Response to Comments on July 9, 2007 Treatability Study Report
Countywide Recycling and Disposal Facility
August 23, 2007

General Comments

GC 1

Based on both laboratory and field data, an exothermic reaction between leachate water and aluminum wastes is generating gases and excessive heat. The gases generated during the treatability study (e.g., hydrogen, carbon monoxide) are consistent with those measured in the landfill. The treatability study was performed to identify potential suppressant agents for this reaction.

The tested suppression agents were intended to mitigate both the gas and heat generation. Subsequently, the endothermic pyrolytic (or, very slow pyrolytic-type) reaction requiring the heat and causing the charred landfill material to be produced would then be expected to cease. Charred material can be produced from pyrolytic reactions (Bradbury et al., 1979; Chen et al., 1997).

GC 2

The experiments conducted utilized actual material from the landfill being exposed to heat. To the best of our knowledge, there are no studies in the peer-review literature that investigate the use of chemical agents for suppressing the aluminum dross hydrolysis reaction. We believe that the use of silicic and phosphate salts were a reasonable approach. Several studies (Chen et al., 1973; Lijklema, 1980; Martin, 1986; Gabelich, 2005) show that the interaction between aluminum species and phosphate can result in precipitation/sorption reactions that can potentially passivate the aluminum–water interface. In addition, both of the commercial fire suppressants that were tested contain surfactants that act both to coat and cool surfaces; use of these commercial agents was also deemed plausible as a potential means to mitigate the aluminum dross hydrolysis reaction. Results from the experiments performed indicate that none of the tested agents were effective in mitigating the hydrolysis reaction(s), and that some of the suppression agents could make the reaction more aggressive. As such, the study yielded useful and informative results.

We believe that the best characterization of the reactions occurring at Countywide is that of a pyrolysis (i.e., very slow pyrolysis) heating of waste material that is initiated and sustained by the proximate exothermic hydrolysis of aluminum waste. It is likely that the lateral extent of waste pyrolysis is limited to areas where sufficient aluminum waste is present in the immediate vicinity. As such, we do not believe that the event will self-sustain beyond the limits of concentrated dross. As such, the treatability study focused on halting the aluminum hydrolysis reaction.

Measurements at the Countywide Recycling and Disposal Facility (CRDF) indicate temperatures elevated above those usually found at such landfills and the observation of gases at concentrations above those typically found at such landfills. The elevated temperatures and the higher concentrations of gases are consistent with exothermic chemical reactions associated with aluminum and its compounds found in dross/waste.

We understand that the OEPA has a different model of the event (although we are not sure what that model is) and believe that continued evaluation, such as that done in this study, will help evolve a mutual understanding and, ultimately, agreement on an approach to mitigate.

GC 3

Although the tested amendments were shown to be ineffective for mitigating the hydrolysis reaction observed in the laboratory, we believe the study objectives were attained:

- Evaluating treatment of combustion processes in the landfill waste was ***not*** a stated objective.
- The exact aluminum composition of the dross material is unknown. The estimated range of aluminum composition in all the dross-like materials is approximately 5.1% to 12.4%, the estimated composition of aluminum in black dross is 10% to 20%. However, the distribution of this aluminum within and between the cells is unknown and the concentrations in the aluminum wastes disposed at CRDF are likely in the low ranges of estimates based on the economics of the secondary aluminum industry. We believe that, if successful, mitigation of the aluminum waste hydrolysis would have occurred via a surface passivation, which could have occurred nearly instantaneously, or more gradually as sorbed/precipitated species began to cover the particle surface. Unfortunately, no evidence of such passivation was observed in the laboratory study.
- The degree of suppression irreversibility would have been evaluated by continued monitoring of gas generation and composition after the hydrolysis reaction had apparently ceased. Again, this did not occur, so no evaluation of suppression irreversibility was possible.
- The final objective can be more clearly stated as "to quantify the overall impacts of amendment addition *with respect to* gas production and composition".

