

Detection of Aluminum Waste Reactions and Waste Fires

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Abstract: Aluminum production wastes (APW) placed in Subtitle D regulated landfills may react exothermically and cause uncontrolled temperature increases, large volumes of explosive and toxic gasses, increases in landfill gas pressure and flow, intense odors, undesirable changes in leachate composition, increased leachate production, and most importantly, smoldering combustion of the surrounding solid waste. The landfill liner and explosive gas extraction and leachate collection systems can be damaged by heat from the reaction and/or accompanying combustion. Slope failure also may result from increased gas and liquid pressures and the reduction of waste mass shear strength attributable to subsurface combustion compounding existing or initiating damage to engineered components. Therefore, landfills that have received APW need early detection of a potential exothermic reaction to respond promptly to prevent subsequent subsurface combustion. This paper presents techniques to quickly evaluate landfill gas and temperature data to determine if an APW reaction is occurring, discusses operational indicator criteria that can be used to differentiate an APW reaction from subsurface combustion or combined reaction/combustion, and provides recommendations for APW disposal that minimize potential for a reaction to occur. DOI: 10.1061/(ASCE)HZ.2153-5515.0000171. © 2013 American Society of Civil Engineers.

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Introduction

The U.S. Department of Energy (U.S. DOE) (1999) estimated that at least one million tons (approximately 1.1 million short tons) of aluminum production wastes (APW) are placed annually in Resource Conservation and Recovery Act (R.C.R.A.) Subtitle D landfills. These waste materials contain variable amounts of aluminum metal and aluminum compounds, such as aluminum carbide, aluminum nitride, and aluminum oxides mixed with sodium and potassium salts and other substances. Aluminum production wastes include materials commonly referred to as dross, white dross, skim dross, rich dross, black dross, and salt cake within the aluminum production industry (Graczyk et al. 1997). These terms are used to

describe the aluminum metal content and morphology of the various wastes removed from the surface of molten aluminum during processing and purification (Manfredi et al. 1997; Shinzato and Hypolito 2005; Szczygielski 2008).

Although APW can remain relatively dormant for years in a landfill, it may react exothermically with liquids present in or introduced into a Subtitle D landfill (Szczygielski 2008). If landfill leachate (or other water-based fluid) contacts APW for a sufficient period of time and dissolves soluble salts from the APW matrix, exothermic chemical reactions can occur. As the dissolution of salts progresses, the pH of the leachate gradually increases as it begins to react with carbides, nitrides, and metal oxides contained in the APW. Some of these reactions generate heat and toxic or flammable gasses such as ammonia and acetylene. When the pH rises to approximately 9.0 or higher, hydroxyl ions in the leachate begin to react with the aluminum metal particles of the APW. This reaction is highly exothermic, rapidly releasing large amounts of heat and hydrogen gas. Internal temperatures of landfill waste masses experiencing this reaction of 88°C (170°F) to 110°C (230°F) have been observed, at which desirable microbial activity is terminated and methane production severely curtailed. These exothermic reactions and associated changes in gas composition and increased gas pressure also may cause intense odors.

The sustained heat generated from this exothermic reaction can cause a subsurface waste fire by igniting the surrounding solid waste through the processes of glowing (contact) or smoldering combustion. The high temperatures generated by the exothermic reaction and exacerbated by smoldering combustion of waste materials also can cause damage to the engineered components of the landfill, e.g., gas collection, leachate collection, and liner systems (Lewicki 1999; Øygard et al. 2005), and even negatively impact slope stability (Stark et al. 2010). Additionally, landfill combustion emits air pollutants, including but not limited to

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particulate matter, carbon monoxide, chlorinated dibenzo-p-dioxins, and chlorodibenzofurans that can pose safety and environmental health threats (Bates 2004; Nammari et al. 2004; Szczygalski 2008).

This paper discusses techniques and operating parameters for determining whether an APW exothermic reaction and/or fire exist in a landfill facility and provides operational indicator criteria for distinguishing between the two. Trend analyses for identifying changes in landfill gas temperature and composition are presented; these techniques can be used as a cost-effective tool to identify a reaction or combustion at an early stage. A case study landfill in which a reaction and subsequent subsurface combustion occurred is used to illustrate the data evaluation techniques and operational indicator criteria presented herein. Conditions caused by the APW reaction at the case study landfill are similar to other landfills that have experienced APW reactions (EnSafe, Inc. 2002; Indiana Department of Environmental Management 2000, 2006; Ohio EPA 2007; Washington State Department of Ecology 2006; U.S. EPA 1995).

Normal Landfill, APW Reactions, and Landfill Combustion Conditions

Normal Subtitle D Landfill Operating Conditions

The normal biological decomposition of municipal solid waste (MSW) occurs in the following generalized phases [Agency for Toxic Substances and Disease Registry (ATSDR) 2001; Haarstrick et al. 2001; Bogner et al. 1996; Barlaz et al. 1989]:

- **Aerobic phase:** Begins immediately after waste placement and continues until entrained oxygen is depleted. Aerobic bacteria consume oxygen while breaking down long molecular chains of carbohydrates, proteins, and lipids that comprise organic waste. The primary byproducts of this process are water and carbon dioxide.
- **Anaerobic acid phase:** Begins after aerobic decomposition is complete and oxygen levels have dropped below 2% volume-to-volume ratio (v/v). Anaerobic bacteria convert Phase I organic compounds into organic acids (propionic, butyric, and carboxylic) through hydrolysis. The pH of the waste mass drops from approximately 7.5 S.U. to approximately 5.5 S.U. Primary byproducts include carbon dioxide and hydrogen. During this phase, landfill gas is typically composed of 20–60% v/v carbon dioxide (concentration increasing), 10–20% hydrogen (concentration increasing), and 50–30% v/v nitrogen (concentration decreasing).
- **Methane production phase:** Begins when certain anaerobic bacteria consume organic acids and form acetate, raising the waste mass pH to levels favorable for the growth of methane-producing archaea (>7.0 S.U.), which consume acetate, carbon dioxide, and hydrogen and generate methane. Landfill gas is typically composed of 40–60% v/v carbon dioxide and 45–60% v/v methane with <1% v/v hydrogen.

