Ohio EPA

State of Ohio Environmental Protection Agency

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August 7, 2007

Tim Vandersall
General Manager/Engineer
3619 Gracemont St. S.W.
East Sparta, Ohio 44626

RE: **Countywide Recycling and Disposal Facility, 3619 Gracemont St. S.W., East Sparta, Ohio 44626, Stark County, Treatability Study Report, Supplement to the Fire Suppression Plan, Order 8 of the DFF&Os of March 28, 2007**

Dear Mr. Vandersall:

The Ohio Environmental Protection Agency (Ohio EPA) has completed its review of the July 9, 2007 Treatability Study Report (the Report) for the above referenced Facility. Countywide RDF (Countywide) has provided the above submittal as a supplement to the Fire Suppression Plan, Order 8 of the Director's Final Findings and Orders of March 28, 2007. While not addressing the Fire Suppression Plan itself, Ohio EPA has substantial comments regarding the Treatability Study. Ohio EPA requests Countywide address the following comments:

General Comments:

GC 1) Focus of the Treatability Study
The Introduction section of the report states, "*Presented herein are the results of a laboratory treatability test to evaluate the application of various suppression agents for mitigating the reaction between aluminum waste and leachate water present in the Countywide Landfill.*"

Finding 43 of the March 28, 2007 Director's Final Findings and Orders states the following: "*A chemical reaction involving large amounts of aluminum waste and producing elevated temperatures has been and is still occurring at the Facility. In addition, a fire involving the rapid thermal decomposition of solid waste producing carbon monoxide in excess of 1000 ppmv, or "fire" as referred to in OAC Rule 3745-27-19(E)(3)(a), has been and is still occurring at the Facility and Respondent has failed to act immediately to control or extinguish the fire in violation of OAC Rule 3745-27-19(E)(3)(a).*"

Ohio EPA has retained qualified experts in fire science[1], landfill fire identification and suppression[2], and chemistry[3] to assist with the evaluation and remediation of the ongoing situation at Countywide Landfill. Based on their visual inspection of the area of settlement, drill cuttings, visible emissions, and review of data, these experts have concluded that a fire is present within the waste mass in addition to the exothermic reaction of the aluminum production wastes. Additionally, Ohio EPA contacted other experts in fire science[4] and landfill fire identification and suppression[5], who, based on information provided to them via telephone discussions, expressed an opinion that a fire is likely present at Countywide Landfill.

The Report evaluates several means of suppressing the exothermic reaction of aluminum production wastes with water (leachate), but does not evaluate any means of suppressing the smoldering fire that exists within the organic waste mass at Countywide Landfill. In fact, the Report appears to imply that a smoldering fire does not exist at Countywide Landfill based on the experimental results[6]. The experimental results do not allow any conclusions to be made.

Ohio EPA requests from CWRDF, based on the Report and all other pertinent data collected to date, an explanation and technical justification of the option(s) CWRDF is currently evaluating to suppress the aluminum production waste reaction <u>and</u> extinguish the smoldering fire within the waste mass at the landfill.

GC 2) Overall Study
Ohio EPA and its experts believe this study lacks methodological detail and yields only questionable results.

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[1] Vytenis Babrauskas, Ph.D., Fire Science Protection

[2] Todd Thalhamer, California Registered Professional Civil Engineer, Cal-EPA/California Integrated Waste Management Board, and Lieutenant, El Dorado Hills Fire Department

[3] Carl Heltzel, Ph.D., Organic Chemistry

[4] Personal communication, William M. Pitts, Ph.D., Physical Chemistry, National Institute of Standards and Technology, Building and Fire Research Laboratory, to Jeff Martin, Ohio EPA, February 13, 2007

[5] Personal communication, Tony Sperling, P.E., Ph.D., Geotechnical Engineering, to Ed Gortner, Gina Gerbasi, and Jeff Martin, Ohio EPA, February 12, 2007

[6] Since August 2006, CWRDF has denied that a fire exists within the waste mass at the landfill. Order 41 of the March 28, 2007 Director's Findings and Orders states, "*Respondent has admitted that there is a reaction involving aluminum waste at the Facility, but has denied that there is a fire occurring at the Facility.*"

The Report provides only two references. One reference cites Shaw's own unpublished work, which attempts to assess the effect of adding the sodium salts of the reagents. The pH of each solution was not measured. The other reference, the Krnel study, is not relevant considering the experimental conditions and goals of the research. The Krnel study is based on the effect of adding dilute organic acids to only AlN, not aluminum dross. The study assessed the fire suppression value of hydrated forms of SiO_2 (silicic acid) and phosphoric acid. The Krnel study reported a slight passivation of AlN hydrolysis as a result of the addition of the acidic form of each compound. In each case, the reference reported that when weak, diprotic silicic acids (such as meta silicic acid, H_2SiO_3, or ortho silicic acid, H_4SiO_4), were used, the reaction was hindered but not prevented. When phosphoric acid (H_3PO_4) was used, passivation occurred, but subsequent addition of heat (the pervasive conditions at Countywide) induced hydrolysis of the AlN, indicating that the inhibition of AlN hydrolysis using these reagents is completely reversible.

The experiment did not simulate the actual combustion scenario taking place at Countywide. It appears that the procedures simply allowed for the observation of mild oxidation of dross with water (where the reaction stopped producing gas after two days). Thus, the study really only replicated what was already known about the reaction of aluminum with water. The presence of the suppression reagents as amendments to the dross mixtures did not represent potential solutions for the problem—a fire—since the reaction was not ignited in a self-sustaining manner as the fire is observed to be occurring in the landfill. Given the enormity of the problems occurring at the Countywide site, this study is inadequate and needs to be repeated but with tighter experimental conditions and objectives that are more specifically focused on the Countywide condition.

