Calorimeter Test for Aluminum Production Waste Reactivity

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ABSTRACT: Secondary aluminum production wastes (APWs) are frequently disposed in dry form in Subtitle D non-hazardous waste landfills, where unfortunately they can react adversely with leachate. APW reactions can cause sustained temperature increases that inhibit normal anaerobic biodegradation and potentially reduce the longevity of the waste-containment system. A constant pressure calorimeter test procedure is outlined that can simulate an APW reaction in a landfill environment to evaluate reactivity. The paper discusses the influence of typical APW composition and particle gradation on temperature increase. A procedure to calibrate the calorimeter is recommended.

INTRODUCTION

Aluminum is the most widely used nonferrous metal in the world with applications in world markets such as aerospace, marine industries, transportation, packaging, food, construction, electricity, and medicine. Aluminum is produced by two different routes: primary aluminum production from bauxite ore and secondary production from recycling aluminum from process scrap and used aluminum products. In 2006, the U.S. metal producing sector manufactured approximately 2.28 million Mg of primary aluminum and 3.54 million Mg of secondary aluminum (Menzie et al. 2010) so secondary aluminum now provides more aluminum than primary production. Recycling aluminum requires only about 5% of the energy required for primary aluminum production yet it yields the same quality aluminum as primary smelting (Kammer 1999; Das et al. 2006). As a result in 2003, aluminum recycling in the United States saved more than 1.7×10^{11} kilowatt hours (0.57 quad; BCS, Inc. 2007) of energy or equivalent to 32 600 MW coal-fired power plants. In addition, secondary aluminum production emits 17 times less air pollution, generates between 5 to 9 times less solid waste, and consumes 35 times less water than primary aluminum processing (Drossel et al. 2003). In short, recycling aluminum is more sustainable than primary aluminum production and will continue to grow as more aluminum is consumed.

The wastes produced from aluminum recycling, however, can be problematic when they contain even small amounts of metallic aluminum. Metallic aluminum can oxidize rapidly in acidic or caustic solutions to produce heat and hydrogen gas, as indicated in

Reaction 1. Depending on the aluminum production waste (APW) composition and landfill environment, the heat of reaction can cause sustained temperature increases that inhibit normal anaerobic biodegradation and impact engineered components, e.g., service life of composite liner system, gas vents and wells, and leachate collection systems. In addition, APWs can react adversely with liquids to produce flammable and toxic gases such as hydrogen, ammonia, methane, and hydrogen sulfide. As a result, disposal of such wastes in Subtitle D non-hazardous waste landfills has caused problems requiring expensive remedial efforts (Calder and Stark 2010; Stark et al. 2012; Jafari et al. 2013).

$$Al + 3\,H_2O\,(l) \rightarrow Al(OH)_3 + 3/2\,H_2\,(g) \qquad \Delta H = -415 \text{ kJ/mol} \qquad (1)$$

The potential for exothermic reactions between APW and landfill leachate necessitated development of a simple test to quantify APW reactivity and potential temperature increases after disposal. A constant pressure calorimeter test was developed to simulate an APW reaction in a landfill. The test procedure enables landfill operators and APW generators to quickly evaluate maximum temperature. This paper presents results of the constant pressure calorimeter calibration and preliminary tests performed on APW.

TYPICAL APW COMPOSITION

APW contains variable amounts of metallic aluminum (Al) and aluminum compounds, such as aluminum carbide (Al_4C_3), aluminum nitride (AlN), and aluminum oxide (Al_2O_3) mixed with other substances such as salts and impurities. Types of APW are also referred to as “dross,” “white dross,” “black dross,” and “salt cake.” These terms refer to the amount of aluminum present and the morphology of the wastes raked from the surface of molten aluminum during primary and secondary processing and purification (Manfredi et al. 1997).

