



Countywide Recycling & Disposal Facility

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July 10, 2007

Ohio Environmental Protection Agency, Central Office
Division of Solid and Infectious Waste Management
Attn: Mr. Ed Gortner
P.O. Box 1049
Columbus, Ohio 43216-1049

RE: SUBMITTAL OF TREATABILITY STUDY REPORT
SUPPLEMENT NO. 1 TO THE FIRE SUPPRESSION PLAN, ORDER 8
OF THE DIRECTOR'S FINAL FINDINGS AND ORDERS OF MARCH 28, 2007
COUNTYWIDE RECYCLING AND DISPOSAL FACILITY

Dear Mr. Gortner:

Countywide Recycling and Disposal Facility (Countywide) hereby submits the attached Treatability Study Report as a supplement to the Fire Suppression Plan (FSP) which was previously submitted on May 25, 2007 in accordance with Order No. 8. of the Findings and Orders (Orders) dated March 28, 2007. The treatability study was performed and the report was prepared by our consultant, Shaw Environmental, Inc., in consultation with a team of experts from multiple consultants. A copy of the Treatability Study Report is attached to this letter for your information.

The Treatability Study evaluated five compounds to determine whether they would control or suppress the aluminum reaction in a laboratory setting. The compounds evaluated included magnesium chloride, sodium silicate, sodium phosphate, First Strike® mine firefighting foam concentrate, and FlameOut® concentrate. None of the compounds tested had any effect in controlling or suppressing the aluminum reaction. In fact, one compound, sodium silicate, actually increased the amount of gas generated by the reaction.

Even if a compound that suppressed or controlled the aluminum reaction were to be identified, there remain significant technical and logistical problems that would have to be overcome, as described in the FSP, in order to inject a liquid treatment agent through saturated municipal solid waste so that it would have the desired effect on the aluminum waste. Uniform delivery of any chemical agent (including inert gases) would be difficult, if not impossible to accomplish in the precise amount and concentration of the chemical needed to suppress the reaction over a large area. Past experience suggests that it is difficult if not impossible to deliver a product in a uniform, comprehensive distribution such that the agent reaches all parts of the waste mass. This is because the landfill's waste mass is heterogeneous and will likely contain large, tightly-packed waste masses that will not be able to be reached by such applications.

We await your review and the upcoming opportunity to meet with the Agency to discuss the FSP and the various remedial alternatives discussed within the FSP. If you have questions, please do not hesitate to contact me at (330) 874-3855.

Sincerely,



Tim Vandersall, P.E.
General Manager

cc/ec: Bill Skowronski, OEPA-NEDO
Kirk Norris, SCHD
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Shaw Environmental, Inc.

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July 9, 2007

To: Mr. James Walsh SCS Engineers

From: Charles Schaefer, Ph.D. Shaw Environmental, Inc.

Subject: **Laboratory Testing to Evaluate Potential Suppression Agents
Treatability Report**
Countywide Landfill, Stark County, OH

Introduction

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. The testing was performed by Shaw Environmental, Inc. (Shaw) at their laboratory in Lawrenceville, NJ.

Previously performed studies have suggested that addition of certain salts can hinder the reaction between aluminum metals and water via passivation of the metal surface.^{1,2} The objective of the laboratory study was to evaluate the potential effectiveness of various suppression amendments by estimating the amendment dosage required for treatment, determining how quickly the reaction suppression will occur, verifying that the suppression mechanisms are irreversible, and quantifying the overall impacts of amendment addition on gas production and composition. The treatability testing also evaluated the extent and composition of gas production in the absence of any treatment amendments. A summary of the overall approach and methodologies, experimental data, and a discussion of the results are provided in the following sections.

Experimental Design

Materials

The general approach for evaluating the effectiveness of various suppression agents was to perform small-scale batch tests in the laboratory using “representative” aluminum waste and landfill materials. Aluminum waste material was collected from the landfill at a depth of

¹ Krnel, K.; Kosmac-breve, T., 2000. “*Reactivity of aluminum nitride powder in dilute inorganic acids*”, J. American Ceramic Soc., 83, 1375-1378.

² Cornerstone Environmental Group, LLC, 2006. Report – Gas system operating review at the Countywide Landfill.

approximately 60 ft. below ground surface. The aluminum waste was collected from outside the region where the presumed exothermic aluminum-water reaction was taking place. The aluminum waste appeared dry, and was present in various sizes ranging from a powder to small pieces of approximately 2 cm in diameter. Several of the larger pieces were manually broken to facilitate placement of the aluminum waste into the serum bottles used for the microcosm test.

