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Measurement of chemical leaching potential of sulfate from landfill disposed sulfate containing wastes

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ABSTRACT

A number of sulfate-containing wastes are disposed in municipal solid wastes (MSW) landfills including residues from coal, wood, and MSW combustion, and construction and demolition (C&D) waste. Under anaerobic conditions that dominate landfills, the sulfate can be reduced to hydrogen sulfide which is problematic for several reasons including its low odor threshold, toxicity, and corrosive nature. The overall objective of this study was to evaluate existing protocols for the quantification of total leachable sulfate from solid samples and to compare their effectiveness and efficiency with a new protocol described in this study. Methods compared include two existing acid extraction protocols commonly used in the U.S., a pH neutral protocol that requires multiple changes of the leaching solution, and a new acid extraction method. The new acid extraction method was shown to be simple and effective to measure the leaching potential of sulfate from a range of landfill disposed sulfate-containing wastes. However, the acid extraction methods do not distinguish between sulfate and other forms of sulfur and are thus most useful when sulfate is the only form of sulfur present.

1. Introduction

Many U.S. landfills that receive municipal solid waste (MSW) also receive a variety of non-hazardous industrial wastes and it is important to evaluate the impacts of these wastes on MSW decomposition as well as leachate and gas composition. Examples of wastes that are often disposed in MSW landfills and contain sulfate include ash from coal, wood and MSW combustion processes, and construction and demolition (C&D) waste. When sulfate-containing wastes are co-disposed with MSW in landfills, the sulfate may be reduced to form hydrogen sulfide (H_2S). The presence of H_2S in landfill gas is problematic for several reasons. First, it is corrosive to landfill gas treatment systems, which increases operation and maintenance costs for the landfill gas collection and control system. Second, it is toxic to humans, which presents challenges for occupational safety in enclosed areas at landfills such as subgrade elements of the leachate collection system (Selene and Chou, 2003; WHO, 2000). Levels of H_2S above 10 ppm in volumes (ppmv) are toxic. Third, H_2S has an extremely low odor threshold, 0.02–0.13 ppmv, and fugitive emissions may result in odors (Beauchamp et al., 1984; OSHA, 2005).

Efforts to reduce the emissions of SO_x to the atmosphere have resulted in the installation of flue gas desulfurization (FGD) processes to remove sulfur from combustion off-gas at both coal-fired power plants and MSW combustion facilities. SO_x is removed by the addition of either lime, or in some cases trona which is a sodium carbonate mineral. The result is a solid waste stream that contains either sodium or calcium sulfate. The sodium or calcium sulfate salts are present in different solid residue streams including FGD residue, fly ash that may or may not be combined with the FGD residue, and in the case of MSW combustion residue, a combined stream of bottom ash and fly ash.

Another source of sulfate-containing waste is C&D debris that may contain wallboard which consists of gypsum (i.e., $CaSO_4$). While the composition of C&D waste is highly variable, reports have estimated the drywall content in the range of 17–27% by weight (Cochran et al., 2007; EPA, 1998). In addition to whole C&D waste, a related waste stream is the fines fraction from C&D waste. C&D fines are generated when C&D waste is processed for recycling at material recovery facilities (MRFs). The C&D waste is typically processed through screens that allow material from ~2–7 cm to pass and the fines fraction includes small pieces of drywall, dirt, wood, and concrete. Anderson et al. (2010) reported that C&D fines received at eight Northeastern U.S. landfills contained

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from 0.2% to 12.0% sulfate. These C&D fines have been used as daily cover at landfills which avoids the excavation of off-site soil. Unfortunately, elevated concentrations of H_2S in landfill gas have been attributed to the use of C&D fines as daily cover (Anderson et al., 2010; Lee et al., 2006; Townsend et al., 2000).

Hydrogen sulfide is produced when sulfate is reduced by a microbially-mediated process in which degradable organic matter such as MSW or MSW leachate serves as the electron donor and sulfate serves as the electron acceptor. The sulfur is typically in the form of sulfate (SO_4^{2-}) but may also be in the form of elemental sulfur (S) or sulfite (SO_3^{2-}) (EPA, 1998; EPRI, 2008; Musson et al., 2008).

While the microbiology of H_2S production in landfills is well understood, the H_2S production potential of sulfate-containing wastes is not currently predictable. In the absence of an understanding of the H_2S production potential for specific sulfate-containing wastes, it is difficult to evaluate their impact on the landfill gas (LFG) system. To assess the H_2S production potential, it is necessary to develop a simple and reliable method to estimate the leachable sulfate content in a variety of sulfate-containing wastes. Acid extraction protocols described by the U.S. EPA (U.S EPA, 1996a) and ASTM (ASTM, 2007) are in common use in the U.S. These methods require the use of hot acid (ASTM) and HF (EPA), both of which have severe consequences in the event of an accident that results in some exposure. In addition to the acid extraction protocols, Musson et al. (2008) presented a water extraction procedure to measure the gypsum ($CaSO_4$) content of C&D debris. However, this procedure has not been evaluated for its efficiency on other sulfate-containing wastes and is labor intensive as it requires changing the leaching solution multiple times.