GC 3) Treatability Study Objectives
It appears that the objectives of the proposed research were not met. The objectives, as stated on page 1, paragraph 2, as compared to the apparent outcomes are summarized in the table below:

Objective	Outcome
To evaluate the potential effectiveness of various suppression amendments by estimating the amendment dosage required for treatment.	It is unclear how estimating the amendment dosage required for treatment could be used as a method for evaluating the potential effectiveness of various suppression amendments. The procedure did not prove or disprove the effectiveness of suppression agents for treating ignited landfill waste such as that occurring at Countywide.
To determine how quickly the reaction	Since the concentrations of reactive

suppression will occur.	reagents were never determined (i.e. concentration of Al metal in dross), it would be impossible to express the order of the reaction, the rate of reaction, or the time it would take for the suppression to occur.
To verify that the suppression mechanisms are irreversible.	If the suppression amendments had been successful, the experimental procedure would not have necessarily verified irreversibility.
To quantify the overall impacts of amendment addition on gas production and composition.	The effects of amendment addition on gas production and composition were measured; claiming the overall effects of amendment addition were quantified is a stretch. Furthermore, the validity of the data is questionable.

GC 4) Carbon Monoxide

The Discussion and Conclusions section explains, "*Generation of carbon monoxide up to levels of 500 ppmv were observed. Although the generation of CO is often attributed to combustion, no combustion was observed in the glass serum bottles (i.e., no visible smoke, char, or flame). The mechanism of CO production is unclear, but may be due to the decomposition of volatile fatty acids (VFAs) that are present in the leachate water. VFA concentrations in the leachate water were in excess of 30,000 ug/L. Another possibility is that catalytic reactions could be occurring on the surface of the aluminum waste that act to partially oxidize or reduce carbon sources (e.g. methane, carbon dioxide), subsequently forming carbon monoxide.*"

Fundamental principles of fire science and chemistry do not prescribe that fire necessarily entails the visibility of smoke, char, or flame. Combustion in the interior of porous media will generally show no external signs until the fire is at such a late stage that it is breaking out at the surface. Furthermore, *absence of evidence is not evidence of absence.* It is very likely that the carbon monoxide found in the Report was generated by pyrolysis of organic matter in the landfill solids that were subjected to the experimental conditions. Absent a fire at Countywide, the continued emission of excessive heat (> 170° F) and high concentrations of carbon monoxide (> 1,000 ppmv) would not be occurring within the waste mass through pyrolysis alone.[7]

Ohio EPA was present for the replacement of several gas extraction wells at CWRDF during the period from June 4 through June 13, 2007 and observed the following conditions:

[7] Personal Communication, Vytenis Babrauskas, Ph.D., to Jeff Martin, Ohio EPA, July 18, 2007

- visible emissions from the replacement well borings that appeared to be a combination of water vapor condensation and/or smoke;

- carbon monoxide readings (in the vicinity of the referenced visible emissions) between 30 and at least 500 ppmv (recorded on portable carbon monoxide detectors used for health and safety monitoring by the drilling contractor, the maximum detection limit for the detectors was 500 ppmv);

- organic landfill solids (wood products, yard waste, and paper products) that appeared to be charred, and plastic materials that appeared to be melted;

- waste temperatures typically ranging between 150° and 195° F and boring (down-hole) temperatures as high as 212° F; and

- a very strong burning odor from the waste excavated from the borings.

Ohio EPA has retained qualified experts in fire science[8], landfill fire identification and suppression[9], and chemistry[10] to assist with the evaluation and remediation of the ongoing situation at Countywide Landfill. Based on the experts' visual inspection of the settlement, drill cuttings, visible emission, and review of data, these experts have concluded that a fire is present within the waste mass in addition to the exothermic reaction of the aluminum production wastes. Additionally, Ohio EPA contacted other experts in fire science[11] and landfill fire identification and suppression[12], who, based on information provided to them via telephone discussions, expressed an opinion that a fire is likely present at Countywide Landfill.

Ohio EPA requests that CWRDF please provide the following information:

- copies of published, peer-reviewed scientific studies that evaluate the generation of carbon monoxide from the decomposition of volatile fatty acids. The studies must have been conducted independently of the interests of CWRDF and any consultants retained on their behalf; and

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[8] Vytenis Babrauskas, Ph.D., Fire Science Protection

[9] Todd Thalhamer, California Registered Professional Civil Engineer, Cal-EPA/California Integrated Waste Management Board, and Lieutenant, El Dorado Hills Fire Department

[10] Carl Heltzel, Ph.D., Organic Chemistry

[11] Personal communication, William M. Pitts, Ph.D., Physical Chemistry, National Institute of Standards and Technology, Building and Fire Research Laboratory, to Jeff Martin, Ohio EPA, February 13, 2007

[12] Personal communication, Tony Sperling, P.E., Ph.D., Geotechnical Engineering, to Ed Gortner, Gina Gerbasi, and Jeff Martin, Ohio EPA, February 12, 2007

- copies of published, peer-reviewed scientific studies that evaluate the generation of carbon monoxide from catalytic reactions occurring on the surface of the aluminum production waste that act to partially oxidize or reduce carbon sources (e.g., methane, carbon dioxide) and that were conducted independently of the interests of CWRDF and any consultants retained on their behalf.

GC 5) Experimental Design - Materials
The Materials section of the report discusses the aluminum waste that was used for the testing procedures. The report states that the aluminum production waste was retrieved from Countywide Landfill at a depth of 60 feet.

