Aluminum Waste Reaction Indicators in a Municipal Solid Waste Landfill

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Abstract: Subtitle D landfills may contain aluminum from residential and commercial solid waste, industrial waste, and aluminum production wastes. Some aluminum-bearing waste materials, particularly aluminum production wastes, may react with liquid in a landfill and cause uncontrolled temperature increases, significant changes in gas composition and pressure, nuisance odors, and changes in leachate composition and quantity. Such reactions may also cause degradation of leachate quality (e.g., increased ammonia, sodium, potassium, chloride, and TDS concentrations), combustion of the surrounding waste, damage to engineered components (gas collection systems, leachate collection systems, and liner system materials), and slope instability. Temperatures exceeding 150°C (300°F), generation and accumulation of undesirable explosive and toxic gases (e.g., hydrogen, acetylene, ammonia, carbon monoxide, and benzene), and gas pressures exceeding 210 kPa (30.5 psi) have been observed. Water from leachate recirculation, precipitation, the waste, or groundwater infiltration can initiate the exothermic reaction if aluminum production wastes are present. This paper uses a case history to illustrate some indicators of an aluminum reaction and problems that can develop from such a reaction in a Subtitle D landfill. **DOI: 10.1061/(ASCE)GT.1943-5606.0000581.** © *2012 American Society of Civil Engineers.*

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Introduction

The U.S. Department of Energy (1999) estimates that at least one billion kilograms (two billion pounds) of aluminum production wastes are annually placed in municipal solid waste (MSW) landfills—i.e., landfills whose design is regulated under Subtitle D of the Resource Conservation and Recovery Act (RCRA) (U.S. EPA 2010). Other sources of aluminum in Subtitle D landfills include curbside MSW, industrial wastes, automobiles, and shredder waste. Some of these aluminum-bearing waste materials, particularly aluminum production wastes, may react exothermically with water, including leachate, present in or introduced into a Subtitle D landfill. Aluminum production wastes often represent a large percentage of aluminum within landfills. These waste materials contain variable amounts of aluminum metal and aluminum compounds such as aluminum carbide, aluminum nitride, and aluminum oxides mixed with other substances and are referred to as dross, white dross, black dross, and salt cake. These terms refer to the amount of aluminum metal present and the morphology of the wastes raked from the surface of molten aluminum during processing and purification processes (Manfredi et al. 1997).

While recognizing the distinction among white dross, black dross, salt cake, and other aluminum production wastes (e.g., baghouse dust and shredder waste), for brevity's sake this paper refers to these wastes collectively as aluminum production waste and focuses on recently recognized problems with aluminum production waste in Subtitle D landfills (AZoM 2002; Szczygielski 2007). The authors also recognize that the reaction of aluminum metal with water and the associated generation of heat and flammable gases has been recognized since the 1950s (Chen 1955). The potential hazards of aluminum production waste disposal have been recognized worldwide (Amer 2002; Australian Gov. Dept. of the Environment and Water Resources 2007; Lucheva et al. 2005; Miškufová et al. 2006; Shinzato and Hypolito 2005).

Aluminum Reaction

The most likely reaction of aluminum production wastes in a Subtitle D landfill or nonhazardous industrial landfill is the amphoteric reaction of aluminum with water in the presence of hydroxyl ions (Calder and Stark 2010):

$$Al_{(Metal)} + (OH)^{-1}_{(AQ)} + 3H_2O_{(Liquid)}$$
$$\rightarrow [Al(OH^{-1})_4]^{-1}_{(AQ)} + 3/2H_{2(Gas)} + Heat \qquad (1)$$
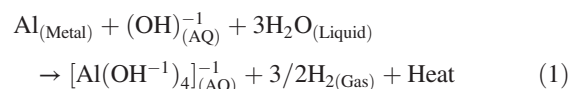
The main characteristics of the amphoteric reaction of aluminum are discussed in Calder and Stark (2010) and are briefly the following:

1. Reaction (1) only stops when the aluminum fuel is exhausted or the water is removed from the waste mass, both of which are difficult to achieve. The resulting exothermic events in Subtitle D landfills typically persist for several years.

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2. Reaction (1) produces hydrogen gas with ignition limits between 4 and 75% (v/v).
3. Controlling the reaction and resulting combustion of the surrounding MSW is difficult because exothermic aluminum reactions are usually unrecognized during their early stages, allowing a large amount of uncontrolled thermal energy (approximately 1 MJ/mol of aluminum) to be released into the waste mass.

Aluminum production wastes can remain dormant for years until sufficient amounts of water (i.e., leachate) dissolve the soluble salt from the waste matrix. With dissolution, the pH of the water gradually increases as it reacts with carbides, nitrides, and metal oxides, generating heat and gases such as methane, ammonia, and acetylene. As the water in contact with the aluminum production waste becomes alkaline (pH $>= 9$), hydroxyl ions begin to react with aluminum metal to produce hydrogen gas. The resulting chemical reactions alter leachate quality; are highly exothermic, increasing waste temperatures in excess of 100°C (212°F); release large amounts of flammable or toxic gases (e.g., hydrogen and ammonia); cause intense nuisance odors; and reduce desirable anaerobic microbial activity present within a landfill.

Aluminum Waste Reaction and Combustion Indicators

Recognizing the indicators of aluminum production waste reactions is important for determining whether a Subtitle D facility is experiencing an exothermic aluminum waste reaction, subsurface combustion, or both. This can be difficult because some indicators, e.g., increased waste mass temperatures, are common to both events, whereas other indicators are event-specific, e.g., the generation of ammonia gas from aluminum production waste reactions and elevated carbon monoxide levels for subsurface combustion. A case history is used to illustrate some of the indicators of an aluminum reaction in a Subtitle D landfill.

Permitted in 1991, the facility initially consisted of 35.7 ha (88 acres), 9.9 million m³ (13 million yd³) of disposal capacity, and Cells 1–6 (Fig. 1). In 2003, the facility received an expansion permit for an additional 69.1 ha (170 acres) of lateral expansion encompassing Cells 7–16 to the north of Cells 1–6. The site accepted more than 5,440 metric tons (6,000 short tons) of MSW per day. The facility operated normally from 1991 until July 2001, at which time the 35.7 ha (Cells 1–6) started exhibiting changes in behavior.