Landfill Solids, which did not contain aluminum waste (or, aluminum waste-like materials), were also collected from the landfill. Landfill solids were collected so as to obtain as representative a sample as possible from within the landfill. Landfill solids consisted of a mixture of paper, metal, plastic, fiber, and some soil. Large objects were removed by hand and the remaining solids passed through a ¼" sieve to facilitate transfer into the serum bottles used for the experiments. After sieving, the solids were transferred to an anaerobic chamber in preparation for their addition to the serum bottles.

Leachate water was collected from three locations: the north above-ground storage tank, the east under-ground storage tank, and the south above-ground storage tank; these leachate waters were combined for the treatability testing. Leachate water was combined in an anaerobic chamber to limit the introduction of air.

The suppression agents selected for treatability testing included the following: magnesium chloride, sodium phosphate, sodium silicate, First Strike[®], and Flame Out[®]. The two commercially-available fire suppression agents, First Strike[®] and Flame Out[®], are aqueous fire suppressants that contain surfactants that allow for wetting and cooling of the fuel surface.

Methodology

Samples were prepared in 160-mL glass serum bottles. A total of 20 bottles were prepared. 50 mL of leachate water was added to each bottle. Treatments and controls were prepared as follows:

Aluminum Waste Control: This control was amended with 35g of aluminum waste, and received no additional amendments.

Aluminum Waste + Landfill Solids Control: This control was amended with 35g of aluminum waste and 25g of landfill solids, and received no additional amendments.

Suppression Treatment 1: Treatment 1 was amended with 35g of aluminum waste, 25g of landfill solids, and magnesium chloride at an aqueous (i.e., leachate) concentration of 0.1 wt%.

Suppression Treatment 2: Treatment 2 was amended with 35g of aluminum waste, 25g of landfill solids, and magnesium chloride at an aqueous concentration of 10 wt%.

Suppression Treatment 3: Treatment 3 was amended with 35g of aluminum waste, 25g of landfill solids, and sodium phosphate at an aqueous concentration of 0.1 wt%.

Suppression Treatment 4: Treatment 4 was amended with 35g of aluminum waste, 25g of landfill solids, and sodium phosphate at an aqueous concentration of 10 wt%.

Suppression Treatment 5: Treatment 5 was amended with 35g of aluminum waste, 25g of landfill solids, and sodium silicate at an aqueous concentration of 0.1 wt%.

Suppression Treatment 6: Treatment 6 was amended with 35g of aluminum waste, 25g of landfill solids, and sodium silicate at an aqueous concentration of 10 wt%.

Suppression Treatment 7: Treatment 7 was amended with 35g of aluminum waste, 25g of landfill solids, and First Strike[®] at an aqueous concentration of 10 wt%.

Suppression Treatment 8: Treatment 8 was amended with 35g of aluminum waste, 25g of landfill solids, and Flame Out[®] at an aqueous concentration of 10 wt%.

All treatments were prepared in duplicate. Serum bottles were capped with a Teflon septum and aluminum crimp seal. 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. Bottle headspace was purged with a 50:50 mixture of carbon dioxide and nitrogen gas; this gas mixture was selected to simulate landfill gases, while at the same time allowing for monitoring of target gas generation. Tedlar bags (0.5 L volume) were attached to each bottle via a needle inserted through the septa of each bottle to facilitate gas collection and monitoring. Tedlar bags were evacuated prior to connecting them to the serum bottles.

The volume of gas production was determined by collecting and measuring the volume of gas generated in each Tedlar bag using 60 mL syringes. The volume of generated gas was measured at t=1 day, 2 days, and 8 days.

Gas composition initially was monitored by sampling the gas collected in the Tedlar bags. However, due to the cessation of any appreciable gas generation, the valves connecting the Tedlar bags to the serum bottles were closed after approximately 12 days and gas samples were collected directly from the headspace of the serum bottles. Gas composition was monitored at t=2, 7, 13, and 20 days. Headspace gases were analyzed for the following:

- methane
- ammonia
- hydrogen
- carbon monoxide
- oxygen
- nitrogen

Background gases carbon dioxide and nitrogen also were analyzed at t=8 days.

Analyses were performed using a thermal conductivity detector, a hydrogen ionization detector, and (for ammonia) Dräger tubes.

Testing was performed for a 3-week duration.

During the final week of the study the temperature was increased to approximately 97 degrees C (207 degrees F) to test the effect of increased temperature on the generation of carbon monoxide.

