

# Classification and Reactivity of Secondary Aluminum Production Waste

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**Abstract:** Aluminum production wastes (APW) are produced during the recycling of aluminum scrap and dross. They are frequently disposed in dry form at Subtitle D nonhazardous waste landfills, where they may react adversely with liquids. Depending on the APW composition and landfill environment, the exothermic reaction can cause sustained temperature increases that inhibit normal anaerobic biodegradation. A constant pressure calorimeter test was developed to simulate the APW reaction in a basic environment and quantify the reactivity. APW reactivity was investigated under varying strengths of sodium hydroxide and particle size. Bench-scale calorimeter experiments show that concentrations greater than 4M NaOH oxidize metallic aluminum and increase temperatures rapidly to 100°C. Lower NaOH concentrations, such as 1M NaOH, are recommended to quantify the APW reaction in a constant pressure calorimeter. APW in neutral solutions was found to be stable, but reducing APW particles through ball-milling exacerbated reactivity. DOI: 10.1061/(ASCE)HZ.2153-5515.0000223. © 2014 American Society of Civil Engineers.

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## Introduction

Aluminum is the most widely used nonferrous metal in the world. It is light, conductive, and corrosion resistant with applications in world markets such as aerospace, marine industries, transportation, packaging, food, construction, electricity, and medicine. Since 1990, total global aluminum production doubled from 28 million t to about 56 million t in 2009 (IAI 2009). Aluminum products are produced by two different routes: primary aluminum production from bauxite ore and secondary aluminum production, i.e., recycling, from process scrap and used aluminum products. In 2006, the U.S. metal producing sector manufactured approximately 2.28 million t of primary aluminum and 3.54 million t of secondary aluminum (Menzie et al. 2010).

Secondary aluminum production is important because the energy required for recycling is only about 5% of that required for primary production yet it yields the same quality aluminum as primary smelting (Kammer 1999; Das et al. 2007). As a result, in 2003 aluminum recycling in the United States saved more than  $1.7 \times 10^{11}$  kWh (0.57 quad) of energy or equivalent to thirty-two (32) 600 MW coal fired power plants (US DOE 2007). In addition, secondary aluminum production emits 17 times less pollution to the atmosphere, generates from 5 to 9 times less solid waste, and

consumes 35 times less water than primary aluminum processing (see Table 1; Drossel et al. 2003). In short, recycling aluminum is truly beneficial and more sustainable than primary aluminum production.

Given the advantages of recycling, market demand for recycled aluminum remains strong due to its inherent low-energy cost compared with primary aluminum smelting. However, the wastes produced from secondary aluminum production can be problematic when they contain metallic aluminum. This is because metallic aluminum can oxidize rapidly to produce heat and flammable gas. As a result, disposal of such wastes in Subtitle D nonhazardous waste landfills has caused problems requiring expensive remediation efforts (Calder and Stark 2010; Stark et al. 2012; Martin et al. 2013). Such problems may have been avoided had a bench-scale test been available for assessing reactivity of specific aluminum production wastes (APWs) prior to disposal in a Subtitle D facility.

The potential environmental hazards of APW disposal are recognized worldwide (Amer 2002; Australian DEWR 2007; Lucheva et al. 2005; Mišková et al. 2006; Shinzato and Hypolito 2005). Tertiary processes developed for recycling hazardous APW into saleable salt fluxes, metal, and value-added nonmetallic derivatives are adversely influenced by the current low cost alternative of landfill disposal (US DOE 2007). The U.S. Department of Energy (US DOE 1999) estimates that at least 1 million t (~1.1 million tons) of APWs are annually placed in Subtitle D nonhazardous waste landfills, i.e., municipal solid waste (MSW) landfills. Accordingly, this paper discusses secondary aluminum production waste products in terms of their respective compositions, reactivity, and potential temperature escalation in a Subtitle D landfill. This paper also discusses current APW waste classification and summarizes two case histories in which APW was evaluated under hazardous waste regulations instead of Subtitle D criteria. Finally, a bench-scale test using a constant pressure calorimeter is presented to help APW generators and Subtitle D landfill operators decide whether a certain shipment of APW will cause an adverse reaction and thus result in excessive increase in landfill temperature.

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**Table 1.** Comparison of Primary and Secondary Aluminum Production Processes (Data from Gil 2005)

| Parameters                               | Primary process | Secondary process |
|--|-----------------|-------------------|
| Consumption of energy (GJ/t Al produced) | 174             | 10                |
| Atmospheric emissions (kg/t Al produced) | 204             | 12                |
| Solid waste (kg/t Al produced)           | 2,100 to 3,650  | 400               |
| Consumption of water (kg/t Al produced)  | 57              | 1.6               |

### 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 oxides ( $Al_2O_3$ ) mixed with salt fluxes, e.g., sodium chloride (NaCl) and potassium chloride (KCl). Such wastes are 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 [Fig. 1(a)] and consist of high metallic Al content (15 to 70%) (Kulik and Daley 1990). Black dross is created during melting of

scrap and recycled aluminum with a salt flux [Fig. 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% Al, 40 to 55% salt flux mixtures, and 20 to 50%  $Al_2O_3$  (Kulik and Daley 1990). To capture metallic Al 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 to 5% Al, 15 to 30%  $Al_2O_3$ , 30 to 55% NaCl, and 15 to 30% KCl, and depending on the scrap type may contain carbides, nitrides, sulfides, and phosphides (Peterson and Newton 2002). Almost 726,000 t (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 [Fig. 1(c)]. Baghouse dusts [Fig. 1(d)] consist of particulates produced during salt cake hammering and crushing and furnace off-gas. To control particulate emissions, lime is usually injected into the foundry ductwork to protect against sparks and improve dust collection. In addition, some heavy metals accumulate in the dust. The collected dust usually meets EPA TCLP (Toxicity Characteristic Leaching Procedure; SW-846 Methods 1311) requirements by mixing a pH buffering agent and an anion. For example, magnesium oxide and triple superphosphate is mixed with the solid waste in the foundry ductwork, and the heavy metals, e.g., zinc, lead, and cadmium, are converted into nonleachable forms in both acidic and nonacidic conditions. Therefore, baghouse dusts usually are a source of hydroxide ions and alkalinity (e.g., pH ~ 13) in landfills when disposed with other forms of APW.



