Aluminum Reactions and Problems in Municipal Solid Waste Landfills

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Abstract: Aluminum enters municipal solid waste (MSW) landfills from untreated raw curbside trash (MSW), industrial waste, and aluminum production wastes variously called dross, baghouse fines, salt cake, and other designations. Aluminum related reactions can arise and become problematic for landfill operations by generating undesirable heat, liquid leachate, and gases, such as hydrogen, hydrogen sulfide, carbon monoxide, and ammonia. Temperature excursions up to ~150°C (300°F) and landfill gas pressures exceeding 210 kPa have been observed. Water from the MSW, precipitation, injection, and/or surface water management can result in sufficient water to trigger problematic aluminum related reactions. Another source of water in a MSW landfill is leachate recirculation, which is not recommended if substantial aluminum is present in the landfill mass because it can lead to a problematic aluminum related reaction. This paper examines the chemical reactions involving aluminum in landfills and the negative consequences of introducing aluminum into MSW landfills regardless of its origin. Proposals for mitigating aluminum reactions are also presented.

Introduction

Large amounts of aluminum can be present in municipal solid waste (MSW) landfills. The major sources of aluminum are domestic waste, industrial solid waste, and aluminum production waste. Aluminum found in domestic waste, i.e., raw municipal solid waste (RMSW), comes from cans, doors, siding, car engine and body parts, wrapping foil, pie plates, frozen food trays, flexible packaging, cigarette and candy wrappings, and a long list of other miscellaneous domestic trash. Curbside recycling is not practical for some of these sources and is not 100% effective. This results in RMSW having sufficient aluminum for adverse reactions, as discussed below. RMSW is frequently incinerated to conserve MSW landfill capacity, designated IRMSW. Incinerators are usually not located at the landfill site so IRMSW must be transported from the incinerator to the landfill. Aluminum from industrial solid waste comes in many forms with automobile production and food packaging being two of many possible sources. Waste from the production of aluminum comes in a variety of forms containing variable amounts of aluminum. The terms "dross," "salt cake," "skim," "rich," "white dross," "black dross," and other designations 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 (King 1987). While recognizing these distinctions, we refer to aluminum production waste collectively herein as dross (Graczyk et al. 1997).

The U.S. Department of Energy (1999) estimated that at least 1 billion kilograms (2 billion pounds) of dross are placed in U.S. landfills annually. Worldwide the aluminum industry produces over 4.5 billion kilograms (10 billion pounds) of aluminum production waste each year [Azom (A to Z of Materials) 2002].

Indiscriminate disposal of aluminum dross in MSW landfills can be problematic because landfills are not inert. Instead, a landfill is a complex active chemical reactor (Ohio EPA 2006, 2007) so various reactions can be occurring during operation and closure. For example, aluminum waste can remain dormant for years in a MSW landfill but chemical reactions can develop when the buried aluminum comes into contact with alkaline water (pH ≥ 9) (Petrovic and Thomas 2008) that enters from a variety of sources, such as alkaline incinerator ash. The resulting aluminum related chemical reactions are highly exothermic (heat producing) which can slow or stop desirable anaerobic microbial activity and ignite or pyrolyze surrounding MSW. Aluminum related reactions can also release large amounts of potentially toxic and/or flammable gases and noxious odors. Underground reactions can consume surrounding MSW that can result in significant settlement of the surface that can damage interim or final cover systems and gas extraction wells and allow additional oxygen and water to enter the waste mass. The additional oxygen can lead to adverse reactions including combustion. The elevated temperatures can also compromise the structural integrity of the landfill liner system and other engineered components.

Aluminum reactions originating from RMSW and dross require separate analysis because the origin and composition of the aluminum in these wastes are different so the reaction components are different. In addition, IRMSW is frequently comingled with RMSW and/or dross and warrants separate treatment because of different compositions. This paper describes the alumi-

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num related reactions that can develop in the various types of MSW landfills: RMSW, IRMSW, industrial waste, and dross landfills, and suggests remedies.

Classification of Aluminum Waste

This section briefly reviews the regulations pertaining to the disposal of aluminum waste in MSW landfills and why aluminum production waste can be legally placed in MSW landfills.

U.S. EPA regulations define a solid waste as any discarded material [40 CFR Secs. 261.2 and 261.4(a)]. A solid waste can be deemed hazardous in two ways that would make it ineligible for disposal in a MSW facility. First, 40 CFR Sec. 261, Subpart D explicitly lists the materials that are defined as hazardous and these materials cannot be placed in a MSW landfill. Aluminum (metal), aluminum production waste, and aluminum dross are not one of the listed materials. Second, if a waste exhibits any one of the four characteristics of a hazardous waste: ignitability, corrosivity, reactivity, or toxicity, the waste is classified as a hazardous waste under 40 CFR Sec. 261, Subpart C and cannot be placed in a MSW landfill. Because of aluminum related problems observed in MSW landfills in the past decade, e.g., Brantley landfill and Ramco Disposal (Swakhamer 2006), ignitable (D001) and reactive (D003) under 40 CFR Sec. 261, , Subpart C are probably most relevant to aluminum wastes rather than corrosive or toxic.