White dross is generated at primary aluminum smelters, extruding plants, sheet mills, foundries, and dies casters (Kulik and Daley 1990). Because these facilities operate without fluxing, white dross skimmed from the furnaces have a grey or metallic white color (Figure 1(a)) and consist of high metallic Al content (15-70%) (Kulik and Daley 1990). Black dross is created during melting of scrap and recycled aluminum with a salt flux (Figure 1(b)). At high molten temperature, the added salt flux becomes dark colored and thus is referred to as “black dross.” The content of the black dross varies depending on the scrap type being charged and the processing conditions, but usually varies from 12 to 18% metallic Al, 40-55% salt flux mixtures, and 20-50% Al_2O_3 (Kulik and Daley 1990). To capture metallic aluminum in white and black dross, they can be melted in a rotary furnace with additional salt flux. The discharge from this process is salt cake. The composition of salt cake depends on the black dross, but it often contains 3–5% metallic Al, 15–30% Al_2O_3, 30–55% sodium chloride (NaCl), and 15–30% potassium chloride (KCl), and depending on the scrap type may contain carbides, nitrides, sulfides, and phosphides (Peterson 2002). Almost 726,000 Mg (800,000 tons) of salt cake is annually landfilled in the U.S. (Sreenivasarao et al. 1997) and is usually disposed in landfills in solid blocks (Figure 1(c)). Baghouse dusts consist of particulates produced during salt cake hammering and crushing and furnace off-gas. These wastes may contain cadmium (Cd) and lead (Pb) above the limits of the EPA Toxicity Characteristics Leaching Procedure (TCLP) test (Hwang et al. 2006; Stanforth 1991) and are frequently disposed of in landfills (Figure 1(d)). Because lime is injected into the foundry ductwork to protect against sparks and improve dust collection, baghouse dusts are a source of alkalinity and aluminum in landfills, which makes this material highly reactive.

(a) white dross (a) black dross

(b) salt cake (c) baghouse dust

FIG. 1. Types of aluminum production waste

ALUMINUM REACTIVITY

Recent case histories indicate that aluminum oxidation (see Reaction 1) can release large amounts of heat and possibly flammable hydrogen gas in the waste (Calder and Stark 2010; Stark et al. 2012). Aluminum naturally forms a thin surface layer of aluminum oxide on contact with oxygen in the atmosphere through a process called oxidation. This surface layer creates a physical barrier to corrosion or further oxidation in most environments. There are several possible mechanisms, however, that can still facilitate aluminum oxidation to occur: (1) mechanical activation, e.g., ball milling, which disrupts the protective oxide layer; (2) AlN, calcium oxide (CaO), and magnesium oxide (MgO) hydrolyze in solution to increase pH and thus corrode the protective oxide layer; (3) KCl and NaCl salts can pit and rupture the oxide layer; (4) hydrogen bubbles in-between aluminum and the oxide layer break apart oxide layer (Petrovic and Thomas 2008).

Laboratory experiments by Huang et al. (2011) and David and Kopac (2012) indicate that APW temperature increase is a function of environmental temperature and APW particle size. Increasing the environmental temperature leads to an increase in reaction rate and thus maximum temperature. For example, Huang et al. (2011) report an average 7°C increase in temperature response for experiments conducted at APW temperatures of 37°C and then 50°C.

Figure 2 shows particle size distributions for a typical black dross and recycled APW. Recycled APW is a post-process treatment that secondary aluminum generators perform that ball-mills, crushes, and then sieves to collect free metallic Al fines. As a result, recycled APW in Figure 2 is uniformly graded with d_{50}~0.2 mm while black dross is slightly uniform. Recycled APW has similar gradation to fine sands whereas black dross is similar to sand with gravel. APW particle size influences temperature response and hydrogen production in Reaction (1) because reducing particle size, e.g., by ball-milling, liberates aluminum fines from the salt residue.