**Fig. 1.** Types of aluminum production waste: (a) white dross; (b) black dross (from Site 2); (c) salt cake; (d) baghouse dust (from Site 2)

## Waste Classification

Residential, institutional, and commercial refuse from a municipality or region comprise the bulk of the waste streams disposed in a Subtitle D landfill. Subtitle D landfills also can accept nonhazardous industrial wastes, which are generally referred to as “special wastes.” For example, APW is generally classified as special wastes in Tennessee Subtitle D landfills. The primary purpose of referring to waste streams as “special waste” is to provide the operator of Subtitle D landfills with a mechanism to ensure that prohibited wastes, especially Resource Conservation and Recovery Act (RCRA) Subtitle C hazardous wastes and TSCA (Toxic Substances Control Act) wastes, are not placed in a Subtitle D landfill. A secondary purpose of classifying certain types of waste as “special waste” is to ensure that receipt of such wastes will not adversely affect the near-term or long-term operation of the landfill.

A solid waste is deemed hazardous in two ways either of which would make it ineligible for disposal in a Subtitle D facility. 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. Metallic Al and APW, including dross, salt cake, and baghouse dust, are not explicitly listed in 40 CFR Sec. 261. 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 APW related problems observed in Subtitle D landfills in the past, e.g., Brantley, Huelger Kronquist, and Arkansas Red River, toxicity, reactivity, and corrosivity under 40 CFR Sec. 261, Subpart C are potentially relevant to APW. Although corrosivity and toxicity can be an issue because APW leachate consists of high concentration of salts and may include heavy metals (arsenic, cadmium, lead, mercury) (Xiao et al. 2005; Swackhamer 2006), reactivity is most applicable to APW because of liquid induced exothermic reactions.

### Site 1—Ohio Landfill

From 1995 through 2008, a MSW landfill located in Ohio (referred to Site 1 herein) received approximately 661,000 t (651,000 tons) of APW. Annually, APW comprises 30 to 50% of the total tonnage (176,000 t). Because another Ohio landfill experienced APW reactions (Stark et al. 2012; Martin et al. 2013), the county health district issued special terms and conditions to prevent a similar situation. The terms and conditions include monitoring leachate characteristics, gas production and composition, and temperatures within the waste mass. The plan requested the facility to characterize the reactivity, ignitability, chemical composition, and leaching characteristics of APW from each generator. Table 2 presents total elemental composition (EPA 3051 Method) for three types of APW. The APW elemental content varies significantly and hence is difficult to interpret, but presumably results from different feedstocks and differences in operating practices. For example, magnesium, iron, manganese, and silicon in APW are linked to alloys used to enhance aluminum properties during production. Chloride, potassium, and sodium with trace amounts of calcium and fluoride in Table 2 are comprised in the salt flux.

Starting in 2007, Ignitability and Dangerous When Wet Tests (CFR Part 173.124) were performed monthly for each APW in Table 2. The ignitability tests proved negative. This test is described in Title 49 Transportation (CFR Part 173.124)—Shippers—General Requirements for Shipments and Packing and involves the reaction of a material with distilled water at 20°C and atmospheric pressure. A “dangerous when wet” material is defined as a

**Table 2.** Site 1 Ohio APW Total Element Content

| Parameter (mg/kg) | Milled black dross | Salt cake | Baghouse dust |
|-------------------|--------------------|-----------|---------------|
| Aluminum          | 114,000            | 142,000   | 35,300        |
| Magnesium         | 57,800             | 26,700    | 10,600        |
| Iron              | 2,030              | 1,710     | 1,970         |
| Manganese         | 533                | 186       | 199           |
| Chloride          | 230,000            | 140,000   | 250,000       |
| Potassium         | 122,000            | 70,900    | 71,300        |
| Sodium            | 97,400             | 86,700    | 66,000        |
| Calcium           | 7,980              | 7,820     | 206,000       |
| Fluoride          | 950                | 640       | 150           |

material in contact with water that becomes spontaneously flammable or gives off flammable or toxic gas at a rate greater than 1 L/kg-h. The Dangerous When Wet Tests were generally below the maximum gas evolution rate of 1 L/kg-h. However, several baghouse dust samples yielded maximum gas evolution rates above 1 L/kg-h, e.g., 3.0, 6.6, and 10.1 L/kg-h. The APW was not deemed hazardous and continued to be disposed at the facility. Although extensive APW characterization and testing was performed, *in situ* waste temperatures over 100°C measured by thermocouples located in landfill gas wells suggest current test procedures do not capture APW reactivity.

### Indiana Landfill

An Indiana secondary aluminum facility generated 3,600 t (4,000 tons) per month of APW from its aluminum dross reclamation process and disposed of these wastes at an onsite monofill. From July 2006 to January 2007, three “thermite fires” (oxidation of metallic Al at high temperatures) occurred in the landfill (RMT, Inc. 2007). Subsequently, the Indiana Department of Environmental Management (IDEM) requested assessment of the APW as a hazardous waste according to 40 CFR Sec. 261, Subpart C. The testing and analysis performed indicated that the three fires were caused by abnormal conditions. The fires ceased after modifications to the mechanical post-process reduced the metallic Al content of the APW being disposed. Specifically, the top screen mesh size was increased from 25.4 mm to 50.8 mm before mechanical grinding. The bottom screen sieve was decreased from No. 16 (1.19 mm) mesh to No. 25 (0.707 mm). The screen size modifications allowed larger APW granules to pass (thereby increasing the post-processed volume of dross to capture more metallic Al before disposal). By retaining more of the crushed metallic Al particles on the final mesh, mainly salts and nonmetal oxides, passed the final sieve and were identified for landfill disposal.

The generator concluded that APW was not a reactive or ignitable hazardous waste under 40 CFR Secs. 261.2 and 261.4(a) because the reaction between APW and water occurred over several minutes to hours. The reaction did not exhibit violent reaction, i.e., characterized by a rapid evolution of energy. Laboratory testing showed that upon contact with water, gas release was slow, at less than 1 L/kg-h in six out of seven hourly increments as measured in the DOT Dangerous When Wet Test (CFR Part 173.124). The reaction between APW and water (under controlled conditions) did not generate toxic gases, e.g., ammonia, acetylene, methane, or sulfur compounds, in a quantity sufficient to present a danger to human health in an outdoor environment (Table 3). Ammonia concentrations were measured using Draeger tubes positioned less than 150 mm above the processed materials. Measured concentrations ranged from 2 to 23 ppm, which is below the OSHA Personal Exposure Limit (PEL) of 50 ppm. The gas composition in Table 3 confirms that hydrogen is the dominant gas generated from APW.