Based on Ohio EPA's discussions at CWRDF with Mr. Michael Beaudoin, P.E., Earth Tech, Inc. on June 4, 2007, the aluminum production waste that was tested was collected from Cell 2 (near PW-111) where, to Ohio EPA's knowledge, evidence of the aluminum production waste reaction or landfill fire indicators have not been observed to date. Mr. Beaudoin showed Ohio EPA samples of the aluminum production waste materials collected; these included black dross, salt cake, and bag house dust as apparently identified on behalf of CWRDF by a former employee of Reynolds Metals.

Ohio EPA requests the following clarification on the type(s) of the aluminum production waste that were used in the experiment:

- please identify the specific type(s) of aluminum wastes that were used for each control and treatment;

- explain how the specific identity of the components, especially aluminum metal, was quantified; and

- Cell 3 has exhibited the most intense aluminum production waste reaction to date. Please provide justification that the aluminum waste types used in the experiment are the same type(s) of aluminum wastes disposed in Cell 3.

In addition, Ohio EPA requests that CWRDF please provide a summary of all aluminum waste types that have been retrieved from the landfill since January 2006 (such as the samples of salt cake from approximately 81 feet below the landfill surface CWRDF and Ohio EPA collected during the installation of replacement landfill gas extraction well W-56R in Cell 4 on June 11, 2007) and whether or not the sample materials have been used for laboratory analyses or testing to date.

The type of aluminum production waste used in the experiment is important because the chemical and physical variation between waste types is likely to influence the observed reaction and reaction products. For example, black dross contains more elemental aluminum than salt cake[13] and therefore is likely to generate greater volumes of hydrogen gas and more heat. In addition, bag house dust is much finer grained than black dross or salt cake and as such may be more reactive as a greater surface area is available for the reaction to occur as a function of smaller particle size.[14]

GC 6) Experimental Design – Materials
The concentrations of aluminum, aluminum nitride, and aluminum oxide in the dross samples were never determined. This should have been a critical initial step in the experimental design; the consequences of this oversight are mentioned in some of the following comments. References for determining the composition of various dross samples are available in the literature[15,16]. Material Safety Data Sheets typically report the hazardous ingredients of aluminum dross (MSDS #04) as:

Hazardous Ingredient	Typical Percent
Aluminum (Al) metal	10 - 70
Aluminum oxides	5 - 20
Mixture of nitrides	2 – 10
Mixture of carbides	1 - 4
Mixture of chlorides	2 - 40
Other impurities	traces

Source: Wise Alloys MSDS, prepared 04/01/99, revised 09/01/04

GC 7) Experimental Design – Materials
The Materials section of the Report explains that the landfill solids used were collected from the landfill to obtain a representative sample of the waste disposed in CWRDF. This representative sample consisted of a mixture of paper, metal, plastic, fiber, and some soil. Large objects were removed by hand and the remaining solids were passed through a 0.25-inch sieve so that the waste could be transferred into the serum bottles used for the experiments.

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[13] Shinzato, M.C., and Hypolito, R., 2005, *Solid waste from aluminum recycling process: characterization and reuse of its economically valuable constituents*: Waste Management, vol. 25, pp. 37-46

[14] Laboratory testing results for aluminum production wastes presented by representatives of Athens-Hocking Reclamation Center during an April 10, 2007 meeting with Ohio EPA indicate that bag house dust is more reactive (i.e., generates more gas when exposed to water) than dross or salt cake

[15] Manfredi, O., Wulth, W., Bohlinger, I. The Chemical and Physical Properties of Aluminum Dross, *Journal of the Minerals, Metals, and Materials Society*, 49 (11) 1997, pp 1047-4838

[16] Graczyk, D., Essling, A., Huff, E., Smith, F., and Snyder, C. "Analytical Chemistry of Aluminum Salt Cake in Light Metals" (R. Huglen, ed.), *Proceedings of the 126th Annual Meeting of the Minerals, Metals and Materials Society: Symposium on Aluminum Dross and Salt Cake* Processing, Orlando, Florida, February 9-13, 1997

Ohio EPA requests that CWRDF provide information to address the following concerns:

- first, please explain where and how the landfill solids used for the experiment were collected, and specifically, whether or not the landfill solids were taken from an area of the waste mass where evidence of the aluminum production waste reaction or landfill fire indicators have been observed to date, and whether or not the landfill solids were taken from an area of the waste mass where leachate circulation has been performed (noting how many times the leachate was recirculated);

- second, please provide the estimated age of the wastes used for the landfill solids sample;

- third, please provide the information (e.g., references, facility disposal records, etc.) used to determine that the landfill solids sample was representative of the waste disposed in the aluminum production waste reaction area at Countywide Landfill. According to U.S. EPA[17], typical municipal solid waste consists of 26% paper and paperboard, 17% food wastes, 16% plastics, 7% yard trimmings, 7% metals, 6% glass, and 21% other wastes by weight. Countywide Landfill's waste composition in the area where dross was placed may differ from these typical proportions, if this is the case, please provide evidence to that fact;

- fourth, please provide a clarification as to the specific wastes categorized as "fiber" (e.g., wood, wood products, and yard waste.) During the installation of replacement gas extraction wells from June 4 through 13, 2007, Ohio EPA observed that wood, wood products and yard waste appeared to be a significant component of the waste in the reaction area;

- fifth, please provide the percentage of soil that was included in the landfill solids used for the experiment. During the referenced drilling, Ohio EPA observed that soil appeared to be a very small proportion of the overall waste volume; and

- sixth, please provide justification that the difference in the degree of compaction between the landfill solids and the actual in-situ waste at Countywide Landfill (1,800 lbs/yd^3)[18] was not a significant factor with respect to the experimental results observed.

