Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Marchioretto, Marina Maya , Bruning, Harry and Rulkens, Wim(2005) 'Heavy Metals Precipitation in Sewage Sludge', Separation Science and Technology, 40: 16, 3393 — 3405
To link to this Article: DOI: 10.1080/01496390500423748
URL: http://dx.doi.org/10.1080/01496390500423748

Separation Science and Technology, 40: 3393–3405, 2005

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390500423748

Heavy Metals Precipitation in Sewage Sludge

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Abstract: There is a great need for heavy metal removal from strongly metal-polluted sewage sludges. One of the advantages of heavy metal removal from this type of sludge is the possibility of the sludge disposal to landfill with reduced risk of metals being leached to the surface and groundwater. Another advantage is the application of the sludge as soil improver. The use of chemical precipitation to remove dissolved heavy metals from sewage sludge implies a high cost for chemicals. This work shows, for real sewage sludge for the first time that the addition of NaOH as first precipitating agent considerably saves the addition of Na_2S, that is one of the most effective metal precipitating agents and also expensive. After solubilization of heavy metals by chemical leaching with previous aeration, the next step was the separation of the sludge solids from the metal-rich acidic liquid (leachate) by centrifugation and filtration. Afterwards, the filtered leachate was submitted to the application of NaOH and Na_2S, separately and in combination, followed by filtration. The results showed that when iron and aluminium are present in the leachate, adsorption and/or coprecipitation of Cr, Pb, and Zn with $Fe(OH)_3$ and $Al(OH)_3$ might occur at increasing pH conditions. The combination of hydroxide and sulfide precipitation was able to promote an effective removal of heavy metals from leachate. Applying NaOH at a pH of 4–5 as a first precipitation step, followed by filtration and further addition of Na_2S to the filtered liquid at pH of 7–8 as a second precipitation step, decreased considerably the dosage of the second precipitant (almost 200 times), compared to when it was solely applied. This has practical applications, as the claimed costs drawbacks of H_2S addition is considerably reduced by the addition of the less expensive NaOH.

Received 5 May 2005, Accepted 10 October 2005

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The best removal efficiencies obtained were: Pb: ~100%, Cr: 99.9%, Cu: 99.7%, and Zn: 99.9%.

Keywords: Anaerobically digested sludge, heavy metals, hydroxide precipitation, sewage, sulfide precipitation

INTRODUCTION

Sewage sludge from municipal wastewater treatment plants is often strongly polluted with heavy metals. To improve the quality of the sewage sludge, heavy metals have to be removed. This can occur by heavy metals solubilization followed by separation of the metal containing sludge liquid phase (usually called leachate), and the sludge solids. In the complete integrated chain of treatment steps necessary for removal of heavy metals, leachate treatment is a key process step not only regarding the technical performance but also with respect to costs and final amount of heavy metals wastes.

The solubilized heavy metals can be removed from the leachate by chemical precipitation. The precipitate formed is removed from the liquid by a second physical separation step, resulting in a smaller amount of metal-rich sludge compared to the initial huge fraction of sludge. The metals precipitation process involves the addition of chemical reagents to adjust the pH of the liquid in such a way that the metals exhibit low solubilities in water and therefore precipitate (1).

Common reagents used include alkalis, such as lime, magnesia, NaOH, $NaHCO_3$, Na_2CO_3. Heavy metals like Cr, Cu, Pb, and Zn do not precipitate at pH below 7, permitting some possibility for separation from ferric iron (2, 3, 4) and aluminium (2, 3), which precipitate at pH below 6.5. The association of heavy metal ions with a ferric or aluminum hydroxide precipitate is controlled by adsorption or coprecipitation. Adsorption implies the two-dimensional accumulation of a metal ion at the interface between a preformed solid and the aqueous phase (2). Coprecipitation implies the simultaneous removal of a metal ion during the formation of the primary metal precipitates (2).