Table 1 presents a summary of operating conditions at Subtitle D landfill under normal operating conditions, an exothermic aluminum waste reaction, and a subsurface fire condition. Three groups of operating parameters are considered: (1) parameters used to evaluate landfill gas and the performance of the landfill gas

Table 1. Summary of Indicator Parameters for Normal Subtitle D Landfill Conditions, Aluminum Production Waste Reaction, and Subsurface Landfill Fire

Subtitle D landfill monitoring parameters	Normal operating conditions	Aluminum production waste reaction	Subsurface landfill fire
Explosive gas extraction system			
Gas temperature	<55°C (131°F) ^a	>60–93°C (>140–200°F)	>60–260°C ^{+b} (>140–500°F ⁺)
Gas pressure (kPa)	<0.5 ^c (bioreactors 0.5–16)	0.5–45 ^{+d}	<0.5 (?)
Gas flow	Facility specific	2–3 x normal ^d	Below normal?
Methane (v/v %)	45–60 ^e	<45 ^d	<15 ^d
Carbon dioxide (v/v %)	40–60 ^e	40–60 ^d	>60 ^d
Carbon monoxide (ppmv)	<20 ^e	100–1,000 ^d	Suspected >100 ^b confirmed >1,000 ^b
% Hydrogen (v/v %)	<1 ^e	20–50 ^d	<1 (?)
Ammonia (ppmv)	0.1–1 ^e	2–15,000 ^d	<0.1–1 (?)
Carbon residue	Not present	Not present	Likely ^b
Leachate			
Leachate temperature	22–33°C ^a (72–91°F)	36–88°C ^d (96–190°F)	36–88°C ^d (96–190°F)
Leachate quantity	0.3 m ³ (72 gal.)/t ^f	5–10 x increase ^d	No increase ^g
Leachate quality	Normal constituent concentration ranges ^h	10–100 x increase, TDS, Na, K, Cl, NH ₄ ^d	10–50 x increase, COD, heavy metals ⁱ
Waste mass			
EGES downhole or waste temperature	30–60°C ^a (86–140°F)	>60–110°C (>140–230°F)	>77–260°C ^{+b} (>170–500°F ⁺)
Open flame	Not present	Not present	Possibly
Smoke	Not present	Not present	Very likely ^b
Steam	Not present	Likely	Likely (if >100 ppmv CO)
Odor (burning, hot, or smoldering)	Not present	Possibly (ammonia odor likely)	Very likely ^b
Landfill settlement (% of initial height)	5–10	Slight increase?	Increase (>30%) ^b

^aU.S. EPA (2006).

^bFederal Emergency Management Agency (2002), subsurface landfill fire indicator.

^cYoung (1989); Hettiarachchi et al. (2007).

^dCase study landfill described herein.

^eAgency for Toxic Substances and Disease Registry (2001).

^fStark et al. (2010).

^gAssuming water is not used as a fire suppressant.

^hReinhart and Grosh (1998); U.S. EPA (1985).

ⁱØygard et al. (2005).

extraction system; (2) parameters used to evaluate leachate conditions; and (3) parameters used to evaluate the waste mass conditions. The parameter values and ranges shown are intended to provide a general understanding of the deviation from normal landfill operating conditions attributable to an exothermic aluminum reaction and/or subsurface fire at facilities that have accepted or are accepting APW, especially facilities that have performed or are performing leachate recirculation (Stark et al. 2012). These parameter values and ranges may not necessarily reflect site-specific conditions observed at every facility because of differences in landfill age, waste composition, waste mass thickness and extent, the amount of APW disposed, and the duration and extent of leachate recirculation activities, especially with respect to the location of APW. Table 1 data are based on published literature, professional experience of the authors, and the case study described subsequently involving a Subtitle D landfill exhibiting an exothermic aluminum reaction and subsurface fire.

Normal Subtitle D Landfill Temperature

Under normal conditions, the temperature of the waste mass and landfill gas generated by a Subtitle D landfill usually ranges between 25 and 60°C (77–140°F) during decomposition Phases II and III (Meima et al. 2008; Mora-Naranjo et al. 2004; ATSDR 2001). Waste temperature is a function of microbial activity present in the waste mass. Two groups of microorganisms (bacteria and methanogenic archaea) are primarily responsible for the biochemical degradation of organic landfill wastes and the generation of heat and methane: mesophilic microorganisms and thermophilic microorganisms. Generally, the propagation and activity of mesophilic organisms is optimized at a temperature range of 30–40°C (86–104°F), whereas the propagation and activity of thermophilic organisms is optimized at a temperature range of 50–60°C (122–140°F) (Mora-Naranjo et al. 2004). Waste temperatures exceeding 60°C (140°F) reduce microbiological activity and seriously decrease the rates of waste decomposition and methane generation (Hassen et al. 2001). Based on published literature, e.g., Meima et al. (2008), waste temperatures exceeding 60°C (140°F) rarely occur under normal landfill operating conditions, and higher temperatures should be taken as an indication of a heating event.

Temperature controls the quality and quantity of landfill gas generated, and therefore is likely the most important parameter for assessing whether or not a Subtitle D landfill is operating normally (Hanson et al. 2010; Crutcher and Rovers 1982). Methane production starts to decrease significantly if the temperature of the waste mass exceeds 70°C (158°F), and bacterial activity and methane production typically stop if the temperature of the waste mass exceeds 80°C (176°F) (U.S. EPA 2006). New source performance standards (NSPS) 40 CFR 60.753 (NSPS 2003) require that a landfill demonstrate that combustion is not occurring within the waste mass if a gas wellhead temperature exceeds 55°C (131°F) because temperatures greater than 55°C (131°F) impede biological decomposition and methane generation (Mora-Naranjo et al. 2004).

Normal Subtitle D Landfill Gas

Landfill gas is composed mostly of methane (45–60% v/v) and carbon dioxide (40–60% v/v) in approximately equal amounts with <3% v/v nitrogen, <1.5% v/v oxygen, <1% v/v hydrogen, and trace concentrations of carbon monoxide and ammonia (Hassen et al. 2001). With respect to carbon monoxide, concentrations in gas generated by normally operating landfill facilities should not exceed 20 parts per million per volume (ppmv) (ATSDR 2001), and concentrations exceeding 1,000 ppmv are indicative of subsurface combustion (FEMA 2002). Bates (2004) concluded that carbon monoxide is not commonly produced by bacteria in landfill environments and suggests that concentrations as low as 2 ppmv

may indicate underground combustion. Thauer (1998) explains that certain methanogenic archaea utilize carbon monoxide as a nutrient; if present in the landfill environment, such methanogens may limit the concentration of carbon monoxide in landfill gas that may be generated by sources other than combustion. If waste mass conditions become intolerable for these methane-producing archaea, carbon monoxide may begin to accumulate at low levels, e.g., <100 ppmv. Finally, in a normally operating Subtitle D landfill, gas does not exhibit anomalously high gas pressures (>0.5 kPa) or gas flow rates, which could be an indication of abnormal activity.

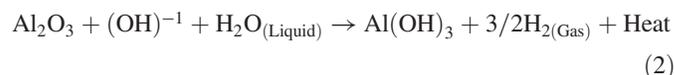
Normal Subtitle D Landfill Leachate

Normal leachate temperature is less than 36°C (96°F), and leachate quality is typical for Subtitle D facilities (Reinhart and Grosh 1998; U.S. EPA 1985). The leachate amount generated is usually predictable given the size and age of the facility. Finally, indicators of active combustion (e.g., flame, smoke, rapid, and excessive settlement) are not present under normal operating conditions.

APW Reaction Indicators

Aluminum production waste reactions and associated subsurface combustion are problematic for Subtitle D landfills because they (1) are challenging to identify and delineate, (2) can remain undetected for a relatively long period of time, (3) are difficult to extinguish, and (4) produce side effects that may damage a facility enough to warrant permanent closure or impact surrounding communities.

