

Municipal sludge ash for abatement of ARD

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Abstract

Abatement of ARD with passive treatment systems can quite often rely only on pH-control if the iron content is high enough and to allow for the formation of ferric hydrous oxides, which act as efficient adsorbents. The stability of ferric hydrous oxides is sensitive to lowering of pH as well as Eh why they must be controlled. Hence, it would be favourable to use a well ordered adsorbent that is stable over time and under the chemical conditions of ARD. Municipal waste water sludge is a growing problem in many countries and incineration under oxidative conditions can be used to oxidize anthropogenic organic molecules which pose a threat to the environment. Sludge ashes rendering from wastewater treatment in which iron is used as a flocculation agent have high concentrations of calcium/magnesium and ferric oxides, and should therefore, in theory be a suitable candidate for treatment of ARD. This study has therefore focused on the ability for these ashes to act as a sorbent for the removal of metals from ARD. The stability and potential release of metals from the material were quantified in batch experiments by extraction at pH 2-10, resulting in equilibrium concentrations (at pH 8) of 11.9, 0.08 and 24.1 mg L⁻¹ for Al, Fe and Mn respectively. However, after washing with water the corresponding values were 0.01, 0.03 and 0.09 mgL⁻¹. In fact, after washing the sludge ash is stable from pH 4 to 10, with only slightly higher concentrations found at pH 2. Batch experiments on metal adsorption from ARD showed more than 99% sorption of Cr, Cu, Pb and V, corresponding values for Co, Ni and Zn were 56, 86 and 34% respectively. The overall results from this study show that sludge ashes are a promising solution for treatment of ARD.

Key words: metals, sorption, equilibrium, sludge, ashes

Introduction

Acidic rock drainage (ARD) typically contains high concentrations of metals, which have a detrimental effect on the life of aquatic systems. Release of ARD constitutes widespread environmental problems and treatment is therefore in many cases demanded. As a consequence, substantial research has been focusing on different treatment options for ARD (Gazea *et al.*, 1996; Akcil and Koldas, 2006; Wei *et al.*, 2014). One of the more intensely studied solutions rely on adsorption of metal ions onto different kinds of adsorbents, including various types of ferric materials (Gitari *et al.*, 2006; Ardau *et al.*, 2014; Florence *et al.*, 2016).

Sludge from municipal wastewater treatment plants (MWWTPs) constitutes a growing problem in many countries, in terms of usage and disposal. The sludge contains high concentrations of phosphorus, which is highly valuable as a fertilizer. However, direct application in agriculture is limited due to the presence of heavy metals, pathogens and a multitude of organic pollutants, as well as the uncertainties regarding the fate of these if applied on arable land (SEPA, 2001). An alternative to direct usage of sludge within agriculture is incineration, where organic material is effectively combusted, leaving an ash residue with high concentration of metal oxides which have high potential for metal adsorption (Hua *et al.*, 2012). Previous studies have shown promising results for the use of sewage sludge ash as sorbents for phosphorus and metals from different kinds of solutions (Pan *et al.*, 2003; Iakovleva and Sillanpää, 2013; Abdulai and Lee, 2016).

When using waste materials for treatment of aqueous solutions, it is of great importance to investigate their chemical stability and potential release of their constituents, in order to ensure their suitability as sorbents (Ardau *et al.*, 2014). The aim of this study was therefore to i) investigate the stability and potential release of metals from sludge ashes at different pH, and to ii) evaluate their capacities to adsorb metals from ARD.

Methods

Municipal sewage sludge from three wastewater treatment plants in mid-Sweden was used in this study and the general properties for the facilities and relevant data for the sludge are presented in table 1. Sludge samples were taken after the dewatering step and stored at 8°C until further processing. After drying at 105°C and they were incinerated at 1000°C using a chamber furnace, the resulting ashes were thereafter crushed to less than 0.1 mm. Equal amounts of ashes from all three facilities were mixed and used throughout this study.