In addition to common alkalis, sulfides such as Na_2S, H_2S, NaHS, or FeS can also be used to precipitate metals and have been applied frequently for metal removal from waste effluents to achieve emission standard limitations (4, 5). The lower solubility of metal sulfides in the acid region below pH 7 permits reduction of metal solubility to values that are orders of magnitude lower than are attainable by hydroxide precipitation (4).

Nowadays, a combination of hydroxide and sulfide precipitation for optimal metals removal is being considered (6). A common configuration is a two-stage process in which hydroxide precipitation is followed by sulfide precipitation with each stage followed by a separate solids removal step. This will produce the high quality effluent similar to that obtained with the sulfide precipitation process. Moreover, it will reduce the consumption of sulfide reagents, which are usually more expensive than hydroxide reagents, and will result in a smaller amount of sludge compared to the hydroxide precipitation process alone (6).

The drawbacks of the chemical precipitation process are related to the amount of chemicals, final amount of wastes, difficulty to separate precipitate and liquid, and of course the costs of chemicals, waste disposal and equipment. These drawbacks are, however, the reason to conduct research in this field, in order to enhance the heavy metals removal processes, as they are still beyond the application in real scale. In this work, the emphasis is the dosage of chemicals required in the process and its consequent cost implication.

This study deals with the precipitation of heavy metals from the leachate, which is separated from the sludge particles by centrifugation and filtration, after the solubilization of the heavy metals. The objective is to get more insight in the feasibility of this process and to improve it either by process optimization or eventually in combination with a slight modification of the process.

MATERIAL AND METHODS

Anaerobically Digested Sludge

The sludge applied in this research originated from an anaerobic sludge digester of a wastewater treatment plant located in Schijndel, the Netherlands.

Heavy Metals Solubilization

To achieve the best conditions for heavy metals solubilization, 1 L sludge samples were subjected to previous aeration, followed by acidification, centrifugation, and filtration. An aeration step was applied due to the results of previous experiments (7) in which Cu solubilization efficiency (with HCl at pH 1) improved considerably (from 30% without aeration to more than 90% with aeration). Both aeration and acidification were applied during 24 hours, with continuous shaking (150 rpm), at 20°C. During aeration the airflow rate was $1.5\,\mathrm{L \cdot h^{-1}}$. Acidification with $13.9\,\mathrm{g \cdot L^{-1}}$ of HCl was applied to decrease the initial pH of the original sludge (around 8) to 1.

The acidified samples were centrifuged at 4000 rpm during 30 minutes. The acidic supernatant containing the dissolved heavy metals (leachate) was filtered by paper filter S&S black ribbon (12–25 mm) to remove residual small particles and the resulting liquid was used in the heavy metals precipitation experiments. The heavy metals concentration in this filtered leachate and in the original sludge is shown in Table 1.

Table 1. Heavy metals content of the original sludge and the leachate used in the precipitation experiments

	Heavy metals content in mg · L^{-1} [% of original sludge]					
Fraction	Al	Cr	Cu	Fe	Pb	Zn
Original sludge (pH = 8)	680	9.2	19.8	500	4.9	35
Leachate (pH= 1)	578 [85]	7.2 [78.3]	18.4 [92.9]	450 [90]	4.8 [99.7]	34 [97]

Precipitation Experiments

The precipitation experiments were done in batch scale in three phases. In the first phase hydroxide precipitation with NaOH was applied in such doses (Table 2) to increase the original pH of the leachate from 1 till 5, 7, 9, and 11. These pH values were chosen based on the theoretical pH values for the precipitation of the heavy metals (shown later). In the second phase, sulfide precipitation with Na_2S was used at the same pH values of the first phase (Table 2). In the third phase of the experiments a combination of hydroxide and sulfide precipitation was investigated. Initially, NaOH was added to the liquid till the pH of 4 and 5 were both achieved (these pH values were chosen according to the results of the first and second phases.

