



BENCH- AND FIELD-SCALE STUDY OF DISPOSAL OF GYPSUM WALLBOARD RESIDUALS

Mackie, Allison L.^{1,3}, Anderson, Robert², and Gagnon, Graham A.¹

¹ Department of Civil and Resource Engineering, Dalhousie University, Canada

² Robert Anderson Consulting, Inc., Canada

³ allisonmackie@dal.ca

Abstract: Waste or residual gypsum wallboard has the potential to generate hydrogen sulphide (H₂S) if disposed in a traditional landfill and most landfills do not accept wallboard for this reason. This study compared five materials in mixtures with residual gypsum wallboard from a wallboard manufacturing plant at bench-scale for the mitigation of sulphide generation: cement kiln dust, pasteurized biosolids, agricultural lime, open hearth slag (OHS), and wood ash. These materials were mixed with gypsum wallboard residuals and placed in vertical columns to which synthetic, de-oxygenated rain water was added weekly. Analysis of leachate from the columns indicated that wood ash and OHS were able to reduce leachate sulphide concentrations most significantly compared to control columns with gypsum residuals only. Wood ash was selected over OHS for field-scale testing due to its proximity. Field test plots were constructed atop a wood ash/pulp mill biosolids landfill, comparing a 1:1 volumetric mixture of wood ash:wallboard residuals with wallboard residuals alone in two separate plots. Both plots were covered with a layer of pulp mill biosolids which effectively prevented any H₂S gas emissions from the landfill. The results of the field study indicate that co-disposal of gypsum wallboard with wood ash can help to reduce generation of H₂S gas and that temperature was a key contributing factor controlling H₂S gas generation.

1 INTRODUCTION

Hydrogen sulphide gas (H₂S) in landfills is generated as a by-product of the respiration of sulphate-reducing bacteria (SRB). Gypsum wallboard contains both the sulphate (SO₄²⁻) and the organic material (i.e., paper backing) required for biological sulphate reduction by SRB to produce H₂S, which is highly toxic in gaseous form. Landfills provide the anaerobic and moist environment required for SRB to thrive. Environmental conditions favoured by SRB are often found at construction and demolition (C&D) debris landfills, where gypsum wallboard is a primary component (Townsend et al. 1999). H₂S gas has a distinct odour of rotten eggs which is detectable by humans at extremely low concentrations (< 10 ppb) and produces mild toxic and neurological effects with long term exposure at low concentrations (1 to 10 ppm) and coma and death resulting from short term exposures at higher concentrations (> 500 ppm; Ko et al. 2015; Kilburn 2003).

Two main options for the mitigation of H₂S gas emission from gypsum wallboard waste or C&D debris landfills are 1) preventing its production or 2) adsorbing it after it's been generated. For option 1, one or more of the environmental conditions necessary for SRB to thrive must be removed (i.e., moisture, absence of oxygen, neutral pH) to prevent the reduction of sulphate to sulphide and thus the production of H₂S. For option 2, various cover materials, from soil to concrete, have been investigated and several have been

shown to be able to adsorb H₂S gas generated from gypsum wallboard in C&D landfills (Yang et al. 2006; Plaza et al. 2007; Bergersen and Haarstad 2008, 2014; Xu, Liu et al. 2010; Xu, Townsend and Reinhart 2010; Sahu et al. 2011; Xu et al. 2011). Specifically, the use of calcium- or iron-based materials, as well as household compost, as covers for landfills containing gypsum wallboard waste have been shown to be effective at adsorbing gaseous H₂S emissions.

The goals of this study were 1) to determine, at bench-scale, which of several additives would best reduce sulphide concentrations and raise pH of leachate when mixed with gypsum wallboard residuals and 2) to monitor field test plots of landfilled materials for sulphide generation.