U.S. EPA uses a test titled "Ignitability of Solids" (SW-846 Method 1030) to determine whether or not a material meets the regulatory definition of ignitability in CFR Sec. 261.21. However, there is no U.S. EPA certified test method for defining wastes as hazardous based on its reactivity. It is anticipated that the reactive test is more relevant to aluminum wastes than ignitability with water but there is no certified test method which results in disposal of aluminum production waste in MSW landfills because the disposal costs are usually less than a hazardous waste facility. Because no federal regulations exist in regard to aluminum, the State of Ohio issued waste advisories (Ohio EPA 2006, 2007) that warn of the problem and provide suggestions for aluminum disposal including the use of a monofill for aluminum production wastes.

The descriptions most relevant for classifying aluminum waste or aluminum production waste as hazardous are as follows:
- 40 CFR Sec. 261.21(a) (2)—It is capable of causing fire through absorption of water and when ignited burns so vigorously and persistently that it creates a hazard.
- 40 CFR Sec. 261.23(a) (2)—It reacts violently with water.
- 40 CFR Sec. 261.23(a) (3)—It forms potentially explosive mixtures with water.
- 40 CFR Sec. 261.23(a) (4)—When mixed with water, it generates toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment.

Given that significant quantities of aluminum and aluminum production wastes are being placed in MSW landfills [Azom (A to Z of Materials) 2002], this paper addresses the potential impact of aluminum waste in terms of the following:
1. Chemical reactions of aluminum in MSW landfills.
2. Chemical reactions of aluminum in terms of the various types of landfills that receive aluminum. This dual approach results in some repetition of material but it facilitates reading and use of the paper.

Table 1. Autoignition Temperatures of Dry Aluminum Powder at Various Oxygen Pressures (G. V. Calder, "Autoignition Temperatures of Dry Aluminum Powder for Various Oxygen Pressure Data," Personal Communication, 2009a)

Temperature (°C)	Pressure (O_2 atmospheres)
77	34
79	6.8
81	1.0
84.3	0.2 (air)

Chemical Reactions of Aluminum

Aluminum can enter a MSW landfill from four major sources: curbside or raw trash (RMSW), ash from incinerated MSW (IRMSW), various private industries, and dross from the production of aluminum metal.
- Dry aluminum metal is flammable at incinerator temperatures ($\approx 850°C$), so IRMSW is not a large source of aluminum metal in MSW landfills because it was burned in the incineration process (details below). Nonetheless, an IRMSW landfill that the writers have worked on has experienced elevated temperatures due to other sources of aluminum.
- Aluminum metal from any source can react with alkaline water that is frequently present in MSW landfills.

Anhydrous Oxidation of Aluminum (in Dry Oxygen/Dry Air)

An important reaction for landfills is anhydrous oxidation that occurs between aluminum and oxygen with or without the presence of water [Reaction (1)]

$$2Al_{(metal)} + 3/2O_{2(gas)} = Al_2O_{3(solid)} + \Delta H^0_{(T)} \tag{1}$$

The molar enthalpy of the oxidation of aluminum is $\Delta H^0_{298} = -1,675.7$ kJ/mol $Al_2O_{3(solid)} = -838$ kJ/mol Al $\approx (-200$ kcal/mol Al) (*Handbook of chemistry and physics* 2003). For comparison, the heat of vaporization of water is ≈ 25 kJ/mol $H_2O \approx (6$ kcal/mol)H_2O. So, the anhydrous oxidation of aluminum produces between 10 and 100 times the heat of vaporization of water (*Handbook of chemistry and physics* 2003).

Aluminum has a molar volume of 10.0 cm^3/mol. 1 mol of Al weighs 27 g, so 1 mol of aluminum is a sphere with a diameter of 2.67 cm. This "small amount" of aluminum releases a large amount of heat ≈ -84 kJ/cm^3 (volumetric basis). This leads to the rule of thumb that the molar heat of reaction (-838 kJ/mol Al) is about ten times the volumetric heat of reaction (-84 kJ/cm^3 Al).

Table 1 presents differential scanning calorimetry data on fine (~ 20 mesh), dry, high purity aluminum powder that shows the autoignition temperature of dry aluminum powder in air or oxygen ranges from about 77°C (170°F) to 84°C (183°F). This temperature range is less than the normal boiling point of water. The autoignition temperature of aluminum varies slightly with gas pressure following an Arrhenius temperature/pressure relation shown below

$$\ln(P_{atm}) = 8.7 \times 10^4/T_K - 246$$
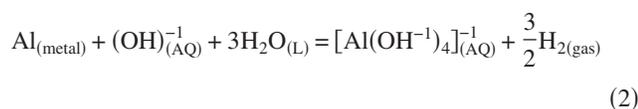
Based on this analysis, the following can be concluded:
1. Under typical incinerator temperatures of $\approx 850°C$ and air, aluminum metal is oxidized (burns) regardless of the presence or absence of water in the incinerator and is not a large

source of aluminum in MSW landfills. Rather, the necessary aluminum for Reaction (1) must originate from RMSW, industrial sources, and/or aluminum production wastes.

2. The particle size of the aluminum is a factor in its autoignition. Consequently, baghouse dust/fines having a large exposed surface area may be more reactive than other forms of aluminum dross in MSW landfills. A landfill currently undergoing an aluminum reaction appears to confirm this statement because the highest temperatures, gas production, and settlement have occurred in baghouse dust disposal areas although detailed records of the exact location and type of the waste are not available (Stark et al., "Aluminum waste reaction indicators in an MSW landfill," *J. Geotech. Geoenviron. Eng.*, unpublished, 2009).