Table 2. Chemical dosages of the precipitating agents

	NaOH			Na_2S		
Experiment	pH[a]	g · L^{-1}	mM	pH	g · L^{-1}	mM
Single precipitation	5	10.7	270	5	11.6	150
	7	11.4	290	7	18.6	240
	9	13.2	330	9	26.3	340
	11	16.4	410	11	35.5	460
Combined precipitation I	4	10.3	260	5	0.042	0.54
				5.5	0.046	0.59
				6	0.049	0.63
				7	0.063	0.81
				8	0.095	1.2
Combined precipitation II	5	10.7	270	5.5	0.003	0.038
				6	0.004	0.051
				7	0.014	0.18
				8	0.056	0.72

[a] The initial pH of the leachate is 1.

The pH 4 was chosen in order to check a lower dosage of NaOH than at pH 5). After NaOH addition the liquids were filtered and submitted to Na_2S addition in doses that reach the pH of 5, 5.5, 6, 7, and 8 (Table 2) (these pH values were selected based on the results of the former experiments). For each precipitation experiment, an amount of 500 ml of leachate was used. After each experiment the liquid was filtered in a paper filter S&S black ribbon (12–25 mm) and two samples were collected and analyzed for their heavy metals (Cr, Cu, Pb, and Zn) content. All the experiments were performed in duplicates, with continuous shaking (100 rpm) during 60 minutes.

Analysis

Heavy metals were analyzed by the Inductively Coupled Plasma—Mass Spectrometry Method (ICP-MS, Elan 6000, Perkin Elmer). ICP-AES (Spectro-Flame FVM04) was used to measure aluminum. Liquid samples (resulted from the extraction experiments) for heavy metals analysis were filtered with paper filters (Schleicher &Schuell no $595\frac{1}{2}$, black ribbon, 12–25 mm), diluted 10 times with HNO_3 (0.14 M), and stored at 4°C before analysis. Solid samples and liquid samples of the original sludge were previously digested in the microwave (MDS-2100 CEM) with addition of aqua regia ($HCl : HNO_3 – 3 : 1$) before final dilution for ICP-MS measurement, following the Dutch norm NEN 6465, as described by Veeken (8). The pH was determined with Knick type 510 pH-meter. For samples agitation, a mixer Snijders Scientific was used and the samples were centrifuged (4000 rpm at 20 minutes) in an IEC Centra MP4. The chemicals used in the experiments were of analytical grade (Merck).

RESULTS

Single Precipitation

In general, sulfide precipitation was more effective in removing all the metals at once even at pH 5. When hydroxide precipitation was applied, Cu removal was very low, independently on the range of the investigated pH. At pH 5, Zn removal was similar to Cu removal, but at higher pH values it improved (Fig. 1).

To improve the understanding of the results of Fig. 1, it is convenient to observe Fig. 2, which was plotted on the basis of the stability constants of the metals complexes and solubility products of minerals involved, considering ionic strength value below 0.1 M (9, 10). In this way, according to Moore (11), the effect of ionic strength on the solubility could be considered negligible in the calculations of the equilibrium relationships of all the species. The initial metals concentration in the leachate is indicated in the curve of

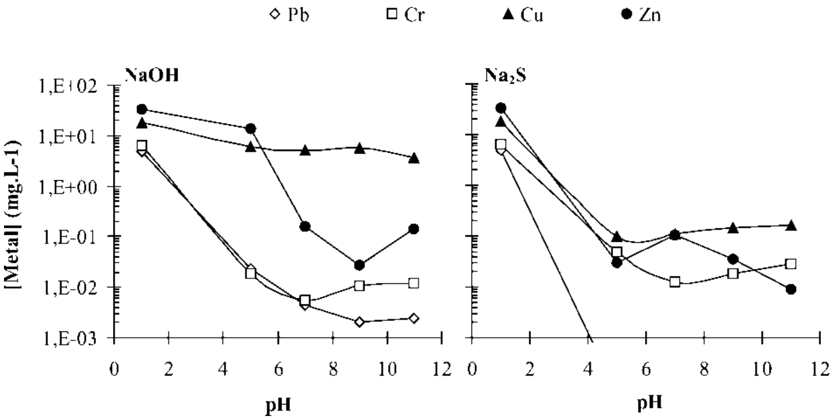

Figure 1. Heavy metals concentration in the remaining liquid after hydroxide and sulfide precipitation followed by filtration (at pH = 1: initial metals concentration in the leachate).