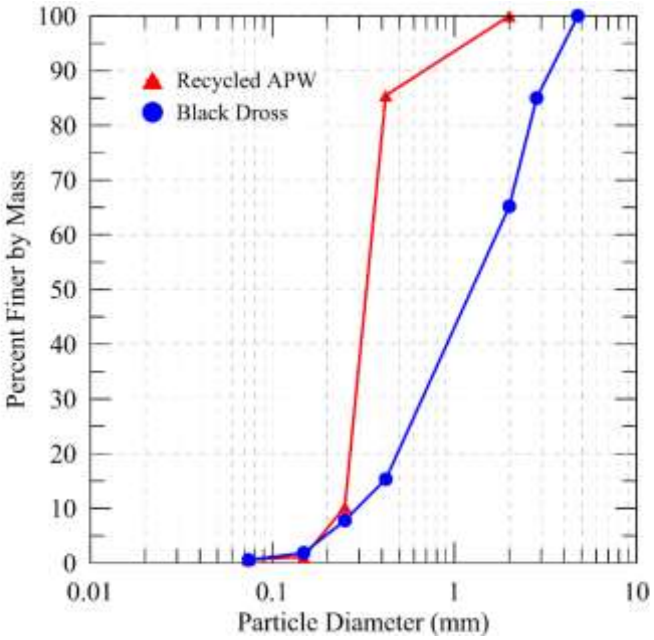

FIG. 2. Particle size of APW

Figure 3 shows temperature response of APW at particle sizes of <0.25 mm, <2 mm, and <9 mm from three different facilities. Tests were performed at ambient temperature of 37°C. The APW samples from Facility 2 consists of 8% metallic Al content which yielded temperatures of 41.1°C, 46.2°C, and 133.2°C for the three particle sizes tested. Because metallic Al is conglomerated with salts and other residues, the smaller particle sizes result in liberation of the aluminum to react with the alkaline liquid. As a result, the maximum temperature increases with decreasing particle size.

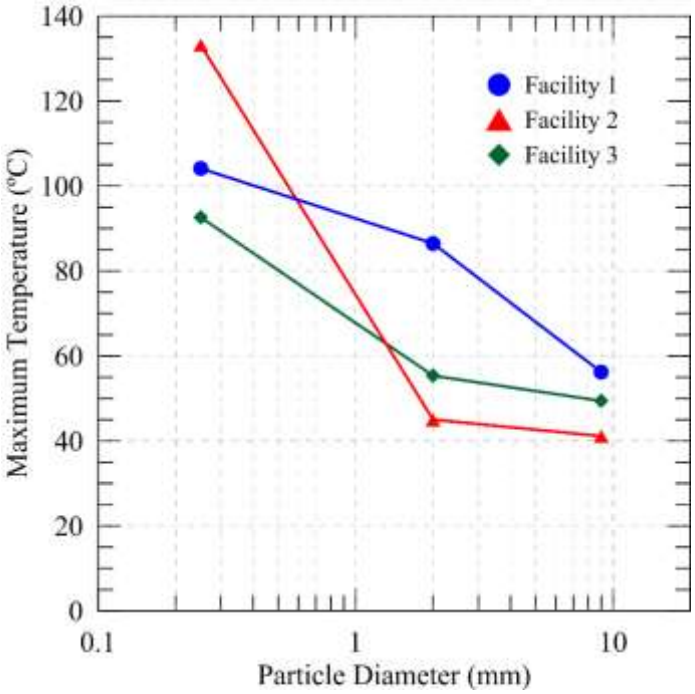

FIG. 3. Effect of particle size (data from Huang et al. 2011)

REACTIVITY TEST

A solid waste is deemed hazardous in two ways either of which would make it ineligible for disposal in a Subtitle D landfill. First, 40 CFR Sec. 261, Subpart D explicitly lists the materials that are defined as hazardous and these materials cannot be placed in a Subtitle D regulated landfill. Second, if a waste exhibits any one of the four characteristics of a hazardous waste, i.e., ignitability, corrosivity, reactivity, or toxicity, the waste is classified as a hazardous waste under 40 CFR Sec. 261, Subpart C and cannot be placed in a Subtitle D facility. Because of aluminum related problems observed in Subtitle D landfills, e.g., Brantley, Countywide, Wabash Alloys, Huelger Kronquist, Red River Aluminum, Washington State-Ramco, etc., a new test and criterion was developed herein to determine whether or not an APW displays the reactivity characteristic under 40 CFR Sec. 261, Subpart C and thus whether the APW should be considered a hazardous waste.

Temperature Criteria

One of the most important parameters used to assess whether or not a Subtitle D landfill is operating normally is temperature (Hanson et. al. 2010; Crutcher et al. 1982) because it reflects the type of anaerobic bacteria present. Anaerobic decomposition proceeds within three temperature ranges: the psychophilic range with temperatures less than 20°C; the mesophilic range with temperatures between 20° and 45°C; and the thermophilic range with temperatures greater than 45°C (Kotze et al. 1969). The anaerobic processes that regulate methane generation occur best within a temperature range of 40^{o} to 42^{o}C for mesophilic bacteria (Hartz et al. 1982). Zinder et al. (1984) suggest thermophilic methanogenesis is optimal at temperatures ranging between 55°C and 60°C. Under normal conditions, the temperature of solid waste and landfill gas generated by an MSW landfill ranges between 25^o and 45^oC (77^o to 113^o F) (ASTDR 2001). New Source Performance Standards (NSPS) (40 CFR 60.753) require that a Subtitle D landfill demonstrate that combustion is not occurring within the waste mass if a gas wellhead temperature exceeds 55°C (131°F). Based on these requirements, the reactivity test was developed to control exothermic reactions so landfill temperatures remain below 65°C (149^oF) to permit waste decomposition and prevent elevated temperatures from impacting engineered components (composite liner system, gas vents and wells, and leachate collection system piping and operation).

