Heavy Metals Sorption by Drinking Water Treatment Byproduct in Jar Tests

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ABSTRACT: Heavy metals contaminants include lead, chromium, arsenic, zinc, cadmium, copper and mercury all of which can cause significant damage to human health and the environment as a result of their mobility and solubility within groundwater. In the Midwest portion of the United States, soil and groundwater based lead, zinc, and cadmium are the prominent pollutants of concern. While remedial technologies exist for heavy metals pollution, the majority of these solutions are expensive to design, maintain, and install. Drinking water treatment waste (DWTW) is a currently landfilled, relatively pure, industrial waste byproduct composed almost entirely of calcium oxide produced during water purification processes. Measured doses of drinking water treatment waste were submerged in synthetic groundwater solutions containing 0.01, 0.1, and 1.0 millimolar concentrations of lead, cadmium and zinc in order to determine if this material could provide remedial measures for heavy metals. In addition, the geomechanical properties and chemical composition of the material were determined. Removal rates varied based upon internal and external water content as well as flocculant formation. However, all tests verify that the material is capable of heavy metals removal at relatively rapid rates. This data suggests that when entrained in a pervious matrix, the reactive nature of the byproduct sorbs ions in solution passing through the matrix.

1.0 INTRODUCTION

Historically, conventional soil remediation of heavy metals depended upon excavation and removal of the contaminated materials and the subsequent disposal of these materials off site. Excavation and disposal is a time consuming, expensive, and disruptive practice that only moved the problematic contaminants without remediation, and did little to reduce long-term exposure. For shallow groundwater contaminated with heavy metals the traditional method of pump and treat relies upon a system of extraction pumps or trenches which draw groundwater to the surface. The groundwater is then treated for heavy metals via chemical manipulation using granular activated carbon, air-stripping, activated sulfur, etc. or disposed of off-site in a similar manner as contaminated soil.

Traditional methods of heavy metals remediation do little to address the source of contamination in the vadose zone, do not remediate low permeability aquifers or aquifers at great depths, and do not adjust well to ground variability over a large site. The state of the art has now advanced to using an in-situ passive treated technology called permeable reactive barriers. Chemical manipulation of the groundwater that formerly took place above ground in pump and treat scenarios is inserted into the ground adjacent to the source of contamination. Groundwater flows freely through the barrier wall, and reacts with the materials contained within to form non-toxic and/or less mobile complexes or precipitates or is permanently sorbed within the reactive materials.

While effective, the design, capital costs of installation, and maintenance of permeable reactive barriers are significant. Ground conditions vary significantly between sites and the design adds significantly to capitol cost investments. Table 1 presents the comparison of costs for existing permeable reactive technology used to treat contaminated groundwater (EPA, 2001). The material costs vary in literature from $450 per ton to $1,500 per ton depending upon the material used, the pH required and the contaminants requiring removal, with an average of 397 tons used per application (EPA, 2001). On average the design costs were $130,000 for multi-stage reactive agents. The drinking water treatment waste cost estimates were determined by applying the average quantity of material reported for the reactive permeable barriers with an average cost of $125 per cubic yard for installation. Yearly operating costs for monitoring were assumed the same as zero valent iron. Although the costs reported are from 2001 and most definitely higher today, a relative comparison of costs suggests that drinking water treatment waste could be a highly desirable solution.