2 MATERIALS AND METHODS

2.1 Materials

Gypsum residuals were sampled from outside of a wallboard production facility in Atlantic Canada. Samples were taken from the anaerobic interior of the piles to ensure SRB were present and in saturated conditions. Bulk density and moisture content (% M) of the gypsum wallboard residuals were approximately 1.2 ± 0.1 g/cm³ and 49 ± 2%. Agricultural lime (pulverized limestone; CaCO₃, 7.0 ± 0.1% M) was contributed by Antigonish Lime (Antigonish, NS, CA), cement kiln dust (CKD; 25% loss on ignition, 43% CaO, 7% available CaO, 0% M) was provided by LaFarge North America (Brookfield, NS, CA), and wood fly ash (0% M) was sampled from a 60-megawatt biomass power plant. Pasteurized biosolids (50 ± 1% M) were produced from municipal biosolids pasteurized using a mix of CKD and quicklime and obtained from the N-Viro[®] facility in Halifax, NS, CA. Open hearth slag (OHS; 11.9 ± 0.1% M) was contributed by Portside Aggregates and taken from the former steel plant site in Sydney, NS, CA. Figure 1 illustrates all materials used in this study, which were used as provided.



Figure 1: Gypsum wallboard residuals and additives used in this study

Simulated rainwater was made following the USEPA's Synthetic Precipitation Leaching Procedure (SPLP) method. A diluted 60/40 w/w sulphuric/nitric acid mixture was used to reduce the pH of pure (Milli-Q) water to 4.20 ± 0.05 (USEPA 1994).

2.2 Bench-Scale Methods

Leachate test columns were constructed of 10-cm diameter acrylonitrile butadiene styrene (ABS) pipe in 40- or 92-cm long sections, as shown in Figure 2, with 6.35-cm of gravel at the bottom covered with geotextile (landscape fabric), followed by 6.35-cm of rinsed and dried sand, then the gypsum waste mixture (19- or 76.2-cm), then 6.35-cm of rinsed and dried gravel at the top. An initial series of 6 columns was constructed: one with gypsum alone plus one of each of the five alkaline materials (i.e., OHS, CKD, wood ash, agricultural lime, and pasteurized biosolids) mixed with the gypsum waste. Preliminary ratios of additive:wallboard residuals (v:v) for the column trials were selected by mixing varying ratios with simulated rainwater to determine the ratio that would give a pH greater than 9.0 and a low S^{2-} concentration. Duplicates were run using a second set of 6 columns at the same initial ratios. The total depth of the waste mixtures was 19-cm and mixtures were placed in the pipe sections by hand to achieve a comparable level of compaction. Additional sets of columns were tested with 1) a different ratio of additive:gypsum residuals and 2) an increased depth of material (i.e., 76.2-cm).

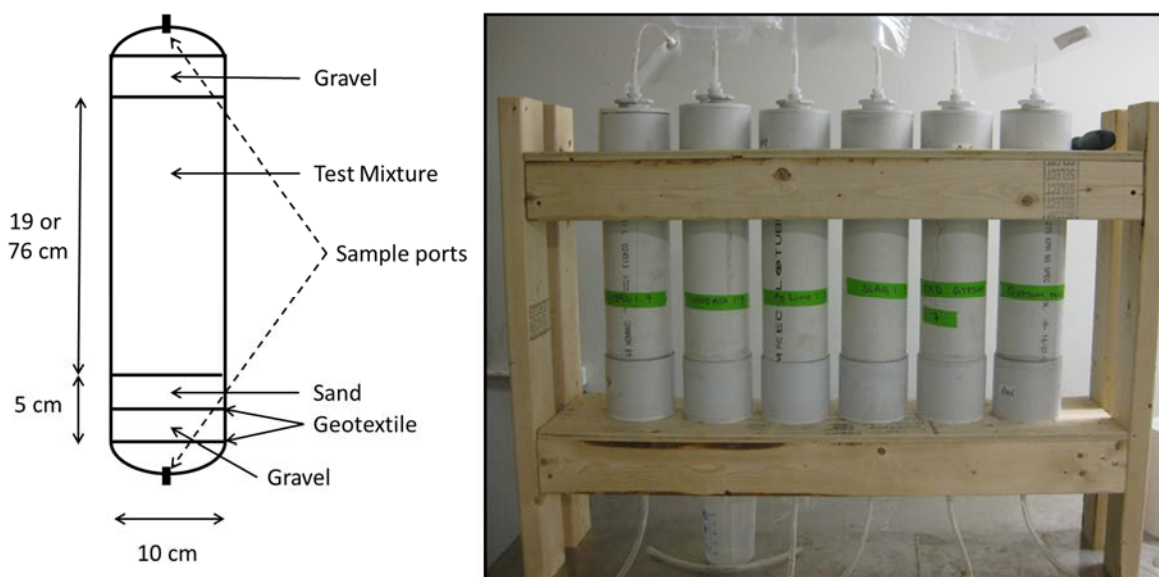


Figure 2: Schematic of column construction (left) and photo of a set of 6 columns (right)