The composite liner systems in Cells 1–3 were constructed over mine spoil material (or structural fill composed of mine spoil over

Fig. 1. Site overview and cell layout

bedrock) and the liner systems in Cells 4–6 are constructed within the upper 6 m (20 ft) of the shale and siltstone bedrock. An inward hydraulic gradient exists on the bottom liner system where it is located below saturated mine spoil. An underdrain system was constructed adjacent to the liner system along the south side of Cell 5D (Fig. 1) during construction of Cells 4–6 to drain groundwater from the mine spoil and divert it away from the waste mass. Although the shale and siltstone bedrock produce too little groundwater to be monitored for detection of landfill gas or leachate releases to groundwater, the unit contains saturated zones and may contribute to the inward hydraulic gradient near Cells 4–6.

The facility accepted between 544,200 metric tons (600,000 short tons) and 1,033,206 metric tons (562,000 short tons) of aluminum production waste from 1991 through 2006. According to the March 2007 Findings and Orders issued by the Ohio Environmental Protection Agency (EPA), the facility placed the aluminum production wastes (mostly black dross or salt cake) in Cells 1, 3, 4A, 4B, 6, and 7 (Fig. 1).

Leachate recirculation began in April 1996 and continued until 2006, when the ongoing exothermic reaction between the aluminum production wastes and recirculated leachate became obvious in Cells 3, 4A, 4B, and 6. In addition to recirculation, the facility performed waste solidification in the areas of Cells 1 and 4A, which involved mixing liquid waste with MSW in unlined pits on the top of the landfill, which likely contributed some additional liquid to the waste, but much less than the 103,102,321 l (27,239,715 gal.) of leachate that were recirculated over approximately 10 years.

The symptoms of the aluminum reaction and associated pyrolysis and combustion of the surrounding MSW usually follow a systematic progression, as follows:
1. Elevated gas and waste temperatures,
2. Decreased methane production and elevated hydrogen or ammonia gas concentrations,
3. Changes in leachate composition,
4. Changes in landfill gas composition and increased gas pressure and flow,
5. Nuisance odors,
6. Increased leachate volume and leachate outbreaks,
7. Unusual and excessive settlement, and
8. Possible slope instability, which occurred in this case history.

Pyrolysis and Combustion

Pyrolysis is generally defined as the chemical breakdown of a substance to lower weight molecules in the presence of heat (Fire 1996). However, chemists sometimes understand pyrolysis as the breakdown of a substance exposed to heat in the absence of oxygen, often at high temperatures (e.g., ≥ 430°C, or 800°F), whereas fire scientists understand pyrolysis to be the process of thermal degradation that allows flaming combustion to self-sustain and spread, i.e., the breakdown of a substance exposed to heat in the presence of oxygen at temperatures as low as 77°C (170°F) (Babrauskas 2003a, b, c; Fire 1996). Pyrolysis is used herein to refer to the thermal breakdown of MSW (in the presence of limited oxygen, generally < 3% v/v) at relatively low temperatures, i.e., 77 to 149°C (170 to 300°F), in response to the exothermic aluminum production waste reaction.

The occurrence of pyrolysis within a waste mass should not be equated with combustion. Pyrolysis is an endothermic process that precedes the exothermic process of flaming or smoldering combustion (Pitts 2007). As such, pyrolysis requires energy input, unlike combustion, does not provide energy output, and is not a self-sustaining process like combustion. Accordingly, indicators of ongoing combustion (e.g., flames, smoke, elevated carbon monoxide, rapid settlement, and elevated waste and landfill gas temperatures)
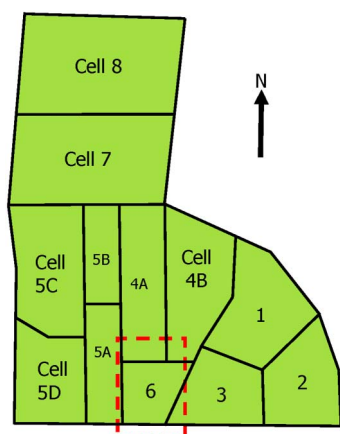
should not be attributed solely to the endothermic process of pyrolysis (Fire 1996).

One of the main problems associated with the heat generated by an aluminum reaction is that the heat can initiate smoldering combustion of the waste mass. Smoldering combustion is a propagating, self-sustained exothermic reaction deriving its principal heat from heterogeneous oxidation of a solid fuel (Babrauskas 2003a, c). Smoldering occurs directly on the surface of a solid fuel (and not in the gas phase, as is the case with flaming combustion) and is therefore not dependent upon pyrolysis for propagation. During smoldering combustion, flames are not produced, and the combustion reaction can occur under the low oxygen conditions (< 3% v/v) that are typical in Subtitle D landfills. Smoldering produces smoke and carbon monoxide, both of which were observed at the subject facility.

Increased Gas and Waste Temperatures

Temperatures in the MSW were measured with thermistors (1) in gas extraction well heads, (2) at various depths in gas extraction wells, (3) in waste boreholes, and (4) in leachate collection pipes. Of the four methods, the direct measurement of temperatures in waste boreholes provided the most accurate data, followed by measuring downhole temperatures in gas wells. Well-head temperatures are easier to obtain than downhole temperatures but are less indicative of actual waste temperature at depth, typically being 11 to 22°C (20 to 40°F) lower than downhole temperatures based on measurements at this site. As opposed to downhole temperatures, well-head temperatures are influenced by heat loss at the well head and ambient air temperature. Measurement of leachate collection system temperatures was primarily performed at this site to evaluate temperature conditions at or near the geomembrane in the single composite liner system, and these temperatures exceeded 85°C (185°F).

Waste temperatures exceeding 143°C (290°F), downhole temperatures reaching 149°C (300°F), and well-head temperatures up to 110°C (230°F) were recorded at this site. As of October 2009, the elevated temperatures in the waste, landfill gas, and leachate collection system had been detected over a period of about 6 years.

Sustained elevated temperatures in excess of 85°C (185°F) can adversely impact the service life and integrity of a landfill gas extraction system, leachate collection system, and materials in the composite liner system (Rowe et al. 2010). The effects of these elevated temperatures on the engineered components are the subject of a separate paper.

The heat generated by an aluminum production waste reaction can adversely impact landfill engineering components and cause smoldering combustion of the surrounding MSW. While the heat generated by the aluminum production waste reaction and heat generated by subsurface combustion may have similar indicators (e.g., increased waste and landfill gas temperatures), other indicators at this site can be attributed to waste combustion (FEMA 2002). These indicators include carbon monoxide concentrations in landfill emissions exceeding 1,000 ppmv for prolonged periods. At this site, carbon monoxide typically ranging from 2,000 to 5,000 ppmv with waste temperatures exceeding 93°C (200°F) were measured. Odors described as hot or burning exhibited by the facility are an indication of possible waste combustion. Smoke was observed at the ground surface of the facility, and substantial steam (possibly mixed with smoke) was emitted from landfill gas well borings. Sootlike material was also observed in the landfill gas extraction system, as was ashlike sediment in the leachate.