Release of metals

Stability and potential release of metals (Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Pb, V and Zn) from the ashes, as well as the impact of washing the ashes with water before extraction, was studied in batch experiments. Washing was done by shaking the ashes with 18.2 MΩ deionized water, which was removed by centrifugation before further treatment. Samples of original and washed ash mixtures were equilibrated with distilled water at five different pH values (ranging from 2 to 10) for 24 hours at room temperature, using a rotary shaker and a liquid to solid ratio (L/S) of 5.

Adsorption of metals

Adsorption of Co, Cr, Cu, Pb, V and Zn to original ashes were quantified at pH 3, 5 and 8 using artificial acid rock drainage (ARD). The elements were chosen according to their chemical properties such as the preference for the formation of cationic and anionic species as well as being common in historic sulphidic mine waste. The ARD was prepared from mine waste from the Ljusnarsberg’s deposit, Sweden, by equilibrating 750 g with 1 L of 18.2 MΩ water for three years. This is a rather weathered material that gives an ARD with pH 2.9, Al 320 mg L⁻¹, Ca 450 mg L⁻¹, Fe 3 mg L⁻¹, K 11 mg L⁻¹, Mg 440 mg L⁻¹, Mn 33 mg L⁻¹ and Na 5 mg L⁻¹ while the anions are dominated by some 5 g L⁻¹ SO₄²⁻. Trace metal concentrations are typically Cd 2 mg L⁻¹, Cu mg L⁻¹, Pb 2 mg L⁻¹ and Zn 600 mg L⁻¹. Due to the relatively low concentrations of trace metals in the ARD, it was spiked with nitrate salts of the metals above, to a final concentration of 0.5 mgL⁻¹. For the subsequent sorption studies, the ARD was mixed with ashes (L/S 10) and shaken at room temperature using a rotary shaker for 24 hours.

Analyses

Metals were quantified with microwave plasma - atomic emission spectroscopy (Agilent 4200 MP AES) after phase separations through centrifugation (4000 rpm, 15 minutes) followed by filtration (0.20 µm). The impact of pH on the metal distribution was statistically evaluated by ANOVA analysis and subsequent Tukey post hoc tests, using the statistical software SPSS Statistics 19. The resulting equilibration concentrations at pH 8 were used for geochemical modeling of saturation conditions using Visual Minteq.

Table 1. Characteristics of the three municipal wastewater treatment plants included in the study

	Örebro	Västerås	Eskilstuna
Connected population (p.e.)	121 000	102 000	85 000
Dimensioned flow (m ³ h ⁻¹)	3 750	4 800	3 090
Precipitation agent	Iron sulfate	Iron sulfate	Iron sulfate
Industries connected (p.e.)	5 700	8 000	7 310
Sludge production (tons year ⁻¹)	11 700	11 900	8 700
Sludge dry weight (%)	27.4	24.3	20.9
Ash content (%)	9.7	10.1	6.3