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[17] U.S. EPA Office of Solid Waste, October 2006, Municipal Solid Waste in the United States: Facts and Figures: EPA530-R-06-011, p. 61

[18] Personal communication, Todd Hamilton, CWRDF, to Jeff Martin, Ohio EPA, May 8, 2007

GC 8) Experimental Design – Materials
In these experiments, large objects were removed by hand and the remaining solids were passed through a 0.25-inch sieve so that the waste could be transferred into the serum bottles used for the experiments. The removal of large objects sets forth a scenario where the scale of the experiment is not representative of conditions at the landfill in terms of size. Please identify the types of "larger objects" that were removed by hand and explain how their removal altered the representative waste stream composition of the landfill solids sample collected for the experiment. In consideration of the fact that particle size may affect combustion and combustion by-products (such as carbon monoxide), please explain why larger reaction containers (serum bottles) were not used to accommodate the representative waste sample.

GC 9) Experimental Design – Materials
The Materials section of the Report explains that leachate used in the experiment was a composite sample collected from the north above-ground storage tank, the east underground storage tank, and the south above-ground storage tank at CWRDF.

Ohio EPA requests that CWRDF please provide the following information:

- the proportions of the composite leachate sample from the three respective collection points (north above-ground storage tank, the east underground storage tank, and south above-ground storage tank); and
- identify which landfill cells are serviced by each of the three collection points.

The leachate used for the experiment represents a water source that has already been affected by the ongoing aluminum production waste reaction and smoldering fire occurring at CWRDF. For example, the aluminum production waste reaction has elevated ammonia nitrogen concentrations in the leachate (2,300 mg/L), as well as the concentrations of chemical oxygen demand (94,000 mg/L), sodium (180,000 mg/L), calcium (5,700 mg/L), potassium (10,000 mg/L), magnesium (1,200 mg/L), and sulfate (7,100 mg/L) and various other leachate constituents.[19]

The anomalous ammonia nitrogen results obtained provide a specific example of the bias of which Ohio EPA is concerned. As the results indicate, very little ammonia gas was produced by the experiment, which is atypical of reactions of aluminum dross and salt cake with water.[20, 21, 22] The reason for the observed low levels of ammonia gas

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[19] Maximum concentrations detected in leachate samples by CWRDF and reported to Ohio EPA during the period from July through December 2006

[20] Shinzato, M.C., and Hypolito, R., 2005, *Solid waste from aluminum recycling process: characterization and reuse of its economically valuable constituents*: Waste Management, vol. 25, pp. 37-46

may be due to high concentrations of dissolved ammonia (ammonium ion) in the leachate that inhibited the production of ammonia gas (equation):

$$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3\uparrow$$

GC 10) Fire Suppression Agents
Two commercial fire suppression agents were used in this experiment. First Strike® is a foam product that, by the manufacturer's instructions, is NOT for use on polar/water miscible fuels[23]; the conditions at Countywide as well as inside the serum bottles used by Shaw would exclude this product from serious consideration. First Strike® is designed for hydrocarbon spills, suppressing fire by being sprayed on and creating a blanket over the hydrocarbon-fuel based fire, starving it of oxygen.

The second commercial fire suppression agent, Flame Out is a proprietary (a well-kept secret) complex blend of alcohols, lipids, and proteins[24]—not an ideal choice when one of the goals of the experiment was to "***quantify*** [emphasis added] *the overall impact of amendment addition on gas production and composition."*

Neither of the commercial fire suppression agents was designed to be placed in a closed system with reagents and water, and then agitated. They are designed to be sprayed onto an ignited fire.

GC 11) Experimental Design – Methodology
The Methodology section of the report indicates that 50 mL of leachate was added to each serum bottle. Ohio EPA requests that CWRDF please explain whether or not the serum bottles were agitated or rotated in any manner during the experiment in an attempt to simulate the percolation of water through the waste mass at Countywide Landfill. Additionally, please explain why the waste samples were saturated, as that aspect of the experiment is not representative of conditions at the landfill (though there are varying degrees of moisture in waste layers).

GC 12) Experimental Design – Methodology
The pH of the samples was not monitored. Ohio EPA request Countywide provide an explanation for this decision to not monitor pH, especially considering the effectiveness

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[21] Lucheva, B., Tsonev, Ts., and R. Petkov, 2005, *Non-Waste Aluminum Dross Recycling*: Journal of the University of Chemical Technology and Metallurgy, vol. 40, no. 4, pp. 335-338

[22] EnSafe, Inc., August 2002, *Superfund Five-Year Review Report, Brantley Landfill NPL Site, Island, Kentucky*: Prepared for United States Environmental Protection Agency, Region IV, Atlanta, Georgia

[23] *Options to the Use of Halons for Aircraft Fire Suppression Systems*. 2002 Update DOT/FAA/AR-99/63, Office of Aviation Research, Washington, D.C. 20591.

[24] http://www.usfoam.com/CatHouse/CatalogDesp.pdf

of the commercial fire suppression agents and the silicate and phosphate reagents are all pH dependent.

GC 13) Experimental Design – Methodology
According to the Report, the experiment was temperature controlled by placing the serum bottles in a 170°F bath, and later increasing the temperature to 207°F. Given the dross and water reaction is exothermic, it would make sense to monitor the temperature of the reaction, rather than control it. If the temperature were monitored, one would gain a better understanding of the temperature range of the reaction and the temperatures the MSW would be exposed to as a result of this reaction (assuming the rest of the experiment was setup and performed appropriately).

GC 14) Experimental Design – Methodology
The Methodology section of the report indicates that the ratio of aluminum production waste (35 g) to other landfill solids (25 g) used for the aluminum waste and landfill solids control and all eight suppression treatments was a 7:5 ratio (58% aluminum waste, 42% other landfill solids).

Ohio EPA requests that CWRDF please provide the following information:

- justification for the aluminum production waste to landfill solids ratio selected for the experiment; and

- whether or not the aluminum waste and other landfill solids were mixed before or after being inserted into the serum bottles, and if not mixed before being placed in the bottles, whether or not the aluminum wastes and other landfill solids were arranged in the bottles as segregated layers (e.g., 25 g of other landfill solids placed over 35 g of aluminum waste).