Changes in Leachate Composition

The leachate composition and quality began to change at this site shortly after leachate recirculation was initiated in 1996. Fluid added to the waste mass via leachate recirculation began to dissolve soluble salts from the aluminum production wastes (primarily black dross and salt cake). As a result, concentrations of sodium, potassium, chloride, and total dissolved solids (TDSs) increased steadily from 1998 to about 2007 and then significantly after 2007, as shown in Fig. 2. The large amount of data shown in Fig. 2 from 2006 to 2008 reflects increased testing after it became obvious that the landfill was performing differently. Sodium, chloride, and TDS concentrations increased nearly one order of magnitude, and potassium concentrations increased nearly two orders of magnitude.
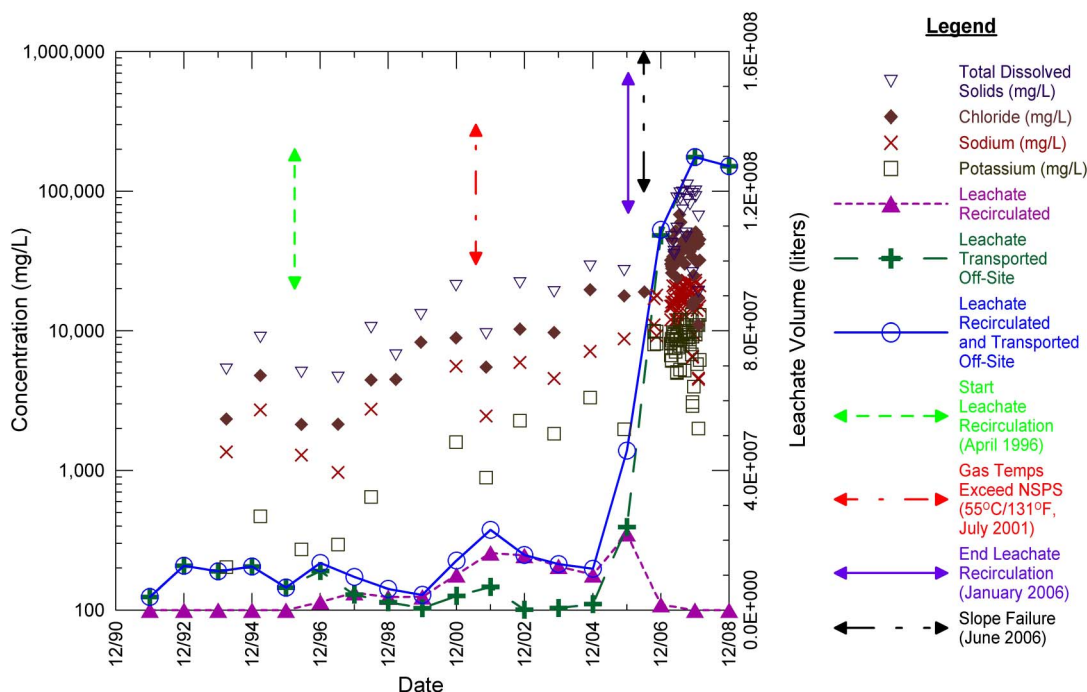

Fig. 2. TDS, chloride, sodium, and potassium trends in leachate, March 1993 through February 2008, and leachate volume generated in 35.7 ha
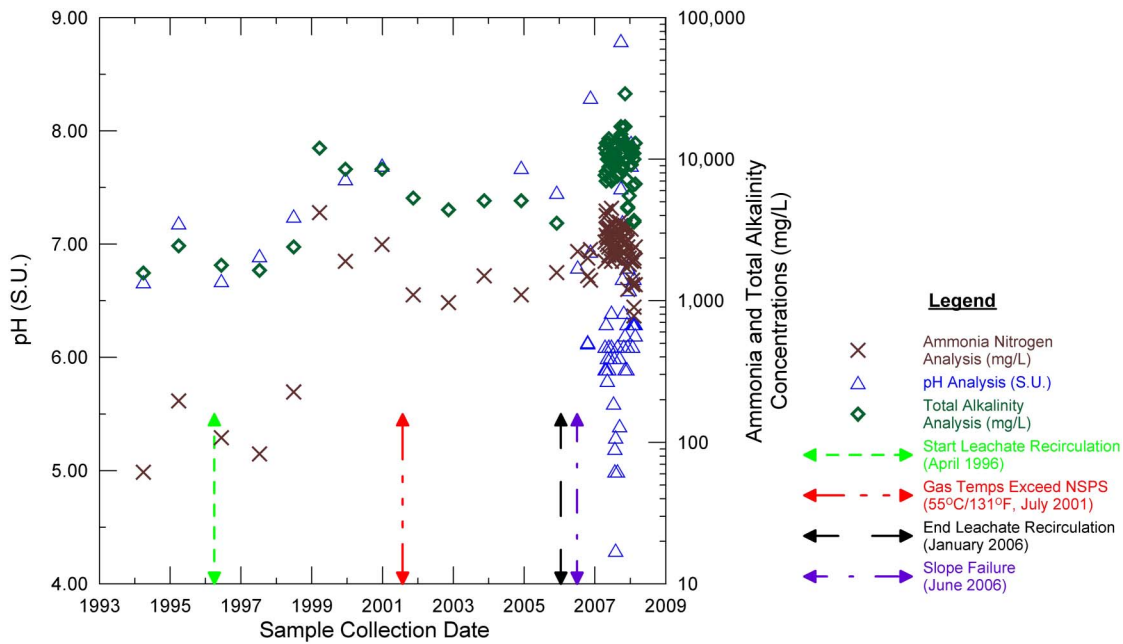
Fig. 3. Ammonia nitrogen, pH, and total alkalinity trends in leachate, March 1993 through February 2008

By 1999, ammonia nitrogen concentrations had increased nearly two orders of magnitude from 1996 and remained relatively high (1,000 to 5,000 mg/L), as shown in Fig. 3. The relatively sudden increase in ammonia nitrogen concentrations was likely caused by the exothermic reaction of aluminum nitride with recirculated leachate and corresponds to elevated landfill gas temperatures and pressures being measured and documented by the higher operating value (HOV) demonstrations that the facility submitted to the regulatory authorities beginning in 2001 and continuing through 2006 to comply with the Clean Air Act New Source Performance Standards (NSPS). Some of the elevated ammonia may be attributed to the normal effects of leachate recirculation because elevated ammonia concentrations up to 1,400 mg/L have been observed in bioreactor and recirculation landfills (Benson et al. 2007).