Results

Rate of Gas Production.

The cumulative volume of generated gas for each treatment is presented in Table 1. Results show that essentially all of the gas generation occurred within approximately 2 days, as gas generation after day 2 was negligible for all treatments. With the exception of Treatments 4 and 6, the volume of gas produced in the microcosm bottles was approximately ($\pm 25\%$) the same. The duplicate Control 2 sample showed very little gas production; this result is not readily explained, but may be due to the quality of the aluminum waste placed in the serum bottle.

The rate and extent of gas production *increased* (relative to the other treatment and controls) for the 10% sodium phosphate and 10% sodium silicate treatments.

To verify that the gas production was due to the presence of the aluminum waste, an additional control was prepared. This controlled was prepared using deionized water only (i.e., no aluminum waste, landfill solids, or leachate). After several days of incubation, no gas generation was observed.

Gas Composition.

Table 2 summarizes the gas composition data. Results indicate that hydrogen, methane, and carbon monoxide were generated in all treatments. Relatively low (<100 ppm-v) levels of ammonia were also generated in most samples. The presence of oxygen likely reflects some infiltration of outside air into the gas collection bags. The decrease in oxygen, as well as the increase in hydrogen, at the $t=13$ day event likely reflects the change in sampling location from the Tedlar bags to the serum bottle headspace, as some gas leakage/diffusion may have occurred through the Tedlar bags.

With the exception of Treatment 4, Table 2 indicates that the primary gas produced was hydrogen. Hydrogen levels in Treatment 6 were greater than the other treatments, suggesting that the presence of the sodium silicate enhanced hydrogen release from the aluminum waste.

For Treatment 4, nitrogen gas composition data showed that nitrogen was the primary gas produced (nitrogen concentrations at $t=8$ days were approximately 25% v/v for all treatments except Treatment 4, which had a nitrogen gas concentration of 44% v/v).

The $t=20$ day sampling results, which were obtained approximately 1 week after increasing the temperature to 97 degrees C, show that methane and carbon monoxide levels did not increase as a result of the increased temperature. Methane and carbon monoxide levels showed a slight decrease, which may be due to leakage and/or additional reactions.

Discussion and Conclusions

Overall results indicate that the aluminum waste reacted with the water to produce hydrogen, methane, ammonia, and (for the case of Treatment 4) nitrogen. Hydrogen, methane, and ammonia production are consistent with the expected hydrolysis products of aluminum waste. The reaction ceased after approximately 2 days.

Total gas, hydrogen, methane, and ammonia production were greatest in the 10% sodium silicate treatment. Sodium silicate may have enhanced the reaction because sodium silicate forms a basic

solution, which may limit (or, reduce the rate of) surface passivation of the aluminum waste. 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. The excess nitrogen production in the 10% sodium phosphate solution is not readily explained.

None of the tested amendments were effective at mitigating the reaction at the selected dosages. This unexpected result is not readily explained, but may suggest that naturally-occurring surface passivation processes dominate relative to any passivation effects produced by the amended suppression agents.

Generation of carbon monoxide up to levels of 500 ppm-v 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.

Tables

Table 1. Cumulative gas volume generated for each treatment. Values for replicate samples are shown.

Time (days)	Cumulative Volume of Gas Produced (mL)									
	Control 1	Control 2	TR1	TR2	TR3	TR4	TR5	TR6	TR7	TR8
1	86 / 95	66 / 16	77 / 89	92 / 94	85 / 71	193 / 181	87 / 79	124 / 121	76 / 94	87 / 90
2	86 / 100	66 / 20	87 / 90	92 / 110	85 / 71	193 / 185	89 / 84	137 / 126	76 / 94	90 / 93
8	86 / 100	66 / 20	87 / 90	92 / 110	85 / 71	193 / 185	89 / 84	137 / 126	76 / 94	90 / 93

Table 2. Gas composition data. Values for replicate samples are shown. NA= Not analyzed. Ammonia was not analyzed after t=7 days because of the limited sample volume in the serum bottle headspace.