GC 15) Experimental Design – Methodology
The Methodology section of the report states, "*Bottles were placed in a constant temperature bath to maintain the temperature at approximately 170 degrees F (77° C), which was the maximum temperature measured in the aluminum waste material during sample collection.*"

Ohio EPA was not aware that a temperature of 170° F was measured in the aluminum production wastes when they were collected. This elevated temperature indicates that these wastes were already reacting with water present in the waste mass at the time they were collected (which possibly introduced some bias into the experimental results). In addition, temperatures in excess of 170° F in the waste mass are indicative of a landfill fire.[25] If the temperature was measured in the waste after it was retrieved from the boring, the temperature of the in-situ waste was likely higher.

[25] Federal Emergency Management Agency, United States Fire Administration, National Fire Data Center,

Ohio EPA requests that CWRDF please explain why the temperature of 170° F was used for the experiment rather than a normal municipal solid waste landfill operating temperature of less than 131°F, which was the approximate landfill temperature before the apparent start of the aluminum production waste reaction during 2001, when elevated landfill gas temperatures and pressures began to be observed.[26]

The use of aluminum production wastes that had partially reacted with landfill fluids (condensate or leachate) may have biased the experiment results. For example, if aluminum wastes that had not already reacted were used the duration of the observed reaction may have been longer and the volume of gas produced may have been greater.

GC 16) Experimental Design – Methodology
The Methodology section of the Report explains that gas analyses were performed using a thermal conductivity detector, a hydrogen ionization detector, and for ammonia, colorimetric indicator (Dräger) tubes. In addition, the two-day and seven-day gas samples were apparently collected using Tedlar® bags.

Based on the cursory discussion provided, Ohio EPA assumes that the hydrogen ionization detector was used to determine concentrations of hydrogen, and the thermal conductivity detector was utilized to determine concentrations of methane, carbon monoxide, oxygen, and nitrogen.

Ohio EPA requests that CWRDF please provide the following information:

- the composition of the carrier gas used for the thermal conductivity analyses;
- a detailed discussion of the methane, ammonia, hydrogen, carbon monoxide, oxygen, and nitrogen analyses, including copies of the published methods that were followed;
- thermal conductivity detectors and hydrogen ionization detectors were used for gas analysis. Discuss what method was used to separate the gases, including whether or not these detectors were attached to a gas chromatograph, and if so, describe the conditions employed (including the carrier gas and type of column), error limits for the procedure, and detection limits of the instruments;

May 2002, *Landfill Fires: Their Magnitude, Characteristics, and Mitigation*: FA-225, p. 14

[26] July 27, 2001 Letter from Khaled Mahmood, EMCON/OWT Solid Waste Services, to Patrick Shriver, Canton City Health Department Air Pollution Control Division, *RE: Establishment of Higher Temperatures for Gas Wells #42 & #56, Countywide Recycling and Disposal Facility (RDF)*

- whether or not the methods used to determine the oxygen or carbon monoxide concentrations were susceptible to interferences from any other gasses or vapors present in the serum bottles;

- a comparison of the accuracy and precision of the thermal conductivity meter analysis of gas concentrations (particularly carbon monoxide) with the accuracy and precision of ASTM Method D 1946; and

- the holding times for all carbon monoxide samples collected in Tedlar® bags.

GC 17) Carbon Monoxide
The Discussion and Conclusions section explains, "*Generation of carbon monoxide up to levels of 500 ppmv were observed. Although the generation of CO is often attributed to combustion, no combustion was observed in the glass serum bottles (i.e., no visible smoke, char, or flame). The mechanism of CO production is unclear, but may be due to the decomposition of volatile fatty acids (VFAs) that are present in the leachate water. VFA concentrations in the leachate water were in excess of 30,000 mg/L. Another possibility is that catalytic reactions could be occurring on the surface of the aluminum waste that act to partially oxidize or reduce carbon sources (e.g. methane, carbon dioxide), subsequently forming carbon monoxide.*"

Fundamental principles of fire science and chemistry support the fact that the absence of visible smoke, char, or flame does not mean there is no fire occurring. *Absence of evidence is not evidence of absence.* It is very likely that the carbon monoxide was generated by pyrolysis of organic matter in the landfill solids that were subjected to the experimental conditions. Absent a fire, the continued emission of excessive heat (> 170° F) and high concentrations of carbon monoxide (> 1,000 ppmv) would not be occurring within the waste through mass pyrolysis alone.[27]

Ohio EPA was present for the replacement of several gas extraction wells at CWRDF during the period from June 4 through June 13, 2007 and observed the following conditions:

- visible emissions from the replacement well borings that appeared to be a combination of steam and/or smoke;

- carbon monoxide readings (in the vicinity of the referenced visible emissions) between 30 and at least 500 ppmv (recorded on portable carbon monoxide detectors used for health and safety monitoring by the drilling contractor, the maximum detection limit for the detectors was 500 ppmv);

[27] Personal Communication, Vytenis Babrauskas, Ph.D., to Jeff Martin, Ohio EPA, July 18, 2007

- organic landfill solids (wood products, yard waste, and paper products) that appeared to be charred, and plastic materials that appeared to be melted;

- waste temperatures typically ranging between 150° and 195° F and boring (down-hole) temperatures as high as 212° F; and

- a very strong burning odor from the waste excavated from the borings.