GC 4

We agree that the carbon monoxide generation in the treatability testing could have been due to a forced pyrolysis of the organic matter. It is important to note that pyrolysis is not the same as smoldering (DiNenno et al., 2002). The aluminum hydrolysis reaction likely is providing the heat source for this pyrolysis within the landfill. Aluminum hydrolysis reactions have been shown to generate temperatures up to approximately 270 degrees F (Hiraki et al., 2007). Additional testing of the heat-impacted landfill solids that were examined at the site may provide further insight to the reaction processes occurring at the landfill.

Supplemental testing of the aluminum waste was performed to further evaluate carbon monoxide production; these data were presented at the July 26 meeting in Columbus, OH. Experiments were performed similar to those described in the previously submitted treatability report. Three treatments containing *aqueous slurries* of 1) leachate + landfill solids (no aluminum waste), 2) leachate + landfill solids + aluminum waste, and 3) deionized water + aluminum waste were prepared in duplicate. Carbon monoxide was measured as a function of time. Results, shown in the Table 1 below, indicate show that maximum CO levels ranging from 440 to 1,200 ppm-v were attained in each sample, and that multiple CO generation mechanisms likely were occurring. This clearly demonstrates, using accepted scientific methods, that CO is produced at elevated levels (440 to1,200 ppmv) in absence of fire.

One possible mechanism for the CO generation, in addition to pyrolysis, is the decomposition of volatile fatty acids (Yu and Savage, 1998; Akiya and Savage, 2004). Catalytic oxidation of methane to carbon monoxide (Bharadwaj and Schmidt, 1995) can occur in the presence of a noble metal catalyst at elevated temperatures. A similar process might be occurring, albeit at a substantially decreased rate and extent, on the surface of the aluminum wastes. A computational study performed by Farcasiu and Lukinskas (2002), in which C-H bond breaking by aluminum species is simulated, suggests that this mechanism might be possible. Metallic aluminum (as well as bimetallic copper-aluminum) acts as a chemical reducing agent in aqueous systems (Lien and Zhang, 2002). This mechanism is analogous to that which occurs using metallic iron, which has been shown to reduce carbon dioxide (Hardy and Gillham, 1995); CO is identified as a potential side-product due to incomplete reduction. Thus, in lieu of these mechanisms, it is plausible that the metallic aluminum in the landfill is reducing carbon dioxide to carbon monoxide. Copies of these references are provided in Attachment 1.

Table 1.
Supplemental treatability testing to evaluate CO generation.

Gas sampling bags were removed after the first day; subsequent gas samples were collected directly from the serum bottle. The Al waste used for this supplemental testing was characterized as baghouse fines.

t=1 day (T=212 degrees F)

Treatment	ppm-v Carbon Monoxide
Leachate + Landfill Solids	36 / 70
Leachate + Landfill Solids + Al Waste	200 / ND
Deionized water + Al Waste	40 / 90

t=4 days (T = 140 degrees F, approx.)

Treatment	ppm-v Carbon Monoxide
Leachate + Landfill Solids	440 / 510
Leachate + Landfill Solids + Al waste	520 / 730
Deionized water + Al Waste	300 / 660

t=6 days (T = 140 degrees F, approx.)

Treatment	ppm-v Carbon Monoxide
Leachate + Landfill Solids	370 / 620
Leachate + Landfill Solids + Al waste	400 / 680
Deionized water + Al Waste	580 / 1,200

NOTES:
CO values less than 100 ppm-v are estimated
ND = non-detect

GC 5

All of the aluminum waste used in the treatability study, as described in the Treatability Study Report, was characterized as black dross. This material, however, should not be confused with black dross as it may be referred to on a MSDS for material used as a raw material in the secondary aluminum process. This black dross sample (as well as samples of saltcake and

baghouse fines) was collected on 17 May 2007 from a hole near PW-111, as noted. The percentages of aluminum and other components were not quantified because we determined that we had a reasonably typical black dross sample, and it was felt that additional analyses would be of limited value. If desired, compositional analyses of the aluminum dross and salt cake materials can be performed.

