

April 25, 2017

[REDACTED]
U.S. Chemical Safety and Hazard Investigation Board
1750 Pennsylvania Avenue, NW, Suite 910
Washington DC 20006

Characterization of Reactants

MGPI Processing Inc. in Atchison Kansas

CASE File No: 2445003

[REDACTED]

CASE Forensics Corporation (CASE), a JENSEN HUGHES company, was directed to test and characterize several fluid chemical samples collected during the U.S. Chemical Safety and Hazard Investigation Board (CSB's) investigation of the formation of a noxious gas plume from the MGPI Processing Inc. facility in Atchison, Kansas on October 21, 2016.

The following is our report regarding our observations and findings. Please note that CASE reserves the right to amend or supplement any of the findings and conclusions presented in this report if new data becomes available.

TASKS PERFORMED

During the course of this examination CASE performed the following tasks:

- a. Reviewed background information.
- b. Conducted a laboratory characterization on five of seven provided samples.
- c. Conducted a filmed simulation of the suspected reaction.
- d. Compiled this report.

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BACKGROUND INFORMATION

Based on a written summary provided by the CSB it is our understanding that in the morning of Friday, October 21, 2016, a tanker truck carrying 30% sulfuric acid (H_2SO_4) likely unloaded the acid into a sodium hypochlorite ($NaClO$) bleach tank at the MGP Ingredients facility in Atchison, Kansas. An ensuing chemical reaction led to an uncontrolled release of an uncharacterized gas plume that impacted 11,000 Atchison citizens in the surrounding community.

During the investigation that followed in the day after the event, the CSB found that the plant has two sodium hypochlorite tanks designated as the “bulk” and “day” tanks. The bulk tank is located outside and the day tank is located inside. The suspected mixing of sulfuric acid and sodium hypochlorite occurred in the outdoor bulk tank, however the day tank may have also been exposed since the tanks are connected by a pipe. The CSB also reported that that bulk tank samples may have been contaminated with “soda ash” (sodium carbonate or possibly sodium bicarbonate) that was used by emergency responders to neutralize the acid. It was also reportedly suspected that the acid in the tanker truck may have been contaminated with a back flow of sodium hypochlorite.

The remnant fluids of the bulk and day tanks were transferred to three new blue poly tanks and stored outside for approximately three days. On October 24, 2016 one sample from each of the blue poly tanks was collected and identified as samples 1 through 3. A fourth sample of residual fluid was collected from the bottom of the bulk tank. The remaining samples, designated as 5, 6, and 7, were collected from the sulfuric acid tanker truck with samples 6 and 7 being collected two months after the incident. The samples were sent to CASE via Clean Harbors Environmental of Lenexa, Kansas. Table 1 lists the samples received by CASE for analysis.

Table 1
Provided Chemical Fluid Samples

Item	Sample Location	Comments
1	Poly Tank #1 from Sodium Hypochlorite Bulk Tank	1 Liter-Mix of reactants
2	Poly Tank #2 from Sodium hypochlorite Bulk & Day Tank	DO NOT TEST per CSB
3	Poly Tank #3 from Sodium Hypochlorite Day Tank	900 mls. Possible mixture
4	Sodium Hypochlorite Bulk Tank Bottom	500 mls
5	Sulfuric Acid from Tanker Truck	100-mls
6	Sulfuric Acid from Tanker Truck	500 mls. 2-months later
7	Sulfuric Acid from Tanker Truck	DO NOT TEST per CSB

LABORATORY ANALYSIS

The laboratory characterization of the provided chemical samples proceeded with a series of analytical tasks prescribed by the CSB in the *CSB MGP Investigation Task Overview*. The analyses proceeded with a visual and olfactory examination of sub-samples that were transferred to sealed laboratory beakers and permitted to stand undisturbed for one week. The pH of each sample was measured using a glass pH electrode pre-calibrated with standardized pH buffers.