Ohio EPA has retained qualified experts in fire science[28], landfill fire identification and suppression[29], and chemistry[30] to assist with the evaluation and remediation of the ongoing situation at Countywide Landfill. Based on the experts' visual inspection of the settlement, drill cuttings, visible emission, and review of data, these experts have concluded that a fire is present within the waste mass in addition to the exothermic reaction of the aluminum production wastes. Additionally, Ohio EPA contacted other experts in fire science[31] and landfill fire identification and suppression[32], who, based on information provided to them via telephone discussions, expressed an opinion that a fire is likely present at Countywide Landfill.

Ohio EPA requests that CWRDF please provide the following information:

- copies of published, peer-reviewed scientific studies that evaluate the generation of carbon monoxide from the decomposition of volatile fatty acids in solid waste landfill leachate. The studies must have been conducted independently of the interests of CWRDF and any consultants retained on their behalf; and

- copies of published, peer-reviewed scientific studies that evaluate the generation of carbon monoxide from catalytic reactions occurring on the surface of the aluminum production waste that act to partially oxidize or reduce carbon sources (e.g., methane, carbon dioxide) and that were conducted independently of the interests of CWRDF and any consultants retained on their behalf;

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[28] Vytenis Babrauskas, Ph.D., Fire Science Protection

[29] Todd Thalhamer, California Registered Civil Engineer, Cal-EPA/California Integrated Waste Management Board, and Lieutenant, El Dorado Hills Fire

[30] Carl Heltzel, Ph.D., Organic Chemistry

[31] Personal communication, William M. Pitts, Ph.D., Physical Chemistry, National Institute of Standards and Technology, Building and Fire Research Laboratory, to Jeff Martin, Ohio EPA, February 13, 2007

[32] Personal communication, Tony Sperling, P.E., Ph.D., Geotechnical Engineering, to Ed Gortner, Gina Gerbasi, and Jeff Martin, Ohio EPA, February 12, 2007

- verify the concentrations of VFAs in Countywide's leachate, which are reported at 30,000 mg/L, which seems to be a very high concentration (30,000 mg/L = 30 g/L).

GC 18) Ammonia
The absence of any appreciable amounts of ammonia gas is surprising to Ohio EPA and raises concerns regarding the reliability of the experiment. Ammonia is commonly produced by the hydrolysis of AlN which is typically present in dross (this reinforces the notion that the determination of the exact composition of the dross samples is critical).

$$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_{3\ (gas)}$$

The hydrolysis reaction is pH dependent[33]; adding a strong acid such as H_3PO_4 will stop the hydrolysis of AlN at room temperature, presumably because of the formation of insoluble phosphate salts on the metal surface[34].
Ammonia is a weak base that is highly soluble in water so that might account for the lack of ammonia gas evolved in the study. Ammonia will partially dissociate in water:

$$NH_3 + H_2O \rightleftharpoons NH_4^+OH^- \rightleftharpoons NH_4^+ + OH^-$$

The chloride, nitrate, and sulfate ammonium salts are highly water soluble so changes in pH will normally have no effect on the formation of ammonium precipitates. Unfortunately for this theory, the solubility of ammonia decreases (increasing its volatility) as pH and temperature increase[35] (and increased temperatures are present at Countywide). Again, the experimental design must include monitoring the pH and temperature of the reactions in order to draw meaningful conclusions.

In addition, perhaps a potential explanation for the lack of ammonia is due to the fact that the dross used in these experiments had already or was currently undergoing the dross/leachate reaction when it was excavated. This concept is supported by the fact that Countywide's consultants report that the waste was hot to the touch, an estimated 170°F, when it was collected. If this is the case, the experimental results would be questionable.

Specific comments:

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[33] Weast, R.C., *Handbook of Chemistry and Physics*. 69th ed. 1988: CRC Press, pp 2348.

[34] Krnel, K., Kosmac, T. "Reactivity of Aluminum Nitride Powder in Dilute Inorganic Acids," *Journal of American Ceramic Society*, 83, **2000**, pp 1375-1378.

[35] Manfredi, O., Wulth, W., Bohlinger, I. The Chemical and Physical Properties of Aluminum Dross, *Journal of the Minerals, Metals, and Materials Society*, 49 (11) 1997, pp 1047-4838.

SC 1) Procedure
In the reported procedure, bottle headspace was purged with a 50:50 mixture of CO_2 and N_2 gas. Tedlar bags, which were evacuated, were attached to the bottles *"via a needle inserted through the septa of each bottle."* It appears the vacuum condition of these evacuated bags would draw in the CO_2/N_2 mixture from the headspace. Please describe the manner in which the gas volumes were addressed.

SC 2) Page 3, Paragraph 7: *"Background gases carbon dioxide and nitrogen also were analyzed at t=8 days."*
Please explain the basis of this.

SC 3) Page 3, Paragraph 6, Sentence 2: *"...**valves*** [emphasis added] *connecting the Tedlar bags to the serum bottles were closed after approximately 12 days..."*
This is inconsistent with the fourth paragraph of page 3 that simply states that the *"Tedlar bags were attached to each bottle via a needle inserted through the septa of each bottle..."* Please clarify this inconsistency, perhaps with a diagram illustrating the experimental setup.

SC 4) Page 3, 4: Nitrogen
It is claimed that nitrogen gas was collected and analyzed, but the exact concentrations of nitrogen gas were not given for any of the trials. On page 4, paragraph 6, it is mentioned that nitrogen concentrations for all treatments at t=8 days were approximately 25% v/v, and 44% v/v for Treatment 4. Since essentially all of the gas generation occurred within approximately 2 days (page 4, paragraph1), please explain why the nitrogen gas concentrations were not presented along with the other gases. Moreover, nitrogen gas is not normally associated with dross chemistry reactions; the authors of the study do not explain why nitrogen gas was monitored nor did they propose a mechanism for the formation of nitrogen gas from the dross reactions.