**Table 3.** Composition of Gas Generated from Indiana Landfill in Laboratory Tests Using U.S. DOT Dangerous When Wet Test (Data from RMT, Inc. 2007)

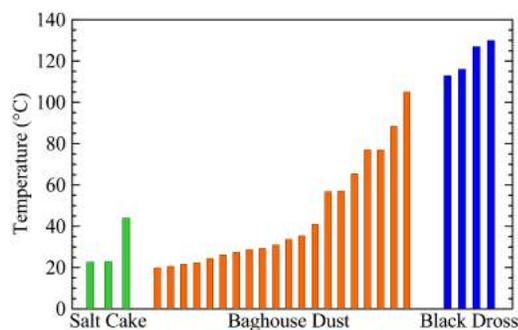
| Gas              | Percent of gas generated |
|------------------|--------------------------|
| Hydrogen         | ≤ 95%                    |
| Methane          | 1 to 5%                  |
| Hydrogen sulfide | <0.2%                    |
| Acetylene        | <0.2%                    |
| Phosphine        | <0.2%                    |
| Arsine           | <0.2%                    |
| Methane thiol    | <0.2%                    |
| Allene           | Below detection limit    |
| Ammonia          | Below detection limit    |

Hence, the metallic Al reaction is the source of a rise in temperature. Based on the data in Table 3, IDEM concluded that APW did not meet reactivity characteristics as described by 40 CFR Part 261.23 and allowed disposal in a Subtitle D facility.

To measure heat generation, the facility immersed the APW in tap water in an insulated chamber. The testing procedure consisted of thoroughly mixing 1 kg of APW and 150 mL of tap water in a plastic beaker. After quickly filling a quart size container with moist APW and placing a thermometer inside the waste, the container was sealed and placed inside an insulated chamber. Fig. 2 summarizes the results that include maximum temperatures of 130°C (266°F). The data show that about one-third of the samples tested exceed temperatures of 65°C, which is an upper bound temperature measured in MSW landfills (Hanson et al. 2010). Although the metallic Al content was not evaluated, the amount of oxidized metallic Al necessary to reproduce temperatures in Fig. 2 was about 1%. This indicates that only a small amount of oxidized metallic Al is required to elevate the temperature to 130°C. Complete metallic Al reaction in the described experiments was unlikely and under more favorable conditions, e.g., finer particle size and a basic solution, higher temperatures should be anticipated.

### Summary of APW Classification

The Indiana and Ohio cases corroborate that APW is reactive but not necessarily hazardous under 40 CFR Sec. 261, Subpart C. Other landfill facilities and researchers (IMP 2002; David and Kopac 2012; Fukumoto et al. 2001; Huang et al. 2011) suggest the reaction is slow and depends on leachate pH. If sufficient time is allowed and an alkaline environment persists, the APW can react and increase temperatures, and thus should not be disposed in MSW landfills. The slow activating reaction is also a drawback

**Fig. 2.** Temperature results from Indiana Landfill APW (data from RMT, Inc. 2007)

of the Dangerous When Wet Test method (40 CFR Sec. 170, Appendix E) because the reacting solution is distilled water, which does not represent actual landfill leachate. Huang et al. (2011) found that APW reaction with water requires over an hour before maximum temperatures are observed. Given the field observations of reactivity (US EPA 1994; Swackhamer 2006; RMT, Inc. 2007; Calder and Stark 2010; Stark et al. 2012) and variability of reactivity test methods, a new test and criterion is proposed to determine whether an APW displays a characteristic of reactivity under 40 CFR Sec. 261, Subpart C and thus whether a specific APW should be considered not suitable for disposal in MSW landfills.

### Reactivity Test Criterion

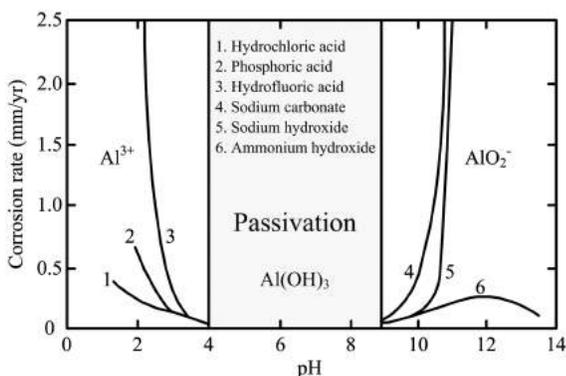
One of the most important parameters used to assess whether or not a Subtitle D Landfill is operating normally is temperature (Hanson et al. 2010; Crutcher et al. 1982). For an active gas collection system that meets New Source Performance Standards (NSPS; 40 CFR 60.753) requirements, landfill gas temperature within each extraction wellhead must be monitored monthly (US EPA 1999). Monitored routinely, temperature provides a reliable parameter to evaluate APW reactivity and landfill behavior.

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). Yesiller et al. (2005) report that most Subtitle D landfills operate in the mesophilic range, although optimal landfill gas production can be achieved in the thermophilic range. The anaerobic processes that regulate methane generation occur best within a temperature range of 40 to 42°C for mesophilic bacteria (Hartz et al. 1982; Mata-Alvarez and Martinez-Viturtia 1986; Pfeffer 1974). Characterizing optimal temperatures in the thermophilic range is less certain. For example, methane production starts to significantly decrease if the temperature of the waste mass exceeds 55°C (Kasali and Senior 1989; Hartz et al. 1982). Zinder et al. (1984) suggest thermophilic methanogenesis is optimal at temperatures ranging between 55 and 60°C. At temperatures beyond 64°C, Ahring et al. (1995) report that acetotrophic methanogens are inhibited and methane production slows or ceases.