Total alkalinity concentrations are also shown in Fig. 3 and correlate generally with the ammonia nitrogen trend. The decreasing total alkalinity trend from 1999 to 2006 may reflect two stages of the aluminum production waste reaction. Initially, the alkalinity of the leachate increases as hydroxyl ions are generated by the reaction of carbides, basic metal oxides, and ammonia gas produced by the exothermic reaction of aluminum nitride. When sufficient concentrations of hydroxyl ions are present, the metal fraction of the aluminum production waste begins to react exothermically, consuming hydroxyl ions and lowering the alkalinity. The pH trend shown in Fig. 3 supports this hypothesis by showing a rising pH trend between 1998 and 2001 and a decreasing trend after 2005. While the measured pH did not exceed 9.0 Standard Units (S.U.), the pH of the fluid in contact with the aluminum production waste probably equaled or exceeded 9.0 S.U. based on the generation of hydrogen gas as shown in Reaction (1).
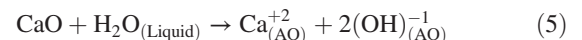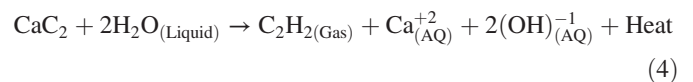
Following the June 2006 slope failure, concentrations of ammonia nitrogen and total alkalinity increased a second time (2,541 mg/L average and 11,034 mg/L average, respectively), and the leachate pH continued to decrease on average (6.42 S.U.) with pH values from 4.30 to 8.80 S.U. These trends may be explained by waste movement within the landfill waste mass associated with the slope failure and subsidence due to consumption of

the waste by combustion. Such slope movements may have exacerbated the ongoing aluminum reaction by allowing leachate to contact aluminum dross and salt cake that had not previously reacted. In addition, the volume of leachate produced by the landfill increased significantly between 2005 (45,687,720 L or 12,070,732 gal.) and 2008 (127,183,949 L or 33,602,100 gal.), as shown in Fig. 2. The increase in leachate volume likely played a role in the continued progression of the aluminum production waste reactions and the associated trends in leachate chemistry by increasing the extent of the reaction.

In summary, the changes in leachate quality are consistent with the dissolution and exothermic reaction of aluminum production waste and the occurrence of smoldering combustion within the waste mass. The elevated concentrations of sodium, chloride, potassium, and TDSs are likely the result of dissolution of the soluble salts, which may comprise as much as 80% of the aluminum production waste by weight. Elevated ammonia nitrogen concentrations are attributed to the reaction of aluminum nitride with leachate [Reaction (2)]:

$$2AlN + 6H_2O_{(Liquid)} \rightarrow 2Al(OH)_3 + 2NH_{3(Gas)} + \text{Heat} \quad (2)$$

Elevated total alkalinity is attributed to the generation of hydroxyl ions from the reactions of leachate with ammonia gas [Reaction (3)], carbides [Reaction (4)], and basic metal oxides [Reaction (5)]:

$$NH_{3(Gas)} + H_2O_{(Liquid)} \rightarrow NH_{4(AQ)}^+ + (OH)_{(AQ)}^{-1} \quad (3)$$

$$CaC_2 + 2H_2O_{(Liquid)} \rightarrow C_2H_{2(Gas)} + Ca_{(AQ)}^{+2} + 2(OH)_{(AQ)}^{-1} + \text{Heat} \quad (4)$$

$$CaO + H_2O_{(Liquid)} \rightarrow Ca_{(AQ)}^{+2} + 2(OH)_{(AQ)}^{-1} \quad (5)$$

The utility of evaluating changes in leachate quality to identify aluminum production waste reactions or subsurface combustion will depend on the configuration of the leachate collection system. If individual areas or cells at a facility can be monitored, then

leachate chemistry observations may provide an early indication of a problem. If leachate is monitored as a composite liquid from many parts of a landfill, gradual changes in leachate quality from a distinct area of the waste mass may be difficult to discern, so significant changes may not be noticeable until the reaction has affected a large area.

Changes in Gas Composition and Landfill Gas Pressure

Changes in landfill gas composition occurred as the aluminum production waste reaction and accompanying waste combustion progressed. The first gas-related indicator of the aluminum production waste reaction was the presence of ammonia, a by-product of the reaction of water and aluminum nitride present in aluminum dross. Hydrogen gas is generated from the amphoteric reaction of aluminum and water in the presence of hydroxyl ions. The generation of hydrogen associated with aluminum production waste [Reaction (1)] appeared to occur after the generation of the ammonia, acetylene, and methane reactions as the pH of the recirculated leachate in contact with the aluminum production waste became more alkaline. Other early-stage aluminum production waste reactions include the generation of acetylene from calcium carbide in aluminum production waste [Reaction (4)] and the generation of methane from aluminum carbide [Reaction (6)]:

$$Al_4C_3 + 12H_2O_{(Liquid)} \rightarrow 4Al(OH)_3 + 3CH_{4(Gas)} + Heat \quad (6)$$
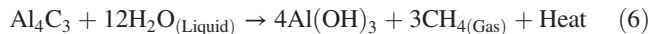
Hydrogen gas is produced as an intermediate compound in the conversion of MSW into methane. During the brief Phase II (acidic) decomposition of landfill waste, which begins after the oxygen in the waste mass has been consumed, hydrogen gas generation begins and landfill gas may consist of as much as 20% hydrogen by volume. Subsequently, the hydrogen component of landfill gas declines to near zero during the start of Phase III (methanogenic) and Phase IV decomposition of waste (constant gas composition and production) as it is converted into methane. At the time of the aluminum reaction and waste combustion at the subject site, the waste was in Phase III to Phase IV decomposition when hydrogen gas levels should typically be less than 0.2% v/v (ATSDR 2001). Instead, the hydrogen gas levels at the site ranged from 20 to 50% v/v. The accumulation of large amounts of hydrogen gas can be problematic because hydrogen is extremely flammable, having an explosive range of 4 to 75% by volume in normal atmosphere. One reason a hydrogen explosion did not occur at this site is that the oxygen level present in the waste mass was generally less than 3% v/v, which is well below normal atmospheric conditions (20.8% v/v). This was accomplished by the installation of a geomembrane over the affected area, which was enlarged as the affected area increased with time. In 2006, Cell 6 and portions of Cells 1, 3, 4A, 4B, 5A, 5B, and 5C were covered with a geomembrane (Fig. 1), and in 2009, Cells 5A, 5D, and 6 were covered, along with portions of Cells 1, 2, 3, 4A, 4B, 5B, and 5C.