Further testing included determining the specific gravity and percent of total solids after evaporation of the fluids and subsequent characterization of these solid fractions. The solids fractions were characterized using Fourier Transform infrared spectroscopy (FTIR) and multi-qualitative/semi-quantitative elemental scanning using a scanning electron microscope equipped with an energy dispersive spectrometer (SEM/EDS). One of the sample fluids was subjected to gravimetric analysis for total sulfate (calculated) as sodium sulfate. The concentration of the sulfuric acid samples was determined using routine general chemistry procedures. The other analyses were conducted under the guidelines of the tests and practices published by ASTM International (ASTM), and listed in Table 2. The analytical results are presented in Table 3.

Table 2
Analytical Methods used by CASE in the Investigation

Analysis	ASTM Designation	Method Practice
pH	ASTM E70	<i>Standard Test Method for pH of Aqueous Solutions with a Glass Electrode</i>
Specific Gravity	ASTM D891	<i>Standard test Methods for Specific Gravity, Apparent, of Liquid Industrial Chemicals (pycnometer method)</i>
Total Solids	ASTM D2369	<i>Standard Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings</i>
FTIR	ASTM E1252	<i>Standard Practice for General Techniques for Obtaining Infrared Spectra for Qualitative Analysis</i>
SEM/EDS	ASTM E1508	<i>Standard Guide for Quantitative Analysis by Energy-Dispersive Spectroscopy</i>
Sulfates	ASTM D516 (Discontinued)	<i>Standard Test Method for Sulfate ion in Water (barium sulfate precipitate technique)</i>
Titration	Standard Applied Chemistry	<i>Titrated with certified 0.5N sodium hydroxide titrant to a phenolphthalein end point.</i>

Table 3
Analytical Results

Sample ID	Visual/Smell	pH	Solids (weight)	Density (g/cm ³)	FTIR	EDS solids	Titration or Sulfates
1 Poly Tank #1 from Sodium Hypochlorite Bulk Tank	Clear, water-like, with strong sulfuric acid odor. No sediment	0.8	21.064 %	1.189	Mixture of sodium bisulfate and sodium sulfate	Oxygen 48.2 % Sodium 26.0 % Sulfur 23.8 % Chlorine 1.9 %	N/A
3 Poly Tank #3 from sodium hypochlorite day tank	Yellow, water-like with chlorine and faint acid odor. Trace brown sediment	12.3	26.247 %	1.213	Sodium chlorate and sodium chloride (bleach evaporates)	Chlorine 46.5 % Sodium 34.1 % Oxygen 15.4 %	1917 mg/L calculated as Na ₂ SO ₄
4 Sodium hypochlorite bulk tank bottom	Clear, water-like with faint acidic odor. No sediment	0.6	13.781 %	1.121	Mixture of sodium bisulfate and sodium sulfate	Oxygen 48.3 % Sodium 25.4 % Sulfur 24.0 % Chlorine 2.2 %	N/A
5 Sulfuric acid from tanker truck	Clear, water-like with faint acidic odor, No sediment.	0.4	Does not fully evaporate 44% weight loss	1.228†	Sulfuric acid	N/A	3.65M
6 Sulfuric acid from tanker truck	Clear, water-like with faint acidic odor. No sediment.	1.31	Does not fully evaporate 46% weight loss	1.227†	Sulfuric acid	N/A	3.83M

† Density consistent with 30 % sulfuric acid (CRC Press Handbook of Chemistry and Physics)

DISCUSSION

The chemical reaction between the subject reactants in the Atchison, Kansas event mimics one process used to generate chlorine gas in the laboratory. The reaction is based on acidifying or lowering the pH a chlorine containing solution or solid that is alkaline or has a high pH. The alkalinity of the solution favors the stability of dissolved hypochlorite ion over chlorine gas. Acidification of the bleach solution causes evolution of green-colored, noxious chlorine gas, which is slightly heavier than air. Test reactions in our laboratory were conducted by adding 50 milliliters of sulfuric acid (Sample Item 6) by a steady continuous flow from a burette into a reaction vessel containing 200 milliliters of 5 % sodium hypochlorite (fresh Clorox® bleach). The test revealed the reaction is non-violent, without a notable generation of heat and results in the formation of small chlorine gas bubbles that rise to the surface to form a layer of gaseous chlorine foam. A film of the reaction was made and is included with this report.