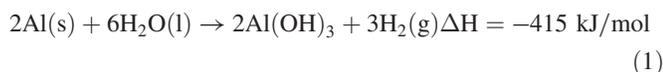
Under normal conditions, the temperature of solid waste and landfill gas generated by an MSW landfill ranges between 25 and 45°C (77 to 113°F) (ASTDR 2001), and the maximum allowable gas wellhead temperature is 55°C (131°F) (40 CFR 60.756). In particular, NSPS (40 CFR 60.753) require that a facility demonstrate that combustion is not occurring within the waste mass if a wellhead temperature exceeds 55°C (131°F). Based on NSPS requirements and anaerobic landfill environment, it is desirable to maintain landfill temperatures below 65°C (149°F) for healthy anaerobic decomposition, optimal methane gas production, and safe landfill operations. Therefore, the reactivity test should yield a temperature less than 65°C (149°F) to ensure NSPS compliance and prevent adverse consequences to landfill engineered components.

### Constant Pressure Calorimeter

APW composition and physical properties, e.g., pH, particle size, and metallic Al content, can vary significantly due to plant operation, smelting furnace, scrap and recycled materials used, salts introduced, etc. The most likely exothermic reaction of APWs in a Subtitle D landfill or nonhazardous industrial landfill involves the amphoteric reaction of metallic Al with water:



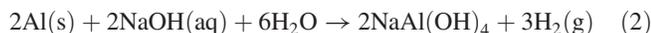
**Fig. 3.** Effect of pH on corrosion of aluminum alloy 1100-H14 by various chemical solutions (data from Hollingworth and Hunsicker 1990)



As an amphoteric metal, trivalent aluminum ( $\text{Al}^{3+}$ ) dissolves in strong acids as well as strong basic solutions (Fig. 3). In addition, Fig. 3 shows that an oxide layer passivates metallic Al between pH of 4 to 9, i.e., metallic Al is corrosion resistant in the atmosphere and almost neutral pH solutions. However, the oxide layer cannot exert its protective effect in strong acidic or basic solutions, which is problematic in Subtitle D landfills because of significant alkalinity in the wastes and accompanying liquid.

The pH value is not the sole parameter influencing the reaction of metallic Al. The lower corrosion rate in ammonium hydroxide demonstrates that the individual ions in the solution are more important than the degree of acidity or basicity. For example, the corrosion rate of metallic Al in a solution of NaOH at 0.1 g/L is 25 times greater than in an ammonia solution at 500 g/L, although both solutions have similar pH values, 12.7 and 12.2, respectively (Vargel 2004). The strong bases and acids in Fig. 3 cause the reaction rate to increase with concentration. In addition to basicity, increasing temperature leads to an increase in rate of chemical reactions. This applies to inorganic acids (HCl) and bases (NaOH), especially when the temperature approaches their boiling point (Vargel 2004). Chatterjee and Thomas (1976) report that aluminum corrosion rates in 200 g/L NaOH solution increase by 20 times for temperatures of 30 to 80°C, respectively. Therefore, depending on the specific chemical ions, concentration, and temperature, the metallic Al reaction in APW can range from superficial etching to rapid corrosion.

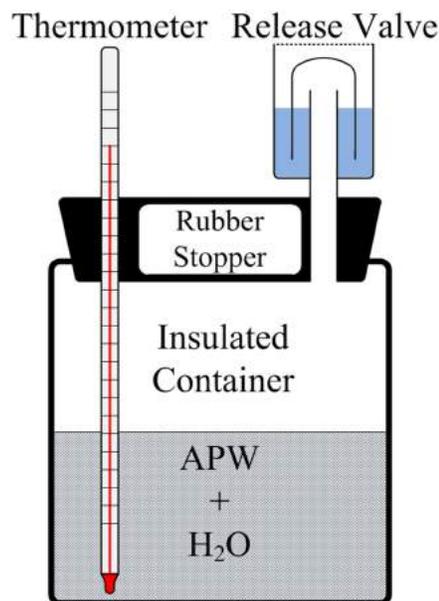
In Reaction (2), metallic Al and NaOH solution combine to yield sodium aluminate [ $\text{NaAl}(\text{OH})_4$ ], hydrogen, and heat. This reaction is the basis of the caustic etching reaction used as the initial operation in aluminum anodizing, i.e., electrolytic passivation process, that increases the thickness of the natural oxide layer:



This important reaction is completed within a few minutes and oxidizes the metallic Al. As a result, the bench-scale experiment developed herein uses Reaction (2) to identify whether the reactivity of the APW is sufficient to elevate temperatures in the landfill and classify as a hazardous waste.

### Constant Pressure Calorimeter Theory

Calorimetry is the quantitative measurement of heat required or evolved during a chemical process (Chang 2005). The proposed



**Fig. 4.** Schematic of constant pressure calorimeter for APW classification

constant pressure calorimeter is shown in Fig. 4 and is an instrument for measuring the heat of reaction during a defined process. In a constant pressure calorimeter, the reaction between a liquid and APW generates heat. Because calorimeter acts as an insulator, minimal heat loss occurs between the calorimeter and the surrounding air, thus creating an isolated system. The heat of reaction ( $q_{\text{rxn}}$ ) is a thermodynamic unit of measurement for calculating the amount of energy (kilojoules; kJ) per mole released in a reaction

$$q_{\text{rxn}} = m_{\text{residue}} c_{p,\text{residue}} \Delta T \quad (3)$$

where  $T$  is temperature ( $^{\circ}\text{C}$ ) and the change in final and initial temperature is  $\Delta T$ ,  $m_{\text{residue}}$  is mass of basic solution and APW (g), and  $c_{p,\text{residue}}$  is the specific heat ( $\text{J/g}^{\circ}\text{C}$ ). The resulting value of  $q_{\text{rxn}}$  is the maximum amount of heat that could be generated in a Subtitle D landfill by a given amount of APW reacting with solution. The  $c_{p,\text{residue}}$  is a weighted average between the specific heats of solution and APW. Using the arithmetic mean of the main constituents (metallic Al,  $\text{Al}_2\text{O}_3$ , NaCl, and KCl), the APW specific heat is about  $0.837 \text{ J/g}^{\circ}\text{C}$  ( $0.2 \text{ cal/g} \cdot ^{\circ}\text{C}$ ). For example, assuming 50 g of APW is reacted in 20 g of water ( $4.186 \text{ J/g} \cdot ^{\circ}\text{C}$  or  $1 \text{ cal/g} \cdot ^{\circ}\text{C}$ ), the  $c_{p,\text{residue}}$  is about  $1.79 \text{ J/g} \cdot ^{\circ}\text{C}$  ( $0.43 \text{ cal/g} \cdot ^{\circ}\text{C}$ ). The example assumes the density of water is constant, but the solution density changes with varying concentrations of basic reagents.