With the generation of ammonia, acetylene, methane, and hydrogen from the aluminum production waste reaction, a dramatic increase in landfill gas pressure occurred. In some areas, a gas pressure of about 50 kPa (7.3 psi) was measured. This positive pressure occasionally manifested itself in "leachate geysers" shooting through the cover soil and reaching 9 to 10.2 m (30 to 40 ft) in the air. These leachate geysers were also encountered when borings were drilled in the waste for gas wells or exploratory purposes. Most, if not all, of the 35.7 ha (88 acres) of the facility were affected by significant gas pressure. These gas pressures contributed to the instability that caused the south slope failure discussed subsequently.

In addition to the increased gas pressure, the facility experienced a substantial increase in gas quantity. During the early phases of the aluminum production waste reaction and associated subsurface combustion (December 2005), the gas flow was about 50 m³/min (1,800 ft³/min). By August 2006, the gas flow was more than 140 m³/min (5,000 ft³/min). The gas flow as of June 2009 was more than 158.9 m³/min (5,639 ft³/min). This substantial increase in gas quantity required a significant enhancement of the gas extraction system, including installation of more than 150 new gas wells, an increased compression/vacuum system, and a 2.0 mm (80 mil) thick HDPE geomembrane over the affected area to improve gas collection efficiency and reduce odors.

The aluminum and water reaction also generated considerable heat. Yeşiller et al. (2005) estimate that normal MSW heat generation ranges from 23 to 77 MJ/m³ (average 50 MJ/m³). Based on the foregoing Reaction (1), 1 m³ of aluminum production waste containing 5% aluminum metal by weight (e.g., salt cake) has the potential to generate up to 40,000 MJ of heat energy, or 800 times the heat energy normally generated by an equivalent volume of MSW. Given this potential energy release, the relationship between heat generation and temperature presented by Yeşiller et al. (2005) suggests that reacting aluminum production waste could raise waste mass temperatures in excess of 204°C (400°F). Elevated temperatures observed at the case-study landfill generally ranged between 60 and 150°C (140 and 300°F).

When the heat from the aluminum production waste reaction initiated smoldering combustion in the surrounding waste mass, the gas composition changed again, with the generation of carbon monoxide and carbon dioxide at concentrations well above those present in typical landfill gas (FEMA 2002; ATSDR 2001), elevated concentrations of certain volatile organic compounds (VOCs) and semivolatile compounds (SVOCs) (Parker et al. 2002; Eklund et al. 1998; U.S. EPA 1991), and concentrations of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) (up to 3,010 pg/m³) that appeared to be comparable to those generated by active waste fires (Ruokojärvi et al. 1995). At the same time, normal levels of methane gas in the waste mass (45 to 60%, ATSDR 2001) rapidly decreased as methanogens died off in response to landfill temperatures rising above 88°C (190°F). Methane production effectively dropped to zero within the 35.7 ha (88 acres) of Cells 1–6 of the waste mass affected by the aluminum reaction and associated subsurface combustion.

Carbon monoxide is primarily a by-product of incomplete combustion due to limited oxygen, i.e., heterogeneous smoldering combustion (Fire 1996). Carbon monoxide may also be produced biologically in temperature-stressed systems, but current guidance on Subtitle D landfill fires suggests that abnormally high carbon monoxide levels (> 200 ppmv) are more likely the product of subsurface combustion than biological activity (FEMA 2002). Carbon monoxide levels in a Subtitle D landfill should normally not exceed 200 ppmv (ATSDR 2001). According to FEMA (2002), landfill fire is occurring when concentrations of carbon monoxide exceed 1,000 ppmv in landfill gas. At this facility, carbon monoxide levels in landfill gas ranged from 1,000 to 8,067 ppmv from April 2006 through November 2007, which is consistent with the process of subsurface smoldering combustion of the waste mass.

Carbon dioxide is normally present in Subtitle D landfills at concentrations ranging between 40 and 60% v/v (ATSDR 2001). However, carbon dioxide levels measured in some gas extraction wells at this facility ranged from 60 to 80% v/v. The increased carbon dioxide levels correlate with higher gas well temperatures (those greater than 88°C or 190°F) and indicate an increase in the efficiency of MSW combustion due to increased heat or increased

Table 1. Comparison of Landfill Gas VOC Concentrations

Landfill gas volatile organic compounds	Case-study landfill		U.S. EPA (1991)		Parker et al. (2002) (see also Eklund et al. 1998)	
	Max. ppmv	Avg. ppmv	Max. ppmv	Avg. ppmv	Max. ppmv	Avg. ppmv
Acetone	3,781	597	32	5.94	21.155	3.688
Benzene	940	219	52.2	3.6	35.737	1.538
Ethyl acetate	1,167	67	20 (single analysis)		—	
Methyl-ethyl ketone	2,373	278	57.5	8.17	20.966	4.615
Tetrahydrofuran	2,678	275	30 (single analysis)		—	
Toluene	769	48	758	59.34	387.777	22.870
Total xylenes	642	29	70.9	17.11	100.917	5.482

availability of oxygen, probably due to cracks in the soil cover caused by excessive settlements and overdrawing of the gas extraction system, discussed subsequently. Carbon dioxide can also be produced biologically and be elevated in concentration when methane production is inhibited. As a result, some of the elevated carbon dioxide may also be derived from methanogens being inhibited as well as combustion but values of 60 to 80% v/v generally exceed those derived from biological degradation.

The aluminum production waste reaction and associated subsurface combustion appear to have significantly increased the landfill gas concentrations of some VOCs. In general, VOC emissions from Subtitle D landfills double with every $-8°C$ (18°F) of temperature increase (ATSDR 2001). From April 2007 through February 2008, seven VOCs were detected in landfill gas samples at concentrations exceeding 1,000 mg/m^3 including acetone, benzene, ethyl acetate, methyl-ethyl ketone, tetrahydrofuran, toluene, and total xylenes. This facility performed a total of 1,362 gas analyses for VOCs, with the referenced compounds being detected in 98 to 100% of the samples.