Table 1. Comparison of Permeable Reactive Barrier Technology (EPA, 2001)

Treatment Strategy	**Drinking Water Treatment Waste**	**Zero Valent Iron**	**Activated Persulfate**	**Pump and Treat**
Contaminants Treated	Particulate, heavy metals,	Heavy metals, chlorinated solvents, NAPLSs	Chlorinated Solvents, Polyfluorinated-alkalates	VOCs, Heavy Metals, Solvents, LNAPLs
Total Average Capitol Costs	$161,000	$730,000	$7,000,000	$4,900,000
Yearly Operating Costs	$120,000	$120,000	$360,000	$770,000
Average Years Operated	No data	6-10	8	6

Heavy metal solubility is highly dependent upon pH, and the removal process is driven also by the reactive material within the barrier. Metals removed by hydroxides include cadmium, chromium (3+), copper, iron, manganese, nickel, lead and zinc (EPA, 1987). Carbonate precipitation effectively remove nickel, cadmium, lead and zinc (EPA, 2001). Sulfide removal includes cadmium, chromium (6+), cobalt, copper, iron, nickel, silver, tin, and zinc (EPA, 2001). Many permeable reactive barriers contain multiple reactive agents or use a staggered multi-stage barrier to correct for the various contaminants in solution.

2.0 Background on Drinking Water Treatment Waste

Surface water treatment processes used by the majority of the United States in metropolitan areas rely on chemical flocculation and filtration to treat sufficient, quality drinking water to support their populations. These processes produce a waste sludge at a rate of 4% by volume of the overall water treated (Sanin et al, 2010) and account for 30 to 40% of the capital cost of the treatment plant, and are approximately 50% of the annual operating costs (Sanin et al, 2010).

Sludge is produced via settling following the chemical processes and are seldom dispersed as the material forms flocculants or flocs. Particles are dewatered into a semi-dry cake and then disposed. The United States produced approximately 7 million metric tons of lime based sludge from drinking water treatment alone in 2010 (Rodriguez et al, 2010). Disposal occurs either via landfill or open evaporating pits near the treatment facility (Nowasell and Kevern, 2014).

Table 2—Chemical Composition of DWTW (Nowasell and Kevern, 2014)

Specific gravity	2.41
Loss on ignition, %	42.59
CaO, %	43.93
SiO2, %	5.84
MgO, %	4.24
Al2O3, %	1.55
Fe2O3, %	0.78
SO3, %	0.31
K2O, %	0.20
P2O5, %	0.10

Note: Wt% < 0.1 are not listed.

Water treatment processes produce a solid sludge formed from particles that agglomerate into flocs (Vesilind, 1994). The flocculants are composed primarily of calcium oxide which is readily re-actable with heavy metals, especially in solution. The sludge contains a bulk water which is easily removed and a bonded water which remains with the floc. Nowasell and Kevern (2014) suggested that the bonded water includes interstitial water, vicinal water and water of hydration (Vesilind, 1994). Interstitial water is solution trapped within the internal pores of the floc. If the floc structure is disturbed or destroyed by drying, interstitial water may be freed to become bulk water. Vicinal water is bonded to the floc surface through hydrogen bonding (Moller, 1983). Hydration water is chemically bonded within the floc particles and can only be removed through thermal drying (Moller, 1983, Tsang et al, 1990). Removal or replacement of the interstitial water as well as the vicinal water with a solution containing a dissolved solute through sorption processes allows the floc particles to react with the dissolved solute in bulk solution (Nowasell and Kevern, 2014). Since water treatment is a very controlled process, the sludge produced is also relatively pure and uniform in nature. The composition of the drinking water treatment waste used here is identical to that presented in Nowasell and Kevern (2014) (Table 2).

3.0 MATERIALS CHARACTERIZATION

3.1 Chemical

The drinking water treatment waste materials used in this study were obtained from Water One in Kansas City, Kansas in as landfilled conditions. Bulk moisture content was approximately 53% on a dry weight basis (Moller, 1983). Specific gravity was tested using and was 2.43. This value is reported as the average of 5 repeated tested values obtained via pycnometer. Values of specific gravity reported in the literature are comparable at 2.62, 2.35 and 2.59 (Baker et al., 2005, Glysson, 1972, Ramer and Wang, 2000). Industrial drinking water treatment is a very rigorous process which appears to produce very slight variations in specific gravity for calcium based sludge. (ASTM, 2010). X-ray florescence (XRF) shows high calcium content with relatively low silicon, magnesium, and aluminum contents (Nowasell and Kevern, 2014) (Table 2). Scanning electron microscopy (SEM) showed conglomerations of calcium carbonate (Nowasell and Kevern, 2014). The pH of the sludge was 11.5 S/U and the cation exchange capacity was relatively high and was measured at of 15.42 cmol(c) kg(-1).