### Calorimeter Equipment and Procedure

The test equipment comprises an insulated calorimeter, NaOH solution, thermometer, and release valve. Typical insulated calorimeters use glass thermal insulation layers and are tightly sealed using a rubber stopper. A variety of NaOH concentrations, e.g., 1M, 2M, and 3M, can be prepared from NaOH pellets purchased at a chemical supply company. Although landfill leachate is usually represented by a pH of about 7 (Barlaz et al. 2010; Kjeldsen et al. 2002; Ehrig 1983), a basic solution is recommended in the test to ensure the metallic Al reacts. This will minimize the reaction time and maximize the temperature rise, i.e., representative APW

reactivity assessment. A release valve serves to dissipate 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.

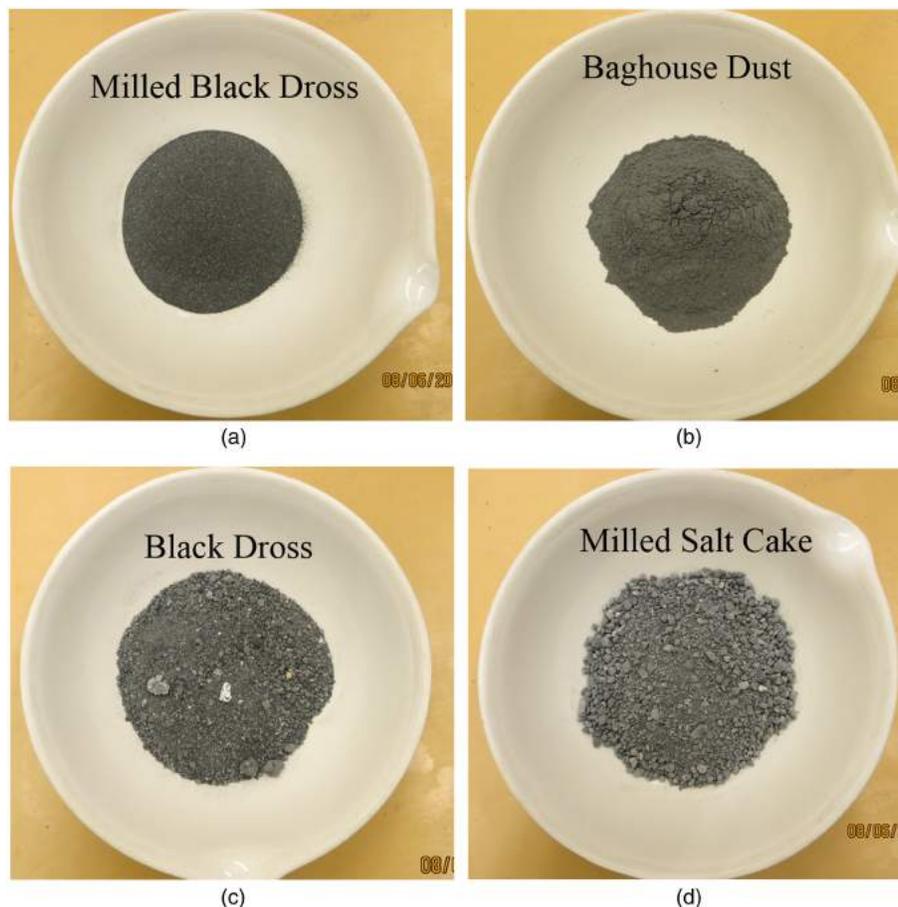
The general test procedure consists of weighing a representative specimen of APW and placing it inside the insulated constant pressure calorimeter (Fig. 4). The volume of NaOH should saturate the APW. This procedure is recommended instead of a solid to liquid ratio because some APW, e.g., baghouse dust, are extremely fine and require additional liquid to saturate and coat all dust particles. The predetermined 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 moist APW. In addition, a release valve is connected to the rubber stopper, which prevents pressure build-up from gas production. The temperature is monitored and recorded at regular intervals, e.g., every 20 s, until the maximum temperature is recorded. Because the heat lost from the insulated container is small, the constant pressure calorimeter provides a representative landfill temperature and heat of reaction. The constant pressure calorimeter is calibrated by evaluating the insulation efficiency of the container. The calibration procedure uses dissolution of NaOH in water and details are provided in Jafari and Stark (2014). They report the heat loss from the calorimeter using NaOH heat of reaction is less than 5% and hence is suitable for measuring APW reactivity.

## Calorimeter Test Results

### Physical and Chemical Properties of APW

APW was sampled from two Subtitle D facilities: Site 1 (Ohio landfill in waste classification section) and Site 2. Fig. 5 presents samples of Sites 1 and 2 APW used in reactivity testing. The APW samples in Figs. 5(a–d) are milled black dross (MBD), baghouse dust (BHD), black dross (BD), and milled salt cake (MSC), respectively. Fig. 6 shows the particle size gradation for both sites. The MBD represents the remaining APW after black dross was mechanically milled and screened for metallic Al, resulting in gap-graded MBD. The BD in Fig. 6 is shown in Fig. 1(b) and is representative of a well-graded fine sand. The MSC originates from mechanical grinding and crushing of salt cake blocks [Fig. 1(c)] and sieving to recover metallic Al captured within the salt flux. The sieve processing results in a coarser gradation than black dross in Fig. 6. BHD is not shown in Fig. 6 because the dust particles are finer than No. 200 (0.074 mm).

The mineral phase of each APW was characterized using XRD. The XRD patterns were collected on a RigakuMiniFlex II Diffractometer from 5 to 110 degrees  $2\theta$  using Cu  $K\alpha$  radiation and scintillation counter with in-line monochromator. The phase identification of samples was carried out using Materials Data, Incorporated (MDI) software suite *Jade 9* and the International Center for Diffraction Data PDF4+ database for reference patterns. After identification, semi-quantitative analysis was conducted on each sample using *Jade 9* whole pattern fitting methods.



