CLASSIFICATION AND REACTIVITY OF SECONDARY

ALUMINUM PRODUCTION WASTE

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1   **Classification and Reactivity of Secondary Aluminum Production Waste**

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4   **ABSTRACT:** Secondary aluminum production wastes (APW) are produced during the melting

5   of aluminum scrap and dross. They are frequently disposed in dry form at Subtitle D non-

6   hazardous waste landfills, where they can react adversely with liquids. Depending on the APW

7   composition and landfill environment, the heat of reaction can cause sustained temperature

8   increases that inhibit normal anaerobic biodegradation. Further, the reaction products can

9   produce flammable and toxic gases such as hydrogen, ammonia, methane, and hydrogen sulfide

10   and cause foul odors in the neighboring area. The potential for exothermic reactions between

11   APW and landfill leachate necessitates the development of a simple test that quantifies reactivity

12   and potential temperature increase and determines which APW are overly reactive and which are

13   relatively inert. A constant pressure calorimeter test is outlined herein that can simulate the APW

14   reaction in a landfill environment.

15   *Keywords:* Landfills, aluminum, hydrogen, salt cake, dross, calorimeter, waste disposal

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INTRODUCTION

Aluminum is a widely used nonferrous metal in the world (IAI 2009), being present in markets such as transportation, packaging, food, construction, electricity, and medicine. Total global primary and secondary aluminum production increased from 28 million tonnes in 1990 to about 56 million tonnes in 2009. Recycled scrap aluminum constitutes about 32% of total production of about 56 million tonnes (IAI 2009). In 2003, the metal producing sector manufactured approximately 2,704,000 tonnes of primary aluminum and 2,820,000 tonnes of secondary aluminum (BCS, Inc. 2007). Recycling aluminum scrap is important because the energy required for aluminum recycling is only about 5% of that required for primary aluminum production yet it yields the same quality aluminum as primary smelting (Kammer 1999; Das et al. 2006). As a result, aluminum recycling in the United States has saved more than $1.7x10^{11}$ kilowatt hours (0.57 quad) of energy in 2003 (BCS, Inc. 2007). In addition, secondary aluminum production process emits seventeen (17) times less pollution to the atmosphere (see Table 1), generates between five to nine (5 to 9) times less solid waste, and consumes thirty-five (35) times less water than primary aluminum processing (Drossel et al. 2003). In short, recycling aluminum is truly beneficial and more sustainable than primary aluminum production.

Given the advantages discussed above, market demand for recycled aluminum remains strong especially due to its inherent low-energy cost compared to primary aluminum smelting. However, the wastes produced from secondary aluminum production can be problematic when they contain metallic aluminum fines because finely divided metallic aluminum can oxidize to produce heat and hydrogen gas. As a result, disposal of such wastes in Subtitle D non-hazardous waste landfills has caused serious problems requiring expensive remediation efforts

41　(Calder and Stark 2010; Stark et al. 2012). Such problems may have been avoided had a simple

42　test been available for assessing reactivity of specific APW prior to disposal.

43

44　**Table 1:　Comparison of Primary and Secondary Aluminum Smelting Processes (data**
45　　　　　　**from Gil 2005)**
46

	Primary Smelting	**Secondary Smelting**
Consumption of energy (GJ/tonne Al produced)	174	10
Atmospheric emissions (kg/tonne Al produced)	204	12
Solid waste (kg/tonne Al produced)	2,100-3,650	400
Consumption of water (kg/tonne Al produced)	57	1.6

47

48　　　The U.S. Department of Energy (1999) estimates that at least one billion kilograms (~2

49　billion pounds) of APWs are annually placed in Subtitle D non-hazardous waste landfills, i.e.,

50　municipal solid waste (MSW) landfills. The APW contains variable amounts of metallic

51　aluminum and aluminum compounds such as aluminum carbide (Al_4C_3), aluminum nitride

52　(AlN), and aluminum oxides (Al_2O_3) mixed with other substances such as sodium and potassium

53　chloride. Such wastes are referred to as "dross", "white dross", "black dross", and "salt cake."

54　These terms refer to the amount of aluminum present and the morphology of the wastes raked

55　from the surface of molten aluminum during primary and secondary processing and purification

56　(Manfredi et al. 1997). Tertiary processes have been developed for separating the components of

57　black dross into saleable salt fluxes, metal, and value-added nonmetallic derivatives such as

58　calcium aluminate additives for low-density cement. The economics of tertiary processing are

59　adversely influenced by the current low cost alternative of landfill disposal (BCS, Inc. 2007).

60   The potential hazards of aluminum production waste disposal are recognized worldwide

61   (Amer 2002; Australian DEWR 2007; Lucheva et al. 2005; Miškufová et al. 2006; Shinzato and

62   Hypolito 2005). Accordingly, this paper discusses secondary aluminum production waste

63   products in terms of their respective compositions, reactivity, and potential temperature

64   escalation in a Subtitle D landfill. This paper also discusses current APW waste classification

65   and summarizes two case histories in which APW was considered to be a hazardous waste so

66   disposal in a Subtitle D landfill was not allowed. Finally, a test procedure using a constant

67   pressure calorimeter is presented to help APW generators and Subtitle D landfill operators

68   decide whether a certain shipment of APW will cause an adverse reaction and increase in landfill

69   temperature.

70

71   **BACKGROUND**

72   One of the most important parameters used to assess whether or not a Subtitle D Landfill is

73   operating normally is temperature (Hanson et. al. 2010; Crutcher and Rovers 1982) because it

74   reflects the type of anaerobic bacteria present.   There are two types of bacteria that dominate in

75   landfills, i.e., mesophilic and thermophilic. Each type of bacteria has a unique operating

76   temperature. Mesophilic bacteria reproduce in a temperature range of 35° to 45ºC (68° to 113ºF)

77   with an optimal temperature of 35ºC (95ºF), while thermophilic bacteria reproduce in a

78   temperature range of 45° to 75ºC (113° to 167ºF) with an optimal temperature of 55° to 65ºC

79   (131° to 149ºF) (Stark et al. 2012). Yesiller et al. (2005) indicate that most Subtitle D landfills

80   operate in the mesophilic range, although optimal landfill gas production can be achieved in the

81   thermophilic range. The mesophilic and thermophilic anaerobic processes that regulate methane

82   generation occur best within a temperature range of 30° to 60^oC (86° to 140^oF), and methane

5

83 generation is optimized at a temperature of 41°C (106°F) (U.S. EPA 2005). Methane production

84 starts to significantly decrease if the temperature of the waste mass exceeds 70°C (158°F), and

85 typically bacterial activity and methane production stop if the temperature of the waste mass

86 exceeds 80°C (176°F). Under normal conditions, the temperature of solid waste and landfill gas

87 generated by an MSW landfill range between 25° and 45°C (77° to 113° F) (ASTDR 2001). New

88 Source Performance Standards (NSPS) (40CFR60.753) require that a facility demonstrate that

89 combustion is not occurring within the waste mass if a wellhead temperature exceeds 55°C

90 (131°F). Based on these requirements, it is desirable to maintain landfill temperatures below

91 60°C (140° F) for healthy anaerobic bacteria growth, optimal methane gas production, minimize

92 APW exothermic reactions, and safe landfill operations.

93

94 **ENIVORNMENTAL REGULATIONS**

95 Residential, institutional, and commercial refuse from a municipality or region comprise the bulk

96 of the waste streams disposed in a Subtitle D landfill. However, Subtitle D landfills also can

97 accept non-hazardous industrial wastes, which are generally referred to as "special wastes." The

98 primary purpose of referring to waste streams as "special waste" is to provide the operator of

99 Subtitle D landfills with a mechanism to ensure that prohibited wastes, especially RCRA Subtitle

100 C hazardous wastes and TSCA (Toxic Substances Control Act) wastesare not placed in a Subtitle

101 D landfill. A secondary purpose of classifying certain types of waste as "special waste" is to

102 ensure that receipt of such wastes will not adversely affect the near-term or long-term operation

103 of the landfill.