p.e. = person equivalents

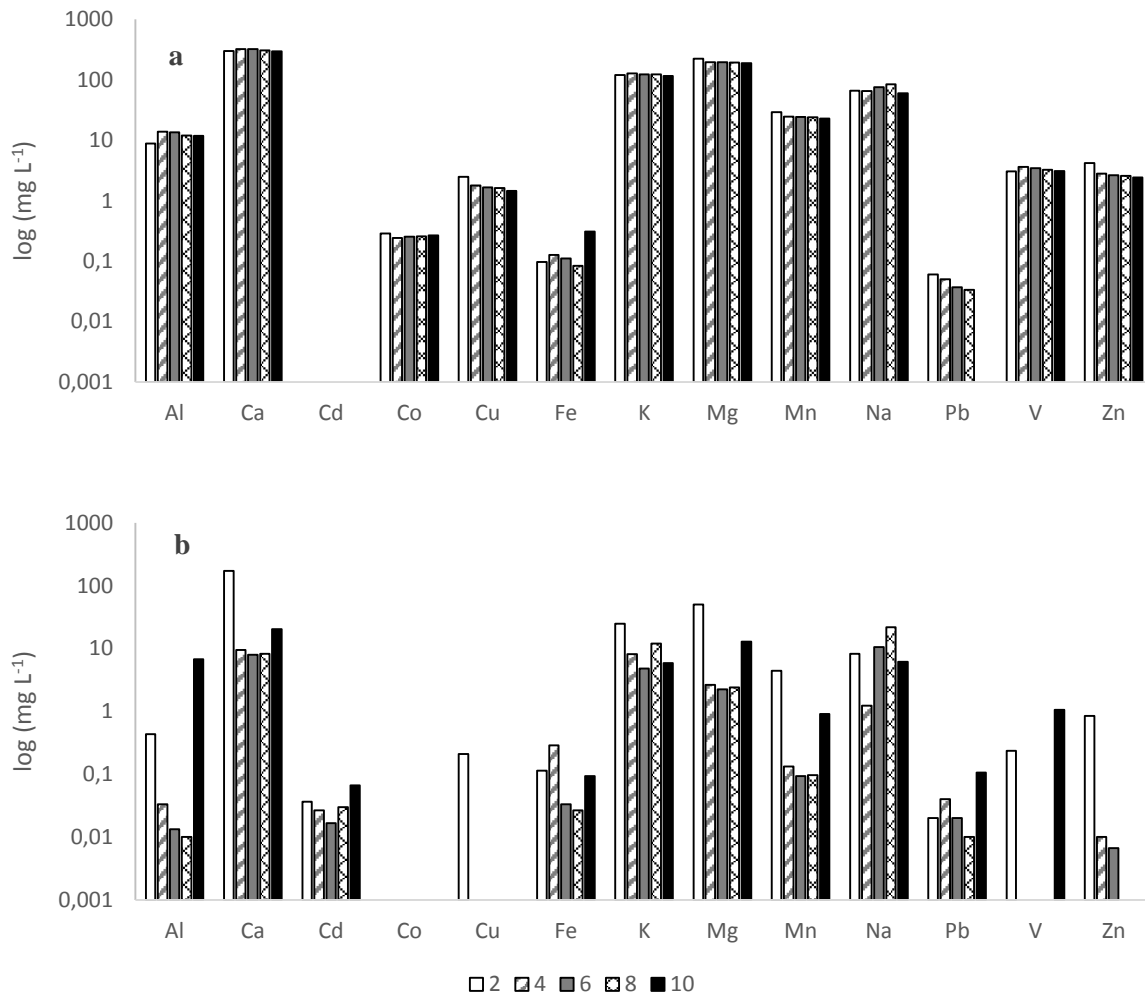


Figure 1 Equilibrium concentrations of selected metals as a function of pH for original (a) and washed (b) municipal sludge ash

Results and discussion

Release of metals

Equilibrium concentrations of metals (Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Pb, V and Zn) after 24 hours can be seen in figures 1 a and b for original and washed ashes, respectively. It is obvious that the leaching of metals is decreased by washing of the ashes. Furthermore, the effect of pH on the leaching process is evidently lower for the original ashes, compared to the washed ones. However, the statistical evaluation suggests that pH is significantly ($p < 0.05$) affecting the release of metals from ashes in both of the set-ups (table 2). As seen in the tables 2a and b, the most prominent differences are found between leaching at pH 2. These results are consistent with a similar study on the use of fly-ashes as adsorbents (Abdulai and Lee, 2016). In that study they concluded that pH had a significant impact on the uptake of metals as it affects the surface of the adsorbent as well as the speciation of the metal ions, and hence their solid/solution distribution. Furthermore, they ascribed the decrease in sorption at low pH, to the increase of hydrogen ions, which act as competitors for the sorption sites. The results in this study also indicate an increase in the release of metals at high pH (figure 1). Similar results have been reported by Gitari *et al.* (2006) who attributed the increase in concentration at high pH to the formation of hydroxyl species. At high pH the formation of negatively charged coordination compounds with ligands such as hydroxide, bicarbonate and carbonate ions, as well as mixed complexes, lowers the affinity for cation-exchangeable sites.

Table 2 a. Comparison of leaching of original sludge ashes at different pH, indicated by bold text.. Significant ($p < 0.05$) differences between equilibrium concentrations at different pH are noted in the matrix.