Constant Pressure Calorimeter

Calorimetry is the quantitative measurement of heat required or evolved during a chemical process (Chang 2005). The proposed constant pressure calorimeter is shown in Figure 4 and is an instrument for measuring the heat of reaction during a defined process. In a constant pressure calorimeter, the reaction between an alkaline solution and APW will generate heat. The heat of reaction (q_{rxn}) is a thermodynamic unit of measurement for calculating the amount of energy (kilojoules; kJ) per mole either released or produced in a reaction.

$$q_{rxn} = m_{residue}\, C_{p,residue}\, \Delta T \qquad (2)$$

where T is temperature (°C) and the change in final and initial temperature is ΔT, $m_{residue}$ is mass of alkaline solution and APW (g), and $C_{p,residue}$ is the specific heat (J/g·°C). $C_{p,residue}$ is a weighted average between specific heats of water (4.186 J/g·°C or 1 cal/g·°C) and APW (0.837 J/g·°C).

Calorimeter Equipment and Procedure

The test equipment is comprised of an insulated calorimeter, an alkaline solution (such as sodium hydroxide; NaOH), thermometer, and release valve. Although aluminum is amphoteric, an alkaline solution simulates field conditions because Huang et al. (2011) report the pH of APW is about ~10.4. Typical insulated calorimeters use glass thermal insulation layers and are tightly sealed using a rubber stopper. A variety of NaOH concentrations, e.g., 20% w/w, can be purchased from a chemical supply company or made using NaOH pellets. This alkaline solution must be strong enough to ensure that the protective oxide layer is corroded and the aluminum is reacted during the test. This will minimize the reaction time and simulate a representative landfill scenario, i.e., middle third of landfill where heat loss is minimal. A release valve serves to release gas pressure generated by the APW reaction. As a result, it is anticipated that this test can be performed quickly at a secondary processor or a landfill weigh station (Figure 5).

The general test procedure consists of a representative specimen of APW that is weighed and placed inside the insulated constant pressure calorimeter (see Figure 4). A predetermined volume of NaOH solution is then added to the APW and quickly mixed by stirring or swirling. The calorimeter is quickly sealed tightly by placing the rubber stopper in the top of the container to prevent heat loss. The change in temperature inside the calorimeter is monitored by inserting a thermometer through the rubber stopper into the saturated APW. The calorimeter should be placed in a pan or on the ground surface because the pressure generated can be great enough to blow the rubber stopper off and cause fluid to be ejected from the calorimeter. A release valve is necessary to release pressure build-up from gas production. In addition, Jafari et al. (2014) found that a strength of 4M (molarity; mole/L solution) NaOH is sufficient to react the metallic Al and prevent forceful gas pressures and safety hazards. The temperature is monitored and recorded at regular intervals, e.g., every 20 seconds, until the maximum temperature is recorded. Because the heat loss from the insulated container is small (measured in calibration tests below), the constant pressure calorimeter provides an upper bound temperature and heat of reaction.

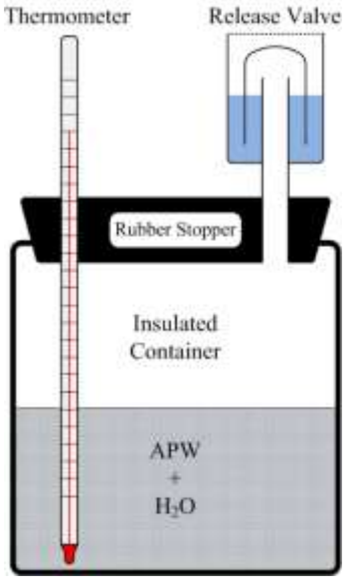

FIG. 4. Schematic of constant pressure calorimeter for APW classification

CALIBRATION OF REACTIVITY TEST

Calibration of the constant pressure calorimeter is recommended before classifying APW as hazardous or non-hazardous. The calorimeter calibration test involves the dissolution of NaOH in water. Reaction (3) is exothermic and generates 44.5 kJ of energy. By measuring ΔT, q_{rxn} (kJ) is computed using Eq. (2). To compare theoretical and experimental results in similar units, the computed q_{rxn} is divided by the moles of NaOH to obtain ΔH (kJ/mol).

