- Federal Highway Administration (FHA). (2000). "An Introduction to the Deep Soil Mixing Methods as Used in Geotechnical Application", US Department of Transportation, Federal Highway Administration.
- Geiger, C. L., Chopra, M., Reinhard, D.R., Burwinkel, S., Quinn, J., Clausen, C.A., Sonawane, A. (1998). "Construction and performance of a field-scale permeable reactive barrier using the deep-soil mixing technique," University of Central Florida.
- Hattaway, J., Hardin, C. D., Daniels, J. L. (2013). "Recommended Guidelines for the Use and Application of the Leaching Environmental Assessment Framework (LEAF) for Coal Combustion Residuals," World of Coal Ash.
- Interstate Technology & Regulatory Council (ITRC), (2011). *Development of Performance Specifications for Solidification/Stabilization. S/S-1.* The Interstate Technology & Regulatory Council Solidification/Stabilization Team. Washington, D.C.
- Jasperse, B. H., Miller, A. D. (1990). "Installation of Vertical Barriers Using Deep Soil Mixing," HazMat Central 1990, Rosemont, Illinois.
- Jayaram, V., Marks, M. D., Schindler, R. M., Olean, T. J., & Walsh, E. (2002). "In Situ Soil Stabilization of a Former MGP Site," Portland Cement Association, Skokie, Illinois.
- Kosson, D.S., Garrabrants, A.C., van der Sloot, H., Thorneloe, S., Benware, R., Helms, G., Baldwin, M. (2012). "The Leaching Environmental Assessment Framework as a Tool for Risk-informed, Science-based Regulation," *Cement Barriers*.
- Larsson, S., (2005). "State of Practice Report" Tyrens AB, SE-118, Royal Institute of Technology, Stockholm, Sweden.
- Liver, Norman L., Mardorf, Erwin C., King, John C. (1954). "Development and Applications of Intrusion Grout Mixed-in-Place Piles", *Civil Engineering*.
- Maher, A., H. Najm, and M. Boile. (2005). "Solidification/stabilization of soft river sediments using deep soil mixing", FHWA-NJ-2005-028 Piscataway, NJ:
 Rutgers, the State University of New Jersey, Center for Advanced Infrastructure & Transportation (CAIT) Civil & Environmental Engineering Department.
- Olson, M. R., Sale, T. C., Shackelford, C. D., Bozzini, C., & Skeean, J. (2012). "Chlorinated Solvent Source-Zone Remediation via ZVI-Clay Soil Mixing: 1-Year Results," *Groundwater Monitoring & Remediation*, 32(3), 63-74.
- Olson, M. R. (2014). "Remediation of soil impacted with chlorinated organic compounds: Soil mixing with zero valent iron and clay," Colorado State University.

Ryan, C. R., and Jasperse, B.H. (1989). "Deep Soil Mixing at the Jackson Lake Dam,"

Proceedings, Foundation Engineering: Current Principles and Practices, held in Evanston, Illinois, on 25-29 June, F.H. Kulhawy, Ed., ASCE, New York, NY, Vol. 1, pp. 354-367.

Immobilization of Cadmium (Cd) and Zinc (Zn) Using Steel Slag Fines

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Abstract: The immobilization potential of dissolved Cd and Zn (each ~750 mg/L) in independently packed columns of freshly crushed steel slag fines (SSF) media was evaluated. The SSF media was characterized as USCS SP type soil with <5% passing the No. 200 (0.075 mm) sieve and the flow rates were on the order of a meter per day with a residence time on the order of 3.5 hours for a 25-cm long column containing approximately 5 kg of SSF media.

The influent pH of the Cd and Zn solutions were on the order of 5.8 and 7.2, respectively, and the pH of the effluent for the test duration of 100 pore volume (PVs) remained above 11.5. The dissolved concentrations of Cd in the effluent remained below the detection limit (0.05 mg/L) for the entire test duration; whereas the Zn concentrations exceeded 1 mg/L at approximately 48 PV.