500-mL of simulated rainwater was added to the upper port of each column weekly for 6 weeks followed by a reduction in the added volume to 100-mL per week for a further 6 weeks and intermittently thereafter. Leachate sampling from the bottom sample port was also performed weekly for the first 12 weeks then intermittently thereafter. Leachate samples were collected in amber glass bottles from the lower sample port and analyzed the same day for SO_4^{2-} , S^{2-} , and pH.

2.3 Field-Scale Methods

Two roughly equally-sized field test plots were constructed on top of an estimated 3.2-ha section in the middle of an estimated 15.4-ha wood ash/pulp mill biosolids landfill in eastern NS, CA: one using a 1:1 volumetric mixture of wood ash and wallboard residuals and the other using wallboard residuals alone (i.e., control plot). This landfill has been and continues to be used to dispose of wood ash and pulp mill biosolids in alternating layers. Gypsum residuals and wood ash were mixed using backhoes prior to placement on the landfill in layers totalling approximately 50- to 100-cm. A 30-cm minimum cover of pulp mill biosolids was used over both test plots. Core samples from 3 sites on each test plot were taken on 8 occasions over a 33-week period from May to September. Core samples were taken by first removing the biosolids layer using a shovel then coring into the residuals using a hand auger. Samples were taken from the top and bottom, just below and above the interfaces with the upper and lower biosolids layers. H_2S gas readings

were also taken in each borehole as well as above the surface of the landfill. Core samples were processed by mixing a 25-g portion with 100-mL of DI water and letting react for 1-hr, filtering through 0.45- μm cellulose nitrate filters, then measuring SO_4^{2-} and S^{2-} . pH was measured on unfiltered samples. Mixing, filtering, and in some cases dilution of the samples prior to S^{2-} analysis may have oxidized some of the sulphides, resulting in underestimated sulphide concentrations.

2.4 Analytical Methods

pH was measured using an Accumet XL50 meter with an Accumet double junction electrode. SO_4^{2-} (detection limits = 2 to 70 mg/L) and S^{2-} (detection limits = 5 to 800 $\mu\text{g/L}$) were measured spectrophotometrically on a HACH DR5000 spectrophotometer using EPA-approved methods. The methylene blue S^{2-} test method used determines total sulphides (e.g., H_2S and HS^-) in water; S^{2-} is generally less than 0.1% of a sample even at pH of 14 (Steudel 2000; Yongsiri et al. 2005). H_2S gas was measured using a Crowcon Tetra personal gas monitor calibrated by Avensys Solutions (Montréal, QC) at concentrations of 25 ppm and 255 ppm.

Error bars on graphs and error terms in text represent one standard deviation from the mean of two columns tested using the same additive ratio for the bench-scale trials and from the mean of 3 boreholes for the field-scale trials. Analysis of variance (ANOVA) was used to determine the statistical significance of differences between test conditions. P-values less than 0.05 indicate that there is a significant difference between the means of the two test conditions analyzed at the 95 % confidence interval (Mac Berthouex and Brown 2005).