	4	6	8	10
2	Al, Cu, Mg, Mn, Zn	Al, Cu, Mg, Mn, Zn	Al, Cu, Mg, Mn, Na, Zn	Al, Cu, Mg, Mn, Zn
4		Na	Na	
6				Ca, Na
8				Na

Table 2 b. Comparison of leaching of washed sludge ashes at different pH, indicated by bold text.. Significant ($p < 0.05$) differences between equilibrium concentrations at different pH are noted in the matrix.

	4	6	8	10
2	Al, Ca, Mg, Mn, Na, V, Zn	Al, Ca, K, Mg, Mn, V, Zn	Al, Ca, Mg, Mn, Na, V, Zn	Al, Ca, Mg, Mn, Na, Zn
4		Na	Na	
6			Na	Na
8				Ca, Na

Differences in equilibrium concentrations as a function of pH in the two set-ups, given as the percentage amounts of metals in leachates from the washed ashes compared to the original ones, are given in table 3. From the table it can be concluded that the metal concentrations are considerably lower in the leachates from washed ashes, compared to original, with iron at pH 2 and 4 being the only exception. This trend is related to the removal of metals present as soluble salts or surface complexes at the solid ashes interface, following the washing. By removing these from the matrix, the amount of metals available for extraction is drastically decreased, thus resulting in lower equilibrium concentrations. The deviation for iron may be explained by a lower proportion of adsorption sites for the hydrogen ions, due to the pre-washing, thereby leading to lower pH and subsequently a more pronounced dissolution of iron-carbonates (Golubev *et al.*, 2009). The presence of siderite (iron carbonate) in the sludge ashes has been confirmed by XRD (data not shown). For the remaining metals, the concentrations in the leachates from washed ashes, compared to the original, are considerably higher for (one or both of) the extremes (pH 2 and 10), as compared to the intermediate pH-interval. This is expected since the majority of soluble metals have been removed in the washing procedure, thereby leading to a limited amount available for leaching at neutral pH. However, the leachability is higher at the pH end-points.

Table 3. Differences between metal concentrations in leachate from original and washed sludge ashes at different pH, given as the percentage share found in washed compared to original ashes.

pH	Al	Ca	Cd	Co	Cu	Fe	K	Mg	Mn	Na	Pb	V	Zn
2	4.9	56.8		0	8.5	117.2	20.5	22.2	15.1	12.4	33.3	7.7	20.2
4	0.2	2.9		0	0	226.3	6.3	1.4	0.5	1.9	80.0	0	0.4
6	0.1	2.5		0	0	30.3	3.9	1.2	0.4	12.9	54.5	0	0.3
8	0.1	2.7		0	0	32.0	9.7	1.2	0.4	25.6	30.0	0	0
10	57.4	6.8		0	19.9	30.4	5.1	6.9	4.0	10.2		34.4	0

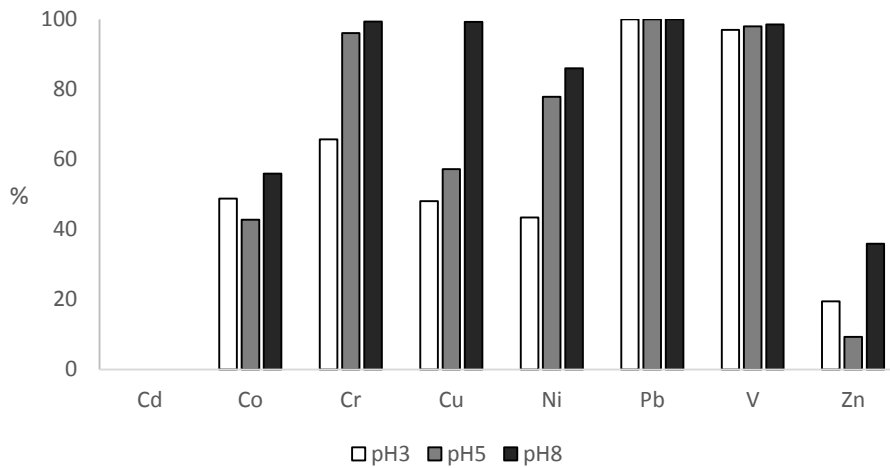


Figure 2. Adsorption (% of total) of metals to sludge ashes as a function of pH.