Based on a comparison of the maximum and average concentrations of these compounds to other concentrations determined by other investigations (Table 1), concentrations of these VOCs in the case-study landfill were one to two orders of magnitude higher than those expected in a normally operating Subtitle D landfill (U.S. EPA 1991). Although total VOC data were not readily

available for review, the data evaluated indicate the VOC component (total concentration) increased significantly in response to the reaction and accompanying combustion. Generally, the total VOC component of landfill gas generated by a normally operating Subtitle D landfill ranges up to 0.1% v/v or 1,000 ppmv (Soltani-Ahmadi 2002).

Several SVOCs were also detected in the landfill gas samples at elevated concentrations, including 1,4-dichlorobenzene (4.0 ppmv max., 0.5 ppmv avg., 84% detection rate), 2-methylphenol (3.2 ppmv max., 0.7 ppmv avg., 5% detection rate), 4-methyphenol (85.8 ppmv max., 3.5 ppmv avg., 85% detection rate), phenol (649.4 ppmv max., 14.4 avg., 92% detection rate), and pyridine (9.6 ppmv max., 1.4 ppmv avg., 16% detection rate). These values are based on 638 samples analyzed between April and December 2007.

The changes in landfill gas composition discussed previously are illustrated in Figs. 4 and 5, which show monitoring results for a horizontal gas collector in the affected area at the subject facility. Between May 2005 and September 2006, the collector generally exhibited normal methane concentrations (50 to 70%), carbon dioxide concentrations (30 to 50%), and landfill gas temperatures ($< 55°C$, $< 131°F$), with the exception of the period between October 2005 and May 2006, when the gas collector was being overdrawn in an effort to control nuisance odors and was pulling
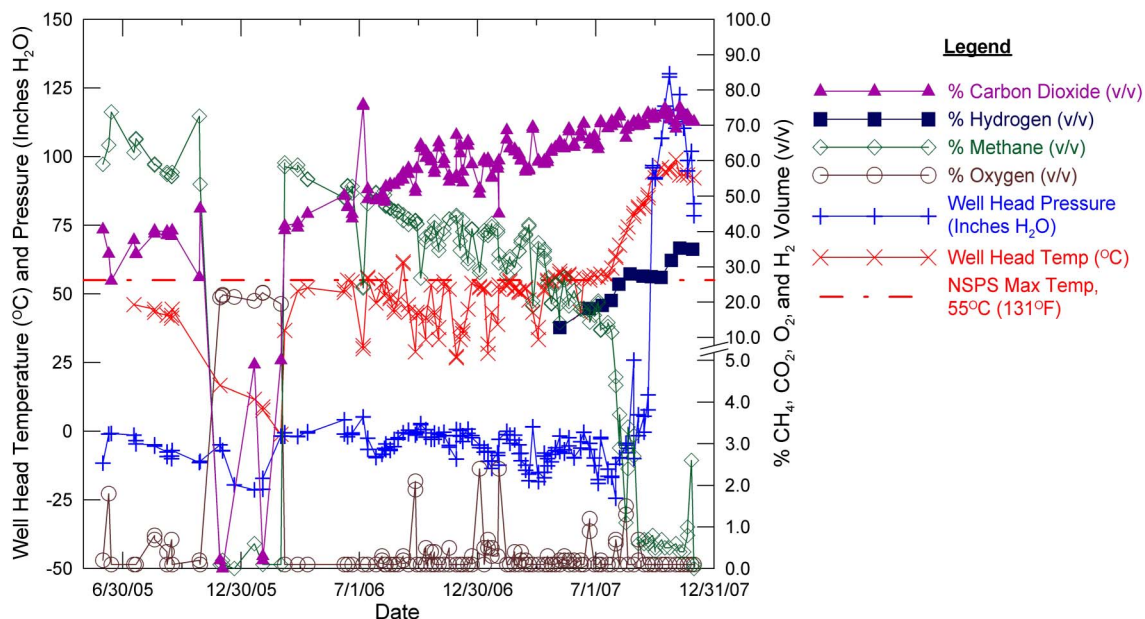
Fig. 4. Horizontal gas collector: carbon dioxide, hydrogen, methane, oxygen, well-head pressure, and well-head temperature trends
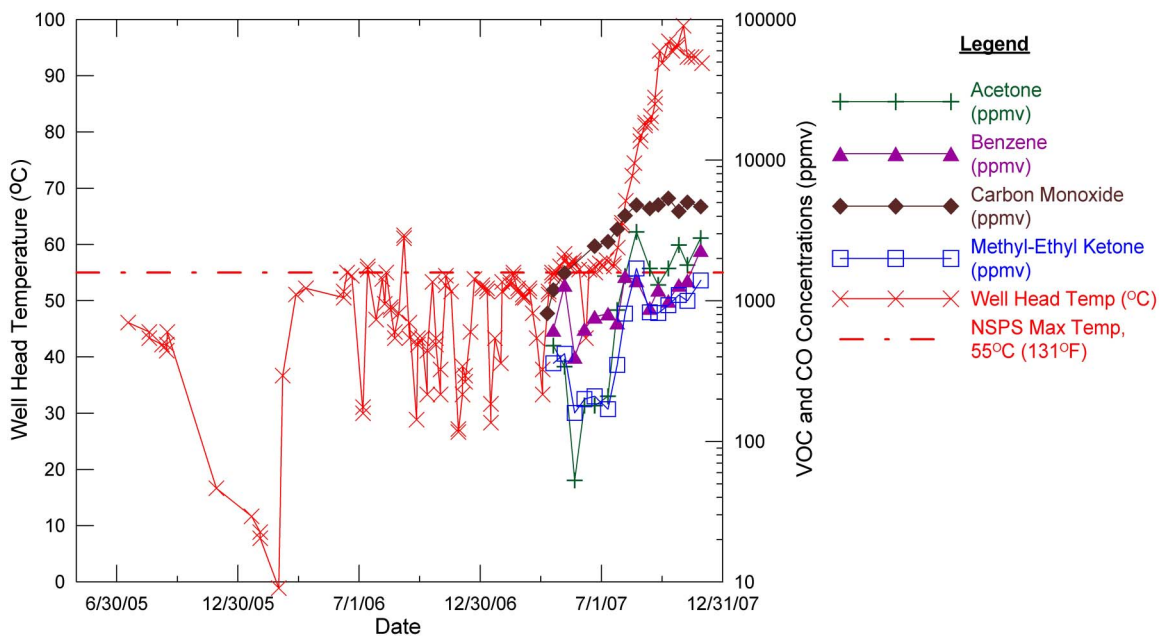
Fig. 5. Horizontal gas collector: volatile organic compound, carbon monoxide, and well-head temperature trends

in ambient air, as indicated by the negative well-head pressure and 20.8% oxygen concentration (Fig. 4).