3 RESULTS AND DISCUSSION

3.1 Bench-Scale Column Trials

3.1.1 Effect of Additive

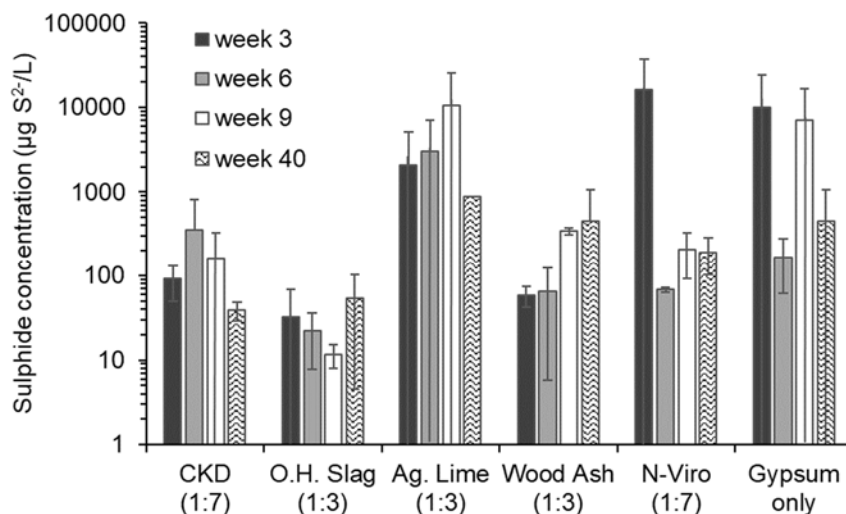


Figure 3: Total sulphides in leachate from columns with varying additives. Note that sulphide concentration is plotted on a logarithmic scale.

Figure 3 shows total sulphide (S^{2-}) concentrations in leachate from columns run with the additives tested in this study. The S^{2-} concentration in leachate samples was highly variable over the course of the study. However, in general, the gypsum-only control and agricultural lime/gypsum mixture resulted in the highest

S²⁻ concentrations while open hearth slag and wood ash resulted in the lowest. No H₂S gas was ever generated from the upper ports of the columns. The S²⁻ analytical method used in this study measures aqueous H₂S and HS⁻, along with some metal sulphides. The pK_a for H₂S to HS⁻ is approximately 7, with H₂S decreasing with increasing pH above 7 (Yongsiri et al. 2005). The leachate from columns in this study had a pH of approximately 7 (Figure 4), therefore, H₂S and HS⁻ should be approximately in equilibrium in solution. Since columns also remained saturated during testing, it is likely that H₂S remained dissolved in solution rather than being emitted in gaseous form. The Henry's Law volatility constant for H₂S in water is approximately 500 atm per mole fraction at 20 °C (Yongsiri et al. 2005 and references therein) which, when expressed as a solubility constant, is 0.001 mol/m³ Pa (Sander 2015 and references therein). For comparison, the solubility constant of CO₂ is estimated to be 0.00034 mol/m³ Pa, while that of methanol is approximately 2.0 mol/m³ Pa.

CKD and pasteurized biosolids were able to raise the pH more effectively than the other additives, as evidenced by their selected additive:residuals ratios of 1:7, compared to 1:3 for the remainder of the additives. CKD consistently had the highest pH over the course of the study, even at the lower ratio compared to other additives (Figure 4). The pH of the other columns was more consistent over the course of the study, with the gypsum residuals-only columns and the agricultural lime columns having the lowest leachate pH (6.8 ± 0.1 and 6.7 ± 0.1, respectively, at week 10), followed by pasteurized biosolids (7.4 ± 0.9), OHS (7.3 ± 0.1), and wood ash (7.2 ± 0.5) mixtures. None of the columns had pH levels above 9 after week 1 apart from CKD.

Both CKD and pasteurized biosolids contain SO₄²⁻ themselves which would add to the SO₄²⁻ available for reduction by bacterial action. For this reason, CKD and pasteurized biosolids were excluded from further column testing, along with agricultural lime due to its poor performance in terms of increasing pH. Due to the poor pH performance of the remainder of the additives during this experiment (wood ash and OHS), subsequent column tests were run with an additive:wallboard residuals ratio of 1:1.