SC 5) Page 4, Paragraph 4, Sentence 4: *"The presence of oxygen likely reflects some infiltration of outside air into the gas collection bags."*
Very high levels of oxygen gas were collected and their concentrations measured, yet O_2 is not typically formed from aluminum dross reactions. For a number of trials, the concentration of O_2 presented in Table 2 exceeded the concentrations of H_2. This is indicative of a seriously flawed experimental procedure.

Problems with the experimental procedures are also indicated after taking a close look at the data in Tables 1 and 2. Consider the volumes of gas produced in each trial as reported in Table 1. If an assumption is made that the gases were generated and collected at STP (close to typical laboratory conditions), the total number of moles of gases for each trial can be calculated. Then from Table 2, the individual concentrations of hydrogen, oxygen, and methane (in ppmv), can be converted to moles (where 1 ppmv of a gas is equivalent to 1 microgram/L). When the moles of the individual gases produced in each trial are added up, there are a number of instances where the sum total number of moles of the individual gases (from Table 2) exceeds the total number of moles of gases collected (in Table 1). The calculations and tabulated results just described are available upon request. When close examination of data from a study reveals such inconsistencies, this is an indication that the experimental procedure is flawed and the results must be examined with suspicion.

SC 6) Page 4, Paragraph 4, Sentence 4: *"The presence of oxygen likely reflects some infiltration of outside air into the gas collection bags."*

Ohio EPA requests that CWRDF please provide a more detailed analysis of and explanation for the source of the oxygen concentrations measured during the experiment.

There appear to be three possibilities for the oxygen generation: the reaction of the aluminum production waste with water (leachate); chemical breakdown of landfill solids as a result of the aluminum production waste reaction; or leakage of atmospheric oxygen into the testing and sampling equipment during the experiment.

Ohio EPA has reviewed the following publications, letters, and Material Data Safety Sheets (MSDS) that provide information regarding the reaction of the various chemical constituents of aluminum dross or salt cake (including but not limited to aluminum metal, carbides, and nitrides) with water:

- *Amer, A.M., November 2002, Extracting Aluminum from Dross Tailings: JOM, pp. 72-75*

- *Chen, W.Y., and S.L. Goldheim, July 1955, Aluminum-Water Hazards: Industrial and Engineering Chemistry, vol. 47, no. 7, pp. 32a-34a*

- *Cotton, F.A., Wilkinson, G., Murillo, C.A., and M. Bochmann, 1999, Advanced Inorganic Chemistry (Sixth Edition): John Wiley & Sons, Inc., pp, 218-222*

- *March 22, 2007 Letter from Jose Cisneros, Chief, Waste Management Branch, United States Environmental Protection Agency Region 5, to Kurt Princic, Manager, Division of Solid and Infectious Waste, Ohio Environmental Protection Agency, Aluminum Dross/Salt Cake Fines Waste Disposal Management Information*

- *EnSafe, Inc., August 2002, Superfund Five-Year Review Report, Brantley Landfill NPL Site, Island, Kentucky: Prepared for United States Environmental Protection Agency, Region IV, Atlanta, Georgia*

- *GFS Chemicals, Inc., June 1997, Material Safety Data Sheet for Aluminum Nitride*

- *Graczyk, D.G., Essling, A.M., Huff, E.A., Smith, F.P., and C.T. Snyder, Analytical Chemistry of Aluminum Salt Cake, in Light Metals (R. Huglen, ed.), Proceedings of the 126th Annual Meeting of the Minerals, Metals, and Materials Society: Symposium on Aluminum Dross and Salt Cake Processing, Orlando, Florida, February 9-13, 1997*

- *Greenwood, N.N., and A. Earnshaw, 1997, Chemistry of the Elements (Second Edition): Elsevier Butterworth Heinemann, pp. 297-303*

- *Fire, F.L., 1996, The Common Sense Approach to Hazardous Materials (Second Edition): Fire Engineering Books & Videos (PennWell Publishing Company), pp. 180, 331-333*

- *Lucheva, B., Tsonev, Ts., and R. Petkov, 2005, Non-Waste Aluminum Dross Recycling: Journal of the University of Chemical Technology and Metallurgy, vol. 40, no. 4, pp. 335-338*

- *Manfredi, O., Wuth, W., and I. Bohlinger, November 1997, Characterizing the Physical and Chemical Properties of Aluminum Dross: JOM, pp. 48-51*

- *Shinzato, M.C., and Hypolito, R., 2005, Solid waste from aluminum recycling process: characterization and reuse of its economically valuable constituents: Waste Management, vol. 25, pp. 37-46*

- *New Jersey Department of Health and Senior Services, August 2003, Hazardous Substance Fact Sheet for Aluminum Carbide*

- *Novelis, 2005, Material Safety Data Sheet for Aluminum Dross (remelting)*

- *Washington State Department of Ecology Toxics Cleanup Program, October 2006, Interim Remedial Action Plan, Ramco Aluminum Waste Disposal Site, Port of Klickitat Industrial Park, Dallesport, Washington*

- *Wise Alloys, September 2004, Material Safety Data Sheet for Aluminum Dross*

These sources document that the reaction of aluminum production wastes with water can produce hydrogen, ammonia, acetylene, methane, ethane, hydrogen sulfide, and carbon dioxide. None appear to indicate that the reaction of aluminum production wastes with water will generate oxygen (O_2) or, as CWRDF has claimed, water (H_2O).[36] Rather, the oxygen released from the Al/H_2O redox reaction forms aluminum hydroxide ($Al(OH)_3$, the mineral Gibbsite). Further, if the reaction of aluminum dross or salt cake were capable of producing the volume of oxygen indicated by the results of the experiment (approximately 5% on average with an observed maximum of 20%) one would expect this characteristic to be documented in published investigations of aluminum production wastes and especially on MSDS sheets, as the generation of substantial amounts of oxygen poses both fire and explosion hazards.