3.2 Geomechanical

In addition to chemical analysis of the drinking water treatment waste the materials were characterized for physical, mechanical and geotechnical properties in order to determine other applications for waste byproduct reuse. The total unit weight (γt), void ratio (e), and degree of saturation (S) of the samples were measured. Atterberg limits (ASTM, 2011b) of the sludge were determined using in situ and oven-dried waste. Standard and modified Proctor compaction tests were conducted on in situ sludge (ASTM, 2012a, ASTM, 2012b) as well as lab vane shear tests conducted (ASTM, 2013b). Consolidation testing was performed on relatively intact specimens (ASTM, 2011a) and permeability tests (ASTM, 2007b) were performed using in situ and dried and compacted specimens.

As seen in Fig. 1, the predominant weighted fraction of the drinking water treatment waste contained particles passing the #200 sieve (0.075 mm diameter), approximately 92% for dried material. Because the material is predominantly flocculants, the bulk samples were very difficult to sieve unless wet sieved. Wet sieving broke apart the flocs in a similar manner as oven drying which produced comparable particle size distributions (Figure 2). Both particle size curves yield a poorly graded fine material with coefficients of uniformity and coefficients of curvature equal to 9.1 and 1.5, respectively. Index properties yielded values of the liquid limit (LL) equivalent to 44, a plastic limit (PL) equal to 27 and a plasticity index (PI) of 17. These values are comparable to values reported in the literature (Glysson, 1972, Baker et al. 2005, Ramer and Wang, 2000). The geotechnical classification of this material is a low plasticity silt.

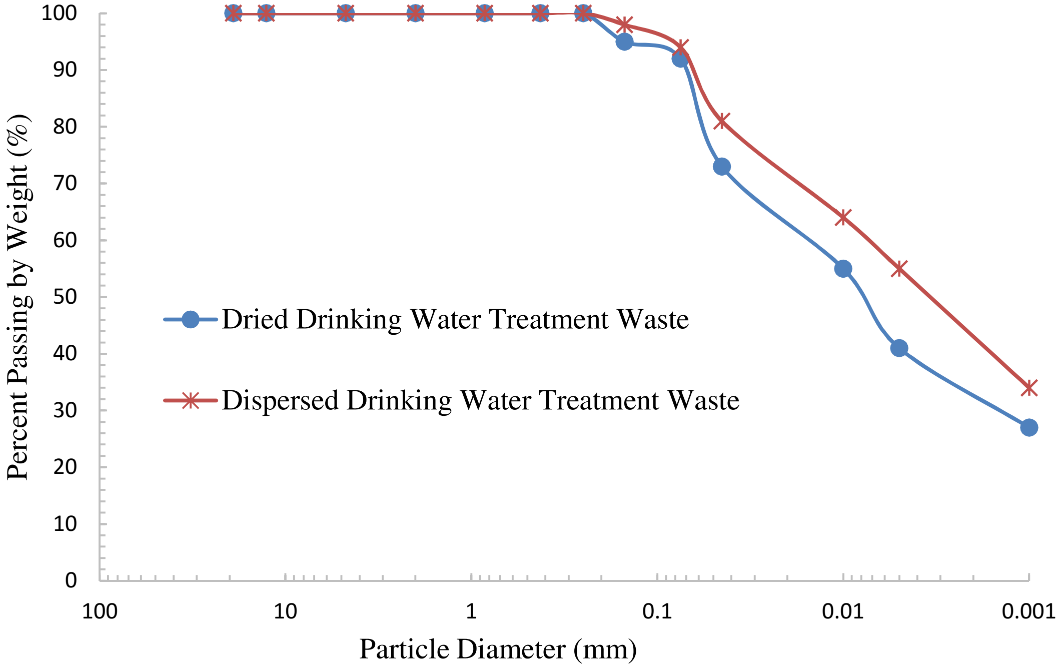

Figure 1 - Particle Size Distribution of Dispersed and Dried Drinking Water Treatment Residuals