t=2 days

Treatment	Hydrogen	Oxygen	ppm-v Methane	Ammonia	Carbon Monoxide
Control 1	87,000 / 64,000	51,000 / 51,000	1,600 / 1,400	<25 / <25	<100 / <100
Control 2	54,000 / 110,000	73,000 / 140,000	900 / 1,200	<25 / NA	<100 / <100
TR1	81,000 / 100,000	42,000 / 36,000	800 / 600	25 / <25	<100 / <100
TR2	90,000 / 120,000	33,000 / 55,000	500 / 600	<25 / 25	<100 / <100
TR3	76,000 / 84,000	40,000 / 45,000	400 / 800	25 / 25	<100 / 100
TR4	45,000 / 29,000	15,000 / 44,000	800 / 700	<25 / <25	<100 / <100
TR5	31,000 / 69,000	19,000 / 28,000	2,400 / 800	25 / 25	100 / <100
TR6	470,000 / 570,000	59,000 / 36,000	21,000 / 26,000	2,000 / 2,500	<100 / <100
TR7	39,000 / 47,000	80,000 / 46,000	400 / 600	25 / 25	<100 / <100
TR8	65,000 / 51,000	38,000 / 49,000	600 / 1,000	25 / 25	<100 / <100

t=7 days

Treatment	Hydrogen	Oxygen	ppm-v Methane	Ammonia	Carbon Monoxide
Control 1	76,000 / 110,000	100,000 / 49,000	4,800 / 6,600	<25 / <25	200 / 100
Control 2	100,000 / 170,000	150,000 / 79,000	6,100 / 6,000	<25 / NA	400 / 500
TR1	260,000 / 200,000	46,000 / 68,000	11,000 / 11,000	<25 / <25	300 / 300
TR2	180,000 / 140,000	66,000 / 93,000	5,500 / 2,900	<25 / <25	200 / 100
TR3	240,000 / 150,000	62,000 / 70,000	7,100 / 5,600	<25 / <25	100 / 200
TR4	110,000 / 79,000	83,000 / 200,000	4,500 / 900	NA / NA	200 / 200
TR5	250,000 / 160,000	77,000 / 52,000	6,600 / 9,100	<25 / <25	200 / 200
TR6	550,000 / 560,000	150,000 / 91,000	56,000 / 62,000	1,400 / 1,200	100 / 100
TR7	140,000 / 130,000	170,000 / 46,000	3,400 / 4,600	100 / 50	200 / 100
TR8	200,000 / 90,000	63,000 / 78,000	6,600 / 3,300	<25 / <25	100 / 100

t=13 days

Treatment	Hydrogen	Oxygen	ppm-v Methane	Ammonia	Carbon Monoxide
Control 1	180,000 / 260,000	23,000 / 33,000	12,000 / 14,000	NA / NA	200 / 200
Control 2	300,000 / 400,000	28,000 / 16,000	13,000 / 9,400	NA / NA	100 / 200
TR1	430,000 / 410,000	12,000 / 8,600	16,000 / 20,000	NA / NA	100 / 100
TR2	330,000 / 410,000	21,000 / 8,900	7,000 / 7,500	NA / NA	100 / 100
TR3	420,000 / 710,000	14,000 / 11,000	14,000 / 17,000	NA / NA	100 / 200
TR4	180,000 / 81,000	33,000 / 41,000	6,100 / 2,900	NA / NA	400 / 400
TR5	380,000 / 550,000	14,000 / 12,000	12,000 / 19,000	NA / NA	200 / 200
TR6	700,000 / 700,000	24,000 / 14,000	48,000 / 57,000	NA / NA	100 / 300
TR7	360,000 / 480,000	28,000 / 6,500	11,000 / 12,000	NA / NA	300 / 100
TR8	530,000 / 350,000	17,000 / 21,000	10,000 / 8,800	NA / NA	100 / 100

t=20 days

Treatment	Hydrogen	Oxygen	ppm-v Methane	Ammonia	Carbon Monoxide
Control 1	NA / NA	NA / NA	5,400 / 6,600	NA / NA	100 / <100
Control 2	NA / NA	NA / NA	5,400 / 5,300	NA / NA	100 / <100
TR1	NA / NA	NA / NA	5,000 / 6,800	NA / NA	100 / <100
TR2	NA / NA	NA / NA	3,500 / 5,100	NA / NA	<100 / <100
TR3	NA / NA	NA / NA	8,200 / 8,900	NA / NA	<100 / <100
TR4	NA / NA	NA / NA	4,200 / 3,700	NA / NA	100 / 200
TR5	NA / NA	NA / NA	11,000 / 4,500	NA / NA	100 / 200
TR6	NA / NA	NA / NA	40,000 / 43,000	NA / NA	100 / 100
TR7	NA / NA	NA / NA	6,500 / 8,000	NA / NA	100 / 100
TR8	NA / NA	NA / NA	8,900 / 4,700	NA / NA	100 / <100