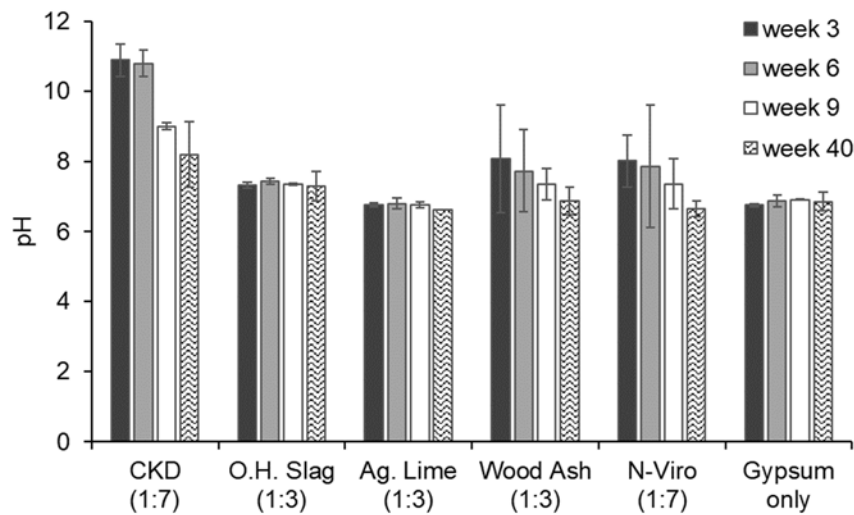


Figure 4: pH of leachate from columns with varying additives

3.1.2 Effect of Column Depth

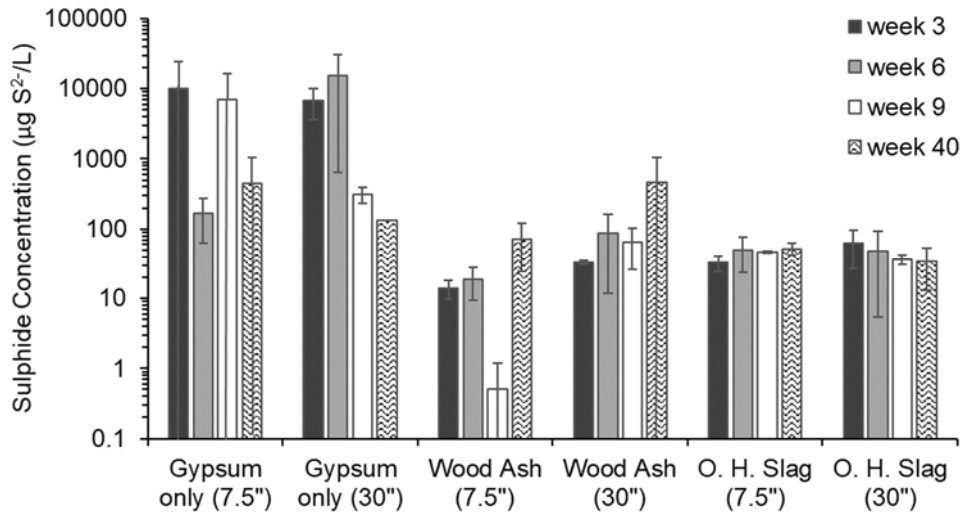


Figure 5: Total sulphides in leachate from columns with varying depths. Note that sulphide concentration is plotted on a log scale.

Increasing depth of material from 7.5" to 30" (19 cm to 76.2 cm) did not appear to have a substantial or consistent influence on S²⁻ generation (Figure 5). Increasing depth also did not result in significantly different pH over the course of the experiment (Figure 6). P-values calculated from ANOVA tests comparing duplicate measurements at each depth for week 2 and week 9 results ranged from 0.15 to 0.43 for S²⁻ and 0.08 to 0.93 for pH. The volume of synthetic rainwater added to the 76.2-cm columns was the same as for shorter columns. The gypsum residuals-only control columns produced much higher S²⁻ concentrations than the 1:1 mixtures with wood ash or OHS, which had comparably low S²⁻ concentrations for the duration of the tests (Figure 5). pH was highest in leachate from wood ash mixture columns and lowest in leachate from gypsum only control columns (Figure 6). This evidence, along with the proximity of the wood ash material to the landfill, led to its selection for field-scale testing.