Total unit weight, void ratio and degree of saturation were measured for samples obtained directly from Water One. Total unit weight (γ_t) varied from 12.3 to 18.5 kN/m^3, varying drastically between shipments. Void ratio of the samples was also variable and was between 2.5 and 1.2 depending. This could be a variation with the depth of embedment of the sample as obtained, but the depth of sampling was not provided by Water One. Total bulk saturation also was variable depending upon the sample state. Saturation was found to be between 75 and 98%. Again, this could be a product of the sampling technique or retrieval of the sample at various depth. Saturation and void ratio varied within the samples themselves which suggests depth of embedment within the lagoon or at least sampling methods controls these two properties. Optimum water content obtained from both standard and modified Proctor compaction tests yielded values of 35%. Maximum dry unit weight (γd) for standard and modified Proctor tests were 12.3 and 14.3 kN/m^3, respectively. Vane shear tests were conducted on approximately 10 samples. Both peak and residual undrained shear strength of the samples were measured and ranged between 20.5 and 58.2 kPa for peak strength. Residual strength ranged between 2.4 and 22.1 kPa. These values seemed to vary similarly to those of void ratio and saturation and could be a product of sampling methodology or depth of embedment.

Partially remolded consolidation tests were conducted on two samples in order to determine the compression index, recompression index and rate of consolidation. Values of the compression index ranged from a high of 0.710 to 0.555. Recompression index values were 0.022 and 0.034. Rate of consolidation was 0.044 and 0.022 cm^2/s for vertical effective stresses ranging from 5 to 2,500 kPa. Permeability was measured for three specimens using compacted standard Proctor procedures and falling head manometers. Average values of permeability (k) at optimum water content $2.5x10^{-5}$ cm/s. Permeability of the material representing in situ measurements was much lower and $1.11x10^{-6}$ cm/s. This could represent displacement of the bulk water and then an increasing resistance to flow due to interstitial forces within the flocculent.

In general, the chemical and geomechanical properties indicate a high calcite content and relatively high pH which suggest a strong probability of heavy metals reactivity. Moreover, it could be potentially used for buffering acidic soils produced in acid mine drainage (AMD). The waste material has a permeability which is greater than most aquifers which may allow for conversion to a permeability reactive barrier. While compaction and consolidation reduce permeability, the peak strength suggests the material could be used for barrier technologies.

4.0 JAR TESTING RESULTS

In order to determine if the drinking water treatment waste materials could react and treat groundwater containing lead, zinc, and cadmium the materials were jar tested. Samples were prepared according to typical laboratory practices and consistent throughout each iteration. DWTW was weighed to 25 grams of dose, ± 0.1 g, of tabulated values and gently stirred for a total of 5 minutes to provide an average sampling of material. Four reagent grade stock solutions were prepared from DI water thoroughly mixed with certified ACS grade reagents (chemical type and Fisher Scientific batch number follow: $CdCl_2$:142892, $PbCl_2$: MKBS4048V, $ZnCl_2$:152361) in uniform concentrations of 1.00, 0.10, 0.01, and 0.00 mM (Figure 2). Doses of drinking water treatment waste were placed in 1L HDPE bottles. Bottles were filled with 750 mL of solution with 3 replicates of each stock solution. One additional control stock solution was prepared without DWTW for each concentration. Jar tests were sealed and well mixed using magnetic stir bars on magnetic stirring tables. After 24 hours, the solutions were removed and 200 mL of solution was acidified the samples analyzed for chemical concentrations of cadmium, lead and zinc via ICP-MS EPA standard 200.8 testing methodology.