the correspondent metal precipitate, as a thick black dot. The initial concentration of Pb is below the curve of $Pb(OH)_2$ ($4.9\,mg \cdot L^{-1}$) and it appears only in the PbS curve. The initial Cu concentration is above the CuS curve ($19.8\,mg \cdot L^{-1}$) and it is not shown either. In Fig. 2 the diagrams of iron and aluminium hydroxides are also shown, in order to elucidate further discussion.

Hydroxide Precipitation

It is clear that Cu, Cr, Zn, and Pb were not able to form hydroxide precipitates at pH values below 6 (Cu), 7.2 (Cr), and 7.5 (Zn) (Fig. 2). Figure 1 shows,

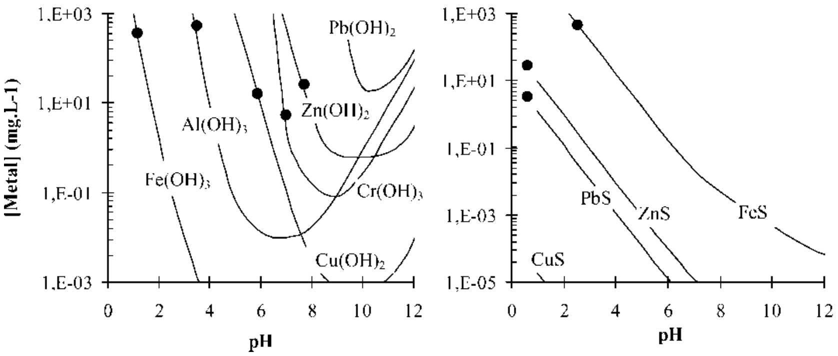

Figure 2. Solubilities of metal hydroxides and metal sulfides as functions of pH (●: initial metals concentration).

however, that more than 99% of Cr and Pb were already removed at pH value of 5. When the pH was higher than 5, Zn removal started and at pH 7.5, more than 99% of this metal was already removed.

Sulfide Precipitation

When Na_2S was applied at pH 5, about 99% of all metals were removed (see Fig. 1). Figure 2 confirms that at pH below 5, ZnS, PbS and CuS precipitates already started to form. Lead was the metal with the highest removal efficiency of all the metals. Figure 1 proves that, at a pH slightly higher than 4, PbS was already almost totally removed. Zinc sulfide removal was less efficient at pH 7 than at pH 5. Comparing both graphs of NaOH and Na_2S in Fig. 1, Cr removal improved when NaOH was applied.

Combined Precipitation

The initial pH values of 4 and 5 were chosen because sulfide precipitation was already efficient at pH 5 (Fig. 1). With initial pH 4 (obtained after precipitation with NaOH), metals were removed at lower pH with the subsequent Na_2S precipitation than when the initial pH value was 5. At the highest initial pH value, the removal of metals by the subsequent sulfide precipitation was more difficult, especially for Cu and Zn.

When more Na_2S was applied, as in the case when the initial pH value was 4 (Na_2S and NaOH doses are shown in Table 2), the formation of Zn and Cu sulfide precipitates occurred at a lower pH value than when less Na_2S was applied (when the initial pH value was 5) (Fig. 3).

It is observed that a high removal efficiency of ZnS can be obtained at a high pH value (Fig. 1 versus Fig. 3 with Na_2S addition), since in all figures the curve of ZnS is still going down at the last pH value measured.