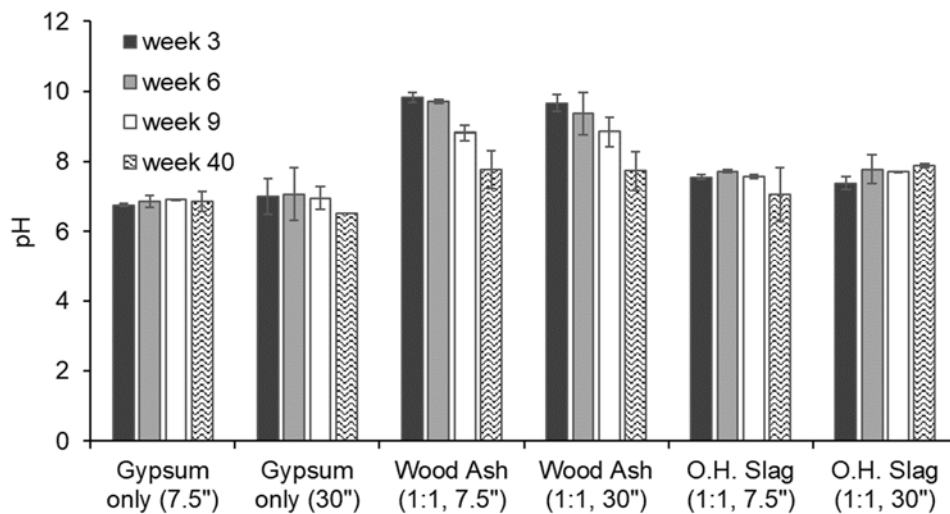


Figure 6: pH of in leachate from columns with varying depths

3.2 Field-Scale Trials

Field test plots were constructed atop an existing wood ash and pulp mill biosolids landfill. Plot A contained a mixture of gypsum wallboard residuals and wood ash at a ratio of 1:1 and plot C contained gypsum residuals only (control). No H₂S gas was ever detected above the surface of the landfill-applied field plots or anywhere near the landfill site once the material was moved and covered with biosolids. H₂S gas within the test plots was not detectable until late June and was detected earlier and in higher concentrations in the gypsum-only plot (C) compared to the gypsum/wood ash mixture plot (A). Readings from both test plots peaked in late August and were above the detection limit of the instrument (>255 ppm) in all boreholes on that sampling visit and the one in late September. H₂S gas diminished to barely detectable levels by November. H₂S becomes less water-soluble with increasing temperature (Yongsiri et al. 2005), therefore increased emission of H₂S gas is expected with increased temperature. Bacterial activity also increases with increasing temperature within the range studied. Both likely contributed to high H₂S gas readings in boreholes during sampling visits when air temperatures were highest. Any H₂S emitted by gypsum residuals applied to the landfill was likely adsorbed by the cover of biosolids.

Figure 7 shows the S²⁻ concentrations found from mixing solid samples from test plot boreholes with pure water were fairly consistent over the course of the study. S²⁻ concentrations spiked during August in both test plots, likely related to the air temperature increasing bacterial activity. Figure 8 shows that, in general, the pH of solid material samples from plot A was slightly higher than that of samples from plot C. However, pH never reached above 9 like it had in the bench-scale trials. This difference was likely due to inadequate mixing at field-scale resulting in pockets of wallboard with no wood ash mixed in as well as the fact that column trials were kept fully saturated while rainfall in field conditions was significantly lower.