Removal rates varied for all solutes from highs of 100% at low concentrations to approximately 90% and follow a linear trend (Figure 2). The average removal rates for lead, cadmium and zinc at low concentrations were 100, 98, and 99%, respectively. Removal rates decreased, as would be expected, with increasing concentrations (Figure 2). At the mid range removal rates for lead, cadmium and zinc were 97, 94 and 95%, respectively. At the highest concentrations tested the removal rates for lead cadmium and zinc were 94, 90 and 90%, respectively.

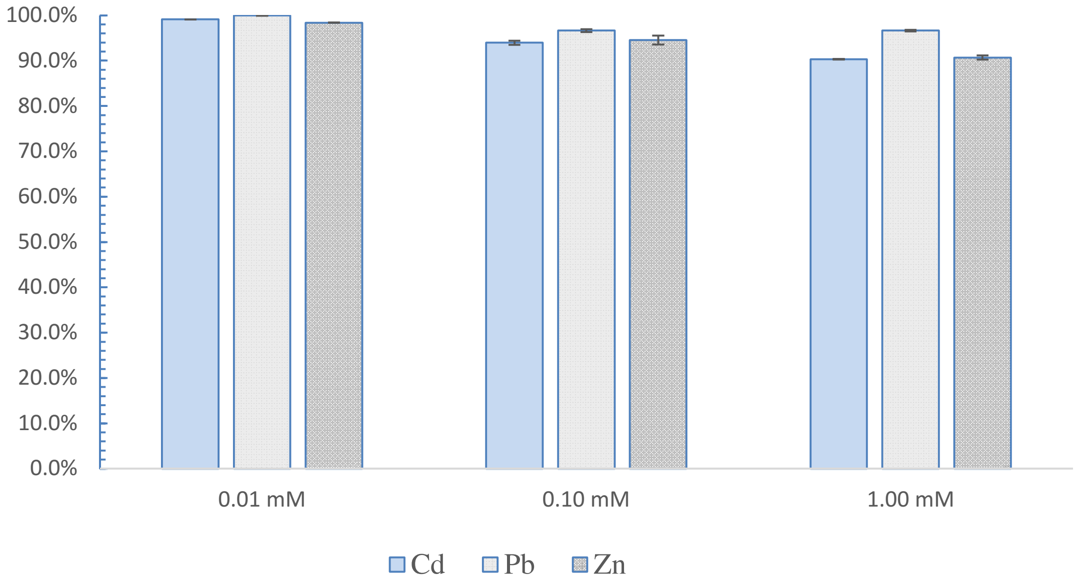

Figure 2- Removal Rates for Lead, Cadmium and Zinc for a 25 gram Dose of DWTW

A linear isotherm was developed for the drinking water treatment waste (Fig.3). Each experiment was duplicated under identical conditions. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

where C_0 and C_e (µg/L) are the liquid-phase concentrations of heavy metals at initial and equilibrium, respectively. V is the volume of the solution (L) and W is the mass of dry adsorbent used (g).

Adsorption isotherm describe how the adsorption molecules distribute between the liquid phase and the solid phase when adsorption reaches equilibrium. The amount of heavy metals adsorbed (q_e) has been plotted against the equilibrium concentration (C_e) as shown in Fig. 3.The R squared value for the trend line is 0.998, which suggests a one for one removal. A possible explanation for this one for one removal trend is that sorption processes are primarily surficial in nature. In order to determine if removal of the heavy metals was permanent we conducted basic column leach tests using neutral pH DI water. The material was flushed with 3 pore volumes of deionized water and the solutions analyzed for heavy metals concentrations via ICP-MS and EPA standard method 200.8. While significant dilution did occur, all values of cadmium, zinc, and lead were non-detectable at the 0.5 parts per billion detection limits of the machine. Column leach tests were chosen as groundwater rarely is influenced by pH's represented by TCLP tests.