Amphoteric Reactions of Aluminum

The most important aluminum related reaction for landfills is its amphoteric reaction with alkaline water at pH ≥ 8 (*Handbook of chemistry and physics* 2003)

$$\text{Al}_{(metal)} + (\text{OH})^{-1}_{(AQ)} + 3\text{H}_2\text{O}_{(L)} = [\text{Al(OH}^{-1})_4]^{-1}_{(AQ)} + \frac{3}{2}\text{H}_{2(gas)}$$

(2)

This is the most probable reaction involving aluminum in MSW landfills because of the presence of water and the common presence of $(\text{OH})^{-1}$ in MSW landfills. Note that this reaction requires no dioxygen (O_2). In addition, neither the anhydrous oxidation nor the amphoteric reaction of aluminum produces water.

The chemical characteristics of Reaction (2) are as follows:

1. Aluminum acts as an "acid" and is an electron-pair acceptor in Lewis acid-base theory because it accepts four electron pairs—one pair from (OH^{-1}) and three pairs from H_2O. These four electron-pair donors act as "bases." Molecular dioxygen, O_2, is neither a reactant nor a product. This distinction is made to avoid confusion because some chemical literature refers to Reaction (2) as the amphoteric "oxidation of aluminum" even though no molecular oxygen is involved.
2. Because $(\text{OH})^{-1}_{(AQ)}$ is required for Reaction (2), the reaction only occurs with water at "high" pH, typically a pH ≥ 8.5.
3. Water donates three of the four electron pairs to aluminum, so water is required for Reaction (2).
4. Reaction (2) produces flammable hydrogen gas. The ignition limits of H_2 and O_2 gases are between 4 and 74% [volume-to-volume ratio (v/v)].
5. In a landfill, both Reactions (1) and (2) can occur simultaneously because dissimilar elements are required for the reactions and these elements may be present.
6. Once the amphoteric reaction of aluminum and alkaline water begins, landfill temperature will increase because of the limited heat dissipation caused by overlying materials which makes reaction suppression difficult. Heat generation will continue as long as the reaction continues. This can lead to combustion of the surrounding MSW and subsequent subsurface carbonaceous fires which are also difficult to suppress. Anoxic (chemically reducing) reactions may also occur, producing toxic and/or noxious gases, such as CO, H_2S, and NH_3.
7. Finally, a large amount of energy is released by Reaction (2). $\Delta H^O_{298} = -843.8 \text{ kJ/mol Al} \approx -1 \text{ MJ/mol Al}$. This means a 2.67-cm sphere of Al contains approximately 1 MJ of thermal energy as discussed above. Combining this thermal en-

ergy with the tons of aluminum disposed of in a MSW landfill and the latent energy stored in a landfill is significant. Thus, when an aluminum reaction occurs in a landfill, it is difficult to control the reaction and burning of the surrounding MSW because of the large amount of energy released. The reaction will stop when the aluminum (fuel) is exhausted but the combustion or pyrolysis of the surrounding MSW can continue for long after.

Water and aqueous alkaline coreactants (OH^{-1}) are usually present in sufficient quantities to continue the aluminum reaction as long as there is aluminum present. Water is usually present in a landfill from a variety of sources including the initial moisture content of the MSW, precipitation during transportation, storage, active waste placement, infiltration through interim waste cover materials especially on slopes where soil placement and compaction are usually less than on the top deck, leachate recirculation, injection of liquids for reaction control or fire suppression, solidification processes on the landfill, or groundwater infiltration if there is no liner system or the liner system has been compromised.

Alkalinity (OH^{-1}) is also usually present in a MSW landfill from a variety of sources, especially calcium carbonate which is present in many landfill components including paper, paints, plastics, and building/construction materials that can contain up to 30% by weight calcium carbonate. Paper is a major component of RMSW and $\text{Ca(CO}_3)$ is often a major component of paper so a significant amount of $\text{Ca(CO}_3)$ usually enters the waste stream from "curbside" trash. Another source of alkalinity is the lime (CaO) added in the incinerator process to capture acidic gases. The lime reacts with water forming slaked lime [Ca(OH)_2]. The Ca(OH)_2 then reacts with carbon dioxide (CO_2) that is abundant in the incinerator effluent, producing another major source of $CaCO_3$. Atmospheric CO_2 can also react with the slaked lime during transportation and placement of the incinerator ash. In summary, there are a number of sources of calcium carbonate in a MSW landfill.

Reaction (2) can also be written as Reaction (3) below by multiplying Reaction (2) by 2 and adding 1 mol of $(\text{H}^+)_{(AQ)}$ to each side of the chemical equation (*Handbook of chemistry and physics* 2003)

$$2\text{Al}_{(metal)} + 6\text{H}_2\text{O} = 2\text{Al(OH)}_3 + 3\text{H}_{2(gas)}$$

(3)

Based on Reaction (3) and the explosive nature of hydrogen, it is recommended that any landfill remediation be designed to capture hydrogen gas to reduce explosive potential and it is a valuable energy resource instead of simply flaring the hydrogen.