Removal of metals from ARD

Sorption of metals from the spiked ARD to sludge ashes, as a function of pH, is shown in figure 2. It is evident that the sorption of several of the metals (Cr, Cu, Ni, Zn) increases with increasing pH as expected and consistent with results reported by Jafaripour *et al.*, 2015. In their study on the use of waste gas sludge to remove metals from ARD they reported increasing removal rates following an increase in pH, which they ascribed to the combined action of adsorption and co-precipitation with other metals. In line with their conclusion, geochemical modeling, based on the results in this study (at pH 8), strongly indicate precipitation of $Pb_3(VO_4)_2(s)$. Hence, in this system the concentrations of vanadium and lead in the solution is depend on each other. As expected for ferric oxides the sorption of zinc is low compared to the other metals. This is mainly attributed to its initially high concentration in relation to available specific adsorption sites (Stumm, 1992). This conclusion is further supported by results from an additional study on the sorption capacity of sludge ashes (table 4), where the initial concentration was only a tenth of the one used in this study, showing an almost quantitative removal of zinc. These experiments were conducted at pH 8 and the over-all results are in agreement with the present study. Based on the amounts of metals bound to the ashes from spiked ARD, estimated sorption capacities for the different metals were calculated as a function of pH (figure 3). As seen in figure 3, the sludge ashes have high capacity to sorb all of the metals in this study. This is especially noticeable for zinc but the significantly higher concentration of this element in the spiked ARD must be taken into account. Considering the high removal efficiencies in figure 2 there are reasons to assume that the process is element, or species, dependent why competition would be minor. This invokes the necessity for more refined studies on the specific sorption mechanisms. Capacities and pH dependence for the individual elements must be determined as well as the impact of ligands in the solution phase since they might compete with the adsorption sites. For a full scale application of sludge ashes it is also important to evaluate its hydrodynamic properties to ensure enough contact time between a running ARD and the sorbent to allow for adsorption to work. Finally, the specificity of the adsorption also encourages for further studies on the possibility for specific metal recovery when the sorbent reaches saturation.

Table 4. Percentage removal of metals from fly-ash leachate using sludge ash as sorbent material.