Calder and Stark (2010) and Stark et al. (2012) discussed the APW reaction and associated chemical reactions that can occur in a Subtitle D landfill. The most likely reactions with APWs in a Subtitle D landfill or nonhazardous industrial landfill involve the amphoteric reaction of aluminum metal with water (Calder and Stark 2010), shown as follows:



These reactions can rapidly release large amounts of heat and hydrogen gas in the waste. These exothermic reactions and associated changes in gas composition and increased gas pressure also usually cause intense and bad odors.

Aluminum production waste reactions can involve pure Al (metal), as shown previously in reactions (1a) and (1b); however, the percentage of pure Al (metal) metal in APW depends on several factors, e.g., the amount of reprocessing to remove valuable Al (metal), and Al (metal) can be trapped between aluminum oxides (Al_2O_3) and a salt flux layer. As a result, APW usually contains mostly aluminum oxide and aluminum nitride (AlN), aluminum carbide (Al_4C_3), and/or aluminum sulfide (Al_2S_3), all of which can combine with water by the reactions shown subsequently and result in ammonia (NH_3), methane (CH_4), and hydrogen sulfide (H_2S) gas being produced, respectively





The indicators of an APW reaction are illustrated using data from a Subtitle D landfill that experienced an aluminum reaction and subsequent subsurface combustion from 2005 to present. In 1991, this facility was permitted and consists of 35.7 ha (88 acres), 9.9 million m³ (13 million yd³) of disposal capacity, and cells 1–6 shown in Fig. 1. In 2003, the facility received a permit for a 69.1-ha (170 acres) lateral expansion that would create cells 7–16. The site accepted over 5,440 t (6,000 short t) of MSW and industrial wastes per day, approximately 2.6% of which consisted of APW (mostly black dross and salt cake) based on a total amount of APW accepted of 544,310 t (600,000 short tons) from 1991–2005 and 5.5 workdays/week. The facility operated normally from 1991 until mid-2005, at which time the 35.7 ha (cells 1–6) started exhibiting significant changes. Some of these changes included bad odors, leachate and gas outbreaks, waste temperatures exceeding 150°C (300°F), landfill gas pressures exceeding 210 kPa, a ten-fold increase in leachate generation, instability of the south slope (see dashed rectangle in Fig. 1), accelerated landfill settlement and soil cover cracking, and changes in leachate and gas composition (Stark et al. 2012). These changes were attributable to an exothermic aluminum reaction that subsequently triggered smoldering combustion of the surrounding waste (Stark et al. 2012). According to the March 2007 findings and orders issued by the Ohio EPA, the facility placed the APW in cells 1, 3, 4A, 4B, 6, and 7 (see Fig. 1).

The facility performed leachate recirculation in cells 3, 4A, 4B, and 6 of the 35.7 ha (88 acres). This recirculation introduced approximately 103,102,321 L (27,239,715 gal.) of leachate into the facility over approximately 10 years (1996–2006). In addition, a waste solidification process was performed in a small area of cells 1 and 4A (see solid rectangle in Fig. 1), which involved mixing liquid waste with solid waste in unlined pits on top of the landfill that likely contributed some additional liquid to the waste mass, but much less than leachate recirculation. Both of these activities contributed moisture to the waste in portions of cells 1, 3, 4A, 4B, and 6 that could have reacted with the buried aluminum waste.

APW Reaction Induced Temperatures

Elevated landfill temperatures are usually the first indicator of an ongoing aluminum production waste reaction at a facility (Table 1). Temperatures in landfill gas wellheads usually rise from 60 to 93°C (140 to 200°F) over a period of several months to several years as the aluminum waste reaction progressively heats the waste mass.

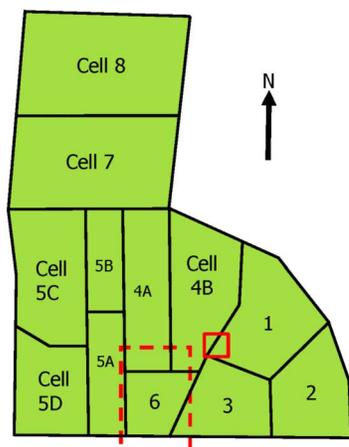


Fig. 1. Overview and cell layout of case study landfill

Elevated temperatures may also be detected in the waste mass or leachate collection system. Sustained elevated temperatures in excess of 93°C (200°F) are typically exhibited by facilities experiencing an active aluminum waste reaction (Ohio EPA 2007). The elevated temperatures may be accompanied by steam and/or smoke emissions from the explosive gas extraction system (EGES) and waste mass.

Downhole temperatures are preferred to temperatures measured at the gas extraction wellhead for this assessment because temperature measurement with depth can be obtained. In addition, downhole temperatures are 5.5–11.0°C (10–20°F) greater than wellhead temperatures, as shown subsequently.

APW Reaction Induced Gas

Changes in landfill gas quantity, pressure, and composition are usually the second indicator of an aluminum waste reaction (see Table 1). As the aluminum waste reaction generates large quantities of hydrogen, ammonia, and trace amounts of other gasses, such as acetylene and alkanes, normal gas flow rates (<50 m³/min) may increase threefold (>150 m³/min). The EGES is gradually overwhelmed, and normal landfill gas pressures (<0.5 kPa) may increase up to two orders of magnitude (50 kPa). For example, in the early phases (December 2005) of the reaction/fire in the case study landfill, the gas flow rate was approximately 50 m³/min (1,800 ft³/min), and gas pressures were typically less than 5 kPa. By August 2006, the gas flow rate was over 158.9 m³/min (5,639 ft³/min), and gas pressure in some extraction wells exceeded 40 kPa.

Approximately 30–50% of landfill gas emissions consist of hydrogen under these circumstances, which is generated by the amphoteric reaction of aluminum metal in the aluminum production wastes with leachate (Calder and Stark 2010). Although the hydrogen concentration of landfill gas may be as high as 20% during the brief acid formation phase of waste decomposition and stabilization, the hydrogen concentration of landfill gas is typically less than 1% (ATSDR 2001). Hydrogen generated by an aluminum waste reaction accumulates in the waste mass and eventually replaces methane in the landfill gas, which ceases to be generated when the waste temperature rises in excess of 77°C (170°F) and methanogens die off.

Ammonia gas is also produced by the APW reaction of leachate with nitrides [see Eq. (3)] present in the aluminum waste; concentrations of ammonia gas as high as 15,000 ppmv have been detected in landfills experiencing an aluminum reaction. Some of the elevated ammonia may be attributed to the normal effects of leachate recirculation, if performed. Elevated ammonia concentrations up to approximately 1,200 mg/L have been observed in bioreactor and recirculation landfill leachate (Benson et al. 2007). The generation of ammonia coupled with the high gas pressures, heating of the waste, and generation of excessive leachate can result in annoying odors that can impact the surrounding community (U.S. EPA 1995).