While the hole near PW-111 was not in Cell 3 (which is exhibiting a strong reaction) this hole yielded examples of black dross, saltcake and baghouse fines, which are the three most prevalent aluminum waste materials landfilled at CWRDF. The temperatures encountered also show that a reaction was present, since we found a temperature as high as 170°F.

In the previous laboratory treatability study (2006), three aluminum wastes were evaluated: a baghouse dust, a shredder delac, and a dross sample from the landfill.

GC 6

The aluminum waste used in the treatability study was, to the best of our knowledge, typical of the aluminum wastes present in the reactive area. Thus, even in absence of a precise distribution of Al species, the results of the treatability study still provide meaningful insight for evaluating potential mitigation agents and reaction products. Whether the carbide percentage was 1% or 3%, or whether the nitride was 3% or 6%, the evaluation of the mitigation agents would not have changed.

GC 7

- The landfill solids were collected from the same borehole used to collect the aluminum black dross waste. Material was collected from 30 to 40 feet and from 65 to 79 feet, respectively. The temperatures ranged from 144°F to 149°F and from 150°F to 170°F, respectively. These temperatures likely were close to the *in situ* temperatures, since the thermometer used for the measurements was buried in the mass of material withdrawn from the hole. While leachate was not recirculated directly over this area, the edge of a recirculation field was located about 100 feet away, so it is possible that the material was exposed to some additional moisture from recirculation.

- Based on a date observed on a section of newspaper in the collected landfill solids, the age of the waste from one zone in this hole is approximately 12 years. Data does not exist to verify the period when material was placed in all areas of this cell.

- The waste contained throughout the landfill is a heterogeneous mixture of household, commercial and non-hazardous industrial waste. The sample was not a scientifically composited sample, but appeared to be representative of the whole of waste secured from the boring.

- The fibrous materials consisted primarily of cardboard and yard wastes.

- Soil (or, soil-like materials) comprised approximately 10% (by volume) of the waste.

- Since the treatability study was designed to evaluate the impact of suppressant on the aluminum hydrolysis reaction, the bulk solids density was not a critical factor in this phase of the evaluation. Solids density and stratigraphy would likely have played a more important role in a pilot demonstration, as these factors would have impacted delivery and distribution of the amendments.

GC 8

Scale and heterogeneity are always issues when performing treatability studies on landfill materials. The approach we used in the current study was similar to the approach used in previous studies Shaw has performed for the USEPA and USACE. Large objects, such as soda cans and intact newspapers, were excluded for purposes of this study. The primary purpose for including landfill solids in the treatability study was to attain geochemical conditions that were reasonably representative of landfill conditions. Small-sized objects typically account for a majority of the solid surface area and subsequent aqueous-solid exchanges. Similar scientific methods have been previously accepted by the USEPA and USACE. It is also important to note that this laboratory study was not intended to replace a pilot-scale test, assuming one of the tested amendments had been successful in mitigating the reaction.

GC 9

The leachate composite consisted of an (approximately) equal volume of each leachate sample. The North storage tank services Cell 4. The east storage tank services Cells 1, 2, and 3. The South storage services Cells 5A, 5B, 5C, 5D, and 6.

Use of leachate water for the treatability testing is preferred, as the landfill leachate water is most representative of the *in situ* geochemical conditions, and any potential *in situ* remedy would need to be demonstrated as effective in the presence of leachate water. Numerous peer-review publications have shown that the geochemistry of natural waters (ground water or leachate water) can have a profound impact on chemical reactions. We feel that good practice suggests use of site-specific waters whenever performing treatability testing.

The AlN hydrolysis reaction, in the presence of excess water, was shown to proceed via an irreversible first order reaction mechanism (Bowen et al., 1990). For this type of mechanism, the kinetics will ***not*** be significantly inhibited by the presence of dissolved ammonia in the aqueous phase. Similarly, hydrogen production from the hydrolysis of Al has been shown to occur as a zero or (nearly) first order reaction (Studart et al., 2005), with no observed dependence on dissolved hydrogen concentrations. An alternate explanation for the lack of reactivity and ammonia production, as discussed during the July 26 meeting, is that the surface of the aluminum waste became partially passivated as a result of exposure to air during collection and transport to the laboratory, and/or that the aluminum dross tested was already partially passivated due to ongoing reaction within the landfill.