In general the jar tests suggest that drinking water treatment waste is capable of heavy metals removal at concentrations found in typical AMD waste sites. Removal may be permanent based upon column leach testing. Further testing is needed to determine how to entrain the waste in a higher permeability structural skeleton.

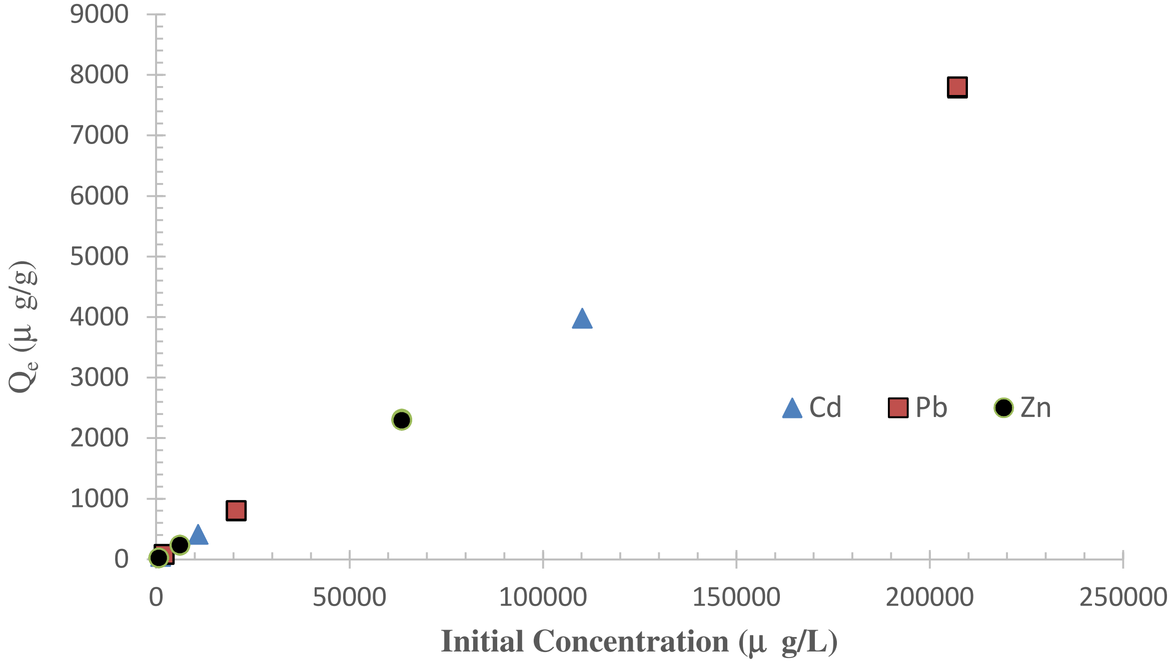

Figure 3- Linear Isotherm of Heavy Metals Removal

5.0 CONCLUSIONS

As a new application, drinking water treatment waste can be used as a remedial measure for typical mining waste sites contaminated with zinc, cadmium and lead. The ability to use large volumes of industrial waste by-product produced from water treatment processes creates a potential for creating a marketable product from a currently landfilled or land disposed of product. Removal rates are comparable to those of current technology and the technology would be much cheaper due to the nature of waste byproduct. The reaction rates for this material appear to be quite rapid, which translates into shorter treatment time, especially if the material is placed within a permeable matrix that allows for free flow of groundwater and maintains the reaction times needed for treatment. In order to design an optimal treatment technology, site specific jar tests and break through curves will be needed for ground conditions where installation may occur. Besides, high reactivity and heavy metals removal, the geomechanical properties of the drinking water treatment waste suggest that the material is relatively stable at depth with sufficient peak and residual strength for embedded depth of typical barriers technologies, as well as permeability The main performance properties tested suggest that the drinking water treatment waste is highly capable of heavy metals removal with little modification.

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