Cd	Cr	Cu	Fe	Li	Mn	Ni	Pb	V	Zn
58,4	100,0	98,8	90,9	9,8	39,4	96,4	94,3	99,9	100,0

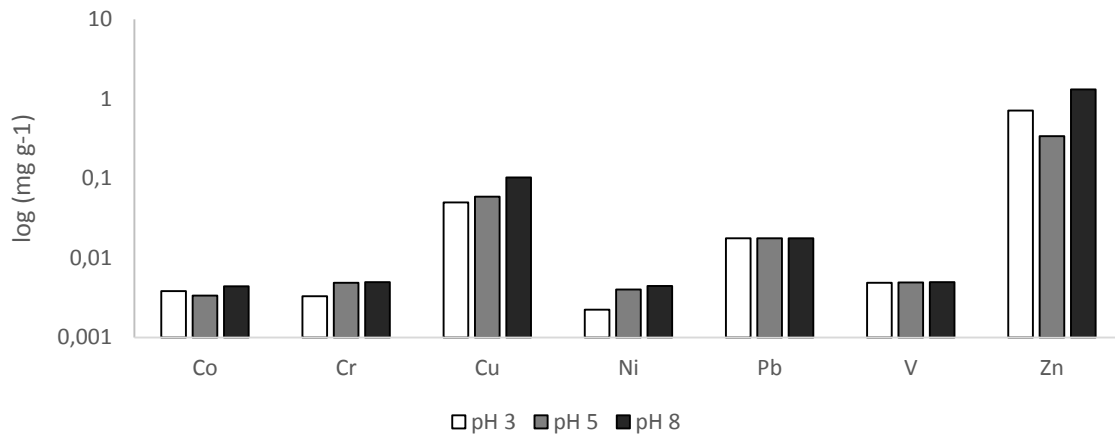


Figure 3. Estimated sorption capacity of sludge ashes as a function of pH

Conclusions

This study provides an initial evaluation of the usage of sewage-sludge-ashes for the removal of metals from acid rock drainage (ARD). Batch studies conducted at different pH has shown that the ashes can remove up to 100% of the ions present in solution, especially at pH 8. Furthermore, it has been shown that by washing the ashes with water prior to usage, the release of metals is significantly reduced. Although further research is needed in order to evaluate its potential as a sorbent, the results from this study show that ashes rendering from incineration of sewage sludge constitutes a promising alternative for treatment of ARD.

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References

- Abdulai, P.J., Lee, S., 2016. Potential use of incineration fly ash as a sustainable low cost material for heavy metals removal from acid mine drainage. *Journal of Korea Society of Waste Management* 33(1), 46-55
- Akcil, A., Koldas, S., 2006. Acid Mine Drainage (AMD): causes, treatment and case studies. *Journal of Cleaner Production* 14, 1139-1145
- Ardau, C., Lattanzi, P., Peretti, R., Zucca, A., 2014. Chemical stabilization of metals in mine wastes by transformed red mud and other iron components: laboratory tests. *Environmental Technology* 35(24), 3060-3073
- Florence, K., Sapsford, D.J., Johnson, D.B., Kay, C.M., Wolkersdorfer, C., 2016. Iron-mineral accretion from acid mine drainage and its application in passive treatment. *Environmental Technology* 37(11), 1428-1440
- Gazea, B., Adam, K., Kontopoulos, A., 1996. A review of passive systems for the treatment of acid mine drainage. *Minerals Engineering* 9(1), 23-42
- Gitari, M.W., Petrik, L.F., Etchebers, O., Key, D.L., Iwuoha, E., Okujeni, C., 2006. Treatment of acid mine drainage with fly ash: Removal of major contaminants and trace elements. *Journal of Environmental Science and Health, Part A* 41(8) 1729-1747
- Golubev, S.V., Bénézeth, P., Schott, J., Dandurand, J.L., Castillo, A., 2009. Siderite dissolution kinetics in acidic aqueous solutions from 25 to 100 °C and 0 to 50 atm pCO₂. *Chemical Geology* 265(1-2), 13-19
- Hua, M., Zhang, S., Pan, B., Zhang, W., Lv, L., Zhang, X., 2012. Heavy metal removal from water/wastewater by nanosized metal oxides: A review. *Nanotechnologies for the Treatment of Water, Air and Soil* 211-212, 317-331
- Iakovleva, E., Sillanpää, M., 2013. The use of low-cost adsorbents for wastewater purification in mining industries. *Environmental Science and Pollution Research* 20, 7878-7899
- Jafaripour, A., Rowson, N.A., Ghataora, G.S., 2015. Utilisation of residue gas sludge (BOS sludge) for removal of heavy metals from acid mine drainage (AMD). *International Journal of Mineral Processing* 144, 90-96
- Johnson, D.B., Hallberg, K.B., 2005. Acid mine drainage remediation options: a review. *Science of the Total Environment* 338, 3-14
- Pan, S.C., Lin, C.C., Tseng, D.H., 2003. Reusing sewage sludge ash as adsorbent for copper removal from wastewater. *Resources Conservation and Recycling* 39(1), 79-90
- Stumm, W., 1992. *Chemistry of the solid-water interface – Processes at the mineral-water and particle-water interface in natural systems*. Wiley. ISBN: 0-471-57672-7
- Swedish Environmental Protection Agency, 2001. Report 5148. Levels of 61 trace elements in sewage sludge, manure, fertilizer, precipitation and soil and crops (in Swedish). ISBN: 91-620-5148-2
- Wei, X., Wolfe, F.A., Han, Y., 2014. Mine drainage: Characterization, treatment, modelin and environmental aspect. *Water Environment Research* 86(10), 1515-1534