GC 10

Both of these commercial products contain surfactants that can cool, coat, and potentially passivate the hydrolysis reaction occurring on the aluminum surface. The use of these commercial products for our application also was discussed with the vendors. In the absence of a commercially-available product for suppression of an aluminum waste hydrolysis reaction, the most scientific and reasonable approach was utilized.

GC 11

Samples were not agitated during the duration of the experiment. Initial field observations suggested that the regions of aluminum activity were in fact water-saturated, or at least very wet. The extent/rate of percolation through these zones is unknown. Furthermore, delivery of any of

the selected amendments would likely have entailed injection of an aqueous solution, resulting in local saturated (or, near-saturated) conditions. We feel that the batch tests employed in the treatability study were appropriate for the stated objectives.

GC 12

We agree that pH can impact the hydrolysis reaction. Final pH values of all the aqueous slurries ranged between 7.0 and 7.5, as measured using pH indicator strips. The exceptions were the MgCl treatment (pH=6.5) and the silicate treatment (pH=11). Consideration of these pH measurements does not change our conclusions of the study.

GC 13

We agree with this point. We performed a preliminary 24-hour screening-test before performing the testing described in the treatability report. This test was performed so we had a general sense of how exothermic and reactive the aluminum waste was prior to setting-up the study. During this preliminary test, we did not observe any temperature increase, as measured qualitatively by handling the glass serum bottles. As discussed under GC9, this lack of reactivity (with respect to heat generation) may have been the result of surface passivation due to exposure to air. Subsequent treatments were heated in order to observe temperatures that were consistent with those measured in the field.

GC 14

This ratio was arbitrarily selected, as information regarding these ratios in reactive landfill locations is unknown. Landfill solids and aluminum wasted were mixed within the bottles.

GC 15

The main purpose of the study was to determine if various suppressant agents could be used to mitigate the hydrolysis reaction. Our thoughts were that, if successful at the bench scale, the selected amendments would be injected into the reactive zone and/or along the perimeter of the reactive zone to decrease the rate of reaction and limit its spread. Thus, we feel it was appropriate to test aluminum waste material that was within the reactive zone.

We agree, as discussed in GC 9 and GC 13, that partial reaction and/or passivation of the aluminum wastes may have occurred prior to the laboratory testing. Indeed, testing of “fresh” or un-reacted dross may have yielded different (i.e., more reactive) results. However, our intent was to obtain an aluminum waste sample representative of current landfill conditions.

GC 16

Details of the gas analytical methods are provided in Attachment 2. Gas samples were collected from the Tedlar bags and/or serum bottles and immediately injected into the gas chromatograph.

GC-17

These reactions are discussed under GC 4. Selected references are provided in Attachment 1. VFA concentrations in each of the three collected leachate waters are summarized below:

Table 2. Concentrations of Volatile Fatty Acids (VFAs) in Samples. All concentrations in mg/L.

	Lactic Acid	Acetic Acid	Propionic Acid	Formic Acid	Butyric Acid	Pyruvic Acid	Valeric Acid
North AST	1020	16900	4110	879	8400	88.7	1180
East AST	711	10200	2800	967	4260	62.6	522
South AST	2590	18700	4640	879	8240	134	1150

GC 18

These issues have been addressed under GC 9, 13, and 15. We agree that partial dissociation of the ammonia may have occurred, thereby reducing gas-phase ammonia concentrations. This process, if occurring, is likely also to be occurring in the landfill itself. Again, this issue does not impact our finding that none of the tested amendments mitigated the hydrolysis reaction (i.e., hydrogen and methane gas production was not reduced by addition of any of the tested amendments).