$$\text{NaOH (s)} \rightarrow \text{Na+ (aq)} + \text{OH- (aq)} \qquad \Delta H= -44.5 \text{ kJ} \qquad (3)$$

Table 1 presents the results for the calorimeter calibration. In Test 1, 7.65 g NaOH (0.191 mole NaOH) is dissolved in 150.19 g H_2O. The measured ΔT was 12.6°C, resulting in q_{rxn}=8.32 kJ and ΔH=43.51 kJ/mol. For Test 1, the error is 2.1%, and the error for all tests is 5.1%. A likely source of error is the measurement of ΔT because the thermometer scale is in increments of 1°C. For example, Test 1 error would have increased from 2.1% to 6% if ΔT was increased by only 0.55°C (1°F).

FIG. 5. Reactivity test performed at Subtitle D Landfill

Table 1. Calibration results for constant pressure calorimeter

Test	NaOH (mole)	H_2O (mL)	ΔT (°C)	q_{rxn} (kJ)	ΔH (kJ/mole)	Error (%)
1	0.191	150.19	12.6	8.32	43.51	2.1
2	0.379	150.32	22.8	15.79	41.65	6.3
3	0.376	150.31	22.4	15.50	41.19	7.3
4	0.209	150.08	13.2	8.75	41.96	5.6
5	0.207	151.27	13.6	9.08	43.86	1.3
6	0.308	187.45	15.6	13.04	42.40	4.6
7	0.217	149.24	13.4	8.85	40.80	8.2

DISCUSSION

The general theory and test procedure to evaluate APW temperature escalation is provided for use by secondary aluminum generators and landfill operators. The following aspects of the reactivity test procedure are being refined to facilitate field implementation:

1. The optimal test conditions should balance the APW sample size, solid to liquid ratio, and strength of NaOH. Because APW is generally transported from generator to the landfill facility by a transfer dump truck, a representative sample size of APW is necessary for the reactivity test. The US DOT Dangerous When Wet test method (49 CFR 170, Appendix E) uses a series of experiments with increasing sample mass, i.e., from 2 mm diameter specimens to 25 g sample, to evaluate gas production. The solid to liquid ratio and strength of sodium hydroxide are also important because enough alkaline liquid should be present to quickly react all metallic Al but highly concentrated sodium hydroxide can be

hazardous and also wasteful. Therefore, the optimal NaOH strength needs to be determined for a feasible sample size.

2. Larger APW particle size decreases the reaction rate and temperature increases. Because APW composition and particle size vary among production processes, the effect of APW particle size should be investigated to determine if screening is required before testing.
3. APW is exposed to the environment during transport, so the initial temperature of the APW can vary depending on climate. For example, an APW may yield lower temperatures during the calorimeter test if transported during freezing temperatures than during hot and humid summer temperatures. As a result, the recommended test temperature is 20°C (68°F), similar to Dangerous When Wet test.

SUMMARY

The following points and recommendations are presented based on the discussion and data presented herein:

1. Although recycling aluminum is sustainable, the disposal of the resulting APW is a concern because of the potential for exothermic reactions. Such problems can be recognized via the proposed calorimeter test that assesses reactivity of specific APW loads or sources prior to disposal.
2. The constant pressure calorimeter test presented herein can be used to predict the maximum temperature generated from an APW reaction in a Subtitle D landfill. Based on methane curtailment at elevated temperatures, the threshold for APW temperatures is 65°C (149°F) to allow normal waste decomposition to continue and prevent elevated temperatures from impacting engineered components, such as the composite liner system, gas vents, and leachate collection system.
3. The recommended reactivity test is being used to develop a standardized calibration procedure as well as to investigate the effect of particle size, testing conditions, ball-milling, and environmental conditions on the maximum temperature increase.
4. Ultimately, proper disposal of APW using the reactivity test can prevent or minimize the aluminum exothermic reaction.

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