The overall objective of this study was to evaluate multiple protocols for quantification of the total leachable sulfate content from solid samples that are frequently disposed in landfills. Existing protocols published by the U.S. EPA (EPA Method 3050B), ASTM (ASTM D2492-02), and Musson et al. (2008) were compared to a new protocol described in this study.

2. Materials and methods

2.1. Experimental design

The protocols evaluated are summarized in Table 1 and include a method developed at NC State University (NCSU protocol), an ASTM method, a U.S. EPA method, and a method described by Musson et al. (2008) that has only been applied to C&D debris. With the exception of the Musson method, the methods rely on a concentrated acid but conditions vary. The U.S. EPA method uses a mixture of HCl, HNO_3 and HF over a period of about 18 h, while the ASTM extraction is only 30 min. As salts are more soluble at low pH, the acid extractions rely on increased solubility to extract sulfate. In contrast, in the Musson method, solids are extracted in deionized water, and the water is changed daily until it is shown that the dissolved sulfate, as measured by conductivity, is below its solubility. In this study, the Musson method was evaluated with both deionized water and synthetic sulfate-free leachate as the extract liquid.

Several factors motivated evaluation of an alternate extraction method including (1) the labor intensive nature of the Musson method, (2) the use of HF in the EPA method which is a particular safety concern, and (3) preliminary observations that the ASTM method at times resulted in seemingly low sulfate values. The NCSU method is in essence a modification of the Musson method in which the extraction is performed using HCl instead of deionized water. The acid dissociation constants (p*K*a) for H_2SO_4 are −3 (p*K*a1) and 2 (p*K*a2) (Snoeyink and Jenkins, 1980). Thus, at pH 1, sulfate will be in the form of HSO_4^- and sulfate will dissolve without being limited by its solubility in water. This eliminates the need to change the extraction fluid as in the method described by Musson et al. (2008). All extraction methods were applied to a range of sulfate-containing wastes (Table 2) and the details of each extraction method are described below.

2.2. Materials

The wastes tested in this study are described in Table 2. The term “coal combustion products” is typically used to represent ash from coal combustion. However, this is an over simplification in the context of sulfate content as there are multiple ashes that can be produced, depending on the configuration of the air pollution control equipment, and therefore multiple scenarios with respect to sulfate concentration. As listed in Table 2, fly ash, bottom ash, FGD residue, and a combination of FGD residue and fly ash were tested separately. All materials tested were dried in an oven at 75 °C, ground in a Wiley to pass a 1 mm screen as needed, and redried.

2.3. Extraction Methods

For the NCSU acid extraction method, 10 g of solid sample were placed into a 2-L plastic bottle with 1.95-L of deionized water and 50-mL of 10 N HCl (final HCl concentration is thus 0.25 N). Bottles were then placed on a shaker table at 100 rpm at ambient temperature for 5 days as sulfate concentrations were shown to stabilize within 5 days in preliminary work that is presented with the Results. After shaking, a 50 mL sample was filtered through a 0.45 μm syringe filter and then analyzed for sulfate (and/or sulfite) by ion chromatography (IC), and total sulfur by inductively coupled plasma (ICP). Samples were frozen prior to analysis.

The ASTM method (ASTM, 2007) was conducted by a commercial laboratory. Briefly, 2–5 g of waste were placed in a 250-mL flask with 50 mL HCl (12 N). The extraction was carried out on a hotplate and boiled gently for 30 min while stirring. Instead of determining the sulfate sulfur gravimetrically as in the ASTM protocol, the total sulfur in the extract sample was analyzed by ICP and reported as sulfate.

Table 1
Comparison of chemical extraction methods for leachable sulfate.

Extraction method	Extraction protocol	
	Reagents	Extraction conditions
NCSU acid extraction	HCl (10 N)	Shake at 100 rpm at ambient temperature for 5 days
ASTM (standard method D2492–02) acid extraction	HCl (12 N)	Stirred on hotplate and boiled gently for 30 min
U.S. EPA (method 3050b) acid extraction	Aqua regia (3:1 ratio of HCl:HNO_3), H_2O_2 (30%), and HF (29 M)	Digested in Aqua regia overnight at ambient temperature and heated on a sand bath with other reagents at 95 °C for 9 h
Musson method	Deionized water or synthetic sulfate free leachate (pH 7.0–7.2)	Shake at 100 rpm at ambient temperature for 30 min with repeated replacement of extraction reagent