When Na_2S was solely applied, the highest removal of Cu occurred at a pH value of 5, whereas in the combined precipitation (with both initial pH 4 and 5) the same removal efficiency was achieved only at a pH 7.

DISCUSSION

This work shows, for the first time, for real sewage sludge, that the addition of NaOH as first precipitating agent considerably saves the addition of Na_2S (almost 200 times) that is one of the most metal precipitating agents. This has practical implications, as the claimed costs drawbacks of Na_2S addition is considerably reduced by the addition of the less expensive NaOH.

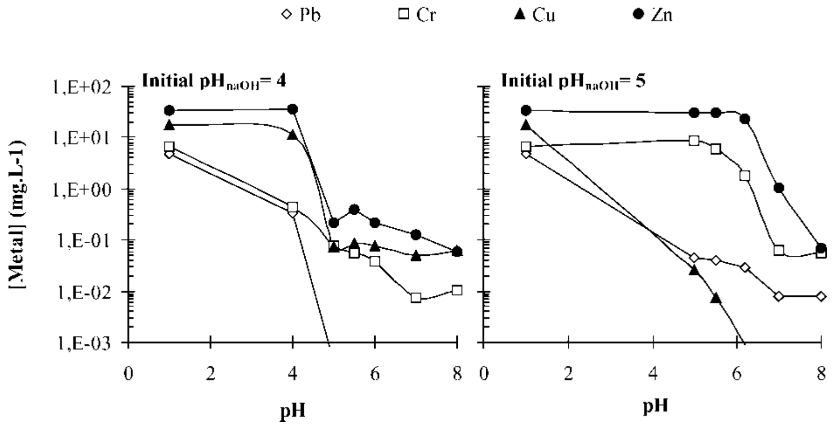

Figure 3. Heavy metals content in the remaining liquid after combined hydroxide and sulfide precipitation followed by filtration (at pH = 1: initial metals concentration in the leachate).

Hydroxide Precipitation

As shown in Table 1, Fe and Al are abundant in the sludge and in the acidified liquid, comparing to the other metals. Figure 2 shows that Fe(III) and Al can start forming hydroxide precipitates at pH 1.3 (Fe) and 3.5 (Al). These curves suggest that adsorption and/or coprecipitation of Cr, Pb and Zn with $Fe(OH)_3$ and $Al(OH)_3$ occurred as the dominant factors in the removal of these metals. In this way, the removals of Cr, Pb and Zn depend on the precipitation of Fe and Al, which act as sorbents (2) and coprecipitants.

The lowest solubility of $Cu(OH)_2$ among other hydroxides (Fig. 2) contradicts the extremely low removal achieved for Cu. On the other hand, when the precipitate has low solubility products, supersaturation is favored and consequently the nucleation rate increases, as the particle sizes decrease (12, 13). According to Veeken et al. (12), the particle size of precipitates depends on the competition between nucleation and crystal growth. When the nucleation rate dominates the crystal growth rate, colloidal particles (<0.05 mm) will result. If the initial concentration of the reactant is high, consequently increasing the concentration of the precipitate, which has a low solubility, the resulting high supersaturation leads to high rates of a primary nucleation (13). In fact, after filtration, the liquid was a bit turbid and this is an indication of the high nucleation rate. This might be a strong reason for the low retention of Cu hydroxide (co)precipitate at the paper filter.

The low Cu removal by coprecipitation with Al and Fe obtained in the present experiments are not in accordance with Lee et al. (2) and Martínez and McBride (3) who found higher removal efficiencies for waters contaminated with acid mine drainage and a synthetic water, respectively. Such differences might be due to the presence of soluble organic matter (SOM) in the leachate (which was probably not present in the waters used by those authors). The affinity of Cu to organic matter is well discussed (14, 15, 16). According to Fletcher and Beckett (17, 18), at a pH value over 7, there is less competition between Cu and other protons for sites on the SOM and thus a high concentration of Cu is likely to be bound to the SOM. These Cu-SOM complexes formed were probably at the colloidal range, which was probably smaller than the filter pore size (12–25 mm) that was used.