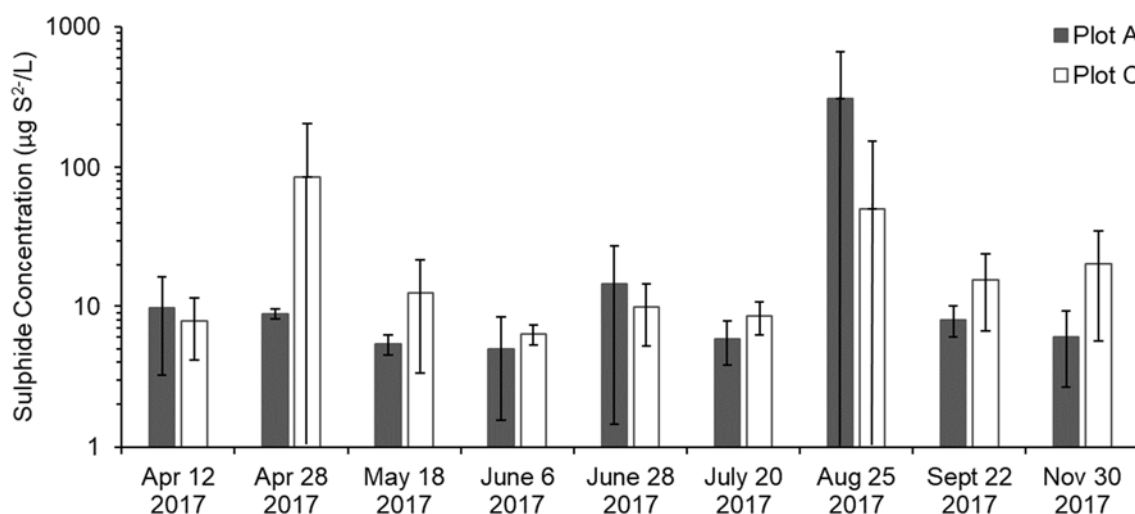


Figure 7: Total sulphides in samples from field test plots. Note that sulphide concentration is plotted on a log scale.

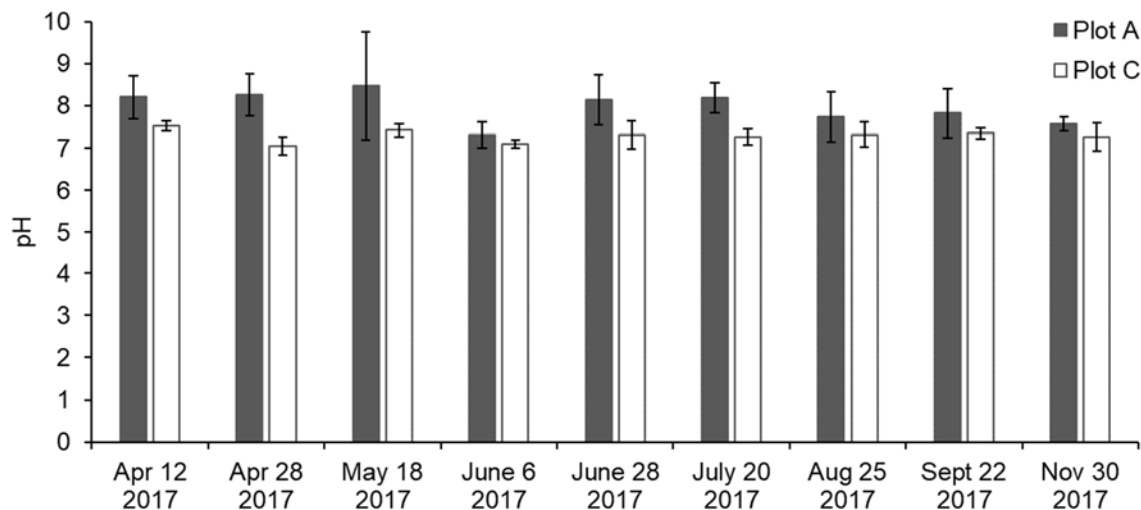


Figure 8: pH of samples from field test plots

4 CONCLUSIONS

5 BENCH-SCALE STUDY:

- No columns produced H₂S gas from upper sample ports during the study.
- Sulphide (S²⁻) concentrations in leachate were lowest in columns with wood ash or OHS at a 1:1 additive:gypsum wallboard residuals ratio.
- After CKD, which contained SO₄²⁻ and therefore was not tested further, pH was highest with wood ash and generally above 9 in columns with a 1:1 ratio of wood ash to gypsum residuals.
- Increased depth of material from 7.5" to 30" (19 cm to 76.2 cm) did not affect S²⁻ concentrations in or pH of leachate.

Field-scale study:

- Hydrogen sulphide (H₂S) gas was never detected above the surface of the landfill. It is likely that any escaping gas was adsorbed by the covering layer of pulp mill biosolids.
- Warmer temperatures led to generation of H₂S gas within both the control pile, plot C, and the gypsum/wood ash mixture, plot A. Detected concentrations took longer to begin in plot A and were observed to be consistently lower in the wood ash mixture. H₂S concentrations in plot C were above the detection limit of the detector (>255 ppm) from late June to late September and in plot A during August and September sampling events.
- Sulphide concentrations in solids mixtures were consistent throughout the study period and were not significantly different between plots A and C.
- pH was slightly but not significantly higher in test plot A compared to control plot C.