Carbon monoxide levels ranging from 100–1,000 ppmv may also be detected in landfill gas at facilities experiencing aluminum waste reactions. The elevated carbon monoxide concentrations are likely generated by smoldering organic wastes (wood and paper) in direct contact with hot APWs that are exothermically reacting with leachate. As discussed previously, an aluminum waste reaction that raises the waste mass temperature in excess of 77°C (170°F) over a period of time can gradually initiate smoldering combustion of paper and wood wastes within a landfill (Babrauskas 2003b, c). Subsurface smoldering has been documented to persist within solid waste landfills between 100 and 125°C (212 and 250°F) (Ettala et al. 1996).

APW Reaction Induced Leachate

Changes in leachate composition and quantity are also important in determining whether or not an APW reaction is occurring. If significant amounts of sodium and potassium chlorides (salt fluxes) are leached from APW, the quality of the leachate will change dramatically; however, this may occur with leachate recirculation too. Salt fluxes are added to aluminum recycling to protect the molten metal from oxidation, help remove superficial aluminum oxide layers, promote coalescence of aluminum drops, and maintain the oxides in suspension (Totten and MacKenzie 2003). Concentrations of sodium, potassium, chloride, total dissolved solids, and chemical oxygen demand have been observed to increase from one to two orders of magnitude. In addition, ammonia nitrogen concentrations typically increase between one and two orders of magnitude and exceed concentrations observed in bioreactor or recirculation landfills (Benson et al. 2007). Elevated concentrations of volatile organic compounds, such as acetone, methyl-ethyl ketone, and benzene may be generated by the pyrolysis or combustion of plastic wastes, fabricated wood wastes, and other waste materials.

A large increase in leachate generation may occur contemporaneously with an aluminum production waste reaction. For the landfill case introduced previously, Stark et al. (2012) showed leachate quantity varied from 3,775,973 L (997,615 gal.) and 23,004,624 L (6,077,840 gal.) from 1991–2004. In 2004, the leachate volume was 11,807,770 L (3,119,622 gal.) and increased approximately four times to 45,687,720 L (12,070,732 gal.) in 2005. The leachate volume continued to increase in subsequent years with 108,953,975 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 increase in leachate production correlated with the onset of the APW reaction; the first reaction indications were observed in 2001 (elevated gas temperatures), and by 2005, the landfill was exhibiting temperatures exceeding 94°C (170°F) and excessive gas pressures, hydrogen, and ammonia gas. Some of the increased leachate quantity was likely the result of leachate recirculation performed from 1998–2006. During this period, 103,102,321 L (27,239,715 gal.) of leachate were recirculated (Stark et al. 2012) over approximately 11 years. However, the 2006 leachate volume total (108,953,975 L or 28,785,700 gal.) exceeded the total amount of leachate recirculated. Other sources that could have contributed to the excessive leachate volume include waste solidification activities, precipitation and ineffective surface water management, water generated by waste heating or combustion, or groundwater infiltration because of a damaged liner system.

In general, the following progression of indicators is characteristic of an exothermic APW reaction in a Subtitle D landfill:

1. Elevated gas and waste mass temperatures;
2. Decreased methane production and elevated hydrogen and/or ammonia gas concentration;
3. Changes in leachate composition;
4. Changes in landfill gas composition and increased gas pressure and flow;
5. Intense and bad odors;
6. Increased leachate volume and leachate outbreaks;
7. Unusually rapid and excessive landfill settlement; and
8. Possible slope instability because of elevated liquid and gas pressure and decreased waste strength (Stark et al. 2010).

Landfill Combustion Indicators

Subsurface combustion consists of waste material undergoing combustion at or below the daily, interim, or final cover system. Little published literature is available on waste fires, so the appendix

provides a detailed review of waste mass combustion and landfill fire characteristics. Subsurface combustion may follow waste mass voids, gradually forming open channels known as worm holes, which greatly increases the complexity of locating the fire and tracking its extent as compared to a waste fire at the landfill surface. In addition to being caused by an exothermic aluminum waste reaction igniting surrounding solid waste materials, subsurface landfill fires may be caused by spontaneous combustion of the waste, inadequate interim or final soil cover allowing excessive air/oxygen inflow to the waste mass, excessive vacuum on the gas extraction system (a common occurrence when methane gas is being collected for energy purposes), and/or an existing or prior surface fire that has gone underground. Typically, subsurface fires are located in areas in which air/oxygen may be infiltrating the waste mass, such as gas extraction wells with poor surface seals or excessive vacuum, uncovered areas, and slopes or grade changes in which soil cover depth is thinner and soil cover compaction is usually less than on a level surface, such as the top of the landfill. However, fire associated with APW reactions may develop in internal areas of the landfill in which APW has been disposed, making detection, delineation, and mitigation even more difficult.

As is the case with exothermic APW reactions, subsurface combustion or fire within Subtitle D landfill waste masses generate excessive heat and elevates gas, waste, and leachate temperatures. In turn, these elevated temperatures create an intolerable environment for mesophilic and thermophilic microorganisms, and methane production decreases. Thus, elevated temperatures combined with anomalously low methane production may be indicative of an APW reaction, a subsurface fire, or both. In the case study described herein, an APW reaction that existed for approximately 4 years apparently ignited a smoldering fire within the waste mass. This is evident because cells 5A–D did not receive APW or undergo leachate recirculation, but have undergone substantial settlement as the waste combustion progressed from the initial reaction area in cell 6 and the southern portion of cell 4B westward (see Fig. 1). Therefore, when investigating the early stages of a landfill heating event with an associated drop in methane production, evaluating parameters that differentiate subsurface combustion from an APW reaction is important to understand the changes occurring within the waste mass and to implement an appropriate response.

A landfill waste mass undergoing subsurface combustion typically exhibits gas temperatures in the range of 60 to >260°C (140 to >500°F) and waste temperatures between 77 and >260°C (170 to >500°F). For comparison purposes, gas temperatures in Subtitle D landfills with APW reactions (without associated combustion) maximize at approximately 93°C (200°F), and waste temperatures maximize at approximately 110°C (230°F) based on observations by the authors. A landfill that is exhibiting such temperatures with excessive gas pressures, decreased methane production, and the generation of elevated levels of hydrogen or ammonia gasses is likely experiencing an APW reaction and not a subsurface fire. However, observation of the conditions associated with an APW reaction does not preclude that an associated subsurface fire exists or is slowly developing. Additional information should be gathered to evaluate the situation.

Subsurface landfill fire indicators include flame within the EGES, exploratory borings, or excavations; smoke; steam; smoldering or hot odors; carbon residue (soot) within the EGES; landfill gas carbon monoxide concentrations exceeding 1,000 ppmv; and unusually rapid and excessive landfill settlement (FEMA 2002). The Subtitle D facility case study discussed herein exhibited all of these indicators with the possible exception of open flame.

A significant amount of rapid and excessive settlement occurred at the case study landfill. Over a 2-year period, over 15.2 m (50 ft)

of settlement occurred in an area of approximately 12.2 ha (30 acres) in which the initial waste thickness was approximately 45.8 m (150 ft). This corresponds to a settlement of 15–18% of the initial waste height per year. This rate also corresponds to 30–35% of the initial height in cell 3 over a 3-year period and is significantly greater than typically observed at Subtitle D landfills, e.g., 5–10% of the initial height over 3–30 years (Edgers et al. 1992; Spikula 1997). In addition, the fire progressed from cell 6 and the southern portion of cell 4B westward until it consumed a substantial amount of waste in cells 5A–D, resulting in significant settlement.