Independent acid neutralization capacity (ANC) testing of Cd- and Zn-spiked SSF media (~500 mg/L each) coupled with geochemical modeling indicated that Cd was insoluble within the SSF. Similar trends were initially observed with the Zn testing suite, except that the aqueous solubility minimum of Zn occurs near pH=9; and its amphoteric behavior above that pH value meant it prematurely broke through the packed SSF column.

INTRODUCTION

Cadmium naturally occurs at a concentration of 0.1–0.5 mg/kg in geologic formations and is commonly associated with zinc, lead, and copper ores. Non-ferrous metal mining and refining, batteries, manufacture and application of phosphate fertilizers, fossil fuel combustion, and waste incineration and disposal are the main anthropogenic sources of cadmium in the environment (ATSDR, 2012). Zinc, on the

other hand, is one of the most common elements with a wide array of applications including metals and metallurgy, bronze, galvanizing applications, paints, ceramics, wood preservation, dyes, topical lotions, creams and so on. Most zinc enters the environment as the result of mining, purifying of zinc, lead, and cadmium ores, steel production, coal burning, and burning of wastes (ATSDR, 2005).

The objective of this study was to assess the metal removal capacity of 9.5 mm minus steel slag fines (SSF) in a column configuration for several metal suites, based on the significant immobilization capacity of the SSF media determined previously in batch TCLP and SPLP leaching experiments (Grubb et al 2010a,b; 2011, 2014). Columns packed with SSF media and were then permeated with metal salt solutions for up to a 100 pore volumes (PVs) at rates consistent with groundwater flow conditions. There was also interest in determining if the metals could then be subsequently recovered, so acid neutralization capacity (ANC) testing of Cd- and Zn-spiked SSF media (10,000 mg/kg each) was completed using the approach outlined by Isenberg and Moore (1992), which is a predecessor for the new USEPA Method 1313.

MATERIALS AND METHODS

SSF media and reagents

The SSF media were characterized as freshly crushed slag particles resembling a SP type soil (9.5 mm minus fraction) by the Unified Soil Classification System (USCS) with <5% passing the 0.075 mm sieve. More details on the physical and chemical characteristics of the SSF media can be obtained from Grubb et al (2011) and will not be repeated here.

The cadmium and zinc salts used for experimentation were: $CdCl_2$ (99.4% purity) and $Zn(NO_3)_2 \cdot 6H_2O$ (99.9% purity), both available from Fisher Scientific (Atlanta, GA). The metal solutions were prepared by dissolving each salt of the corresponding metal in de-ionized (DI) water. Based on the prior thresholding work (Grubb et al 2010a,b), the metals dosing was set at 125% of the metals uptake capacity of the SSF media to promote breakthrough prior to the 100 PV test duration. Accordingly, the target concentrations for Cu and Ni were the aqueous equivalent of 12,500 mg/kg (675 mg/L) based on a 20:1 liquid:solid ratio. Data for the control column appears in Grubb et al (submitted).

Column Experiments

A description of the experimental columns is provided by Grubb et al (submitted). Briefly, the column size was determined in accordance with ASTM D4874 which limits the maximum particle diameter of the material to 1/10 of the inside diameter of the column. As such, the inside diameter was set at 10.2 cm (4 in.). Based on the aspect ratio (H/L) considerations, the compacted height of SSF in the column was 30.5 cm (12 in.). Additionally, an overall column length of 36.8 cm (14.5 in.) was selected to accommodate a 5 cm (2 in.) long influent reservoir placed at the bottom of the column to promote uniform flow.

The columns were packed with approximately 5 kg of dry SSF to achieve a minimum 95% of relative compaction of maximum dry density (MDD) based on the Standard Proctor method (ASTM D698). The exact weight of each packed SSF column and its open PVs (n~0.385 ave) are presented in the summary figures.