104 A solid waste is deemed hazardous in two ways either of which would make it ineligible

105 for disposal in a Subtitle D facility. First, 40 CFR Sec. 261, Subpart D explicitly lists the

106   materials that are defined as hazardous and these materials cannot be placed in a Subtitle D

107   regulated landfill. Aluminum (metal) and aluminum production waste, including aluminum

108   dross, salt cake, and baghouse dust, are not explicitly listed. Second, if a waste exhibits any one

109   of the four characteristics of a hazardous waste, i.e., ignitability, corrosivity, reactivity, or

110   toxicity, the waste is classified as a hazardous waste under 40 CFR Sec. 261, Subpart C and

111   cannot be placed in a Subtitle D facility. Because of aluminum related problems observed in

112   Subtitle D landfills in the past, e.g., Brantley landfill, Countywide, Wabash Alloys, Huelger

113   Kronquist, Arkansas Red River, etc. (see Table 2), toxicity, reactivity, and corrosivity under 40

114   CFR Sec. 261, Subpart C are potentially relevant to APW. Although corrosivity and toxicity can

115   be an issue because APW leachate consists of high concentration of salts (sodium, potassium,

116   chloride) and concentration of heavy metals (arsenic, cadmium, lead, mercury) (Xiao et al. 2005;

117   Swackhamer 2006), reactivity is most applicable because of APW induced exothermic reactions.

118   Table 2 provides a summary of known APW landfills in the United States. Though not a

119   complete list, it is evident that many of the landfills are located in the Northwest, e.g., eastern

120   Washington, and in the Ohio River Valley.

121   Unlike ignitability, there is no U.S. EPA certified test method to determine whether or

122   not a material meets the regulatory definition of "reactivity" or potential heat generation under

123   CFR Sec. 261.21. U.S. EPA withdrew its reactivity method in 1998. The U.S. EPA ignitability

124   test is "Ignitability of Solids" (SW-846 Method 1030) to determine whether or not a material

125   meets the regulatory definition of ignitability in CFR Sec. 261.21.

126

127

128

129

Table 2:   Summary landfills accepting APW

State	Name	City
AR	Red River Aluminum Site	Stamps
AR	Aleris / Wabash Alloys LLC	Benton
CA	Halaco	Oxnard
IL	Hillside	Chicago
IN	Aleris / Wabash Alloys LLC	West Tipton
IN	Wabash Valley Landfill / Reclamation Center	Wabash
IN	Scepter Landfill	Bicknell
KY	Brantley Landfill	Island
KY	Fort Hartford Coal Co. Stone Quarry Site	Olaton
KY	Green River Disposal, Inc.	Maceo
KY	Aleris International	Morgantown
OH	Countywide Landfill	East Sparta
OH	Athens Hocking Reclamation Center	Nelsonville
OH	American Landfill	Waynesburg
OH	Ottawa Landfill	Port Clinton
OH	Uhrichsville Recycling Facility	Uhrichsville
OH	Newark Processing	Newark
OH	Central Waste	Alliance
OH	Cuyahoga Regional Landfill	Solon
OK	IMCO Recycling/ International Metals	Sapulpa
OK	Quarry Landfill	Tulsa
OR	Wasco County Landfill	The Dalles
PA	Gettysburg Foundry	Gettysburg
PA	Rolling Hills Landfill	Earl Township
PA	Sitkin Smelting and Refining	Maitland
TN	Environmental Waste Solutions	Camden
TN	Middle Point Landfill	Murfreesboro
TN	Mt. Pleasant Landfill	Mt. Pleasant
WA	Aluminum Recycling Corporation / Hillyard Processing	Spokane
WA	Heglar Kronquist	Spokane
WA	RAMCO	Dallesport
WA	Mica Landfill	Mica
WA	Aluminum Recycling Trentwood	Spokane
WA	Roosevelt Regional Landfill	Roosevelt

130

131   • 40 CFR Sec. 261.21 (a) (2) — It is capable of causing fire through absorption of water

132   and when ignited burns so vigorously and persistently that it creates a hazard.

133   • 40 CFR Sec. 261.23 (a) (2) — It reacts violently with water.

134   • 40 CFR Sec. 261.23 (a) (3) — It forms potentially explosive mixtures with water.

8

135 • 40 CFR Sec. 261.23 (a) (4) — When mixed with water, it generates toxic gases, vapors,

136 or fumes in a quantity sufficient to present a danger to human health or the environment.

137

138 For comparison purposes, European Union regulations do not allow APW disposal in MSW

139 landfills. European legislation explicitly classifies salt slags and black dross from secondary

140 smelting, waste from treatment of salt slags and black dross, and primary smelting slags and

141 white dross as hazardous waste (European Commission 2000). Waste properties which render

142 APW a hazardous material in Europe (European Commission 2000) consist of the following:

143 • "Highly flammable – substances and preparations which, in contact with water or damp

144 air, evolve highly flammable gases in dangerous quantities."

145 • "Irritant – non-corrosive substances or preparations which through immediate prolonged

146 or repeated contact with the skin or mucus membrane can cause inflammation."

147 • "Harmful – substances and preparations which, if they are inhaled or ingested or if they

148 penetrate the skin, involve limited health risk."

149 • "Substances and preparations capable by any means, after disposal, of yielding another

150 substance, e.g. leachate which possess any of the characteristics listed above."

151

152 **CASE STUDIES OF APW CLASSIFICATION**

153 This section provides a summary of APW reactivity and classification at three landfill facilities.

154 APW classification was not performed at the first case study, and the resulting exothermic

155 reactions led to a subsurface smoldering event. The final two cases classified the APW and the

156 results are presented herein.