Attempting to locate or otherwise characterize subsurface combustion based on subsidence alone is not recommended because substantial settlement usually occurs after subsurface combustion has already occurred in an area. Thus, the area of active combustion may be elsewhere by the time considerable settlement is observed. Evaluation of other indicators outside of areas of active subsidence is critical to locate and characterize subsurface combustion for suppression purposes.

For comparison with the progression of an aluminum reaction, the following indicators are characteristic of the progression of a subsurface fire in a Subtitle D landfill:

1. Elevated landfill gas and waste mass temperatures;
2. Decreased methane production (without elevated hydrogen or ammonia concentrations);
3. Elevated carbon monoxide concentrations;
4. Flame, smoke, steam, smoldering odors, and/or EGES combustion residue; and
5. Unusually rapid and excessive landfill settlement.

Trend Analysis to Assess APW Reaction and Combustion

A rapid investigation after the development of an APW reaction or subsurface combustion is essential to evaluate, locate, delineate, and suppress the reaction and/or combustion in a manner that is protective of human health, safety, and the environment. In addition, responding quickly to a reaction or combustion can reduce the associated costs of regulatory compliance, remedial actions, repair or replacement of landfill engineered components, and the potential for litigation, e.g., a citizens' lawsuit for damages associated with adverse health effects and/or loss of property value. Thus, regularly performing data trend analyses determine if and when a landfill deviating from normal operating conditions can be beneficial.

Fig. 2 is a plot of methane versus carbon monoxide concentrations and is referred to as the 15/1,500 or 15/15 graph. The data used to generate the 15/1,500 graph were obtained from landfill gas samples collected from multiple vertical wells and horizontal gas mains at the case study landfill previously described during April 2006. Horizontal gas collection mains are large-diameter smooth-walled high-density polyethylene (HDPE) pipes that were connected to certain gas wells and conveyed the collected and large volume of gas to the corresponding flare. This collection system enabled gas to be collected from certain gas wells to determine the landfill areas experiencing combustion or reaction. These collection mains also allowed gas to be sampled so the gas could be directed to the flare, or combustible gas added to make the gas more combustible. Gasses were measured biweekly at the landfill gas extraction system.

The gas wells sampled were located throughout the 35.7 ha, and every gas well was sampled except those that were not accessible because of filling with liquid or pinching off because of melted plastic. Three groups of behavior are apparent from various areas

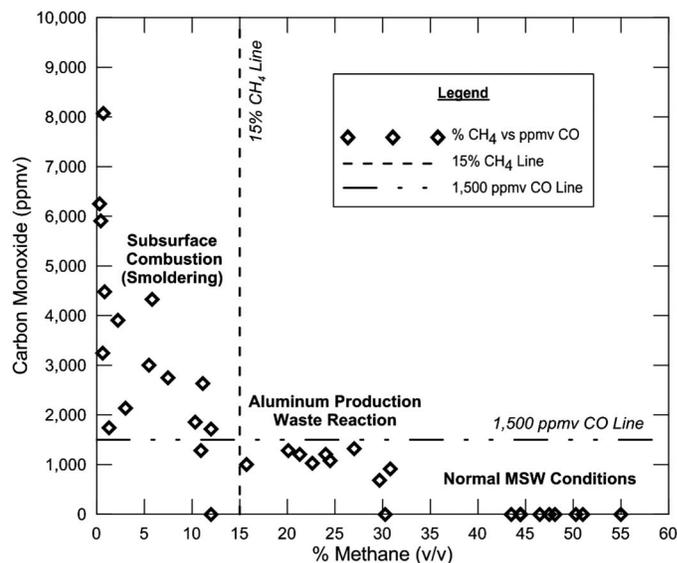


Fig. 2. Methane versus carbon monoxide concentrations in landfill gas extraction wells and associated horizontal gas mains

of the landfill in April 2006: (1) normal MSW conditions with landfill gas methane concentrations ranging between 40 and 45% v/v and carbon monoxide concentrations <100 ppmv; (2) aluminum production waste reaction with methane concentrations ranging between 15 and 35% v/v and carbon monoxide concentrations ranging up to 1,500 ppmv; and (3) subsurface combustion (smoldering) with methane concentrations less than 15% v/v and carbon monoxide concentrations exceeding 1,500 ppmv. A carbon monoxide concentration of 1,500 ppmv was utilized as an indicator of combustion instead of 1,000 ppmv as suggested by FEMA (2002) to clearly identify locations of self-sustaining subsurface combustion from locations undergoing an aluminum production waste reaction with minor contact combustion. The 15/1,500 graph can be used to quickly identify areas within the waste mass where a subsurface aluminum reaction and/or combustion has developed, thereby facilitating cost-effective design and implementation of additional investigative and suppression efforts.

Fig. 3 shows gas wellhead temperature, pressure, and selected gas component trends (methane, carbon dioxide, hydrogen, and oxygen) for a horizontal gas main at the subject landfill and corresponding wellhead temperature and pressure data. Hydrogen concentrations were measured using Summa canisters that were analyzed by a commercial laboratory for a variety of constituents, including hydrogen using ASTM D1945—"Standard Test Method for Analysis of Natural Gas by Gas Chromatography" (ASTM 2003).

Prior to October 2005, the average methane concentration was approximately 60% v/v with an average temperature of approximately 38°C (100°F). An excessively high vacuum was applied to the horizontal gas main between October 2005 and March 2006 in an effort to control odors. During this time period, methane and carbon dioxide concentrations were less than 10% v/v, and the temperature was below 16°C (60°F). These data indicate that a substantial volume of ambient air was being drawn into the waste mass (as evidenced by normal atmospheric oxygen levels of approximately 20.8% v/v), which caused the sharp decrease in observed methane and carbon dioxide concentrations during this period. From March 2006 through August 2006, the vacuum was reduced, and conditions in the vicinity of the horizontal gas main returned to normal, as shown in Fig. 3. Beginning in

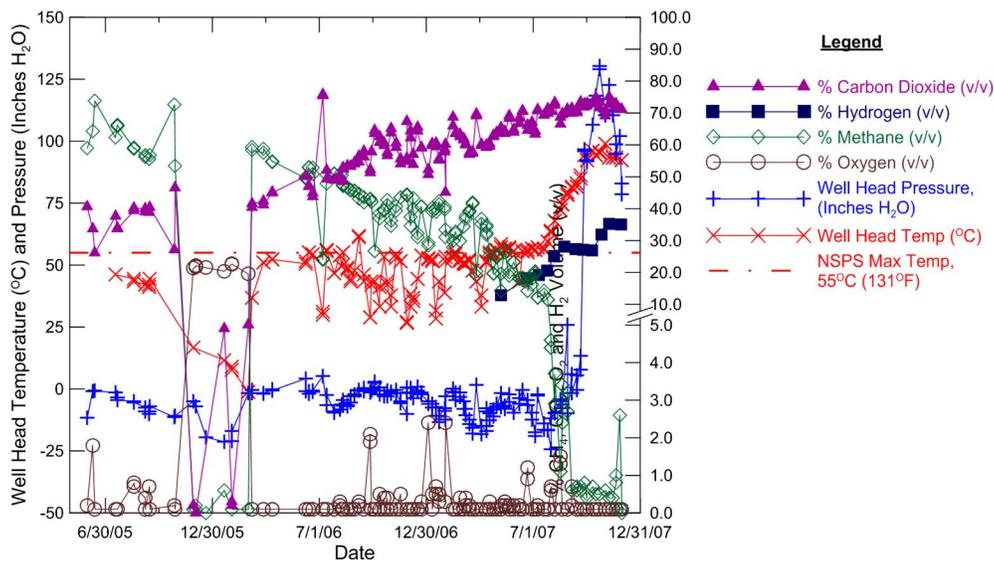


Fig. 3. Wellhead and horizontal gas main temperature, pressure, methane, carbon dioxide, oxygen, and hydrogen trends