While Reactions (2) and (3) are thermodynamically equivalent, Reaction (2) gives a better understanding of the conditions and species present under alkaline reaction conditions in a MSW landfill. Either way, both reactions yield explosive H_2 gas which presents a number of operational and personnel safety issues for a MSW landfill. Gaseous hydrogen can also react with ambient oxygen to produce water [Reaction (4)], which can facilitate Reaction (2)

$$\text{H}_{2(G)} + \frac{1}{2}\text{O}_{2(G)} = \text{H}_2\text{O}_{(L)}$$

(4)
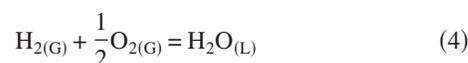
Reactions (2) and (4) are both exothermic, $\Delta H^0_{298} = -402.8 \text{ kJ/mol Al}$ and $-190.6 \text{ kJ/mol H}_2\text{O}_{(L)}$, respectively (*Handbook of chemistry and physics* 2003), so the enthalpy change of the combined reactions is

$$Al_{(metal)} + (OH)^{-1}_{(AQ)} + \frac{3}{2}H_2O_{(L)} + \frac{3}{4}O_{2(G)} = Al(OH)^{-1}_{4(AQ)} + \Delta H^O_{298}$$
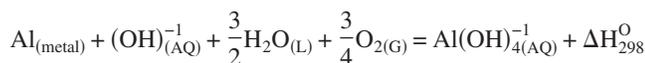
$$\Delta H^O_{298} = -831.5 \text{ kJ/mol Al} = -30.8 \text{ kJ/gm Al} \qquad (5)$$

This sequence of chemical reactions can be contrasted with the reaction of iron, which can also be placed in a MSW landfill and has been proposed as the source of heat (Klein et al. 2003). The reaction of both iron and aluminum with water is exothermic. However, in contrast to aluminum, the reaction of iron does not produce a soluble reaction product. Instead iron "rusts" and the reaction products (various iron oxides) are not water soluble. Also in contrast to aluminum, iron is not amphoteric. So, while both metals react readily with acids at low pH, iron reacts sluggishly at neutral or alkaline pHs and does not pose the same reaction risk that aluminum does in a MSW landfill or in groundwater remediation applications.

Chemical Reactions of Aluminum in Various Landfill Types

This section discusses the possible aluminum related reactions in terms of the various types of landfill wastes that may be comingled with aluminum. It is anticipated that these classifications are useful to landfill operators because operators can relate the waste(s) that their facility accepts to the aluminum related reactions that may occur and the potential impacts on their landfill. The following seven combinations of MSW landfill waste streams and/or aluminum are listed and reviewed below:

1. Waste containing only raw curbside trash (RMSW);
2. Waste containing only incinerated MSW (IRMSW);
3. Waste containing both (1) and (2) mixed;
4. Waste containing aluminum production waste, dross;
5. Waste containing RMSW (1) and dross mixed;
6. Waste containing (4) and (2) mixed (IRMSW and dross); and
7. Waste containing (4) and (3).

Not all of these possible waste streams/landfills are equally feasible for various reasons but for completeness all are listed as "possibilities" for an aluminum related reaction.

Waste stream (1) is probably the most common scenario with waste stream (3), RMSW+IRMSW, being common in certain areas, e.g., east coast of the United States, where incineration is frequently used to conserve landfill space. Waste streams (5) and (7), dross and RMSW and/or IRMSW are usually common in states with aluminum production facilities. Presently there are 15 states that produce a significant amount of aluminum production waste, with Ohio and Tennessee each having five aluminum smelting facilities that produce aluminum production wastes. Thus, waste streams (5) and (7) are common in Ohio and Tennessee. Recent case histories in Ohio and Indiana suggest that waste streams (5) and (4), respectively, can lead to unanticipated temperature excursions and gas emissions (Stark et al., unpublished, 2009). Based on several elevated temperature incidents, Ohio EPA (2006, 2007) recommended that aluminum production waste be stored in a monofill [waste stream (4)] with a daily cover to reduce the amount of water that contacts the waste. However, a monofill can also experience an aluminum reaction as occurred in 2006 in Indiana because water from precipitation contacted the dross. The chemical composition of the daily cover must also be examined because the buried dross and ever-present water could become reactive if the daily cover contains substances that raise the pH ≥ 8.5. Specifically, the pH of a saturated solution of

$Ca(CO_3)$ that enters the waste stream from many sources is about 9.5 ± 0.2 which is alkaline enough to initiate the aluminum amphoteric reaction.

Chemical Reactions in MSW Landfills Accepting Only RMSW [Waste Stream (1)]

Landfills accepting *only* RMSW [untreated "curbside trash," waste stream (1)] are common. Even if aluminum recycling is practiced, some aluminum metal [$\approx 2\%$ (4.9 million m^3) to 6% (18.7 million m^3)] can enter a RMSW landfill via various trash components, e.g., cans, doors, siding, car engine and body parts, pie plates, frozen food trays, flexible packaging, etc. (U.S. EPA 2005). This *usually* would not pose a risk for aluminum related reactions because the pH of RMSW is relatively neutral, the amount of aluminum is small, and the aluminum is dispersed throughout the waste mass. However, should the RMSW landfill begin to accept IRMSW [waste stream (3)], the pH of the incoming waste can be greater than the prior waste and aluminum related reactions can be initiated as discussed in the next section.

Chemical Reactions in MSW Landfills Accepting RMSW and IRMSW [Waste Stream (3)]

One east coast landfill accepts 20% by weight RMSW and 80% by weight IRMSW and experienced elevated temperatures because the following three ingredients needed for the amphoteric reaction of aluminum were present, namely:

- High alkalinity (from IRMSW and possibly RMSW);
- Metallic aluminum (from RMSW); and
- Water (usually present in all MSW landfills from a variety of sources).