**Fig. 5.** Samples of APW tested: (a) Site 1 milled black dross; (b) Site 1 baghouse dust; (c) Site 2 black dross; (d) Site 2 milled salt cake

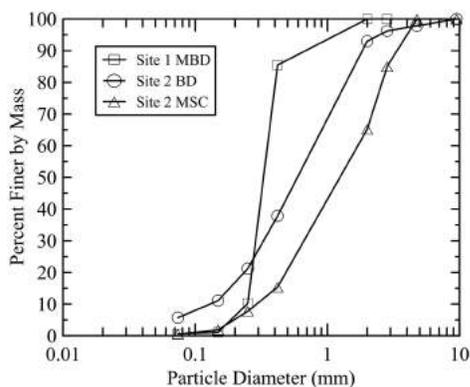


Fig. 6. Particle gradation of Site 1 and Site 2 APW

The dominant minerals in the salt cake samples are summarized in Table 4 and comprise metallic Al, corundum ( $\text{Al}_2\text{O}_3$ ), sylvite (KCl), halite (NaCl), and spinel ( $\text{MgAl}_2\text{O}_4$ ). Some of the samples also contained quartz ( $\text{SiO}_2$ ) and periclase (MgO). The average metallic Al content is about 2% for both sites, which is lower than average values reported in the literature. XRD results summarized in Table 4 also identified aluminum oxycarbide ( $\text{Al}_2\text{CO}$ ), which is more commonly found in APW as  $\text{Al}_4\text{C}_3$ . Alumina and carbon react in the furnace to form  $\text{Al}_2\text{CO}$ . Then, additional carbon and  $\text{Al}_2\text{CO}$  combine to yield  $\text{Al}_4\text{C}_3$ . The XRD results also did not identify AlN even though an ammonia odor was noted from the APW during the reactivity experiments. AlN and  $\text{Al}_4\text{C}_3$  demonstrate that certain mineral phases are present in APW but may not be identified. Therefore, XRD results should provide only a general overview of APW composition.

### Effect of NaOH Concentration

Experiments were performed on APW to investigate the role of metallic Al reaction on temperatures in a landfill. The test procedure consists of dosing 50 g of APW in 20 mL of NaOH solution and measuring the temperature increase. Fig. 7 shows the effect of NaOH molarity (mole NaOH/L solution; M) on the APW from Sites 1 and 2. As the concentration of NaOH increases from 1 to 15M, the maximum temperature and reaction rate increase significantly. For example, Fig. 7(a) shows the MBD in 15M NaOH solution reaches a maximum temperature of about 130°C in about 2 min. This reaction is violent and characterized by forceful gas release. Temperatures in the range of 100 to 110°C are

Table 4. Summary of APW Mineral Phases

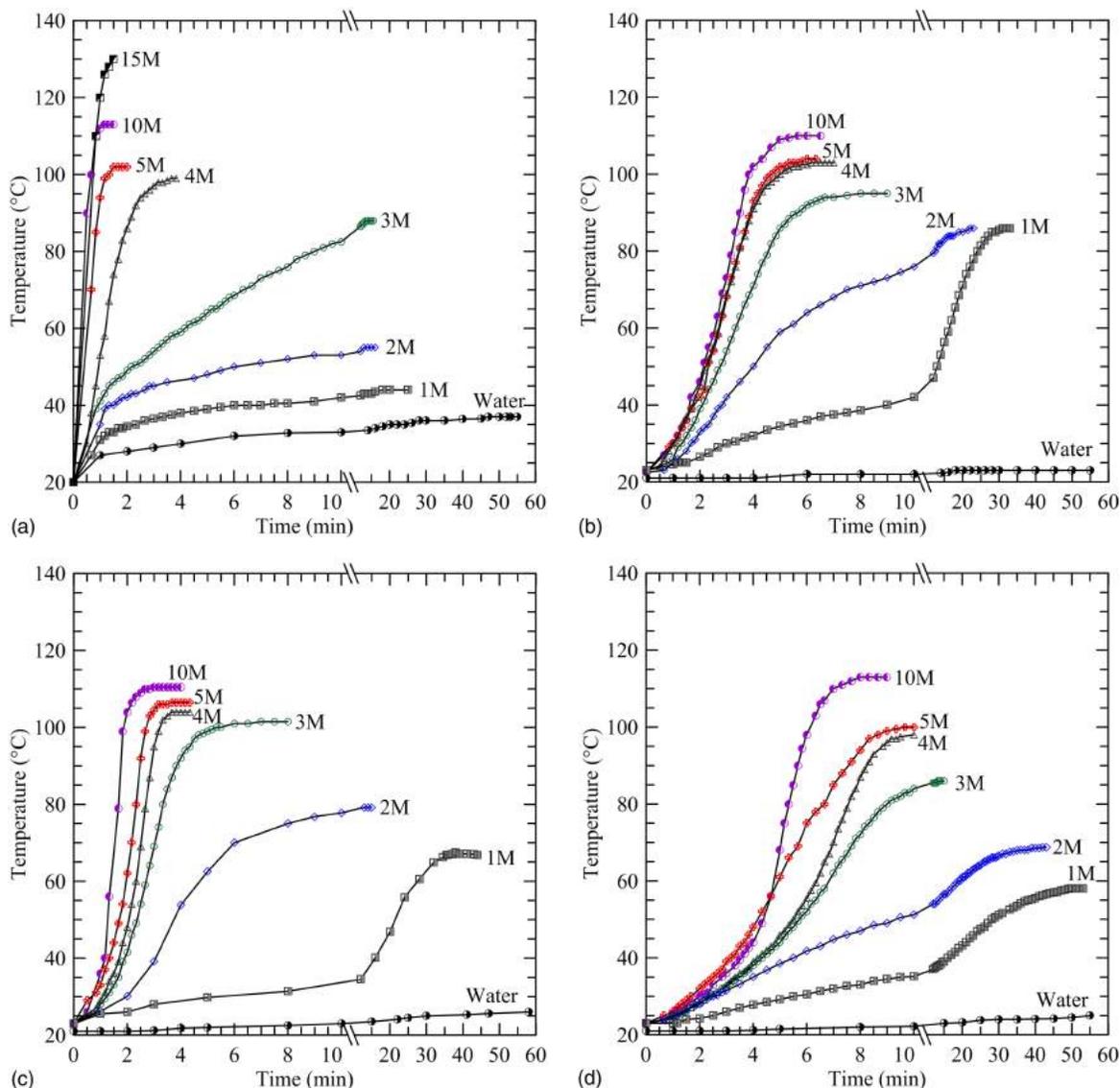
| Mineral phase (%)                      | Site 1 |      | Site 2 |      |
|--|--------|------|--------|------|
|  | MBD    | BHD  | BD     | MSC  |
| Al                                     | 3.8    | 1.1  | 3.1    | 0.5  |
| $\text{Al}_2\text{O}_3$                | 4.8    | 8.5  | 8.3    | 8.6  |
| KCl                                    | 9.3    | 23.1 | 18.2   | 14.3 |
| NaCl                                   | 38.2   | 32.4 | 42.3   | 33.8 |
| $\text{MgAl}_2\text{O}_4$              | 6.7    | 30.9 | 16.1   | 34.4 |
| $\text{Al}_2\text{CO}$                 | 3.5    | 3.7  | 6      | 6    |
| C                                      | 4.3    | 0.9  | —      | —    |
| $\text{KMgCl}_3(\text{H}_2\text{O})_6$ | 29.4   | —    | —      | —    |
| MgO                                    | —      | —    | 5.3    | 1.2  |
| $\text{SiO}_2$                         | —      | —    | 0.7    | 0.2  |
| Pb                                     | —      | —    | —      | 2    |