A general reaction between sulfuric acid and sodium hypochlorite that produces chlorine gas and sulfate salt, is shown below. Other byproducts (acid and sulfate salts) may also be produced.

1. Sulfuric acid (H₂SO₄) combined with sodium hypochlorite bleach (NaClO) results in the formation of hypochlorous acid (HClO) and sodium sulfate salt (Na₂SO₄) which remains dissolved in the solution.



2. The hypochlorous acid then partially breaks down into the hypochlorite anion (OCl⁻) and hydrogen cation (H⁺)



3. The acidic pH of the solution results drives the reaction to the right and promotes the release of chlorine gas (Cl₂).



DATA INTERPRETATION

Interpretation of the data shown in Table 3 is itemized below. Photos of the sample are shown in Photographs 1-3.

1. The density or specific gravity of the acid samples from the tanker truck (item 5 and 6) correlates with published data on the density of 30% solution of sulfuric acid (see http://www.sschemical.com/wp-content/uploads/2013/05/Conversion_Table.pdf).
2. EDS data shows no evidence of elements other than those found in sodium hypochlorite and sulfuric acid. The relative concentrations of the detected elements to the stoichiometric concentration of sodium sulfate and/or sodium bisulfate (Items 1 and 4) could not be balanced. This information suggests the solids incorporate a variety of residual sodium salts.
3. The FTIR data reveals that the evaporated solids in (Item 1 and 4) yield the same spectrum and most closely compare with a mixture of sodium sulfate and sodium bisulfate (NaHSO₄). The solids from Item 3 (sodium hypochlorite day tank) were found to be a spectral match to evaporated solids of sodium hypochlorite Clorox bleach. Figure 1 shows the FTIR spectral comparison of the solids from Item 4).
4. The presence of sulfates in Item 3, which was below the EDS detection limit for sulfur, indicates this sample had been contaminated with some sulfuric acid.