Neither X-ray diffraction analysis nor X-ray photoelectron spectroscopy (G. V. Calder, "Autoignition temperatures of dry aluminum powder for various oxygen pressure data." personal communication, 2009a) detected any aluminum metal in the incinerator ash from this east coast site. These analytical methods are sensitive to $\sim 0.1-0.5\%$. The ash was generated at three different incinerators. The absence of aluminum in the ash is not surprising because the metallic aluminum in the RMSW is burned at incinerator temperatures of $\approx 850 \degree C$ which consumes the aluminum as discussed above.

However, a high incineration temperature ($\approx 850 \degree C$) generates acidic gases, such as HCl, SO_2, SO_3, and NO_x from the incinerator effluent, which is predominantly CO_2. The acidic gases are usually removed by adding CaO "lime" to the incinerator effluent. CaO readily reacts with water forming $Ca(OH)_2$, "slaked lime" (Misra et al. 1993), which also neutralizes acidic gases. Even though the addition of CaO is stressed here, incinerator ash also usually contains other metal oxides, such as MgO, Na_2O, K_2O, and Al_2O_3 and these were detected in ash from the east coast facility. These oxides can hydrolyze on contact with water, yielding the hydroxides $Mg(OH)_2$, NaOH, KOH, and $Al(OH)_3$, or react with CO_2 forming the corrresponding carbonates. So incinerator effluent is likely to be alkaline (pH ≥ 9) with $Ca(CO_3)$ being the primary source of alkalinity. In addition to incinerator ash, RMSW (curbside trash) can contain a significant amount of $CaCO_3$ because $CaCO_3$ is used in paper, cardboard, various building materials including dry wall, concrete, paints, and many other products. A reasonable assumption for MSW landfills is that calcium carbonate is present as a component of both RMSW and IRMSW. Therefore, if sufficient aluminum is

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located in one area of this type of landfill, all of the ingredients are present for the amphoteric reaction of aluminum to occur.

A final cover system is usually not installed over the waste for a long time after waste filling to allow for waste settlement, which results in the ingredients being in thermal and in chemical contact with the atmosphere. The final cover system usually contains a geomembrane and a low permeability compacted soil layer that can isolate the reaction components from the atmosphere and precipitation and oxygen which can sustain combustion resulting from the reaction. Installing a final cover system is beneficial in separating the reaction ingredients from the atmosphere but a final cover system may not be desirable if the landfill is already experiencing elevated temperatures. The final cover can result in heat being trapped below the cover which can initiate or propogate the combustion and/or pyrolysis of the surrounding MSW. The final cover system can also disturb the steady-state exchange of gases, heat, and water with the atmosphere causing the landfill temperature to exceed 100°C. This exchange with the atmosphere provides a significant heat sink for the heat generated within the landfill. If heat generation is not too fast, evaporation puts a "cap" on the maximum temperature of the landfill ($\leq 100°C$), the normal boiling point of water. Unfortunately, temperatures above 60°C impair anaerobic microbial activity, which is undesirable. In addition to trapping heat, a final cover system can also trap undesirable gases, such as hydrogen, which may result in the accumulation of explosive amounts of H_2 because of the low vapor transmission rate of geomembranes (Koerner 1997) unless a sufficient gas extraction system is installed and operated. This risk is significant because of the wide hydrogen ignition *range* [4–74% (v/v)] and its ignition *rate*—explosive.

There are some management strategies for MSW landfills that accept both RMSW and IRMSW. One strategy (not recommended) is the random mixing of RMSW and incinerator ash because the intermingling of the aluminum (fuel) and the alkaline material (coreactant) facilitates the reaction of aluminum, which is undesirable. A better strategy is to layer the waste and the ash in a "club sandwich" configuration to segregate the aluminum and soluble alkaline water at least to some degree and possibly limit the aluminum reaction to layers of material instead of the entire landfill.

The pH of the leachate at the bottom of one RMSW +IRMSW landfill experiencing elevated temperatures is essentially neutral, pH≈7, although the total dissolved solids (salts) are high (G. V. Calder, "MSW landfill composition at site experiencing elevated temperatures." personal communication, 2009b). The neutral leachate is significant because incoming ash, about 80% of the mass in this landfill is IRMSW, is highly alkaline, pH≈9–11, but the leachate has a pH of ≈7. This large decrease in pH, a factor of 100–10,000, indicates that significant neutralization occurs in the landfill. It is anticipated that this decrease in alkalinity is possible because of the following:

1. The reaction of aluminum consumes a significant amount of Ca(CO$_3$).
2. Calcium carbonate undergoes other reactions in the landfill. For example, various organic carboxylic acids from the oxidation of carbonaceous materials are abundant. These neutralize residual alkaline substances forming "weak acid"/ "weak base" salts. These salts tend to form near neutral salt solutions in water.

The practical significance of the neutral (pH≈7) leachate is that trying to adjust the pH of the landfill by injecting an acidic "neutralizing" agent may be futile because of the following:

1. No benefit accrues by adding a neutralizing agent when the leachate pH is essentially neutral.
2. Pumping aqueous agents into a landfill uniformly is difficult because of retarding back pressure and channeling.
3. The amount and cost of the reagent needed to change the pH, or alter other chemical reactions, are likely prohibitive because of the large quantity required, even if it could be distributed uniformly throughout the landfill.
4. Diffusion of liquids into a dense heterogeneous solid matrix is also usually slow and not uniform.