Fig. 4 indicates the development of subsurface combustion (in conjunction with the aluminum production waste reaction), with methane and carbon dioxide concentrations diverging during July 2006 and the methane concentration decreasing to near zero by August 2007. Carbon monoxide levels began exceeding 1,000 ppmv during April 2007 and rose to approximately 5,500 ppmv during October 2007 (Fig. 5).

By September 2006 the gas temperature was fluctuating close to the NSPS limit ($< 55°C$, $< 131°F$), whereas the methane concentration began to gradually decrease. This was likely due to heating of the waste mass in the vicinity of the collector to temperatures exceeding $88°C$ ($190°F$), which started killing methanogens. Methane concentrations declined more rapidly in April 2007, when the accumulation of hydrogen gas indicated the presence of an aluminum production waste reaction within the area of influence of the collector (Fig. 4). As hydrogen concentrations increased to about 35% v/v in October 2007, the waste temperature increased to approximately $93°C$ ($200°F$), with carbon monoxide levels exceeding 5,000 ppmv and carbon dioxide levels near 70% v/v. In addition, the well-head gas pressure increased rapidly from approximately 0.5 m (20 in.) to 3.6 m (140 in.) of water (Fig. 4). Landfill gas VOCs (acetone, benzene, and methyl-ethyl ketone) increased over one order of magnitude between April and October 2007 (Fig. 5).

Nuisance Odors

The facility generated strong to intense odors from 2005 to July 2009. Initially, citizens complained about an odor that they described as "sweet," like "rotting apples," and "hot." During spring 2007, the odor began being described as "burning" or "solventlike," and others likened it to a diesel fuel or coke furnace odor. From January to August 2006, over 660 odor complaints were filed with state and local regulatory agencies. Citizens complained of burning eyes and throats, headaches, nausea, and other symptoms when the odor was present. One local school closed its ventilation system as the teachers' and students' eyes and throats were irritated by the odor. The odor was more pronounced when drilling or other such activities occurred at the landfill. The leachate itself had a reaction

odor that was strong and irritating, and odor complaints often increased when the facility experienced leachate outbreaks or geysers.

To address the numerous odor complaints, the facility significantly enhanced the gas extraction system. Additional vacuum was applied to mitigate odors, and the facility also used the enhanced gas extraction system to control the positive pressure caused by the aluminum production waste reaction. However, increasing the vacuum increased the likelihood of oxygen infiltration into the waste mass and initiating (or supporting) subsurface combustion, as illustrated by Fig. 4. The increased vacuum at the case-study facility may have been facilitating oxygen infiltration and fueling subsurface combustion, at least until a temporary geomembrane cover was installed over at least portions of Cells 2–6.

Increased Leachate Volume and Leachate Outbreaks

The aluminum reaction in the subject facility began after the initiation of leachate recirculation, which commenced in 1996, as shown in Fig. 2. From 1999 until 2005, most of the leachate generated was recirculated, so the volume of leachate transported off-site during this period was minimal. Leachate recirculation ended in 2006, when it was obvious that the landfill was exhibiting abnormal characteristics.

From 1991 through 2004, the 35.7 ha comprising the initial facility generated between 3,775,973 L (997,615 gal.) to a maximum of 23,004,624 L (6,077,840 gal.), as shown in Fig. 2. In 2004, the leachate volume was 11,807,770 L (3,119,622 gal.). In 2005, the leachate volume increased to 45,687,720 L (12,070,732 gal.) and continued to increase in subsequent years with 108,953,875 L (28,785,700 gal.) in 2006, 129,785,758 L (34,289,500 gal.) in 2007, and 127,183,949 L (33,602,100 gal.) in 2008.

The total 103,102,321 L (27,239,715 gal.) of leachate that was recirculated at the facility over approximately 10 years is assumed to be the primary source of the leachate volume increase. As noted earlier, waste solidification activities contributed some moisture to the waste mass, but probably much less than recirculation activities. The facility performed leachate recirculation via a trench distribution system and additionally had obtained approval from

the state regulatory agency to inject leachate directly into gas extraction wells, which is an unusual practice. However, the amount of leachate generated by the effects of the reaction and subsequent combustion significantly exceeded the total amount of leachate recirculated. For example, from 2006 through 2008 the annual volume of leachate generated (Fig. 2) (~120,000,000 L or 31,700,000 gal.) exceeded the total amount of leachate recirculated from 1996 to 2006 (103,102,321 L or 27,239,715 gal.). In addition, the total volume of leachate generated from only 2006 through 2008 (363,214,857 L or 95,961,653 gal.) far exceeded the total amount of leachate recirculated from 1996 to 2006 (103,102,321 L or 27,239,715 gal.).

Infiltration of precipitation is not thought to have contributed significantly to the increased leachate volume because most of the 35.7 ha had been covered with a 2.0 mm (80 mil) thick HDPE geomembrane to control odors since 2006. However, prior to the placement of the geomembrane, significant surface-water ponding occurred within a large bowl-shaped area at the top of the landfill created by rapid settlement of the underlying waste.

Other potential sources of the excess leachate include water generated by the heating or combustion of organic wastes (waste moisture content), noncombustion chemical or biochemical reactions, and possibly inward gradient groundwater infiltration through the heat- or slope-movement-impacted liner system.

Approximately 65% of MSW is comprised of paper, cardboard, wood, yard wastes, and food scraps (U.S. EPA 2005). The heating, pyrolysis, and combustion of these materials could account for a significant amount of excess water. The typical moisture content of MSW is 10 to 20% by weight and may reach 30% by weight if leachate recirculation is performed. Water is a major combustion product, along with carbon monoxide and carbon dioxide. In the case of a rapidly spreading flaming fire with little or no associated aluminum production waste reaction, the moisture in the waste is driven ahead of the fire as water vapor (steam) and does not increase the volume of leachate (Øygard et al. 2005). However, in the case of an aluminum production waste reaction with associated smoldering combustion, as the waste mass is heated, the moisture concentration of the landfill gas increases, and a high degree of saturation is maintained as long as the waste continues to generate excess water vapor. As the saturated gases move to cooler regions of the landfill, the water vapor condenses, with the excess water being reabsorbed by the waste or becoming leachate. Because of the readsorption of at least some of the water, the large increase in leachate volume is not attributed solely to waste moisture content.