157

158 **Countywide Reclamation Disposal Facility (CWRDF) – Ohio**

159 Permitted in 1991, CWRDF consists of 35.7 hectares (88 acres) or 9.9 million m^3 (13 million

160 yd^3) of disposal capacity. CWRDF accepted roughly between 0.6 million tonne (600,000 tons)

161 and 1 million tonne (560,000 tons) of APW from 1991 through 2006. The facility began leachate

162 recirculation in April 1996. However, in 2006 leachate recirculation ceased when the ongoing

163 exothermic reaction between APW and recirculated leachate became obvious. Measurement of

164 leachate collection system temperatures near the geomembrane in the single composite liner

165 system exceeded 85°C (185°F). Waste temperatures exceeding 143°C (290°F), downhole

166 temperatures reaching 149°C (300°F), and well-head temperatures up to 110°C (230°F) were

167 recorded at this site. In addition, the heat generated by APW reaction caused smoldering

168 combustion of the surrounding MSW. As of October 2012, the elevated temperatures in the

169 waste, landfill gas, and leachate collection system had been detected over a period of about 9

170 years. The APW reaction and subsurface smoldering has required expensive remedial measures,

171 e.g., installation of over 100 additional gas wells, increased leachate collection removal and

172 treatment from 15 million to 132 million liters/year, excavation of an isolation break, and

173 construction a flexible membrane liner cover to decrease emanating hazardous and noxious

174 odors. The use of the simple reactivity test may have identified the highly reactive nature of this

175 APW before landfill disposal which may have obviated these remedial measures.

176

177 **Brantley Landfill - Kentucky**

178 Brantley Landfill encompasses approximately 1.6 hectare of a 14.2 hectare parcel located in

179 Island, Kentucky (US EPA 1994). Approximately 227,000 tonnes (250,000 tons) of salt cake

180 fines were placed in Brantley Landfill from 1978 until its closure in 1980 (Swackhamer 2006).

181 The waste was deposited below the groundwater surface, thus threatening public and private

182 wells ground water within about 5 km of the site.

183   In 1979 the Kentucky Division of Air Pollution Control conducted a compliance

184 inspection based on complaints from 200 area residents living within a 400 m radius that

185 ammonia odors were emanating from the landfill during disposal activities. During Kentucky

186 Department of Environmental Pollution (KDEP) inspections, officials noticed vigorous reactions

187 with water and received complaints of irritating gas emitting from the landfill. Soil beneath the

188 landfill cap was contaminated with heavy metals including chromium, copper, aluminum,

189 magnesium, and sodium. This discovery prompted the U.S. EPA in 1980 to classify salt cake

190 fines as a hazardous waste under the reactivity criterion. In 1981 Barmet Aluminum Corporation

191 filed a federal civil action against the U.S. EPA and KDEP protesting regulation of salt cake

192 fines as a hazardous waste. The hazardous waste classification was subsequently removed. The

193 Brantley Landfill is still listed on the National Priorities List due to elevated ammonia and metals

194 concentrations in the subsurface.

195

196 **Wabash Alloys Landfill - Indiana**

197 Wabash Alloys generated 3,600 tonnes (4,000 tons) per month of APW (dross mill silo fines)

198 from its dross reclamation process and disposed of these wastes at an onsite monofill (RMT, Inc.

199 2007). From July 2006 to January 2007, three thermite (oxidation of aluminum at high

200 temperatures) fires occurred in the landfill. Subsequently the Indiana Department of

201 Environmental Management (IDEM) requested assessment of the APW as a hazardous waste

202 according to 40 CFR Sec. 261, Subpart C. The testing and analysis performed indicated that the

203 three thermite fires were caused by abnormal conditions and the thermite fires ceased after

204 modifications were made to reduce the metallic aluminum content of the APW being disposed.

205 Specifically, the top screen mesh size was increased from 25.4 mm to 50.8 mm during post-

206 processing after smelting. The bottom screen sieve was decreased from No. 16 (1.19 mm) mesh

207 size to No. 25 (0.707 mm). The screen size modifications allowed larger APW granules to pass

208 (thereby increasing the post-processed volume of dross to capture more metallic aluminum

209 before disposal); and by retaining more of the crushed metallic aluminum particles on the final

210 mesh, mainly salts and non-metal oxides passed the final sieve and were identified for landfill

211 disposal.

212   Wabash Alloys concluded that APW was not a reactive or ignitable hazardous waste under

213 40 CFR Secs. 261.2 and 261.4(a) because:

214 • The reaction between APW and water occurred over several minutes to hours sothe

215   reaction did not exhibit violent reaction, which is characterized by a rapid evolution of

216   energy.

217 • Laboratory testing showed that upon contact with water, gas release was slow, at less

218   than 1 liter/kg-hour in six out of seven hourly increments as measured in the DOT

219   Dangerous When Wet Test (CFR Part 173.124). This test is described in Title 49

220   Transportation (CFR Part 173.124) – Shippers - General Requirements for Shipments and

221   Packing and is used to determine whether the reaction of a material with distilled water at

222   20°C and atmospheric pressure. Dispersion modeling of the APW reaction with water

223   indicated insufficient hydrogen gas was released to generate a vapor cloud explosion in

224   an outdoor environment. A dangerous when wet material is defined as a material in

225   contact with water that becomes spontaneously flammable or gives off flammable or

226   toxic gas at a rate greater than 1 liter per kilogram of the material per hour.

227   • The reaction between the APW and water (under controlled conditions) did not generate

228   toxic gases, e.g., ammonia, acetylene, methane, or sulfur compounds, in a quantity

229   sufficient to present a danger to human health in an outdoor environment (see Table 3).

230   Ammonia concentrations were measured using Draeger tubes positioned less than 150

231   mm above the processed materials. Measured concentrations ranged from 2 to 23 ppm,

232   where the OSHA Personal Exposure Limit (PEL) is 50 ppm.

233

234 Based on the data in Table 3, IDEM concluded that APW did not meet reactivity characteristics

235 as described by 40 CFR Part 261.23.

236
237 **Table 3.**   **Composition of gas generated from Wabash dross mill waste in laboratory**
238   **tests using U.S. DOT Dangerous When Wet Test (data from RMT, Inc. 2007)**
239

Gas	Percent of Gas Generated
Hydrogen	≤95%
Methane	1 to 5%
Acetylene	<0.2%
Allene	Below detection limit
Ammonia	Below detection limit
Hydrogen Sulfide	<0.2%
Methane Thiol	<0.2%
Phospine	<0.2%
Arsine	<0.2%

240
241
242   To measure heat generation in this case, Wabash Alloys immersed the APW in tap water

243 in an insulated chamber. The testing procedure consisted of thoroughly mixing 1 kg of APW and

244 150 mL of tap water in a plastic beaker. After quickly filling a quart size container with moist

245 APW and placing a thermometer inside the waste, the container was sealed and placed inside an

246 insulated chamber. Fig. 1 summarizes the results that include maximum temperatures of 130°C

247 (266°F). The red dashed line at 60°C denotes the landfill temperature where bacteria growth is

248   inhibited and methane gas production decreases. This data shows that one-third of the samples

249   tested exceeded this threshold. Because the aluminum content in the samples was not evaluated,

250   the amount of aluminum oxidized in the test was estimated to be about 1% metallic aluminum

251   (Al). This means only a small amount (1%) of Al is required to elevate the temperature to

252   130°C. Complete aluminum oxidation is unlikely and under more favorable conditions (e.g.,

253   finer particle size under alkaline conditions) higher maximum temperatures would have resulted.