In order to simulate groundwater flow conditions in the laboratory study, an average groundwater velocity of 0.00092 cm/sec (950 ft/year) was used, which can be easily accommodated in a poorly-graded sand (SP) under a hydraulic gradient of 0.001 to 0.0001 m/m. The average flow rate corresponded to a volumetric injection rate of 4.5 mL/min and an average column retention time of approximately 3.5 hours.

The effluent solutions were sampled at pre-established time intervals and the total volumes of the permeated solutions were recorded. The pH of the effluent was recorded using an Accumet AR20 pH–meter. All samples (single replicates) were stored in the refrigerator at a temperature of 4°C before they were analyzed for metals by ICP-OES.

Sample Preparation for ANC tests

To gauge the ability of SSF to immobilize each heavy metal, SSF was intentionally and individually spiked with 10,000 mg/kg of the target metal, based on a 20:1 liquid:solid ratio. Aqueous metal solutions were individually prepared by dissolving the corresponding salt in de-ionized water to achieve each target dose depending on the metal (see above). The SSF material was wetted with spiked water and mixed with a stainless steel spoon to achieve a moisture content of approximately 16%. The spiked SSF material was then stored in sealable plastic bags and allowed to mellow for approximately 30 days (some minor carbonation may have occurred). After mellowing, all the samples were air-dried and used for analytical testing.

ANC procedure

ANC tests were conducted for control (raw SSF; see Grubb et al 2010a) and metalspiked SSF samples. The ANC test procedure was based on the Generalized Acid Neutralizing Capacity test (Isenburg and Moore, 1992). The procedure consisted of equilibrating the soil samples to increasing equivalents of acid per kilogram of dry soil. Specifically, 6.5 g dry weight of each sample was placed in a series of 130 mL bottles. For all samples, incremental amounts of 15.8 N nitric acid (HNO₃) were added to the sample (total liquid volume 130 mL), using a liquid:solid (L:S) ratio of 20:1. The resultant slurries (in triplicate; A to C) were tumbled in a standard TCLP rotating extractor for 48 hours. The supernatants were then filtrated through a 0.45 μ m nylon membrane filter, and the pH of the leachate was recorded using an Accumet AR20 pH–meter. All samples were stored in the refrigerator at a temperature of 4°C before they were analyzed by ICP-OES.

Modeling

To determine if the release of metals was solubility controlled (aqueous system), the concentration-pH behavior of each heavy metal was simulated using Visual

Minteq, Version 2.61 (David and Allison, 1999). The target dose of each heavy metal was used as the control concentration (Co), e.g., 500 mg/L.

The aqueous database of Minteq was augmented with the aqueous data of the relevant species cited from literature. Table 1 presents the aqueous reactions used to determine Me-H₂O solubility curves in Minteq, in the absence of atmospheric carbon dioxide. The solubility curves for different elements obtained from the Minteq model were plotted with the experimental data (see below). It is worth noting that all Minteq simulations conducted herein were run for pure systems and did not consider complex phenomena due to multi-element or multi-mineral systems such as the ones at hand. For example, Grubb et al (2011) shows the mineral phases of the SSF media determined using quantitative x-ray powder diffraction. Also, adsorption modules were also not considered in the simulation runs.

Table 1: Aqueous reactions used to determine the Me-H₂O solubility curves in MINTEQ

Aqueous Reactions	log K
$Cd^{2+} + H_2O = CdOH^+ + H^+$	-10.097^{a}
$Cd^{2+} + 2H_2O = Cd(OH)_{2(aq)} + 2H^+$	-20.294^{a}
$Cd^{2+} + 3H_2O = Cd(OH)_3^{-} + 3H^{+}$	-33.3 ^a
$Cd^{2+} + 4H_2O = Cd(OH)_4^{2-} + 4H^+$	-47.288^{a}
$2Cd^{2+} + H_2O = Cd_2OH^{3+} + H^+$	-9.397^{a}
$Cd^{2+} + 2H_2O = HCdO_2^{-} + 3H^{+}$	-33.34 ^b
$Zn^{2+} + H_2O = ZnOH^+ + H^+$	-8.997^{a}
$Zn^{2+} + 2H_2O = Zn(OH)_{2(aq)} + 2H^+$	-16.894^{a}
$Zn^{2+} + 3H_2O = Zn(OH)_3^{-} + 3H^{+}$	-28.391 ^a
$Zn^{2+} + 4H_2O = Zn(OH)_4^{2-} + 4H^+$	-41.188^{a}
$2Zn^{2+} + H_2O = Zn_2(OH)^{3+} + H^+$	-8.997^{a}