consistently observed in 4, 5, and 10M NaOH for all APW samples. Experiments generally peaked at a temperature of 100°C because additional heat produced by the aluminum reaction vaporized moisture into steam. The 4 and 5M NaOH solutions yield similar temperatures of 100°C, but the reaction rate of 4M is slightly slower, as illustrated in Figs. 7(a and d). A larger decrease in maximum temperature and reaction rate is observed for 3M NaOH solutions. This indicates that sufficient hydroxide ions are not present in 3M NaOH to react the metallic Al and increase temperatures to 100°C. In Fig. 7(b), the baghouse dust in 3M NaOH reacts quicker due to the finer particles, i.e., increased surface area, and additional basicity (e.g., lime) present in baghouse dusts. Higher maximum temperatures (85°C) and reaction rates were also observed for baghouse dust in 1M and 2M NaOH. Figs. 7(a and d) illustrate that APW in 10M NaOH generates substantially greater temperatures (above 110°C) than 5M NaOH. Both APW samples in Figs. 7(a and d) are milled before landfill disposal, which may explain the slower reaction rates at lower NaOH concentrations.

In Figs. 7(c and d), the black cross is more reactive than the milled salt cake. Using 4M NaOH solution as an example, the milled salt cake requires about 9 min to reach 100°C, but the black cross increases to 105°C in about 3 min. Fig. 7 demonstrates that in a strong basic environment, APW reacts to produce elevated temperatures and flammable, malodorous gases. APW reactivity in water, however, is slower and results in a temperature increase of 5 to 17°C. In comparison, Huang et al. (2011) measured temperature increases of 3.4 to 64.1°C with an average of 22°C for 39 APW samples tested in distilled water and two initial temperatures (37 and 50°C). Huang et al. (2011) report pH and XRD patterns but not APW particle gradation. Trends relating pH or metallic Al content to temperature increase were not directly correlated by Huang et al. (2011). More likely, APW reactivity in neutral solutions is governed by the fines content and lack of basicity to facilitate the reaction.

The 4M NaOH experiments generate temperatures of 100°C because the strong alkaline solution drives the metallic Al reaction. However, the hydroxide ions in the 3M NaOH concentration are consumed prior to 100°C and so 3M NaOH increases temperatures to 80°C. Decreasing reactivity is also observed for 1 and 2M [Figs. 7(a and d)]. APW samples tested in Fig. 7 have low metallic Al content, i.e., XRD results indicate an average of 2%, and they likely represent lower APW reactivity spectrum. As a result, the recommended alkaline concentration to evaluate APW reactivity is 1M NaOH with a maximum concentration of 2M NaOH.

Fig. 7 temperatures rapidly increase from 23°C to about 105°C in less than 10 min. Slower reaction rates in milled APW corroborates that milling and recovering metallic Al in APW also reduces reactivity. The XRD analyses verify that low concentrations of metallic Al in APW can generate high temperatures under strong basic conditions. The rapid reaction rate observed in Fig. 7(b) is attributed to additional alkalinity in the form of lime in the baghouse dust. The reactivity of milled black dross in water, shown in Fig. 7(a), may be attributed to the fine particle size. Because XRD results only provide semiquantitative results, the metallic Al content in Table 4 may be higher than actually identified. A reliable method of evaluating metallic Al content is to directly measure the volume of hydrogen gas produced. For example, ASTM D6356 (2011) provides a procedure to measure the amount of hydrogen gas generation potential of aluminum emulsion roof coating.



**Fig. 7.** Effect of NaOH strength on temperature response for (a) Site 1 milled black dross; (b) Site 1 baghouse dust; (c) Site 2 black dross; (d) Site 2 milled salt cake

### Effect of Milling APW

After skimming salt residue from the smelting furnace, metallic Al entrapped in APW is recovered by impact milling. This process deforms or grinds the malleable metallic Al and reduces the size of brittle oxide and salt phases. Because aluminum will not break in the milling process, it will be screened out in the coarser fractions. The coarser fractions represent as low as 15% of the total weight of the milled APW but can contain as much as 80% metallic Al (Karvelas et al. 1991). After screening ball-milled black dross, Fair et al. (1987) found that 5.2% of the mass passing the No. 100 mesh (0.15 mm) can be metallic Al.

Impact milling recovers aluminum from APW before final disposal but also generates finer APW particles, which may liberate entrapped aluminum and increase APW reactivity. Fair et al. (1987) report that after impact milling 26.3% of APW was finer than No. 100 (0.15 mm) mesh. In comparison, laboratory ball-milling grinds particles to finer than the No. 200 sieve (0.074 mm), so use of ball-milled material will represent a conservative estimate on APW reactivity. Fig. 8 compares Site 2 black dross for original particle

gradation and ball-milled samples (<0.074 mm). Using a 4M NaOH solution, the effect of ball-milling slightly increases reactivity. More importantly, ball-milling increased temperatures from 25 to 60°C in water. Although ball-milling conservatively reduces particle gradation to below 0.074 mm, the milling processes can exacerbate APW reactivity in neutral pH solutions.