254   In summary, metallic aluminum content of APW is a key factor responsible for temperature

255   escalation in Subtitle D landfills.
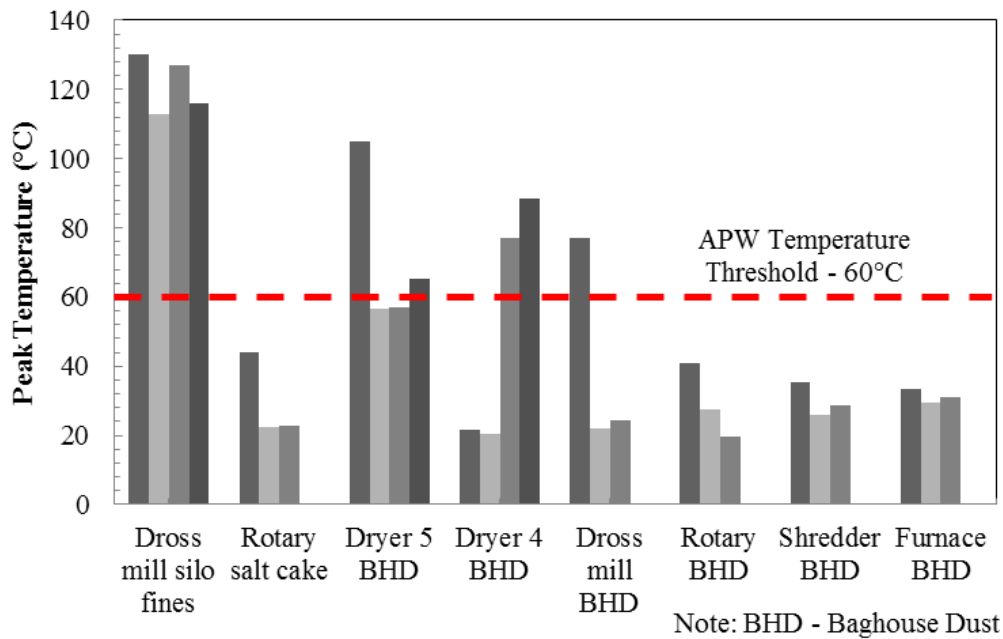
256

257   **Figure 1: Temperature results from Wabash Alloys APW (data from RMT, Inc. 2007)**

258

259   **Summary of APW Classification**

260   The CWRDF case highlights the consequences of temperature escalations due to APW reactions

261   in a MSW landfill. The Brantley and Wabash Alloys cases indicate that APW is reactive but not

262   necessarily hazardous under 40 CFR Sec. 261, Subpart C. The Brantley case suggests that the 40

263   CFR Sec. 261.23 (a) (2) reactive criterion is applicable to APW but testing at Wabash Alloys and

264   other facilities (IMP 2002; David and Kopac 2012; Fukumoto et al. 2001; Huang et al. 2011)

265   suggest the reaction is slow depending on liquid alkalinity. If sufficient time or alkalinity is

266   allowed, the APW may be classified as hazardous. The slow activating reaction is also a

267   drawback of the Dangerous When Wet test method (40 CFR Sec. 170, Appendix E??????)

268   because the reacting solution is distilled water. At near neutral pH conditions, the solubility of

269   metallic aluminum in APW is low so the reaction is slow because aluminum is not readily

270   available. An alkaline solution can accelerate the APW rate of reaction and hydrogen gas

271   production because it increases the solubility of metallic aluminum.

272   Given the field observations of reactivity (US EPA 1994; Swackhamer 2006; RMT, Inc.

273   2007; Stark and Calder 2010; Stark et al. 2012) and variability of reactivity test methods, a new

274   test and criterion is proposed herein to determine whether an APW displays a characteristic of

275   reactivity under 40 CFR Sec. 261, Subpart C and thus should be considered a hazardous waste.

276

277   **TYPICAL APW COMPOSITION**

278   Generation and composition of metallic aluminum and alkalinity are briefly reviewed in this

279   section to ensure development of a reactivity test that will capture the range of materials being

280   produced and model worse case reactions in a landfill.

281   **APW Generation**

282   Secondary aluminum production involves the following two general categories of operation:

283   scrap pretreatment and smelting/refining. Pretreatment operations include sorting, processing,

284   and cleaning scrap. Smelting/refining operations include cleaning, melting, refining, alloying,

285   and pouring of aluminum recovered from scrap. The main features of secondary aluminum

286   production are the diversity of the raw materials and the variety of furnaces used. Typical

287   sources of aluminum scrap are process scrap, used beverage cans (UBCs), foils, extrusions,

288   commercial scraps, turnings, and rolled or cast metal. The type of raw material and its

289   pretreatment determine the selection of the type of furnace, either reverberatory or rotary salt

290   melting furnaces.

291   General scrap recovery uses gas-or oil-fired reverberatory furnaces, typically of 18 to 100

292   tonne (20 to 110 tons) capacity (Viland 1990). A salt flux layer on the surface of the molten

293   aluminum bath to protect the molten aluminum from oxidation and to improve metal recovery. A

294   salt flux layer consists generally of a mixture of potassium chloride (KCl) and sodium chloride

295   (NaCl). The selection of the types of salt fluxes depends on the type of raw material and on the

296   furnace. These salt fluxes have multiple functions (IAI 2009) some of which are:

297   •   allow heat transfer to the metal and contribute to the isolation of the metal from the

298   atmosphere.

299   •   mechanically disperse the oxides and metal substances or solid nonmetal substances

300   present in the furnace.

301   •   some salt fluxes can react chemically with the aluminum oxides, dissolving them.

302

303   Dross production at a typical secondary smelter with reverberatory furnaces is about 15%

304   of the metal charge where dross contains 8 to 12% metallic aluminum. While this is typical for a

305   specific smelter, some dross may contain as much as 80% aluminum (Viland 1990). In 1996,

306   U.S. secondary smelters consumed 1.44 million tonnes of scrap with a calculated metallic

307   recovery of 1.1 million tonnes (Plunkert 1996), which suggests that about 24% of the scrap

308   charge is lost as aluminum and aluminum oxide in the dross. Viland (1990) reports for every

309   454 tonnes (1 million pounds) of scrap processed, 345 tonnes (760,000 pounds) of secondary

310   aluminum is produced, and 109 tonnes (240,000 pounds) of dross residues and 1,360 kg (3,000

311   pounds) of baghouse dusts are generated both of which are usually disposed.

312

313   **APW Composition**

314   The APW contains variable amounts of metallic aluminum and are referred to as "dross", "white

315   dross", "black dross", and "salt cake." This section briefly discusses these terms or

316   classifications.

317

318   *White Dross*

319   The generation of white dross occurs at primary aluminum smelters, extruding plants, sheet

320   mills, foundries, and dies casters (Kulik and Daley 1990). Because these facilities operate

321   without fluxing, dross skimmed from the furnaces have a grey or metallic white color (see Fig.