September 2006, the wellhead temperature reached the NSPS 40 CFR 60.753 (NSPS 2003) limit (55°C, 131°F) and stayed around the NSPS limit through July 2007. During this period of small temperature rise, methane concentrations fell to less than 30% v/v, whereas carbon dioxide concentrations rose to over 65% v/v. During August through November 2007, a rapid rise in temperature (55 to 99°C; 131 to 210°F) was accompanied by a sharp decline in methane concentration to less than 5% v/v, an increase in carbon dioxide concentrations in excess of 70% v/v, and an increase in hydrogen to approximately 30% v/v occurred. The increase in hydrogen was likely generated by the progression of the APW reaction and corresponded with the increased temperature, increased pressure, and decreased methane.

Fig. 4 presents the ratio of average monthly methane to carbon dioxide flow rate and carbon dioxide concentration during the period of May 2005 through December 2007 for the horizontal gas main evaluated in Fig. 3. The average monthly flow rates of methane and carbon dioxide were calculated by multiplying the

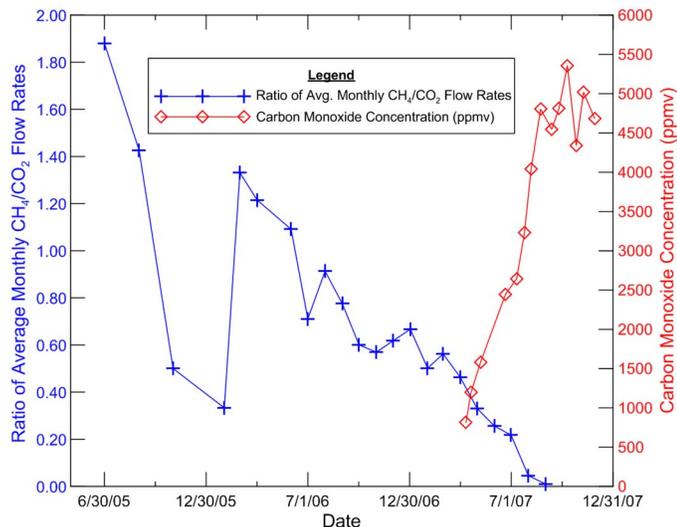


Fig. 4. Horizontal landfill gas main average monthly ratio of methane/carbon dioxide flow rate and carbon monoxide trends

average monthly percentage of methane and carbon dioxide gas by the average monthly adjusted flow rate at the wellhead. Average monthly wellhead temperatures were used to standardize the flow rates to 20°C (68°F). The advantage of using methane and carbon dioxide flow rates rather than just concentrations is that flow rate is a measure of the actual gas production from the waste mass, whereas concentration is simply a measure of the percentage of gas. Therefore, evaluating flow rates gives a better indication of the dynamics of the ongoing reaction and/or combustion activity than evaluating only gas concentration measurements. In general, the ratio of methane/carbon dioxide flow rate should exceed 0.5 and generally be about unity for a normally operating Subtitle D landfill (ATSDR 2001). From March through September 2007, the flow ratio declined from approximately 0.5 to near zero as carbon monoxide concentrations increased from approximately 800 ppmv to nearly 5,500 ppmv, indicating the presence of subsurface combustion in the vicinity of the gas wells supplying this horizontal gas main. Other indicators of a significant change in behavior were the rapid decline in the flow ratio from June 2005 to February 2006, which appears related to a large increase in vacuum applied to the gas extraction system. The vacuum was reduced around February 2005, and the ratio of flow rates increased to approximately 1.4. From February 2005, the flow ratio declined rapidly again and reached nearly zero by September 2007. During this time, the carbon monoxide concentration trend increased rapidly to approximately 5,000 ppmv. The divergence of the ratio of methane to carbon dioxide flow rate and concentration of carbon monoxide is a good indicator of deviation from normal landfill behavior to subsurface combustion, and should be considered when investigating a landfill elevated temperature event.

Fig. 5 shows the temperature trends for the subject landfill. Combustion occurred because of the intense heat from the dross reaction igniting the surrounding waste. Temperature measurements with depth show that hot spots occurred at both shallow and deep depths and in the presence of low oxygen. The hot spots were initially located in areas of dross. Contributing to the waste combustion in the presence of low oxygen was the presence of coal in the interim soil cover material that also could smolder and generate heat with low oxygen.

Wellhead and downhole temperature data were obtained from a single vertical gas extraction well at four depths between the

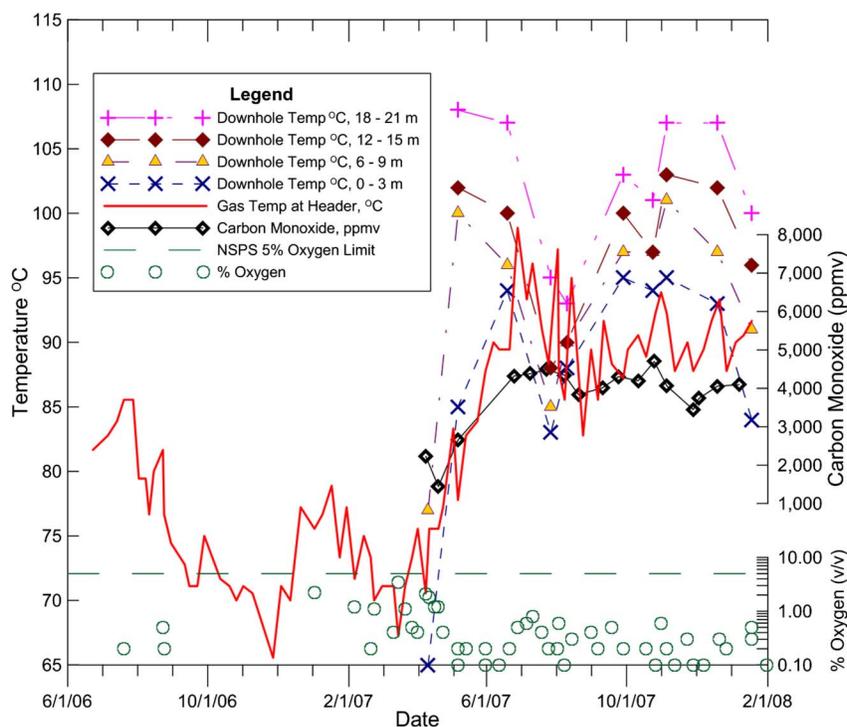


Fig. 5. Vertical landfill gas extraction wellhead temperature, carbon monoxide, and oxygen trends