Water formed from noncombustion chemical or biochemical reactions occurring in the waste mass also may have contributed to the excessive leachate volume. For example, hydrogen and oxygen react to produce water [Reaction (7)]:

$$H_{2(Gas)} + \frac{1}{2}O_{2(Gas)} \rightarrow H_2O_{(Liquid)} + Heat \qquad (7)$$
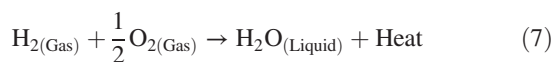
Oxygen levels from gas extraction wells in the waste mass generally were being maintained at or below 1.5% v/v, which would severely limit the amount of water generated from this reaction if it were occurring.

The sidewall liner on the south side of the landfill in the vicinity of Cell 6 may have been damaged due to the high temperatures, gas pressures, leachate chemical composition, or the 2006 slope failure. If the liner was compromised, groundwater from the adjacent mine spoil and underlying shale and siltstone bedrock could have migrated into the waste mass and contributed to the excessive leachate volume because the liner system is below the zone of saturation in the mine spoil.

The increased volume of leachate contributed to the many leachate outbreaks at the facility. Outbreaks appeared to be projected ahead of the reaction and combustion as leachate was pushed away from areas of high temperature to areas of lower temperature along with elevated gas pressures. Additionally, convection of landfill gas may have facilitated redistribution of water within the waste mass, with hot, moisture-rich landfill gas (including water vapor from the pyrolysis or combustion of waste) moving from areas of high temperature to areas of lower temperature, where a portion of the water vapor component of the gas condensed and contributed to the leachate volume. When leachate outbreaks occurred on a bench instead of a slope, gas bubbles could be seen bubbling up through ponded leachate.

Unusual Settlement

The aluminum production waste reaction and associated smoldering combustion progressed in stages through the facility, with atypical landfill settlement being its final manifestation. The magnitude of this settlement, 30 to 35% of the initial height in Cell 3, is greater than settlement normally observed in a Subtitle D landfill, e.g., 5 to 10% of the initial height over 30 years (Edgers et al. 1992; Spikula 1997). Since April 2006, approximately 1,224,000 m³ (1,600,000 yd³) of settlement volume has occurred based on the vertical decrease in height over the lateral extent of the reaction/combustion area. This has resulted in the settlement of the top of the landfill by more than 21.2 m (70 ft) where the initial waste thickness was about 45.8 m (150 ft), or 40 to 45% of the initial height. The settlement is attributed to the reaction and subsequent combustion because the volume of waste in the landfill had to be reduced (i.e., consumed by the reaction or combustion) for such abnormally extensive and deep settlement to develop. Combustion is evident because the large settlement occurring in the various portions of Cell 5 is not due to an aluminum reaction as no dross was placed in these cells according to the March 2007 Findings and Orders issued by the Ohio EPA.

Before an area was covered with a geomembrane, substantial cracking of the interim soil cover was observed due to this rapid settlement. This cracking helped illustrate the magnitude and direction of settlement and slope movement that was occurring as a result of the consumption of the waste materials and south slope instability, respectively. In some areas, the tension cracks had a width of over 0.3 m (1 ft). As the middle to lower portion of the waste column was consumed by the reaction and combustion, the top and sides of the landfill collapsed inward, creating a large bowl-shaped structure at the top of the landfill and flattened slopes. This is also occurring along the west slope as the waste is consumed in the various portions of Cell 5.

Slope Instability

An indirect effect of the reaction and combustion that occurred during the various stages of the event described previously is the failure of a portion of the south slope at the subject facility (see dashed red box in Fig. 1). Monitoring stakes installed near the middle of the slide area showed a movement of 4.3 to 6.1 m (14 to 20 ft) from July 13 to October 2, 2006. The total movement was greater because the slope movement started long before July 13, 2006. In fall 2006, the facility constructed a large soil buttress to try to stop the ongoing slope movement. However, the stability of the south slope continued to be a concern until significant settlement reduced the slope height and inclination in this area due to waste being consumed by the reaction or combustion. The slope failure resulted in waste being conveyed outside the permitted limit.

An indirect effect of the reaction and combustion on slope stability is the effect on the shear strength of the waste.

Stark et al. ([2008](#)) model the stress-dependent nature of the Mohr-Coulomb strength envelope for MSW (1) for effective normal stresses less than 200 kPa using c' and ϕ' of 6 kPa and 35°, respectively, and (2) for effective normal stresses greater than or equal to 200 kPa c' using ϕ' of 30 kPa and 30°, respectively. These strength parameters are significantly greater than the c' of 0 kPa and ϕ' of 20° reported for thermally degraded waste at this site ([Stark et al. 2010](#)). This friction angle is also substantially lower than friction angles suggested for biologically degraded waste, e.g., 30° ([Kavazanjian 2008](#)), because MSW organic components, including reinforcing materials, were significantly charred or reduced to ash by the reaction or combustion. Therefore, absent a substantial reduction in slope height and inclination, facilities experiencing a reaction or combustion could be less stable simply due to a large reduction in MSW strength even if elevated gas and liquid pressures are not present.

Conclusions and Recommendations

The following conclusions and recommendations are presented based on the data presented previously:

1. An aluminum reaction in a Subtitle D landfill can produce many undesirable effects that can adversely affect its behavior and operation. The manifestations of the aluminum reaction and resulting MSW combustion at this site, in order, are elevated temperatures, decreased methane production and elevated hydrogen or ammonia concentrations, changes in leachate and gas composition, elevated liquid and gas pressure, nuisance odors, increased leachate and gas quantities, leachate outbreaks, and unusual settlement. These abnormal conditions can cause other adverse impacts, such as slope failure, damage to the composite liner system and gas control system, and groundwater contamination.

2. The most likely cause of uncontrolled temperature increases involving aluminum waste is a hydrogen-producing amphoteric reaction of aluminum under alkaline conditions of pH $\geq$ 9.0. This reaction also can be responsible for excessive accumulation of hydrogen in landfill gas.

3. Leachate recirculation should not be performed in Subtitle D landfill cells that contain aluminum production waste, and conversely, aluminum production waste should not be placed in cells where leachate recirculation has occurred.

4. Thermistors should be installed in areas accepting aluminum production waste to reliably detect increasing temperature trends as early as possible.

5. Subtitle D landfills should establish baseline chemistry for landfill gas, condensate, and/or leachate (depending on the leachate collection system design) generated under normal operating conditions, including typical concentration ranges for methane, carbon dioxide, carbon monoxide, hydrogen, VOCs, SVOCs, alkalinity, ammonia, chloride, metals, pH, or total dissolved solids depending on the media. Trend analysis or other statistical methods can then be performed using these data to identify significant changes in measured parameters and serve as a warning system for exothermic reactions or subsurface combustion.

Acknowledgments

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