Chemical Reactions in MSW Landfills Accepting RMSW, IRMSW, and Dross [Waste Streams (5)–(7)]

When a MSW landfill accepts a combination of dross, RMSW, and/or IRMSW [waste streams (5)–(7)], the ingredients for Reaction (2) are present and probably in sufficient amounts to be problematic. The large amount of aluminum present in dross can result in a substantial amount of aluminum reacting and overwhelming the previous steady-state temperature condition. This can cause an overall landfill temperature to increase above 100°C, resulting in other reactions and by-products, such as combustion or pyrolysis of the surrounding MSW. The high temperature can also cause increased generation of explosive hydrogen and noxious gases, such as ammonia and hydrogen sulfide. Indeed, the odor of ammonia gas is one of the identifying characteristics associated with landfill dross problems. Ammonia gas is produced from the reaction of water and aluminum nitride (AlN) present in dross (Fukumoto et al. 2001)

$$AlN + 3H_2O = Al(OH)_3 + NH_3 \qquad (6)$$
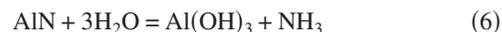
The odor of ammonia gas (NH_3) near a problematic landfill is evidence that the environment is alkaline. If the environment were acidic, the ammonium ion $(NH_4)^{+1}$ would be the predominant nitrogen species, and that ionic species is nonvolatile.

Hydrogen sulfide (H_2S) gas can also be produced from aluminum sulfide present in dross by Reaction (7) (absoluteastronomy.com/topics/Aluminium_sulfide, 2009)

$$Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S \qquad (7)$$
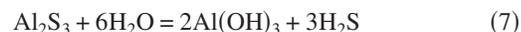
Reactions (6) and (7) are illustrative. The actual reaction mechanisms and chemical species must be determined experimentally.

When carbonaceous matter is present from any waste stream and the temperature is sufficiently high, it can combust, producing carbon dioxide and additional heat (*Handbook of chemistry and physics* 2003)

$$C + O_2 = CO_2(-393.5 \text{ kJ/mol}) \qquad (8)$$

RMSW is usually the major source of carbon (C) in a landfill but another source at some sites is coal from mine spoil that is included in daily or final cover material. This coal can undergo ignition due to elevated temperature from an aluminum reaction. Thus, if the elevated temperature is anticipated/encountered, coal and other carbon based materials should not be used in the daily or final cover soil because the coal can ignite and add additional heat that can prolong or increase the problem. Coal fires are notoriously difficult to extinguish which prolongs the elevated temperature for a substantial amount of time. For example, a coal mine fire in Centralia, Pennsylvania (http://www.offroaders.com/album/centralia/centralia.htm) has been burning for decades. It was inadvertently started around 1962 when RMSW was burned in an abandoned coal strip mine, which unfortunately was connected to a coal seam running near the surface. The burning

RMSW ignited the exposed coal seam and the fire propagated underground. For the next 2 decades, workers battled the fire, flushing the mines with water and fly ash and excavating the burning material in an attempt to find the boundaries of the fire and suppress or at least contain it. By the early 1980s the fire had affected approximately 81 ha and homes had to be abandoned as CO levels reached life threatening levels. After about 50 years and 40 million dollars, the fire still burns through old coal mines and seams under the town and the surrounding hillsides.

If sufficient oxygen is present for complete combustion of the carbon/coal, the products are CO_2 and heat. If insufficient oxygen is present for complete combustion, the reaction product is toxic carbon monoxide (CO) and heat (*Handbook of chemistry and physics* 2003)

$$C_{(solid)} + \frac{1}{2}O_2 = CO_{(gas)} + (-110.5 \text{ kJ/mol}) \qquad (9)$$
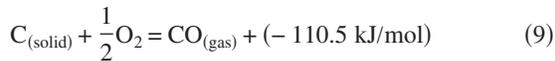
CO levels over 6,000 ppm have been detected at a MSW landfill that is undergoing an aluminum related reaction (Stark et al., unpublished, 2009). CO levels over 1,000 ppm (0.1%) and temperatures above 100°C are usually indicators that a carbon fueled fire is occurring concurrent with, or instead of, an aluminum fueled reaction (Stark et al., unpublished, 2009). Aluminum fueled reactions and carbon fueled fires are not mutually exclusive and can occur concurrently in the same landfill if the requisite conditions are present.

Reactions of ADW in MSW Landfills [Waste Stream (4)]
This waste, collectively referred to here as dross, contains from 10 to 70% aluminum (Stark et al., unpublished, 2009). The chemistry of such sites differs from conventional MSW sites discussed above, so it is treated separately in this section. These sites are designated aluminum dross waste (ADW) sites which correspond to waste stream (4).

Dross contains oxidized aluminum (alumina, Al_2O_3), small particles of aluminum metal, large amounts of MgO and $Mg(AlO_4)_2$ from the recycling of magnesium-aluminum alloys, SiO_2, AlN, Al_4C_3, CaO, and other transition metal oxides such as Fe_3O_4 (Ghorah et al. 2004). In some cases the amount of elemental aluminum can be as high as 90% of the total amount of solids (Kos 1995), although most dross contains about 50% metallic aluminum (Das et al. 2007). The high metal content of dross and the increasing cost of aluminum are creating more interest in recovery but dross recycling [Azom (A to Z of Materials) 2002] has not proven economical to date despite the millions of kilograms of dross produced each year (Broughton and Seldman 1992). Thus, the majority of dross will probably continue to be placed in MSW landfills for the foreseeable future. However, if U.S. EPA develops an objective test to determine whether or not a waste meets the reactive criterion under 40 CFR Sec. 261, Subpart C as suggested below and aluminum is classified as a hazardous waste, dross recycling may become economical.