Oxygen generation from chemical breakdown of landfill solids as a result of the aluminum production waste is also very unlikely. The source of all the detected oxygen must therefore be the leakage of ambient air into the gas collection bags and serum bottles.

Based on the average oxygen concentration of 5.27% by volume (the arithmetic average of all reported oxygen concentrations), on average approximately 25% of the volume of each gas sample analyzed consisted of ambient air infiltration (5.27% average O_2 infiltration / 20.9% O_2 atmosphere x 100 = 25.2%). Oxygen concentrations ranged from 0.7% to 20.0%, and accordingly the ambient air infiltration ranged from 3.3% to 97% of the gas sample volume.

The infiltration of ambient air appears to represent a significant source of error with respect to accuracy of all gas concentrations reported. For example, the oxygen concentration in the second sample analyzed for Treatment 4 (TR4) at 7 days is reported to be 200,000 ppmv, or 20% by volume. The reported hydrogen, methane, and carbon monoxide concentrations for this sample are 7.9 % (79,000 ppmv), 0.09% (900 ppmv), and 0.02% (200 ppmv), or approximately 8% of the total sample volume. If 97% of the sample was ambient air (20.9% O_2, 78.1% N_2) based on a detected oxygen concentration of 20%, then the sum of the other detected gas concentrations should not have exceeded 3% (97% + 3% = 100%).

Cornerstone Environmental Group's February 13, 2007 letter report submitted to Ohio EPA and the Canton City Health Department Air Pollution Control Division on behalf of CWRDF (*Countywide Recycling and Disposal Facility, East Sparta, Ohio, Summary of Heat and Subsurface Conditions*) presents a summary of the results of the aluminum production waste testing performed on behalf of CWRDF by American Analytical Laboratories during May, June and July 2006 (*Republic Countywide Landfill Gas Evolution Testing Revision 1* dated August 21, 2006). The results of this study indicate the following in comparison to the Treatability Study Report:

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[36] Landfill Reaction Analysis – Countywide RDF, April 11, 2007

- carbon monoxide (CO) was not detected in the gas evolved from the reaction of aluminum production wastes analyzed using method GPA 2172-92 (note also that no other solid waste materials were included in the experiment);

- water (H_2O) was not reported to be produced by the reaction;

- gases detected in the gas evolution samples included hydrogen, methane, oxygen, nitrogen, and carbon dioxide; and

- the ratios of oxygen to nitrogen in the samples approximate the ratio of oxygen to nitrogen in ambient air (1:4), indicating that air infiltration likely occurred and biased the results.

The Cornerstone Environmental Group report concludes that, "*The lack of CO during this aluminum reaction leads us to believe that the CO found in some CWRDF LFG wells is a result of heat reacting with MSW via pyrolysis.*"

Again, whereas carbon monoxide may be generated by forced pyrolysis, this fact does not support CWRDF's claim that a fire is not present in the landfill waste mass. Absent a fire, the continued emission of excessive heat (> 170° F) and high concentrations of carbon monoxide (> 1,000 ppmv) would not be occurring within the waste mass through pyrolysis alone.[37]

SC 7) Page 5, Paragraph 1, Sentence 1: *"This result also suggests that the cessation of activity after 2 days in the other treatments is likely not due to stoichiometric depletion in the aluminum waste, but rather due to naturally-occurring surface passivation processes."*
Without any initial measurement of the amount of aluminum present, it is not appropriate to link activity cessation to stoichiometric depletion in the aluminum waste. Surface-passivation processes need to be explored further and on a stoichiometric basis.

SC 8) Page 5, Paragraph 3, Sentence 1: *"Generation of carbon monoxide up to levels of 500 ppmv were observed."*
This statement, made in the Discussion and Conclusion section is misleading, and given the importance of the high concentrations of CO at the Countywide site, this statement warrants further investigation. Only a single trial generated CO at 500 ppmv, and on page 4, the first paragraph mentions that this "*sample showed very little gas*

[37] Personal Communication, Vytenis Babrauskas, Ph.D., to Jeff Martin, Ohio EPA, July 18, 2007

production; this result is not readily explained..." –in fact, both trials of Control 2 that reportedly generated the highest levels of CO had unexplainably low volumes of total gas generated. Good practice would have suggested that these trials be repeated, but it appears they were not.

SC 9) Page 5, Paragraph 3: Carbon Monoxide Production Mechanism
This paragraph suggests that the mechanism of CO production is unclear, but goes on to propose that the CO may be coming from decomposition of volatile fatty acids present in the leachate water. While Ohio EPA believes this is highly unlikely, a simple trial would have dismissed this suggestion. Rather than the additional control trial described on page 4, paragraph 3, where only deionized water was used, a trial containing aluminum waste, landfill solids and deionized water (no leachate) should have been run.

The last sentence of paragraph three on page 5 provides an alternative suggestion for the formation of CO (which only occurred in the errant Control 2 trials). It was suggested that CO may be forming from partial oxidation or reduction of CH_4 or CO_2 via "*catalytic reactions occurring on the surface of the aluminum waste....*" Using inexpensive aluminum waste to break the very strong C-H bonds of methane would be an important discovery indeed and worthy of further experimentation. The report does not attempt to explain why the same catalytic oxidation or reduction reactions are not taking place to any appreciable extent in the other trials.

Ohio EPA appreciates the opportunity to comment on the Treatability Study Report and trusts these comments are helpful in continuing efforts to understand and address the subsurface fire present at Countywide.

Should you have any questions, please contact me at 614-644-2621, or contact Jeff Martin at 614-728-5360 or Gina Gerbasi at 614-728-5325.

Sincerely,

Ed Gortner
Enforcement Coordinator, Ohio EPA
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EG/GG/sw

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