### Discussion

The constant pressure calorimeter experiments with NaOH demonstrate that APW is highly reactive yet APW can remain dormant for years in MSW landfills until some event inadvertently causes the waste to come into contact with an acidic or basic leachate. For example, APW reactions occurred after facilities in Ohio (Stark et al. 2012; Martin et al. 2013) and Tennessee began recirculating leachate. MSW landfill leachates consist of dissolved organic matter, inorganic components, heavy metals, and organic compounds (Christensen et al. 1994). The pH levels are initially acidic (5 to 6) during the transition period from aerobic decomposition to stable

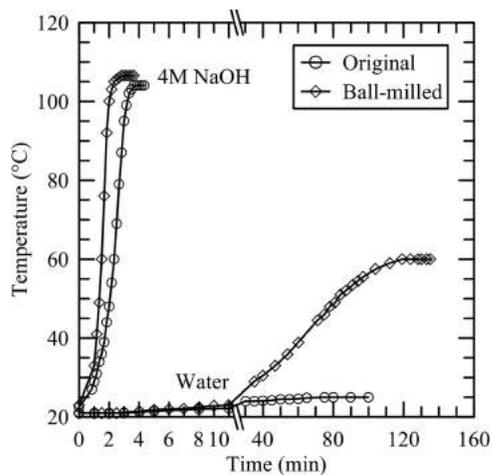


Fig. 8. Effect of ball-milling on Site 2 black dross

methane production. After methanogenic decomposition is established, pH levels increase to average values of 7 to 8 (Ehrig 1983; Kjeldsen et al. 2002). The role of leachate chemical characteristics on initiating the metallic Al reaction is currently unknown. More likely, the leachate serves to saturate the dry APW, where the dissolution and reaction of other APW constituents activate that the metallic Al reaction. Huang et al. (2011) report that the pH of APW is about 10.5. Possible APW constituents responsible for increasing pH are MgO, CaO, AlN, and others. The reactivity increases for APWs comprised of basic pH and a large percentage of fines, e.g., baghouse dusts. Baghouse dusts are, in some instances, even more basic with pH values of 13 because of the addition of hydroxide ions to control sparks in ductwork and prevent leaching of heavy metals. As a result, moisture introduced into the landfill reacts with carbides, nitrides, and metal oxides and hence increases waste pH. The basic conditions begin to react with metallic Al to elevate temperatures and produce hydrogen gas.

*In situ* landfill temperatures have been measured above 100°C in APW disposed facilities. For example, Site 1 (Ohio Landfill) is measuring downhole temperatures in gas wells. In May 2008, temperatures measured at 8 m (26 ft) and 20 m (65.5 ft) below the ground surface (bgs) were about 96°C (205°F). Over 2 years later (September 2011) the temperatures decreased to ~70°C (158°F) at 8 m bgs but remained nearly constant at 93°C at 20 m bgs. The temperature decrease at 8 m bgs indicates that the metallic Al rapidly oxidizes after disposal, i.e., when soil cover is minimal and precipitation can infiltrate into the waste. As the waste height increases, moisture infiltration into the lower waste layers decreases. Because the reaction is self-sustaining with liquid, heat loss is greater than heat generation and temperatures begin to decrease. The temperatures at 20 m bgs illustrate that minimal heat loss occurs in the middle third of the landfill. In the reactivity test, the insulated constant pressure calorimeter serves to simulate the center of the landfill where heat loss is minimal. The basic solution serves to accelerate the metallic Al reaction so the test completes in several minutes.

The bench-scale reactivity test involves performing a temperature test at the generator or landfill weigh station to estimate the temperature rise that could occur in the landfill. The optimal test conditions should balance the strength of NaOH, solid to liquid ratio, APW sample size, and testing temperature. 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. As indicated in Fig. 6, APW particle

gradation can vary based on the type of waste. APW fines are more reactive than the coarse fraction, so the landfill operator should pass the APW through a No. 40 mesh (0.425 mm) to obtain a representative sample. This sample, consisting of APW fines, is then used to measure 50 g for the reactivity test. If the APW consists primarily of lumps and granules, the sieve size may be increased to No. 10 (2.00 mm) and the sample mass increased to a reasonable value.

In addition, APW can be exposed to cold climates during transport as well as warmer temperatures when disposed in MSW landfills. Because metallic Al corrosion is influenced by temperature, a standard temperature is required. For instance, Huang et al. (2011) performed APW reactivity tests in distilled water and temperatures of 37 and 50°C to simulate temperatures in landfills. They report that at 50°C maximum temperatures increased by an average of 7°C compared with 37°C. The proposed calorimeter test, however, is recommended to be performed at a standard temperature of 20°C (68°F), similar to the Dangerous When Wet Test. The standard temperature permits a baseline temperature for landfill operators to compare APW reactivity and ensures testing conditions are consistent between landfills, secondary aluminum generators, and other facilities.

## Summary

Although recycling aluminum is beneficial and sustainable, the disposal of the resulting solid waste is a concern because of potential APW exothermic reactions. A review of two active sites indicate that APW is reactive but not necessarily classified as hazardous under 40 CFR Sec. 261, Subpart C. Potential problems can be avoided by the proposed calorimeter test that assesses reactivity of specific APW loads or sources prior to Subtitle D disposal. The reactivity is assessed via the maximum temperature generated by an APW reaction. The maximum recommended temperature for Subtitle D landfills is 65°C (149°F) to permit waste decomposition and prevent elevated temperatures from impacting engineered components (composite liner system, gas vents, and leachate collection system).

Calorimeter experiments at varying NaOH strengths show temperatures rise to 100°C. The optimal concentration of NaOH was determined to be 1 to 2M NaOH which provides sufficient hydroxide ions to react the metallic Al and fulfill the objectives of a rapid procedure to evaluate APW reactivity in an basic environment. XRD analyses or hydrogen gas production can complement the reactivity tests by corroborating the amount of Al present and similar temperature increase and reaction rates.

The progression of APW reactions in landfills is dependent on the presence of moisture via leachate recirculation, precipitation, groundwater, waste processing, and other sources. The basic APW, especially baghouse dusts, and moisture react with the nitrides, carbides, and salts to further increase the pH. After temperatures and pH begin to increase above background levels, the protective oxide layer is corroded and metallic Al reacts to produce heat and hydrogen gas. In the reactivity test, the insulated constant pressure calorimeter serves to simulate the center of the landfill where heat loss is minimal. The bench-scale test using a constant pressure calorimeter is presented to help APW generators and Subtitle D landfill operators decide whether a certain shipment of APW will cause an adverse reaction and temperatures in the landfill and whether the APW should be classified as hazardous using the reactivity criterion.

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