Differences between the field study and bench study results (i.e., lower field pH, no H₂S gas generation in columns) were likely due to inadequate mixing and lower rainfall (i.e., less saturation) in the field compared to bench study. Mechanical mixing in the field resulted in pockets of gypsum without wood ash and saturated conditions in the column trials led to sulphides remaining in dissolved form and not being released as gas.

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References

- Mac Berthouex, P. and Brown, L.C. 2002. *Statistics for Environmental Engineers*, 2nd Ed., CRC Press, Boca Raton, FL, USA.
- USEPA 1994. *Synthetic Precipitation Leaching Procedure*. EPA Method 1312. Washington, DC, USA.
- Bergersen, O. and Haarstad, K. 2008. Metal Oxides Remove Hydrogen Sulfide from Landfill Gas Produced from Waste Mixed with Plaster Board under Wet Conditions, *Journal of the Air & Waste Management Association*, 58(8): 1014-1021.
- Bergersen, O. and Haarstad, K. 2014. Treating landfill gas hydrogen sulphide with mineral wool waste (MWW) and rod mill waste (RMW). *Waste Management*, 34(1): 141-147.
- Kilburn, K.H. (2003). Effects of hydrogen sulfide on neurobehavioral function. *Southern Medical Journal*, 96(7): 639-647.
- Ko, J.H., Xu, Q., Jang, Y.-C. 2015. Emissions and Control of Hydrogen Sulfide at Landfills: A Review, *Critical Reviews in Environmental Science and Technology*, 45(19): 2043-2083.
- Plaza, C., Xu, Q., Townsend, T., Bitton, G., Booth, M. 2007. Evaluation of alternative landfill cover soils for attenuating hydrogen sulfide from construction and demolition (C&D) debris landfills. *Journal of Environmental Management*, 84: 314-322.
- Sahu, R.C., Patel, R., Ray, B.C. 2011. Removal of hydrogen sulfide using red mud at ambient conditions. *Fuel Processing Technology*, 92(8): 1587-1592.
- Sander, R., 2015. *Compilation of Henry's law constants (version 4.0) for water as solvent*. *Atmospheric Chemistry & Physics*, 15(8): 4399-4981.
- Stuedel, R. 2000. The chemical sulfur cycle. *Environmental technology to treat sulfur pollution: Principles and engineering*, P.N.L. Lens and L. Hulshoffpol, eds., International Water Association, London, 1-31.
- Townsend, T.G., Jang, Y., Thurn, L.G. 1999. Simulation of construction and demolition waste leachate. *Journal of Environmental Engineering*, 125(11): 1071-1081.
- Xu, Q., Townsend, T., Bitton, G. 2011. Inhibition of hydrogen sulfide generation from disposed gypsum drywall using chemical inhibitors. *Journal of Hazardous Materials*, 191(1): 204-211.
- Xu, Q., Townsend, T., Reinhart, D. 2010. Attenuation of hydrogen sulfide at construction and demolition debris landfills using alternative cover materials. *Waste Management*, 30(4): 660-666.
- Xu, Q., Liu, F., Townsend, T.G., Abichou, T., Chanton, J. 2010. Tire-Derived Steel for Hydrogen Sulfide Removal in Landfill Cover. *Pract. Period. Hazard. Toxic Radioact. Waste Management*, 14(3): 211-214
- Yang, K., Xu, Q., Townsend, T.G., Chadik, P., Bitton, G., Booth, M. 2006. Hydrogen sulfide generation in simulated construction and demolition debris landfills: Impact of waste composition. *Journal of the Air & Waste Management Association*, 56(8): 1130-1138.
- Yongsiri, C., Vollertsen, J. Hvitved-Jacobsen, T. 2005. Influence of wastewater constituents on hydrogen sulfide emission in sewer networks. *Journal of Environmental Engineering*, 131(12): 1676-1683.