The reaction of aluminum in an ADW landfill is the same as Reaction (2). This reaction requires both $(OH)^{-1}_{(AQ)}$ and $H_2O_{(L)}$. The origin of $(OH)^{-1}_{(AQ)}$ in a MSW landfill is both RMSW and IRMSW if $Ca(CO_3)$ is present. As discussed above water is usually present in MSW landfill from a variety of sources including precipitation, injection, leachate recirculation, and/or groundwater infiltration if there is no liner system or if the liner system has been damaged and an inward gradient exists. Thus, the main question concerning whether or not Reaction (2) will occur is whether the three ingredients (aluminum, alkalinity, and water)

are able to interact with each other sufficiently in the landfill. If the answer is yes, then Reaction (2) will occur in the MSW landfill and will most likely cause serious operational problems. If the answer is no, then Reaction (2) will not likely occur and the landfill will operate normally.

At least one facility that recirculated leachate in a MSW landfill containing a substantial amount of aluminum production waste has experienced a significant exothermic reaction (Stark et al., unpublished, 2009). At this site 103 ML of leachate were recirculated over about 11 years. This initiated an aluminum reaction that consumed the surrounding MSW. This site is now generating about 132.5 ML of leachate per year after the reaction and combustion started (Stark et al., unpublished, 2009). Prior to the reaction/fire, the maximum annual leachate volume was about 2 ML. Specifically, in 2004 the landfill generated about 12 ML of leachate. In 2005 when the reaction/fire was first reported, the leachate volume increased to 46 ML. The leachate volume increased significantly afterward with 109 ML in 2006, 130 ML in 2007, and 127 ML in 2008 (Stark et al., unpublished, 2009). The amount of leachate generated by the reaction and subsequent fire significantly exceeds the amount of leachate recirculated. For example, in 2006–2009 the annual volume of leachate generated exceeded the total amount of leachate recirculated over about 11 years, i.e., 103 ML. The sources of the additional leachate include the waste itself, liquid injection to accelerate or suppress the reaction or fire, respectively, water/liquid from precipitation, surface water management, and groundwater infiltration due to a damaged liner system (Stark et al., unpublished, 2009). The "black leachate," which has a viscosity similar to used motor oil, is high in dissolved solids, organic material, and ammonia (Stark et al., unpublished, 2009) and required special treatment.

The selected remedial measure at this site simply allowed the reaction(s) and combustion of the surrounding waste to run their various courses (Stark et al., unpublished, 2009). To date, the reaction and combustion have been occurring for about 4 years and are slowly migrating through the 35.6-ha MSW landfill. This migration of the reaction and combustion has resulted in vertical settlement of the affected areas of 10–20 m since 2005 or an annual settlement of 2.5–5.0 m. This has resulted in the top of the landfill settling 30–35% of the initial height. Typical settlement in a MSW landfill settlement ranges from 5 to 10% of the initial height over 3–30 years (Edgers et al. 1992; Spikula 1997).

If these exothermic aluminum reactions are allowed to occur unabated, the heat load will likely overwhelm the heat dissipation capacity of a typical MSW site. Consequently, the temperature is no longer "capped" by the boiling point of water, and other new reactions possibly producing noxious products such as ammonia and hydrogen sulfide that will likely dominate the landfill gaseous effluent.

Temperatures exceeding 150°C (300°F) have been measured in this MSW landfill (Stark et al., unpublished, 2009). These high temperatures also pose a risk to the integrity of the landfill liner system and other engineered components.

Sites where significant amounts of aluminum production wastes have been deposited [waste streams (4)–(7)] pose additional environmental and health issues. Two studies (Azom (A to Z of Materials) 2002; Szczygielski 2007) recognize the hazards of aluminum dross. Another study has implicated exposure to landfill gases to reproductive problems, such as low birth weight, premature birth, and smallness for gestational age (Goldberg et al. 1995b). Another study focused on the effects of exposure to a continuous release of fugitive toxic gases and contaminated soil from an uncapped MSW landfill in Montreal, Canada (Goldberg

et al. 1995a). The gas collection system of this landfill detected human carcinogens, such as benzene, vinyl chloride, and other halogenated hydrocarbons. This study also showed that men living in the exposure zone closest to the site had a statistically significant elevated risk of prostate, stomach, liver, and lung cancer. Women living in the area also showed higher incidence of stomach and cervical cancers (Goldberg et al. 1995a).

The acute toxicity of gaseous landfill emissions, such as CO, H_2S, NH_3, and $HC \equiv CH$ (acetylene) among others, is well known, and the risk factors are exacerbated by landfill fires (FEMA 2002). Another concern about landfill fires, regardless of origin, is the emission of organic combustion and pyrolysis products. An important class of such combustion products is "dioxins." This family of stable toxic substances accumulates in the fatty tissues of all life forms. A large body of toxicological data available is in the literature, (U.S. EPA 2008) Office of the Science Advisor website, concerning the health risks of dioxins and is not repeated here.

