# **REACTION AND COMBUSTION INDICATORS IN MSW LANDFILLS**

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# ABSTRACT

Municipal Solid Waste (MSW) landfills may contain aluminum from residential and commercial solid waste, industrial waste, and aluminum production wastes. Some aluminum-bearing waste, particularly aluminum production wastes, may react exothermically with liquid within a landfill and cause uncontrolled temperature increases, significant changes in gas composition and pressure, nuisance odors, changes in leachate composition and quantity, consumption of the surrounding waste, and damage to engineered components. This paper discusses techniques for determining whether an exothermic aluminum waste reaction and/or combustion exists in an MSW landfill facility and provides recommendations for the safe disposal of aluminum production waste.

#### **INTRODUCTION**

Sources of aluminum in MSW landfills include curbside municipal solid waste, industrial wastes, and aluminum production waste such as dross, salt cake, baghouse dust, and shredder waste. Some of these aluminum-bearing waste materials, particularly aluminum production wastes, may react exothermically with water-based fluids present in or introduced into an MSW landfill. Waste products from aluminum manufacturing 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", "skim dross", "rich dross", "black dross", and "salt cake". These terms refer to the amount of aluminum metal present and the morphology of the various wastes raked from the surface of molten aluminum during processing and purification processes (Manfredi et. al., 1997).

Aluminum production wastes can be disposed in MSW landfills because this waste is not presently categorized as hazardous under 40 CFR §§ 261, subpart D which explicitly lists the materials that are defined as hazardous. Aluminum waste products, e.g., dross, salt cake, baghouse fines, etc., are not listed under 40 CFR §§ 261, subpart D, and are not a hazardous waste pursuant to federal law. Under 40 CFR §§ 261, subpart C, if a waste exhibits one of the following four characteristics of a hazardous waste, i.e., ignitability, corrosivity, reactivity, or toxicity, the waste is categorized as hazardous and cannot be disposed in an MSW landfill. However, there is no U.S.EPA certified test method for defining wastes as hazardous based on their reactivity (Calder and Stark 2010). This paper discusses techniques for determining whether an aluminum waste reaction and/or combustion exists in a facility and presents recommendations for aluminum waste placement.

The U.S. Department of Energy (U.S. DOE) (1999) estimates that at least one billion kilograms (two billion pounds) of aluminum production wastes (collectively referred to as "dross") are annually placed in U.S. MSW landfills. The majority of the primary aluminum smelters in the U.S. are located either in the Pacific Northwest or the Ohio River Valley, and the majority of secondary aluminum smelters are located in Southern California and the Great Lakes Region (U.S. EPA, 1995). Fifteen states produce a significant amount of aluminum production waste, with Ohio and Tennessee each having five aluminum smelting facilities.

# ALUMINUM REACTION AND COMBUSTION INDICATORS

Quickly determining whether or not a subsurface aluminum waste reaction and/or combustion is occurring can facilitate evaluation, delineation, and suppression of the event in a manner that is protective of human health, safety and the environment. In addition, responding quickly to a reaction or combustion event can reduce the associated costs of regulatory compliance, remedial actions, repair or replacement of landfill engineered components, and help reduce the potential for litigation to recover damages associated with adverse health effects and/or loss of property values. The following paragraphs present some techniques for determining whether an aluminum production waste reaction and/or combustion is occurring. To utilize these techniques, regular trend analyses should be performed to determine whether or not the landfill is deviating from its initial or normal operating conditions.

#### **Landfill Gas Indicators**

Figure 1 is a plot of methane versus carbon monoxide concentrations and is referred to as the "15/1500" or "15/15" graph. The data used to generated the 15/1500 graph were obtained from landfill gas samples collected from multiple vertical wells and horizontal collectors at an MSW landfill experiencing an aluminum reaction and subsequent MSW combustion and pyrolysis that began in April 2006.

Three groups of behavior are apparent from the 15/15 graph: "Normal MSW Conditions" with landfill gas methane concentrations ranging between 40% and 45% v/v (volume/total volume) and carbon monoxide concentrations <100 ppmv; "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 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 (rather than 1,000 ppmv; FEMA 2002) to better identify locations of self-sustaining subsurface combustion from locations undergoing aluminum production waste reactions.



Figure 1. Methane versus Carbon Monoxide Concentrations in Gas Extraction Wells

A "15/15" graph can be developed for an MSW landfill and used to identify areas within the waste mass where a suspected subsurface aluminum reaction and/or combustion event may be developing or occurring. Comparison of initial carbon monoxide and methane concentrations with subsequent measurements over time will facilitate cost effective design and implementation of additional investigative and/or suppression/isolation efforts. Figure 1 can be used as a general indicator of whether or not a reaction and/or combustion is occurring at MSW landfills which have insufficient carbon monoxide data to develop a facility-specific "15/15" graph.