322   2). White dross has a high metallic aluminum content (15-70%) (Kulik and Daley 1990). The

323   aluminum metal converts to aluminum oxide rapidly because of high temperature and an oxygen

324   rich environment.

325

Figure 2:   **White dross excavated during gas well drilling in a Subtitle D landfill experiencing an aluminum reaction**

Black Dross

Black dross is created during melting of scrap and recycled aluminum. Salt fluxes are added to the scrap to lower the melting point of the mix (700-800°C). At high a molten temperature, the added salt flux becomes dark colored and thus is referred to as "black dross." At temperatures above the melting point of the salt flux mixture, the black dross (see Fig. 3) consists of two immiscible liquid phases, i.e., aluminum metal and liquid salt containing oxide particles and films. The metal content of the black dross varies depending on the scrap type being charged and the processing conditions, but usually varies from 12 to 18% (Kulik and Daley 1990). The oxide content of the black dross is approximately equal to the salt flux content. The aluminum metal settles in the molten solution and the liquid salt is maintained near the surface and captured for disposal.

341

Figure 3:   Pile of black dross disposed in APW monofill

343

Salt Cake

The composition of salt cake depends on the black dross, but it often contains 3–5% Al, 15–30%

Al_2O_3, 30–55% NaCl, and 15–30% KCl (Peterson 2002). Almost 726,000 tonnes (800,000 tons)

of salt cake is annually landfilled in U.S. (Sreenivasarao et al. 1997) and is usually disposed in

landfills in solid blocks (see Fig. 4).

349

Figure 4:   Pieces of salt cake disposed in APW monofill (photo courtesy of E. Gortner)
351

352

353 *Baghouse Dust*

354 Baghouse dusts consist of particulates produced during salt cake hammering and crushing and

355 furnace off-gas. These wastes may contain cadmium (Cd) and lead (Pb) above the limits of the

356 EPA Toxicity Characteristics Leaching Procedure (TCLP) test (Hwang et al. 2006; Stanforth

357 1991) but are frequently disposed of in landfills (see Fig. 5). Although some hazardous volatiles

358 accumulate in the dust, the collected waste usually can meet EPA TCLP requirements by mixing

359 a pH buffering agent and an anion. Stanforth (1991) developed a patented pH buffering agent

360 and anion, i.e., magnesium oxide and triple superphosphate, respectively, that converts heavy

361 metals, e.g., zinc, lead, and cadmium, into non-leachable forms in both acidic and non-acidic

362 conditions. The patented system focuses on acidic and neutral water conditions to simulate the

363 worst-case leaching condition typically found in an actively degrading Subtitle D landfill, i.e.,

364 slightly acidic with a pH of about five, and in industrial landfills where it is exposed to neutral

365 water such as rain. The magnesium oxide (MgO) and triple superphosphate $Ca(H_2PO_4)_2$ is mixed

366 with the solid waste in the foundry ductwork before the dust is collected from the waste gas

367 stream. Lime is also injected into the foundry ductwork to protect against sparks and improve

368 dust collecting. As a result, baghouse dusts usually contain both magnesium oxide and lime,

369 which are a source of alkalinity in landfills when disposed with other forms of APW.

370

371

Figure 5:   **Sacks of baghouse dust being placed in APW monofill**
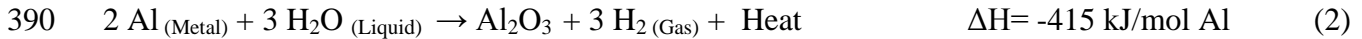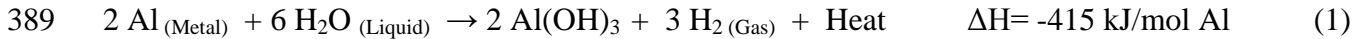
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374

CONSTANT PRESSURE CALORIMETER TEST

This section describes a calorimeter test that can be used to assess the reactivity of APW before

it is accepted for disposal in a Subtitle D landfill.   This section presents the preliminary

equipment and test procedure to assess whether or not the APW is "reactive" under 40 CFR Sec.

261, Subpart C and provides an insight to the impact of the APW after disposal in a Subtitle D

landfill.

381

Purpose

APW composition (e.g., alkalinity, particle size, aluminum content, etc.) can vary significantly

due to plant operation, smelting furnace, scrap and recycled materials used, salts introduced, etc.

The most likely reactions of APWs in a Subtitle D landfill or non-hazardous industrial landfill

involve the amphoteric reaction of aluminum with water (Calder and Stark 2010) as shown

below:

388

389     $2\ Al_{(Metal)} + 6\ H_2O_{(Liquid)} \rightarrow 2\ Al(OH)_3 + 3\ H_{2\ (Gas)} + $ Heat $\Delta H = -415$ kJ/mol Al   (1)

390     $2\ Al_{(Metal)} + 3\ H_2O_{(Liquid)} \rightarrow Al_2O_3 + 3\ H_{2\ (Gas)} + $ Heat $\Delta H = -415$ kJ/mol Al   (2)

391

392   At near neutral pH conditions, the solubility of trivalent aluminum is low so the reaction can

393   only proceed slowly, if at all. Under acidic or alkaline conditions, however, the solubility of

394   trivalent aluminum is high enabling oxidation of finely divided metallic aluminum to proceed

395   quickly. This is the basis of the well-known caustic etching reaction used as the initial operation

396   in aluminum anodizing where the aluminum surface is almost instantly etched when immersed in

397   strong caustic solution described by the following equation:

398

399          $2\ Al_{(Metal)} + 2\ NaOH + 2\ H_2O \rightarrow 2\ NaAlO_2 + 3\ H_{2\ (gas)} + $ Heat   (3)
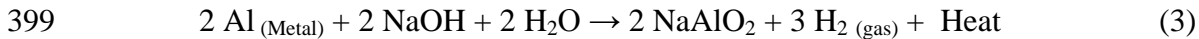
400

401   In Reaction (3) Al (metal) and NaOH solution combine to yield $NaAlO_2$ (sodium aluminate),

402   H_2 gas, and heat. This important reaction is completed quickly, within a few a minutes, and

403   oxidizes all of the aluminum. Thus, the reactivity of APW will depend not only on metallic

404   aluminum content and particle size, but also on the alkalinity of both the APW and landfill

405   leachate.

406   Therefore, a simple experiment that can be conducted before an APW is loaded at the

407   generator or is unloaded at aSubtitle D landfill is needed to identify whether the reactivity of the

408   APW is sufficient to elevate temperatures in the landfill and induce expensive remedial

409   measures. The experiment involves performing a temperature test at the generator or landfill

410   weigh station to simulate the temperature rise that would occur in the landfill if the APW is

22

411   subjected to a alkaline leachate. The test uses a strongly alkaline solution to accelerate the

412   reaction rate so that a worst case scenario is simulated. A side benefit of this test is that it

413   indirectly measures the metallic aluminum content in the APW so that the generator will be more

414   aware of product losses before disposal and actions for better process control can be

415   implemented to capture the remaining aluminum.