^aVisual Minteq ver 2.61; ^bPourbaix, 1966.

RESULTS & DISCUSSION

Cd Column

Figure 1 shows the dissolved and total concentrations of Cd and pH of the effluent from the packed SSF column. The influent pH of the Cd laden solution was approximately 7.25. The test results for the Cd suite column indicated that the column breakthrough occurred at approximately 13 PVs, based on total Cd concentrations versus the DL. The dissolved Cd concentrations were always below the DL through to test completion, while the measured total concentrations exceeded the TCLP-Cd criteria at about 20 PV, and gradually increased to 200 mg/L at 100 PV. This is still less half of the injected concentration.

From the dissolved concentration perspective, the SSF packed column was more efficient in removing more overall Cd than predicted by the batch studies



FIG 1. Cd effluent concentrations and pH from a packed SSF column (v_{ave} = 0.00092 cm/sec).



FIG 2. Zn effluent concentrations and pH from a packed SSF column ($v_{ave} = 0.00092$ cm/sec).

(Grubb et al. 2010a) which was already at 99%, as C/C_o was greatly suppressed (~0.02 max.) up to 100 PVs. The real issue from a practical standpoint to increase the design life of the packed SSF column is what to do about the total (or suspended) concentrations. One approach to immobilize all Cd (e.g. totals), would be to use a sand column in series after the SSF column to trap the suspended solids. Based on the insolubility of otavite (CdCO₃) above pH 8, a carbonate sand would likely be both very effective and preferred. Both media (SSF, carbonate sand) are readily available and cost effective.

Zn Column

Figure 2 shows the dissolved and total concentrations of Zn and pH of the effluent from the packed SSF column. In influent pH of the Zn laden solution was approximately 5.8. The test results for the Zn suite column indicated that the initial column breakthrough occurred at approximately 21 PVs (vs DL). The USEPA secondary drinking water criteria of 5 mg/L was exceeded at about 30 PV based on totals, whereas complete breakthrough occurred at about 80 PV (i.e. $C/C_o=1$).

Since Zn in pure water experiences its minimum solubility at approximately pH~9 (as will be shown below) the persistently elevated pH (~12.5) in the packed SSF column meant that the Zn was not efficiently immobilized. This points to the alternate possibility of using blast furnace slag fines (BFF) as a filter media given its natural pH (~11; Grubb et al 2012) is much closer to that where the solubility of Zn is minimized (a somewhat greater natural solid phase pH is desired to account for the acid solution).

ANC Testing

Figure 3 shows the ANC plot for Cd, which expresses the Cd concentrations as a function of pH in the SSF media based on the 10,000 mg/kg spike (e.g. 500 mg/L as maximum soluble concentration based on 20:1 L:S ratio) against the detection limit (DL) and the USEPA TCLP-Cd criteria. A representative titration curve for SSF media is reported by Grubb et al. (2011). The Cd-H₂O solubility curve simulated using MINTEQ is also shown, having a Cd insolubility region beginning at pH=8. Cd is also shown to be amphoteric in that the solubility begins increasing again at approximately pH 12 which does not occur in an open system—the curve remains flat as CdCO₃ is insoluble above pH 8-9.