landfill surface and a depth of 21.4 m (70 ft) below the landfill surface. In addition, carbon dioxide and oxygen data were obtained and also are plotted in Fig. 5. These data illustrate two important characteristics of subsurface combustion. First, comparison of the header and downhole temperatures in Fig. 5 indicate that downhole temperatures typically exceed wellhead temperatures by 5.5–16.5°C (10–30°F) depending on the depth, i.e., the greater the depth, the greater the temperature difference. Second, although the oxygen level never exceeded the NSPS limit of 5% v/v during the monitoring period from June 2006 through February 2008, the increase in low-level oxygen concentrations after March 2007 appears to correlate with the observed temperature increase (68.3 to 98.9°C; 155 to 210°F) and increase in carbon dioxide concentration (approximately 1,400 to 4,700 ppmv). These data suggest that under conditions of ongoing APW reaction, small but persistent influxes of oxygen are sufficient to sustain smoldering combustion, even if such concentrations are less than that required to sustain flaming combustion (<15% v/v). Thus, minimizing or even eliminating oxygen intrusion is extremely important through additional cover soil and/or geomembrane.

Summary and Recommendations

Aluminum production waste reactions and subsurface combustion can significantly impact the behavior and operation of a Subtitle D landfill, and if not addressed quickly, can result in serious damage to the gas extraction, leachate collection, and liner system, instability of the waste mass, and may adversely affect the local community. Such situations usually cause a response by local, state, and potentially federal agencies, can severely interrupt the normal operation of the facility, and may result in costly corrective measures and litigation for the facility owner/operator.

Some indicators of APW reactions in Subtitle D landfills are similar to those caused by subsurface combustion, so it may be difficult to differentiate between these events. Both produce large

amounts of heat, and APW reactions may cause subsurface waste combustion at some facilities. Therefore, understanding the causes and nature of APW reactions and combustion is important so these two events can be distinguished in the field. Further, understanding the landfill operating parameters to evaluate, and when and how to evaluate them is important to quickly identify and respond to a reaction and/or combustion before the situation becomes unmanageable and presents a threat to human health, the environment, and the facility.

Operating parameters that can be used to evaluate a Subtitle D landfill for the presence of an APW reaction or subsurface combustion or to distinguish between the two include (1) landfill gas temperature and composition (especially hydrogen, methane, and carbon monoxide); (2) leachate quality (especially sodium, potassium, chloride, total dissolved solids, and ammonia) and quantity (unexpected increases); and (3) waste mass emissions (odor, steam, smoke, and flame), temperature, and settlement rate. A trend analysis of changes in landfill gas and waste temperatures and gas composition (hydrogen, methane, carbon dioxide, carbon monoxide, and oxygen) can be helpful and cost-effective in determining the onset of a reaction or fire.

Calder and Stark (2010) presented several operational procedures that can reduce the potential for an APW reaction and include that APW should not exceed 5% (by weight) of the total monthly waste acceptance of the facility, APW tonnage should not exceed 10% of the average daily tonnage, APW should be immediately buried to minimize contact with precipitation, and APW should not be placed in areas where leachate recirculation is occurring, or conversely, leachate recirculation should not be used in areas where APW has been placed.

If aluminum waste is accepted, the placement location and tonnage of aluminum waste placed should be carefully mapped and documented so that if a problem develops, the responding agencies can assess the extent of the problem. Then, place aluminum waste in a monofill.

Appendix. Review of Landfill Combustion/Fires

Occurrence of Landfill Fires

In 2002, the United State Fire Administration (2002) estimated that 8,400 fires occur at Subtitle D landfill facilities every year. The majority of landfill fires that occur are relatively small, easily contained events at the working face that are suppressed by the landfill operator. Such fires generally do not result in operational problems or regulatory violations and are not typically reported to the regulatory community. These operational fires do not pose a serious threat to the public, environmental control systems, or site personnel. However, although the majority of fire events are small and operational in nature, larger events do occur in the United States. The impacts of major landfill fires to public health, the environment, landfill control systems, landfill operation, and fire suppression and emergency response resources can be severe (Bates 2004).

Types of Combustion

In general, combustion is a self-sustained, exothermic reaction between a fuel and oxidizer (Babrauskas 2003a; Warnatz et al. 1996; Griffiths and Barnard 1995; Kuo 1986). Based on the tetrahedron of fire theory (Fire 1996), four conditions must be present for combustion to occur: (1) a fuel source, (2) an oxidizer, (3) an energy (ignition) source, and (4) a self-sustaining chain reaction of burning. Although the first three conditions are available at all Subtitle D landfills, a fire will start only if the fourth condition develops. Two types of fires and two types of combustion can develop in Subtitle D landfills: surface fires, which are generally occurrences of flaming combustion, and subsurface fires, which are generally occurrences of smoldering combustion (Bates 2004).

Once initiated by a heat source, flaming combustion occurring at the surface of a waste mass can quickly become a self-propagating chain reaction, i.e., flammable gasses are continuously generated by pyrolysis of the fuel (the chemical breakdown of a substance to lower weight molecules in the presence of heat), and gradually the flames move outward from the point of ignition, consuming more and more fuel. Flaming combustion is not possible in highly confined situations because of a phenomenon known as quenching distance. Quenching distance is the minimum height of a channel through which a flame can propagate. Thus, subsurface flaming combustion can only develop if substantial voids or cavities are present in the waste mass, which are not likely attributable to waste compaction during disposal and the weight of the overlying waste. Another factor that inhibits the development of subsurface flaming combustion is oxygen concentration. Under most circumstances, flaming combustion is retarded if the oxygen level drops below 15% v/v, and flaming propagation will generally cease at oxygen concentrations below 10% v/v (DeHann 2007).

The second type of fire that can impact a Subtitle D landfill is glowing or smoldering combustion. Glowing and smoldering combustion are similar phenomena, with the only difference being that smoldering combustion is self-sustained, whereas the more general concept of glowing combustion also includes (1) reactions that are not self-sustaining and occur solely because of the presence of an external heat source; and (2) the type of smoldering in which light is emitted (Babrauskas 2003a; Pitts 2007).