Summary and Recommendations

The data presented herein indicate that the likely cause of uncontrolled temperature increases in landfills is the reaction of aluminum and water under alkaline conditions (pH $\geqslant$ 9).

The anhydrous oxidation of aluminum in dry air appears less likely than the amphoteric reaction of aluminum because of the presence of alkaline water in these facilities. Any buried aluminum metal can react with alkaline material forming the water soluble product, $[Al(OH^{-1})_4]^{-1}_{(AQ)}$. However, temperatures above $100°C$ can boil or push water and/or steam from the reaction area, possibly resulting in enough oxygen being present for anhydrous oxidation of aluminum to occur in local "hot spots" or in larger areas, if enough water is removed. These circumstances or the ignition of hydrogen gas can lead to combustion and/or pyrolysis of the surrounding MSW.

ADW landfills contain a large amount of potential thermal energy that presently is not being used. Reaction (2) provides a means of tapping this energy source by converting the energy to electrical power and/or heat. Both the aluminum and hydrogen reaction products are used so that the only volatile product of the reaction is water. There are no volatile organic compounds, so the reaction is clean and "green." These concepts are currently being researched by the writers.

The following actions are recommended to reduce the potential for aluminum related problems in MSW landfills based on at least five MSW landfills that have experienced or are experiencing elevated temperatures investigated by the writers.

Administrative Recommendations

U.S. EPA should develop an objective test to determine whether or not a waste meets the narrative description of "reactive" under 40 CFR Sec. 261, Subpart C instead of the current subjective process which results in reactive aluminum dross being placed in MSW landfills.

U.S. EPA should develop guidelines for testing frequency and reporting to ensure that reactive wastes are not placed in MSW landfills.

Change state law to prohibit disposal of aluminum production waste in MSW facilities because it may be quicker than changing

40 CFR Sec. 261, Subpart D which lists hazardous materials and 40 CFR Sec. 261, Subpart C which classifies a waste as hazardous if it exhibits reactivity.

It should be the responsibility of the landfill operator to report the results of reactive and "ignitiability" tests to the U.S. EPA and state regulatory agencies not the generator because the landfill operator initially will have to address the problems that develop, not the generator. In addition, the generator may have a conflict of interest concerning the results.

Operational/Technical Recommendations

"Waste" should be analyzed to ensure that aluminum waste, including dross, does not contain any banned metals that would classify the waste as hazardous, thus making it unsuitable for disposal in a MSW landfill.

Aluminum waste should not exceed 5% (by weight) of the total monthly waste acceptance of the facility. In addition, the aluminum waste tonnage should not exceed 10% of the average daily tonnage received on any given day.

Aluminum waste should be immediately buried to minimize dust dispersion and contact with precipitation, e.g., rain and/or snow. Alternatively, the facility should consider not accepting aluminum waste on precipitation days.

Aluminum waste should not be mixed with tire shreds or fly ash because of possible alkaline reactions, moisture, and heat.

Aluminum waste should not be placed in landfill areas where leachate recirculation is occurring and conversely leachate recirculation should not be used in areas where aluminum waste has been placed.

If aluminum waste is accepted the placement location and tonnage of aluminum waste placed should be carefully mapped and documented so if a problem develops, the responding agencies can assess the extent of the problem. In a recent aluminum waste problem (Stark et al., unpublished, 2009), the facility claimed that these records were lost which made assessing the extent of the problem and possible remedial measures difficult.

Place aluminum waste in a monofill. However, two elevated temperature events occurred in an aluminum production waste monofill in Indiana in recently placed waste at or near the working face so it is important to cover the monofill as soon as possible (Stark et al., unpublished, 2009).

Another option is to dispose aluminum waste in a residual waste landfill with other inorganic nonalkaline industrial wastes, such as foundry sand, gypsum (calcium sulfate $CaSO_4 \cdot 2H_2O$), or steel manufacturing wastes. However, the potential reactivity of aluminum waste with other substances, even *inorganic* substances in the landfill, should be examined to ensure that there are no potential reactions.

Last, but not least, the heat generated from an aluminum related event might be captured using a Stirling engine concept. A Stirling engine consists of two heat exchangers. The first heat exchanger, the primary heat exchanger, uses a high boiling, high heat capacity fluid, typically liquid water and/or steam buried in the hot landfill. Basically this is an automobile radiator. This fluid (water/steam) drives itself to the surface due to the pressure difference. A second heat exchanger at the surface uses a fluid with a much lower boiling point than the primary fluid so that its vapor pressure at temperatures $\geqslant 100°C$ is greater than water. The two fluids are in thermal but not physical or chemical contact. The primary fluid vaporizes the secondary fluid, which now is at a high pressure ($P \geqslant 1$ atm). This high pressure fluid drives a turbine or piston. The cycle, once stabilized, operates continuously.

The first fluid, for example, could be water/steam. A candidate for a second fluid is sulfur hexafluoride (SF_6) which is nontoxic, nonflammable, and is already used commercially in similar applications. The turbine or piston is then used to generate electrical power, or the heat itself could be distributed and used for any number of heating purposes. While mentioned here, this concept is the subject of ongoing research. Depending on the particular circumstances at a particular landfill, maybe a second heat exchanger may not be needed, or SF_6 may not be the best fluid for the second stage.

Acknowledgments

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