416

417   **Theory**

418   Calorimetry is the quantitative measurement of heat required or evolved during a chemical

419   process (Chang 2005). The proposed constant pressure calorimeter is shown in Fig. 6 and is

420   an instrument for measuring the heat of reaction during a defined process.
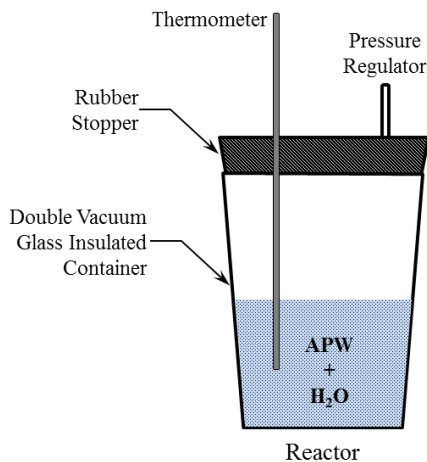
421

422   **Figure 6: Schematic of constant pressure calorimeter for APW classification**

423

424   In a constant pressure calorimeter, the reaction between water and APW will generate heat.

425   Because the calorimeter acts as an insulator, minimal heat loss will occur between the

426   calorimeter and the surrounding air, creating an isolated system. The heat of reaction (q_{rxn})

427   is defined as the quantity of heat exchanged with the surroundings in restoring the

428   calorimeter to its initial temperature in units of kilojoules (kJ) or calories (cal).

$$q_{rxn} = m_{residue} * C_{p,residue} * \Delta T \qquad \text{Eq. (1)}$$

429   where T is temperature (°C) and the change in final and initial temperature is ΔT, m is mass

430   of alkaline water and APW (g), and $C_{p,residue}$ is the specific heat (J/g °C). $C_{p,residue}$ is a

431   weighted average between specific heats of water and APW, which are 4.186 J/g·°C (1

432   cal/g·°C) and about 0.837 J/g °C (0.2 cal/g·°C), respectively, and is estimated by Eq. (2).

433   APW specific heat is an arithmetic mean of the main constituents Al (metal), Al_2O_3, NaCl,

434   and KCl.

$$C_{p,residue} = \frac{m_{H_2O} * C_{p,H_2O} + m_{APW} * C_{p,APW}}{m_{H_2O} + m_{APW}} \qquad \text{Eq. (2)}$$

435

436   For example, assuming 25g of APW reacts with 10 mL of water, the $C_{p,residue}$ is about 3.46

437   J/g·°C (0.826 cal/g·°C) using Eq. (2). The resulting value of q_{rxn} is the heat that will be

438   generated in a Subtitle D landfill by the APW reacting with water.

439

440   **Calorimeter Equipment and Procedure**

441   The test equipment and recommended procedure for conducting a constant pressure

442   calorimeter test to evaluate APW reactivity is presented in this section. The test equipment is

443   comprised of an insulated calorimeter, sodium hydroxide (NaOH) solution, thermometer, and

444   pressure regulator. Typical insulated calorimeters use glass thermal insulation layers and are

445   tightly sealed using a rubber stopper. A variety of NaOH concentrations, e.g., 20% w/w, can

446   be purchased at a chemical supply company. This alkaline solution must be strong enough to

447   ensure all of the aluminum can be reacted and that an excess is present to maintain strong

448   alkaline conditions as the reaction proceeds. This will minimize the reaction time and

449   maximize the temperature rise. A pressure regulator serves to release gas pressure generated

450   by the APW reaction. To simplify and reduce testing time, the production of gases such as

451   ammonia, methane, and hydrogen sulfide gas production are not measured. As a result, it is

452   anticipated that this test can be performed quickly at a secondary processor or a landfill
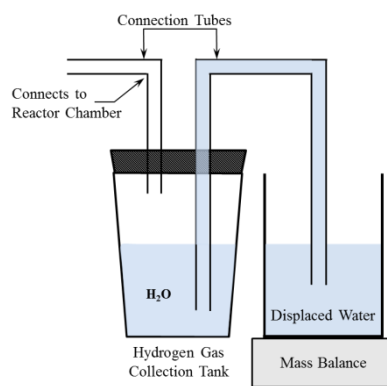
453   weigh station.

454   The general procedure consists of a representative specimen of APW is weighed and

455   placed inside the insulated constant pressure calorimeter (See Fig. 6). After a predetermined

456   volume of NaOH solution is added to APW and mixed thoroughly for a few moments by

457   shaking and swirling, ensuring the reaction goes to completion. The calorimeter is sealed

458   tightly by placing the rubber stopper in the top of the container to prevent heat loss. The

459   change in temperature inside the calorimeter is monitored by inserting a thermometer through

460   the rubber stopper into the moist APW (see Fig. 6). In addition, a pressure regulator, i.e., a

461   release valve, is necessary to release pressure build-up from gas production. The temperature

462   is monitored and recorded at regular intervals, e.g., one minute, until the maximum

463   temperature is recorded. Because the heat lost from the insulated container is small, the

464   constant pressure calorimeter provides an upper bound temperature and heat of reaction.

465   If the APW generator or analyst desires, the aluminum content can be estimated by

466   measuring the volume of hydrogen gas generated from the reaction. Fig. 7 shows how the

467   calorimeter can be modified to include two calorimeters (reactor and hydrogen collection

468   tank) and a displaced water beaker to measure the volume of hydrogen gas generated. The

469 procedure for this experiment follows the constant pressure calorimeter procedure described

470 above with a few additional preparation steps. First, fill the Hydrogen Collection Tank

471 (HCT) until it is almost full of water and seal it with a rubber stopper. Fill the Displaced

472 Water (DW) beaker with water such that the connection tube from the HCT is submerged

473 (see Fig. 7(a)). Establish a siphon from the HCT to DW beaker by "pushing" water through

474 the system from the Reaction Chamber connection tube (see Fig 7(b)). It is important to

475 remove all of the air bubbles in the siphon connection tube. Finally, connect the tube from

476 the Reaction Chamber to the HCT. Before starting the APW reaction, the DW beaker is

477 placed on a balance and the initial mass of water and beaker is measured. In Fig 7(c), the

478 hydrogen gas produced by the APW reaction flows via connection tube to HCT and pushes

479 water into the DW beaker. The change in mass of DW beaker is measured at the end of the

480 test and can be converted to a volume of displaced water. The test is complete after observing

481 the maximum temperature and the calorimeter reaches ambient temperature. This ensures the

482 reaction has been completed at a constant pressure. Assuming minimal hydrogen gas is lost

483 from the system, the volume of hydrogen gas produced is equal to volume of displaced

484 water.