Subsurface fires occurring within a landfill waste mass typically propagate through smoldering combustion. Unlike flaming combustion, the smoldering combustion reaction occurs directly on the surface of a solid fuel and not in the gas phase, i.e., combustion of flammable gasses produced by the process of fuel pyrolysis. Once a smoldering fire is initiated, the reaction rate is generally limited by

the amount of oxygen available at the fuel surface, and therefore, smoldering is generally sensitive to factors affecting the amount of oxygen reaching the fuel surface (Pitts 2007). Smoldering fires will propagate at oxygen concentrations below 3% by volume (DeHann 2007). With respect to the occurrence of subsurface landfill fires, recognition of this fact is critical to understanding the potential consequences of overdrawing a landfill gas extraction system and fundamental to operating a gas extraction system in compliance with state and federal regulations. Smoldering combustion may develop at relatively low temperatures, and has been documented in a wood member exposed to heating at temperatures as low as 77°C (170°F) for time periods ranging from several months to several years—the concept of a fixed (handbook) ignition temperature does not apply under these circumstances (Babrauskas 2003b, c). Accordingly, an APW reaction that develops within a Subtitle D landfill and raises the waste mass temperatures in excess of 77°C (170°F) over a period of several years (such as in the case described previously) can initiate smoldering combustion of surrounding paper and wood wastes within a landfill.

Both flaming and smoldering combustion reactions can be extinguished by removing sufficient heat from the system. Flaming combustion is easier to extinguish than smoldering combustion because flaming (gas-phase) combustion is readily quenched by heat removal and cannot be sustained at low temperatures. Smoldering combustion reactions can persist at low temperatures and low oxygen concentrations that make it difficult to extinguish in a landfill. Thus, smoldering combustion is more likely encountered underground and harder to extinguish because reducing oxygen and/or removing heat are difficult in a landfill.

Combustion Byproducts

In addition to heat, other combustion by-products include gasses (mostly carbon monoxide and carbon dioxide), vapors (mostly steam), and smoke (particulate matter). These products may be indicative of either a surface or subsurface fire and can be used to evaluate the presence of a landfill fire, particularly a subsurface fire.

Both types of combustion (flaming and smoldering) produce carbon monoxide and carbon dioxide, although in different amounts. The rate at which a landfill fire produces carbon monoxide is dependent on the size of the fire, type of combustion, and available oxygen. Flaming combustion is more efficient than smoldering combustion and tends to produce primarily carbon dioxide with a small carbon monoxide component, whereas smoldering combustion is less efficient and produces carbon monoxide as the primary combustion product. Smoldering combustion can produce carbon monoxide concentration of 1–10% (10,000–100,000 ppm), whereas flaming combustion generally produces less than 0.02% (200 ppm) carbon monoxide (DeHann 2007). Therefore, if elevated carbon monoxide ($\geq 1,000$ ppm) concentrations are encountered within a landfill or gas extraction system, a smoldering event is most likely occurring. Concentrations of carbon monoxide exceeding 100 and 1,000 ppmv in landfill waste masses are considered to be indicative and confirmation of an active landfill fire, respectively (FEMA 2002).

Other combustion by-products include smoke and steam. Recognizing the difference between smoke and steam is important when evaluating whether or not a subsurface fire is present because it is often difficult to identify a subsurface fire, particularly in the incipient stages. Smoke, which consists of combustion products—particulate matter, gasses (primarily carbon monoxide and carbon dioxide), and water vapor—generally appears hazy and exhibits a bluish-gray color. Conversely, steam consists mostly of water vapor

and generally appears cloudy with a white to whitish-gray color. Smoke is always an indicator of active combustion, whereas steam indicates either (1) heating of the waste mass from biological decomposition or an exothermic chemical process, both of which may or may not be associated with subsurface combustion; or (2) heating of the waste mass attributable to subsurface combustion.

Subsurface landfill fires (smoldering combustion) may not generate substantial amounts of readily visible smoke. The absence of smoke is not confirmation that a subsurface fire does not exist, because as smoke from a subsurface fire migrates upward through the waste mass, the waste materials can filter the particulate matter, resulting in surface emissions that can appear to be steam, i.e., mostly water vapor, carbon monoxide, and carbon dioxide. Steam and smoke are not necessarily distinguishable in the field based solely on visual appearance and the process of identifying or characterizing surface emissions because smoke or steam is often difficult and contentious because of the potential legal implications and regulatory consequences of a subsurface landfill fire. Accordingly, a landfill inspector should always examine surface emissions carefully for a bluish tint before assuming that an emission is simply steam from heating of the waste mass. A more definitive way to characterize surface emissions is to measure the carbon monoxide concentration. If the steam contains carbon monoxide in excess of 100 ppm, it is indicative of combustion within the waste mass (FEMA 2002), and additional investigation should be performed. If carbon monoxide is in excess of 1,000 ppm, a subsurface fire is usually present.

At landfills with thermal heating events caused by the rapid oxidation of APW by water, steam may be observed at the landfill surface or within the waste mass (e.g., rising from a boring or gas well). Such an emission may consist mostly of water vapor generated from heating of the water and/or waste mass, or it may be associated, at least in part, by smoldering combustion in the waste mass that was initiated by an exothermic APW reaction.

Combustion versus Pyrolysis

Pyrolysis is generally defined as “the chemical breakdown of a substance to lower weight molecules in the presence of heat” (Babrauskas 2003a). However, the disciplines of chemistry and fire science define pyrolysis differently (Babrauskas 2003a), and understanding the distinction between the two definitions is important for Subtitle D landfills.

From a chemist’s perspective, pyrolysis is the breakdown of a substance when exposed to heat in the absence of oxygen, whereas the fire scientist defines pyrolysis to be the process of thermal degradation that allows flaming combustion to self-sustain and spread, i.e., the breakdown of a substance when exposed to heat in the presence of oxygen. As discussed previously, smoldering and glowing (contact) combustion does not involve pyrolysis because the combustion reaction occurs on the surface of the solid, whereas flaming combustion is combustion of the flammable gasses produced by pyrolysis. Therefore, smoldering combustion can occur without pyrolysis from the fire scientist’s perspective, but at the same time generates heat that can cause pyrolysis of surrounding materials (e.g., paper or wood) from the chemist’s perspective. This also can lead to difficult and contentious discussions about whether a fire or pyrolysis is occurring in a Subtitle D landfill because of the legal implications and regulatory consequences of a fire. In other words, it is more desirable to have a pyrolysis event than a subsurface fire.

The occurrence of pyrolysis within the waste mass because of heat generated by an aluminum reaction, smoldering combustion, or any other heat source should not be confused or equated with

combustion. Pyrolysis is an endothermic process that precedes the exothermic processes of flaming or smoldering combustion (Pitts 2007). As such, pyrolysis requires energy input; therefore, unlike combustion, pyrolysis does not provide energy output and is not a self-sustaining process. Accordingly, indicators of ongoing combustion (e.g., flames, smoke, elevated carbon monoxide concentrations, abnormal settlement, and/or elevated waste and landfill gas temperatures) cannot be attributed solely to the endothermic process of pyrolysis.

Although the development and propagation of smoldering combustion is independent of pyrolysis, the pyrolysis of organic fuel materials exposed to heat generated by smoldering combustion can still occur (just as it occurs during flaming combustion). Plastic waste materials generally do not experience pyrolysis, because plastics usually melt and behave like combustible liquids before pyrolysis can occur (Fire 1996). In the aforementioned case study landfill, heat generated by the APW reaction pyrolyzed MSW fuel materials, e.g., paper and wood, but the critical issue at hand was the ongoing APW reaction and associated smoldering combustion causing the pyrolysis.

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