Sulfide Precipitation

The threshold for increasing the solubility of zinc sulfide is at the pH range of 5, as ZnS removal was less efficient at pH 7 than at pH 5. However, Figure 2 cannot confirm this explanation. The residual concentrations of Zn (around 0.05 mg/L) and Cu (around 0.1 mg/L) at pH value of 8 were also obtained by Bhattacharyya et al. (19).

CuS should present the highest removal efficiency of all the other metal sulfides (Fig. 2). But this is not observed in Fig. 1. Despite the relatively high range of removal, there might be some factors affecting Cu removal. A possible explanation is the fact that CuS has a very low solubility comparing with ZnS and PbS. As explained before, the low solubility product favors the decrease in the particle sizes (12, 13). This was confirmed by the experiments, because the filtrated liquid was somewhat dark turbid. In addition, in the case of sulfide precipitation, it is not possible to affirm that the formation of Cu-SOM complexes would occur when the pH value was up to 7. Moreover, the slight decrease in CuS removal at a pH value over 6, as shown in Fig. 2, could be due to the change in the solubility of CuS at this pH. However, Fig. 2 cannot confirm this assumption.

Chromium (III) sulfide is not likely to occur here, because in water this is a very unstable form (20). When Na_2S was applied, it seems that Cr was still being removed by adsorption and coprecipitation with $Fe(OH)_3$ and $Al(OH)_3$ that might be present in the liquid as long as the pH value increases. Comparing both graphs of NaOH and Na_2S in Fig. 1, Cr removal was better when NaOH was applied, since $Fe(OH)_3$ and $Al(OH)_3$ might be formed in larger extend than when Na_2S is used.

Combined Precipitation

Before explaining the results shown in Fig. 3, it is important to understand what happened with the heavy metals when NaOH was previously applied. From the results of single precipitation (Fig. 2), all the metals, with exception of Cu, were probably adsorbed and/or coprecipitated with $Fe(OH)_3$ and $Al(OH)_3$ at pH over 5 (Zn) or below 5 (Cr and Pb). Figure 3 shows that at pH 5 Cr and Pb were better removed than at pH 4. This might be due to the fact that at the higher pH value, $Fe(OH)_3$ and $Al(OH)_3$ were better formed, as presented in Fig. 2. As observed before, Cr achieved its best removal efficiency at pH 7.

In the case of Cu, in the combined precipitation (with both initial pH of 4 and 5) the best removal efficiency was achieved only at pH 7, whereas when Na_2S was solely applied, the same removal efficiency occurred at pH 5. These differences are due to the low initial Cu removal obtained when NaOH was applied. As mentioned before, although Cu achieved high removal efficiency, in theory (see Fig. 2) this value should be even higher. The formation of Cu-SOM complexes and the low solubility of $Cu(OH)_2$ and CuS are the probable reasons for this fact.

Furthermore, when the pH value is raised to 4 or 5 by NaOH, it should be increased another 3 pH-units by Na_2S to obtain the highest metals removal (Fig. 3). The option with less Na_2S dosage seems to be advantageous since this chemical is at least 4 times more expensive than NaOH (per mol) and more toxic. Comparing the chemical doses required for single sulfide precipitation and the amount of Na_2S needed for the combined precipitation, in the second case much less precipitant (almost 200 times less) is needed to achieve the same metals removal. This can be observed in Table 3, where the highest removal efficiencies obtained are displayed.