From approximately $pH\sim5.5$, Cd concentrations in the SSF media are suppressed well below the theoretical solubilities. Above approximately pH 7 (based on data interpolation), the SSF media has effectively immobilized the equivalent of 10,000 mg/kg while passing the TCLP criteria. Above $pH\sim9$, Cd was essentially non-detectable.

Figure 4 shows the ANC plot for Zn. Zinc behavior appears to be largely pH controlled, and the relative proximity of the Zn concentrations in the SSF media to the theoretical water solubility curve suggests that the SSF media does not significantly suppress the Zn concentrations, they are merely pH controlled. Above $pH\sim10$, the SSF media shows some increased immobilization above straight pH



FIG 3. ANC-derived total Cd concentrations equilibrated with SSF media for a 10,000 mg/kg Cd(II) spike.



FIG 4. ANC-derived total Zn concentrations equilibrated with SSF media for a 10,000 mg/kg Zn(II) spike.

CONCLUSION

Packed column testing using steel slag fines (SSF) media illustrated the significant ability of this granular media to immobilize approximately 750 mg/L Cd, and to a lesser degree Zn, owing to its amphoteric pH behavior. At groundwater flow rates on the order of 1 m/day, dissolved Cd concentrations were essentially non-detect for the entire 100 PV test duration, whereas the total (suspended) concentrations reached about 200 mg/L by test completion. In actual practice, the use of sand filters immediately downgradient of the packed SSF column would resolve the suspended solids issue.

The batch ANC testing for Cd and Zn using 500 mg/L equivalent dosing levels mirrored the results of the packed column tests. Cd concentrations were suppressed by the SSF media below the predicted water solubility over a broad range of pH, whereas Zn appeared to be primarily pH controlled.

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REFERENCES

- ATSDR (2005). *Toxicological Profile for Zinc*, U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, Atlanta, GA, September, 352 pp.
- ATSDR (2012). *Toxicological Profile for Cadmium*, U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, Atlanta, GA, September, 487 pp.
- David, S.B., and Allison, J.D. (1999). *Minteqa2, An equilibrium metal speciation model: User's manual 4.01.* Environmental Research Lab., USEPA, Athens, GA.
- Grubb D.G., Wazne, M., and Jagupilla, S.C. (2010a). "Metals immobilization using slag fines." *Protection & Restoration of the Environment X*, Corfu, Greece, July 5-9, pp.8 (CD-ROM).
- Grubb, D.G., Wazne, M., Jagupilla, S.C., and Malasavage, N.E. (2010b). "Arsenic immobilization using slag fines," Protection & Restoration of the Environment X, Corfu, Greece, July 5-9, pp.8 (CD-ROM).

- Grubb, D.G., Wazne, M, and Malasavage, N.E. (2010c). "Characterization of slag fines for use as a dredged material amendment," *GeoFlorida 2010: Advances in Analysis, Modeling and Design*, Geotechnical Special Publication No. 199, D. Fratta, A.J. Puppala, and B. Muhunthan (eds.), ASCE, pp. 10.
- Grubb, D.G., Wazne, M, Jagupilla, S.C., and Malasavage, N.E. (2011). The beneficial use of steel slag fines to immobilize arsenite and arsenate: Slag characterization and metal thresholding studies, *ASCE J. Hazardous, Toxic and Radioactive Waste*, 15(3), 130-150.
- Grubb, D.G., Jagupilla, S.C. and Wazne, M., (submitted). "Simultaneous immobilization of copper (Cu), nickel (Ni) and lead (Pb) using Steel Slag Fines," *Geo-Chicago 2016*, pp.8.
- Isenberg, J., and Moore, M. (1992). "Generalized acid neutralization capacity test, stabilization, and solidification of hazardous, radioactive, and mixed wastes." ASTM STP 1123, T. M. Gilliam and C. C. Wiles, eds., Vol. 2, ASTM, Philadelphia, 361–377.
- Pourbaix, M. (1966). *Atlas of electrochemical equilibria in aqueous solutions*. Oxford, New York, Pergamon Press.