485
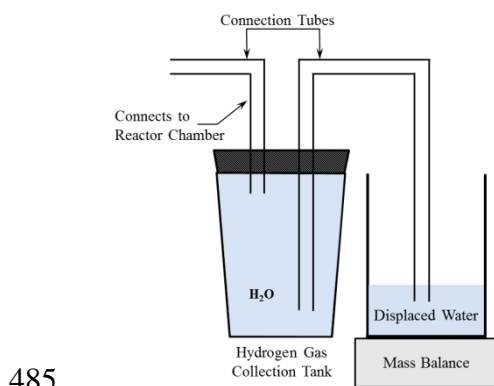
486 **(a) Stage 1 Fill completely HCT**   **(b) Establish a siphon from HCT to DW beaker**
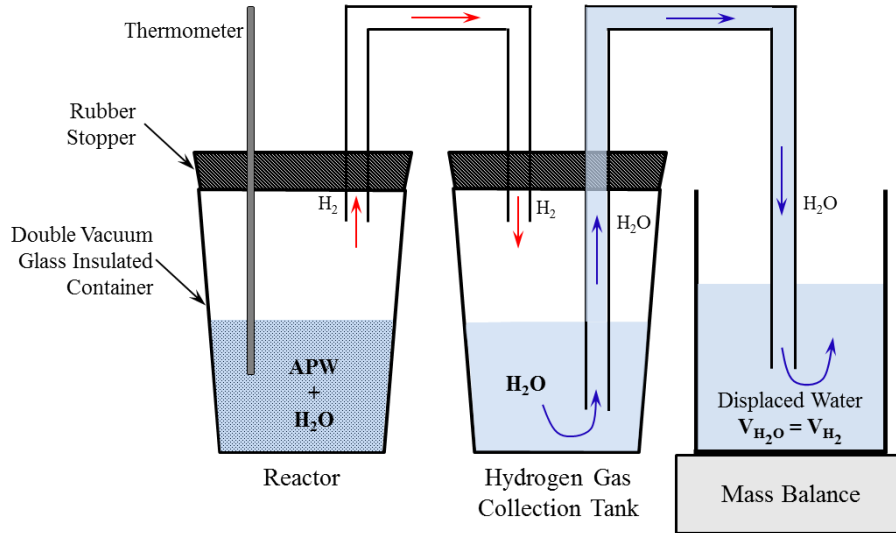
(c) Compete test setup with Reaction Chamber

Figure 7: Test to estimate aluminum metal content from APW reaction in calorimeter

The percentage of aluminum is obtained using Eq. (3):

$$Al\ (\%) = H_2\ gas\ (L) \times \frac{P_{atm}}{R*T} \times \frac{2\ mol\ Al}{3\ mol\ H_2} \times \frac{M_{Al}}{mol} \times \frac{1}{M_{initial}(g)} \tag{3}$$

where R is the ideal gas constant 0.082057 (L·atm/K·mol), P_{atm} is atmospheric pressure (1 atm), T is in units of Kelvin (K), $2\ mol\ Al/3\ mol\ H_2$ is the molar ratio of Al and H_2 reaction coefficients shown in Reaction (3), M_{Al} is the molar mass of aluminum (27 g/mol), and $M_{initial}$ is initial mass of APW sample (25 g). Because temperature is evaluated in Kelvin (K), Eq. (4) converts degree Celsius to Kelvin:

$$T\ (K) = 273°C + °C \tag{4}$$

PRELIMINARY TEST RESULTS

500 Preliminary reactivity experiments were performed on APW to investigate the role of metallic

501 aluminum content and hydrogen gas production on temperatures in a landfill. The test method

502 involved measuring hydrogen gas production via Reaction (3), after metallic Al and NaOH

503 solution were combine to yield $NaAlO_2$ (sodium aluminate), H_2 gas, and heat. The test procedure

504 consisted of sampling 25 g of APW and placing in 40 mL of 25% w/v NaOH solution. The

505 volume of gas was measured using a gas collection tube. Table 4 presents the hydrogen gas

506 production and computed aluminum content for five samples.

507

508 **Table 4: Preliminary APW Reactivity Test Results**

Sample	Description	H_2 Gas (mL/gm APW)	Metallic Al Content (%)	q_{rxn}, Heat of Reaction (J)
Dross-1	Fines from secondary aluminum recovery process	131.8	9.9	~149,00
Dross-2	Gray color pebbles and dust	365.4	27.4	~408,00
Dross-3	Metallic aluminum fines, dust, floor sweepings	420.9	31.5	~470,000
Baghouse Dust-1	Dark gray, finely divided dry powder, strong ammonia odor	4.4	0.3	~5,000
Baghouse Dust-2	Very fine gray powder	9.9	0.7	~11,300

509

510

511 After measuring the volume of hydrogen gas, the equivalent amount of metallic aluminum

512 present was computed using Reaction (3) and Eq. (3). The heat generated, e.g., kJ or calories,

513 was estimated from Reaction (3), i.e., ΔH= -415 kJ/mol Al. From Table 4, the back-calculated

514 metallic Al content ranges from 0.3% to 31.5%. In particular, the baghouse dust is not reactive

515   due to the small hydrogen production while the dross samples indicate high metallic aluminum

516   content which could be captured with additional processing.

517   Because the maximum reaction temperatures were not measured, the heat of reaction was

518   used to estimate temperatures in a landfill setting. The change in temperature, ΔT, is estimated

519   using Eq. (1), where m is 65 g, $C_{p,residue}$ ~2.9 J/g·°C and is estimated using Eq. (2), and q_{rxn} (see

520   Table 4). For example, the Dross-1 sample generated ~149,000 J of energy thus the computed

521   ΔT is about 790°C. This means complete oxidation of 9.9% metallic aluminum can increase

522   temperatures by ~790°C. In a landfill the observed maximum temperatures will be less because

523   complete aluminum oxidation may not occur and heat can be lost through the landfill surface.

524   An APW monofill in Ohio is measuring downhole temperatures of ~96°C (220°F). The

525   metallic aluminum content of APW at this facility is unknown but the downhole temperatures

526   illustrate the effect of heat loss via conduction. In May 2008, temperatures measured at 8 m (26

527   ft) and 20 m (65.5 ft) below ground surface (bgs) were about 96°C (220°F). In September 2011,

528   over a two-year period, the temperatures decreased to ~70°C (158°F) at 8 m bgs but remained

529   constant at 93°C at 20 m bgs. It is likely that heat loss at the surface and waste insulation

530   contributed to the temperature change at 8 m bgs. Fig. 8 presents a possible relationship between

531   metallic aluminum content, heat loss, and maximum temperature in a landfill setting. It is evident

532   that temperatures can dramatically increase depending on the percent aluminum oxidized and

533   heat loss through the landfill cover. The maximum temperatures are capped at 100°C because

534   downhole temperatures measured at an APW monofill are ~96°C, or near the boiling point of

535   water. Even though the reactivity test results provided herein are preliminary, they show the

536   ability of the calorimeter to measure hydrogen gas and back-calculate metallic aluminum

537 content. The final development of the test protocol and interpretation of results is currently in

538 progress so the results can be used in field applications.