It is clear the advantage of the combined hydroxide and sulfide precipitation over the single sulfide precipitation, in terms of Na_2S dosage and removals of Cu and Cr (Table 3). For the main goal of this research it is appropriate to find the lowest cost solution, where the heavy metals are removed to acceptable concentrations, enabling the discharge of the liquid. For sure a proper destination for the metal concentrated sludge must be attended and

Table 3. Highest heavy metal removal efficiencies achieved at different process conditions

	pH		Dosage (mM)		Heavy metal			
Situation	NaOH	Na_2S	NaOH	Na_2S	Cu	Cr	Pb	Zn
Na_2S	—	5	—	150				
Removal (%)					99.4	99.2	100	99.9
[Metal] ($mg \cdot L^{-1}$)[a]					0.1	0.05	0	0.03
NaOH + Na_2S	4	7	260	0.81				
Removal (%)					99.7	99.9	100	99.7
[Metal] ($mg \cdot L^{-1}$)[a]					0.05	0.007	0	0.1
NaOH + Na_2S	5	8	270	0.72				
Removal (%)					99.7	99.9	100	99.9
[Metal] ($mg \cdot L^{-1}$)[a]					0	0.06	0.008	0.07

[a] Heavy metal concentration remaining in the leachate after precipitation and filtration.

the possibilities of heavy metals recovery from this sludge should be also evaluated. In that respect, the presence of aluminium and iron in the sludge leachate is a relevant fact.

When a mixture of heavy metals is present in the liquid to be treated, it is likely that each metal precipitate particle size evolutes differently from the others. Therefore, in practice, it might be difficult to find an optimal crystal growth rate for all the metals studied An interesting alternative to the use of chemically produced sulfide compounds is the application of the biogenic hydrogen sulfide formed from sulfate reduction by hydrogen consuming sulfate-reducing bacteria (21, 22). Biogenic sulfide precipitation has been investigated for treatment of acid mine drainage and industrial wastewaters (22, 23). This option is also very promising in the treatment of sewage sludges aiming at heavy metals removal. Especially when metals sulfate are present in the leachate, which is a result, for instance, of the sludge acidification with sulfuric acid produced by bioleaching process.

CONCLUSIONS

With the combination of hydroxide and sulfide precipitation followed by a separation process, highly effective separation of heavy metals from the metal-rich acidic liquid (leachate) is obtained. The leachate is resulted from the separation with the sludge solids by centrifugation and filtration. Before the separation step, the sludge is previously aerated and acidified in order to promote heavy metals solubilization.

The dissolved heavy metals present in the leachate are precipitated. The prior addition of NaOH (until a pH of 4 and 5 is reached), followed by Na_2S addition (until a pH of 7 to 8 is reached) allows for a considerable reduction of Na_2S dosage, important from an economic point of view.

Moreover, when iron and aluminium are present in the leachate, adsorption and/or coprecipitation of Cr, Pb, and Zn with $Fe(OH)_3$ and $Al(OH)_3$ might occur at increasing pH conditions.

ACKNOWLEDGEMENTS

This research was supported by CNPq (Project 200.808/98-2), an entity from the Brazilian Government for the development of science and technology.

REFERENCES

1. Freeman, H.M. and Harris, E.F. (1995) Precipitation of Metals from Ground Water. In *Hazardous Waste Remediation: Innovative Treatment Technologies*; Technomic Publishing: Basel, Switzerland.