Specific Comments

SC 1

The gas sampling bags collapse (i.e., deflate) when a vacuum is drawn on them. Thus, when the bags were connected to the serum bottles, there was no vacuum applied to the bottle.

SC 2

These background gases were analyzed to determine if there were any appreciable changes from baseline.

SC-3

The gas sampling bags are manufactured with a valve to allow for gas sampling. It was the port on this valve that was connected to the serum bottles.

SC 4

Nitrogen gas was analyzed simply for completeness at t=8 days only; this gas was not routinely analyzed. We agree that nitrogen production is not expected from an aluminum waste hydrolysis reaction. We can only speculate that addition of elevated phosphate levels somehow resulted in nitrogen production, which is consistent with our observations. This unexpected result exemplifies our difficulty in understanding the geochemistry of this complex system. We feel that, overall, this is a minor point in the findings of the study.

SC 5

Leakage of oxygen into the samples was noted in the report. This issue was somewhat mitigated when sampling was performed directly from the serum bottles (discussed under SC-6 below)

The gas volume and gas composition values are consistent. Using an average final value of 350,000ppm-v of hydrogen gas as a basis, and assuming a gas volume of approximately 0.2 L

(this is approximately the sum of the serum bottle headspace volume and the volume of the partially inflated gas collection bag), the hydrogen volume generated was 70 mL. Potential generation of gases not analyzed in this study (e.g., H_2S) would add to this value. Thus, the gas composition data is in reasonable agreement with the gas volume data (with the exception of Treatments 4 and 6, where additional hydrogen or nitrogen gas was generated).

SC-6

We agree, as indicated in our report, that the source of oxygen is likely due to infiltration of ambient air during the sample collection process (i.e., leakage near the sampling port during sample collection). We do not assert that the oxygen is the result of the aluminum hydrolysis reaction, although we do not have the data to definitively eliminate this possibility. We acknowledge that leakage/sampling issues likely resulted in measurable (approximately 25%, generally) error in gas measurements during the t=2 and 7 day sampling events, and may have resulted in a decrease in measured Al hydrolysis gases. Samples were collected directly from the serum bottles beginning at t=13 days; a substantial decrease in oxygen concentrations was observed coincident with this change in sampling methodology.

It is noted that, despite this issue with leakage, results among the treatment and controls can still be compared with each other. We believe that results indicate that none of the tested amendments were effective for mitigating the reaction, as measured gas volumes and hydrogen levels in the treatments were greater than or equal to those in the controls.

SC-7

We generally agree with this statement. However, the point we were trying to make in the report is that, in the presence of 10% sodium silicate, the extent of the reaction was greater (as indicated by the increased volume of hydrogen, ammonia and methane gas generation) than in the other treatments. We speculate that this might be due to diminished surface passivation in the silicate treatment. Additional studies would be needed to further evaluate this assertion.

SC-8

We agree that the 500 ppm-v of CO in the duplicate control (with the anomalously low gas volume) should be evaluated with caution. However, 300 ppm-v of CO was observed in Treatment 1, 400 ppm-v of CO was observed in Treatment 4, and 200 ppm-v of CO were observed in Control 1. Thus, the 500 ppm-v CO value, when compared to the other values, did not appear anomalously high.

As presented by Shaw during the July 26 meeting, additional samples were prepared to further evaluate CO production. These data also are presented under our response to GC 4. Average CO levels were on the order of 500 ppm-v, with one duplicate sample generating 1,200 ppm-v.

SC-9

As discussed in SC-8 above, CO was observed in several of the treatments. Additional evaluation of CO production also was performed (see Table 1 under GC 4).

While the exact mechanism(s) for CO generation in the aluminum and leachate systems are not yet determined, the mechanisms discussed under GC 4 provide possible explanations. We feel that the aluminum metal is more likely to reduce CO_2 to CO rather than to oxidize CH_4 to CO.

However, a computational study performed by Farcasiu and Lukinskas (2002), in which C-H bond breaking by aluminum species is simulated, suggests that the latter mechanism is possible.

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