#### Landfill Temperature Indicators

Temperatures in MSW landfills can be evaluated using four measuring methods: (1) measuring temperatures at the top of gas wells (well head temperatures), (2) measuring temperatures at various depths in gas wells (downhole temperatures), (3)

directly measuring waste temperature by installing thermistors in waste boreholes, and (4) measuring leachate temperatures by inserting thermistors in leachate collection pipes. Of the four methods, the direct measurement of waste temperatures by thermistors has provided the most accurate temperature data, followed by measuring downhole temperatures in gas wells. Well head temperatures are the easiest to obtain, but are less indicative of actual waste temperature at depth because they are typically 11.1 to 22.2°C (20 to 40°F) lower than peak downhole temperatures based on measurements at this MSW landfill. Well head temperatures are generally lower than downhole or direct waste temperatures due to heat loss within gas extraction wells and ambient temperature influence.

Figure 2 shows well head temperature and selected gas component trends (methane, carbon dioxide, hydrogen, and balance gas, i.e., the proportion of gas not consisting of the sum total of methane, oxygen, and carbon dioxide) for a horizontal collector at an MSW landfill experiencing an aluminum reaction and subsequent MSW combustion from May 2005 through December 2007. Prior to October 2005, the average methane concentration was about 60% v/v with an average temperature of about 38°C (100° F). An excessively high vacuum was applied to the horizontal collector between October 2005 and March 2006 in an effort to control nuisance odors being generated by the MSW landfill. During this time period, methane and carbon dioxide concentrations were less than 10% v/v and the temperature was below  $16^{\circ}$  C ( $60^{\circ}$  F). These data indicate that a substantial volume of ambient air was being drawn into the waste mass (75 to 80% balance gas) which caused the sharp decrease in methane and carbon dioxide concentrations during this period. During March 2006 the vacuum was reduced which resulted in a rapid decrease in the percentage of balance gas. As the vacuum was reduced, conditions in the vicinity of the horizontal collector returned to normal as shown in Figure 2. Beginning in September 2006, the wellhead temperature reached the New Source Performance Standards (NSPS) (40 CFR 60.753) limit (55° C, 131° F) and fluctuated around the NSPS limit, slowly increasing through July 2007. During this period of gradual temperature rise, methane concentrations fell to less than 30% v/v while 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 concentration in excess of 70% v/v, and an increase in balance gas (consisting mostly of hydrogen from the aluminum waste reaction) to approximately 30% v/v. The increase in hydrogen was generated by the progression of the aluminum waste reaction and corresponds with increased temperature and decreased methane concentration.

If baseline data, i.e., initial readings, are collected at an MSW landfill, these initial readings can be used to detect and evaluate early deviations from normal operating conditions. The comparison of such trends can be of value in understanding the nature, location, and extent of the "heating event", identifying potential problems with operation of the Explosive Gas Extraction System (EGES), and in selecting and implementing remedial measures to control or extinguish an exothermic reaction or subsurface combustion.

Figure 3 shows the temperature trends for the same MSW landfill experiencing an aluminum reaction and subsequent MSW combustion. Well head temperature and downhole temperature data were obtained from a single vertical gas extraction well at four intervals between the landfill surface and a depth of 21.4 m (70 feet) below the landfill surface. In addition, carbon dioxide and oxygen data are also plotted in Figure 3. These data illustrate two important characteristics of subsurface combustion. First, comparison of the header and downhole temperatures indicate that downhole temperatures typically exceed well header temperatures by 5.6 to -16.7°C (10 to  $30^{\circ}$ F) depending on the depth, i.e., the greater the depth, the greater the temperature difference because of higher temperature at depth. Secondly, although the oxygen level never exceeds 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 concentrations (approximately 1,400 ppmv to 4,700 ppmv). These data suggest that under conditions of ongoing aluminum waste 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).



Figure 2. Horizontal Gas Collector Temperature, Methane, Carbon Dioxide, Balance Gas, and Hydrogen Trends