2. Lee, G., Bigham, J.M., and Faure, G. (2002) Removal of Trace Metals by Coprecipitation with Fe, Al and Mn from Natural Waters Contaminated with Acid Mine Drainage in the Ducktown Mining District, Tennessee. *Applied Geochemistry*, 17: 569–581.
3. Martínez, C.E. and McBride, M.B. (2000) Aging of coprecipitated cu in alumina: Changes in structural location, chemical form, and solubility. *Geochimica et Cosmochimica Acta*, 64 (10): 1729–1736.
4. Brooks, C.S. (1991) *Metal Recovery from Industrial Waste*; Lewis Publishers, Inc.: Chelsea, Michigan, USA.
5. Peters, W.R. and Khu, Y. (1988) The effect of tartrate, a weak complexing agent, on the removal of heavy metals by sulfide and hydroxide precipitation. *Particulate Science and Technology*, 6: 421–439.
6. Wastewater Treatment Technologies. (1998) In *Development Document for the CWT Point Source Category*; U.S. Environmental Protection Agency, EPA: Washington DC, USA.
7. Marchioretto, M.M. (2003) *Heavy Metals Removal from Anaerobically Digested Sludge*; PhD thesis, Wageningen University: Wageningen, The Netherlands.
8. Veeken, A. (1998) *Removal of Heavy Metals from Biowaste*; PhD thesis, Wageningen University: Wageningen, The Netherlands.
9. Stumm, W. and Morgan, J.J. (1996) Precipitation and Dissolution. In *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd Edition; John Wiley and Sons, Inc.: USA.
10. Smith, R.M. and Martell, A.E. (1981) Inorganic Complexes. In *Critical Stability Constants*; Plenum Press: New York, USA; Vol. 4.
11. Moore, J. (1976) *Physical Chemistry*; Prentice-Hall, Inc.: New Jersey, USA.
12. Veeken, A.H.M., de Vries, S., van den Mark, A., and Rulkens, W.H. (2003) Selective Precipitation of Heavy Metals as Controlled by a Sulfide-Selective Electrode. *Separation Science and Technology*, 38 (1): 1–19.
13. Mersmann, A. (1999) Crystallization and Precipitation. *Chemical Engineering and Processing*, 38: 345–353.
14. Marchioretto, M.M., Bruning, H., Loan, N.T.P., and Rulkens, W.H. (2002) Heavy Metals Extraction from Anaerobically Digested Sludge. *Water Science and Technology*, 46 (10): 1–8.
15. Solís, G.J., Alonso, E., and Riesco, P. (2002) Distribution of Metal Extractable Fractions During Anaerobic Sludge Treatment in Southern Span WWTPs. *Water, Air, and Soil Pollution*, 140: 139–156.
16. Zufiaurre, R. and Olivar, A., and Chamorro, P., et al. (1998) Speciaton of Metals in Sewage Sludge for Agricultural Uses. *Analyst*, 123: 255–259.
17. Fletcher, P. and Beckett, P.H.T. (1987) The Chemistry of Heavy Metals in Digested Sewage Sludge—I. Copper(II) Complexation with Soluble Organic Matter. *Water Research*, 21 (10): 1153–1161.
18. Fletcher, P. and Beckett, P.H.T. (1987) The Chemistry of Heavy Metals in Digested Sewage Sludge—II. Heavy Metal Complexation with Soluble Organic Matter. *Water Research*, 21 (10): 1163–1172.
19. Bhattacharyya, D., Jumawan, A.B., Jr., and Grieves, R.B. (1979) Separation of Toxic Heavy Metals by Sulfide Precipitation. *Separation Science and Technology*, 14 (5): 441–452.
20. Weast, R.C. (1979) *CRC Handbook of Chemistry and Physics*, 60th Edition; CRC Press, Inc.: Boca Raton, Florida, USA.
21. Gilbert, O., Pablo, J., Cortina, J.L., and Ayora, C. (May 12–17, 2002) Treatment of Acid Mine Drainage by Sulphate-Reducing Bacteria Using Permeable Reactive

Barriers: from Laboratory to Full-Scale Experiments. In *The Sulfur Cycle in Environmental Biotechnology: Options for Sulfur and Heavy Metal Removal/Recovery*; Summer School: Wageningen, The Netherlands.

22. Tabak, H.T. and Govind, R. (May 12–17, 2002) Advances in Biotreatment of Acid Mine Drainage and Biorecovery of Metals. In *The Sulfur Cycle in Environmental Biotechnology: Options for Sulfur and Heavy Metal Removal/Recovery*; Summer School: Wageningen, The Netherlands.
23. Foucher, S., Battaglia-Brunet, F., Ignatiadis, I., and Morin, D. (2001) Treatment by Sulfate-Reducing Bacteria of Chessy Acid-Mine Drainage and Metals Recovery. *Chemical Engineer Science*, 56: 1639–1645.