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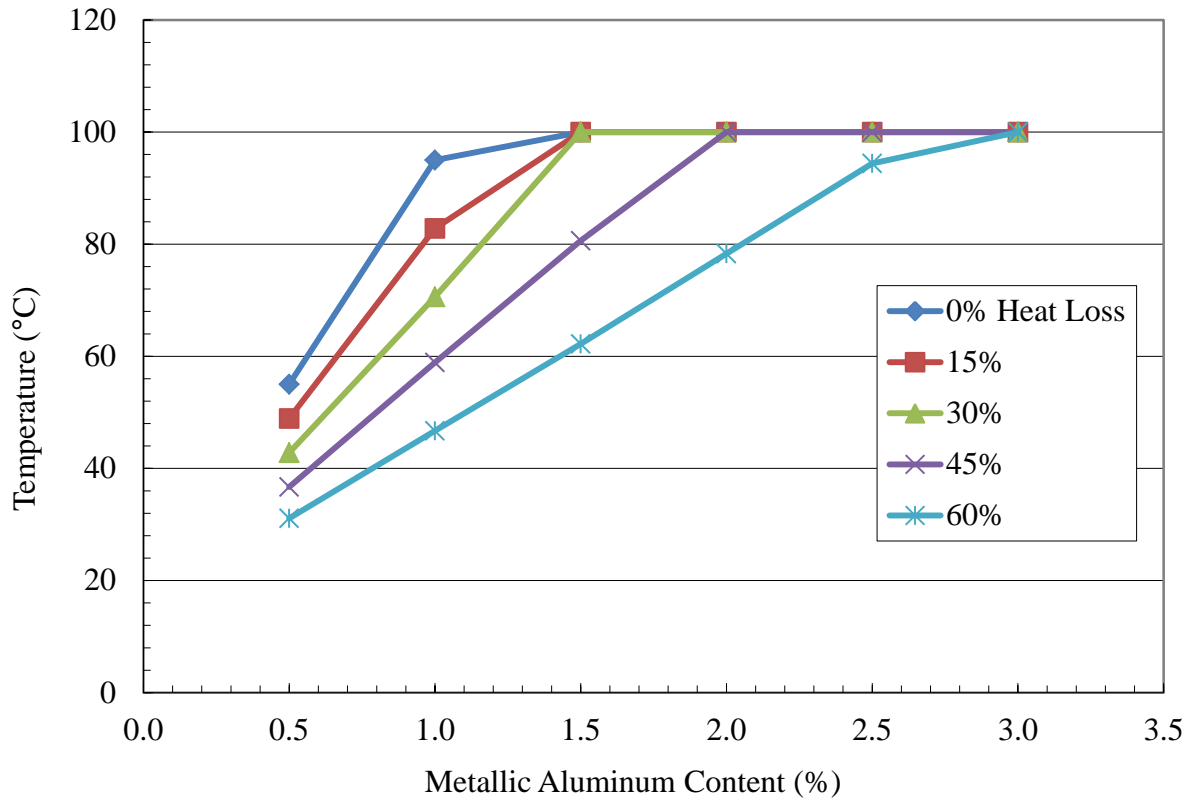
540

541 **Figure 8: Effect of aluminum content on maximum reaction temperature**

542

543 **DISCUSSION**

544 The general theory and test procedure to evaluate APW temperature escalation and metallic

545 aluminum content is provided for use by secondary aluminum generators and landfill

546 operators. The following aspects of the reactivity test procedure are being investigated to

547 facilitate field implementation:

548   1. Calibration experiments for the constant pressure calorimeter and hydrogen gas

549   measuring procedure are recommended to verify reproducibility and accuracy, i.e.,

550   produces stoichiometric equilibrium quantities of q_{rxn} and hydrogen gas, before using

551   to classify APW as hazardous or non-hazardous. A possible calibration test involves

552   aluminum powder with sodium hydroxide which produces a known amount of heat

553   and hydrogen gas that can compared to the theoretical values in Reaction (1).

554   2. The optimal test conditions should balance the APW sample size, solid to liquid ratio,

555   and strength of sodium hydroxide. Because APW is generally transported from

556   generator to the landfill facility by a transfer dump truck, a representative sample size

557   of APW is necessary for the reactivity test. The US DOT Dangerous When Wet test

558   method (49 CFR 170, Appendix E) uses a series of experiments with increasing

559   sample mass, i.e., from 2 mm diameter specimens to 25 g sample, to evaluate gas

560   production. In addition, the solid to liquid ratio and strength of sodium hydroxide are

561   important because enough alkaline liquid should be present to quickly react all

562   metallic aluminum but highly concentrated sodium hydroxide can be hazardous and

563   also wasteful.

564   3. Huang et al. (2011) found that as APW particle size decreases the reaction rate and

565   temperature increases. Because APW composition and particle size vary among

566   production processes, the effect of APW particle size should be investigated to

567   determine if screening is required before testing.

568   4. Ball-milling of APW can liberate metallic aluminum fines from granules of salt flux.

569   In addition, the crushing and grinding can mechanically activate the aluminum by

31

570   breaking the protective oxide layer and oxidizing the free metallic aluminum. In this

571   case, oxidation can decrease the metallic aluminum content before reactivity testing.

572   5. Huang et al. (2011) reports that increasing the initial starting reaction temperature can

573   increase the maximum temperature measured. Because APW is exposed to the

574   environment during transport, the initial temperature of the APW can vary depending

575   on climate. As a result, testing at varying initial temperatures or recommending a test

576   temperature, e.g. Dangerous When Wet test uses 20°C, requires further investigation.

577   6. During the hydrogen gas measuring procedure, the volume of gas changes with

578   temperature, so a correction factor may be necessary for landfill conditions.

579

580 **CONCLUSIONS**

581 The following conclusions and recommendations are presented based on the discussion and data

582 presented herein:

583   1. Although recycling aluminum is truly beneficial and sustainable, the disposal of the

584   resulting solid waste is a concern because of APW exothermic reactions. Such problems

585   can be avoided by the proposed calorimeter test that assesses reactivity of specific APW

586   loads or sources prior to disposal.

587   2. The constant pressure calorimeter test presented herein can be used to predict the

588   maximum temperature generated from an APW reaction. The maximum recommended

589   temperature for Subtitle D landfills is 60°C (140°F) to permit waste decomposition and

590   prevent elevated temperatures from impacting engineered components (composite liner

591   system, gas vents, and leachate collection system).

592   3. A procedure is also described herein to estimate the aluminum content of APW from the

593   calorimeter test. The estimated aluminum content can be used to judge if further APW

594   recycling is economical. The final decision on whether or not to accept APW for disposal

595   in a Subtitle D landfill is the responsibility of the landfill owner or manager, but the

596   proposed calorimeter test provides a practical means for estimating the potential landfill

597   temperature increase due to the APW.

598   4. The recommended reactivity test is being used to determine a calibration procedure as

599   well as to investigate the effect of particle size, testing conditions, ball-milling, and

600   environmental conditions on the maximum temperature increase and production of

601   hydrogen gas.

602

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