# **Methane Gas Indicators**

Figure 4 presents the ratio of average monthly methane to carbon dioxide flow rates and carbon monoxide concentration trend during the period of May 2005 through December 2007 for the horizontal collector evaluated in Figure 2. The average monthly flow rates of methane and carbon dioxide were calculated by multiplying the average monthly percentages of methane and carbon dioxide by the average monthly adjusted flow rate at the well head. Average monthly well head

temperatures were used to standardize the flow rates to  $20^{\circ}$ C (68°F). The advantage of using flow rates rather than concentrations is that flow rates are a measure of actual gas production from the waste mass, whereas concentration is simply a measure of gas constituent percentages. Therefore, the ratio of the average monthly methane to carbon dioxide flow rates provides an indication of the relative activity of the aluminum production waste reaction and/or subsurface combustion in the vicinity of the collector. In general, the ratio of methane to carbon dioxide flow rates should exceed 0.5 and generally be about unity for a normally operating MSW landfill. From March through September 2007, the flow rate 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 horizontal collector. The divergence of the ratio of methane to carbon dioxide flow rates and increasing carbon monoxide concentration demonstrates deviation from normal landfill behavior in response to subsurface combustion. Another indicator of a significant change in normal landfill behavior is the rapid decline in the flow rate 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 2006 and the flow rate ratio increased to about 1.4. From February 2006 the flow rate ratio again declined rapidly in response to heating of the waste mass, and was almost zero by September 2007.



Figure 3. Temperature, Carbon Monoxide, and Oxygen Trends for Aluminum Production Waste Reaction and Combustion



Figure 4. Horizontal Gas Collector Average Monthly Ratio of Methane/Carbon Dioxide Flow Rate and Carbon Monoxide Trend

#### **Changes in Leachate Composition and Quality**

At the same MSW landfill that was experiencing an aluminum reaction and a subsequent subsurface combustion used in Figure 2, 3, and 4, the leachate composition and quality began to change 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 potassium, sodium, chloride, and total dissolved solids (TDS) increased steadily between 1998 and 2008 as shown in Figure 5. Sodium, chloride, and TDS concentrations increased nearly one order of magnitude and potassium concentrations increased nearly two orders of magnitude.

By 1999 ammonia nitrogen concentrations also increased nearly two orders of magnitude and remained relatively high (1,000 to 5,000 mg/L). 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 gas and liquid pressures being measured and documented by Higher Operating Value (HOV) demonstrations which the facility submitted to the regulatory agencies beginning in 2001 and continued through 2006 to comply with NSPS. If such changes in leachate composition are identified early, more substantive investigations can be initiated to determine the nature, location, and extent of the "heating event" so that appropriate measures to isolate and contain the event can be implemented in a timely fashion.



Figure 5. Potassium, Sodium, Chloride, and TDS Trends in Leachate, March 1993 Through February 2008

# ALUMINUM WASTE PLACEMENT RECOMMENDATIONS

This section briefly presents some suggestions for the safe disposal of aluminum production waste. Calder and Stark (2010) present additional placement recommendations.

- Aluminum production waste should not exceed 5 to 10% of the total monthly waste acceptance rate by weight of the MSW facility. In addition, the aluminum waste tonnage should not exceed 10 to 15% of the average daily tonnage received on any given day.
- Aluminum production waste should not be mixed with tire shreds, fly ash, or bottom ash because of possible alkaline conditions and high moisture content that can trigger a reaction.
- Aluminum production waste should not be mixed with high moisture content wastes such as sludge that does not fail the paint filter test.
- Aluminum production waste should not be placed in landfill areas where leachate recirculation is occurring, and conversely leachate recirculation should not occur in areas where any aluminum waste has been placed.
- Aluminum production waste should not be exposed to significant rain events and should be covered with soil daily.
- If aluminum production waste is accepted, the placement location and tonnage of aluminum waste placed should be carefully documented to facilitate prompt assessment and remedial response if a problem develops.

• Aluminum production waste monofills may be a better alternative than disposing of aluminum wastes in MSW landfills. Monofills also may facilitate future reclamation of the aluminum waste if economically feasible.

# SUMMARY

The following is a summary and some recommendations for detection and remedial actions for aluminum production waste reactions and MSW landfill fires:

- Normal, reaction, and combustion related operating parameters are presented to facilitate determining whether or not a facility is experiencing an aluminum reaction and/or subsurface combustion.
- Leachate should not be recirculated if aluminum production waste may be present in the waste mass.
- An aluminum reaction in an MSW landfill can produce many undesirable effects that can significantly impact the behavior and operation of the landfill. The manifestations of an aluminum production waste reaction and associated MSW combustion, in order, are increased gas and waste temperatures; decreased methane production and elevated hydrogen and/or ammonia gas production; changes in leachate composition; changes in gas composition and nuisance odors, increased landfill gas pressure and flow, increased leachate volume and outbreaks, and unusually rapid and excessive settlement. These conditions can also cause other adverse impacts to the facility and surrounding environment, such as slope failure, damage to the composite liner system, and groundwater contamination.
- MSW landfills should develop meaningful fire contingency plans and sponsor training with the local emergency service agencies so they are prepared to deal with an aluminum reaction and/or subsurface combustion.
- Remedial measures for landfill reactions and subsurface combustion usually includes excavation of an isolation break, "burning out", excavation of the problem area (if detected in an early stage), odor mitigation, and various injection technologies.

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