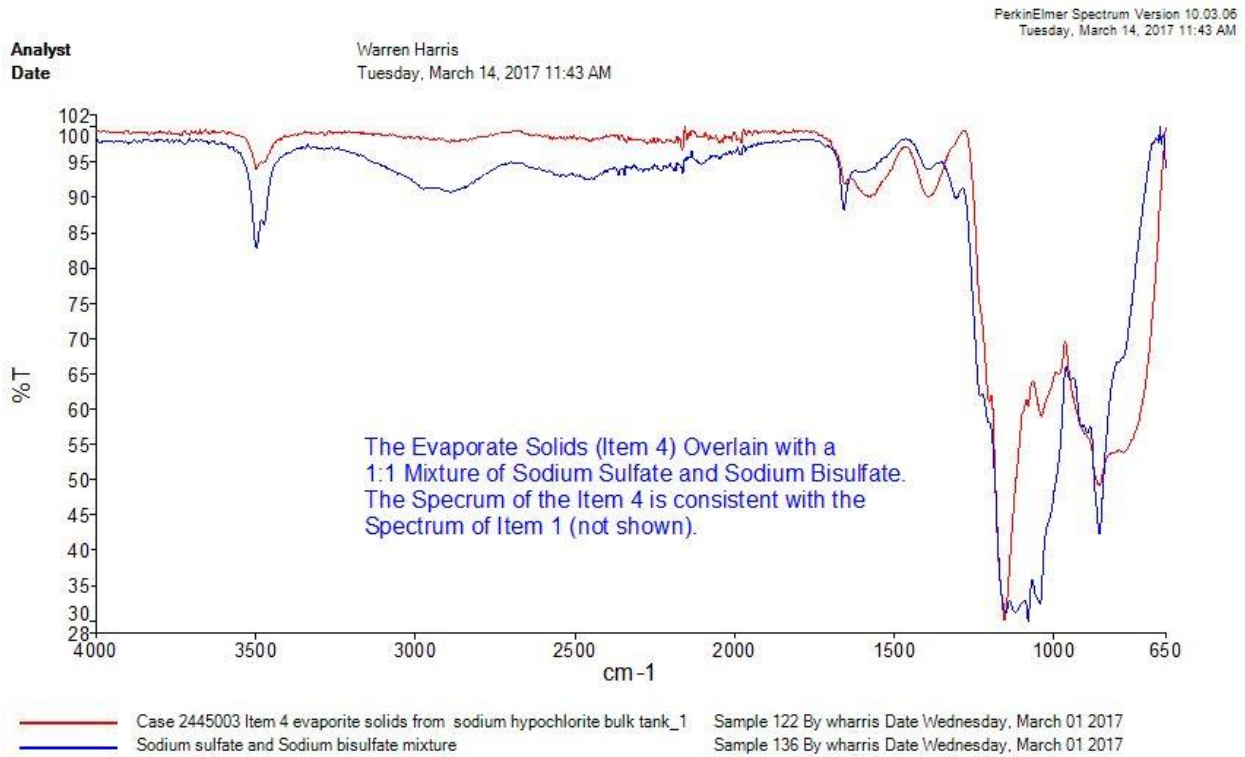
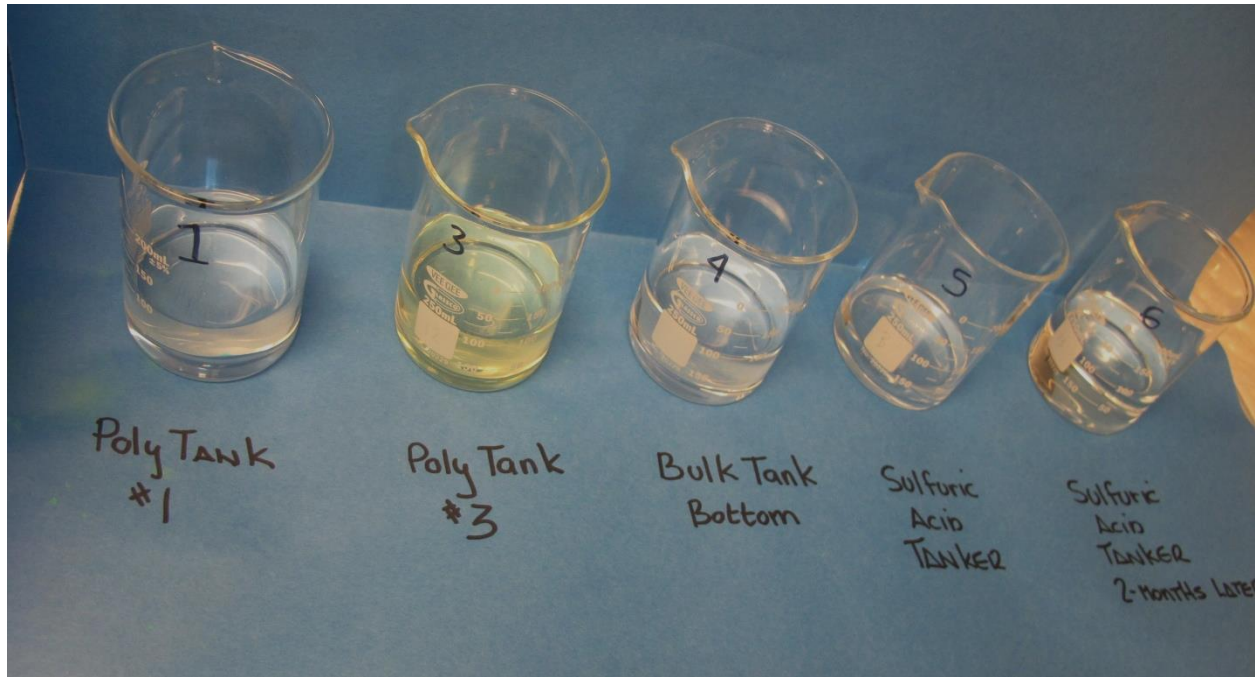


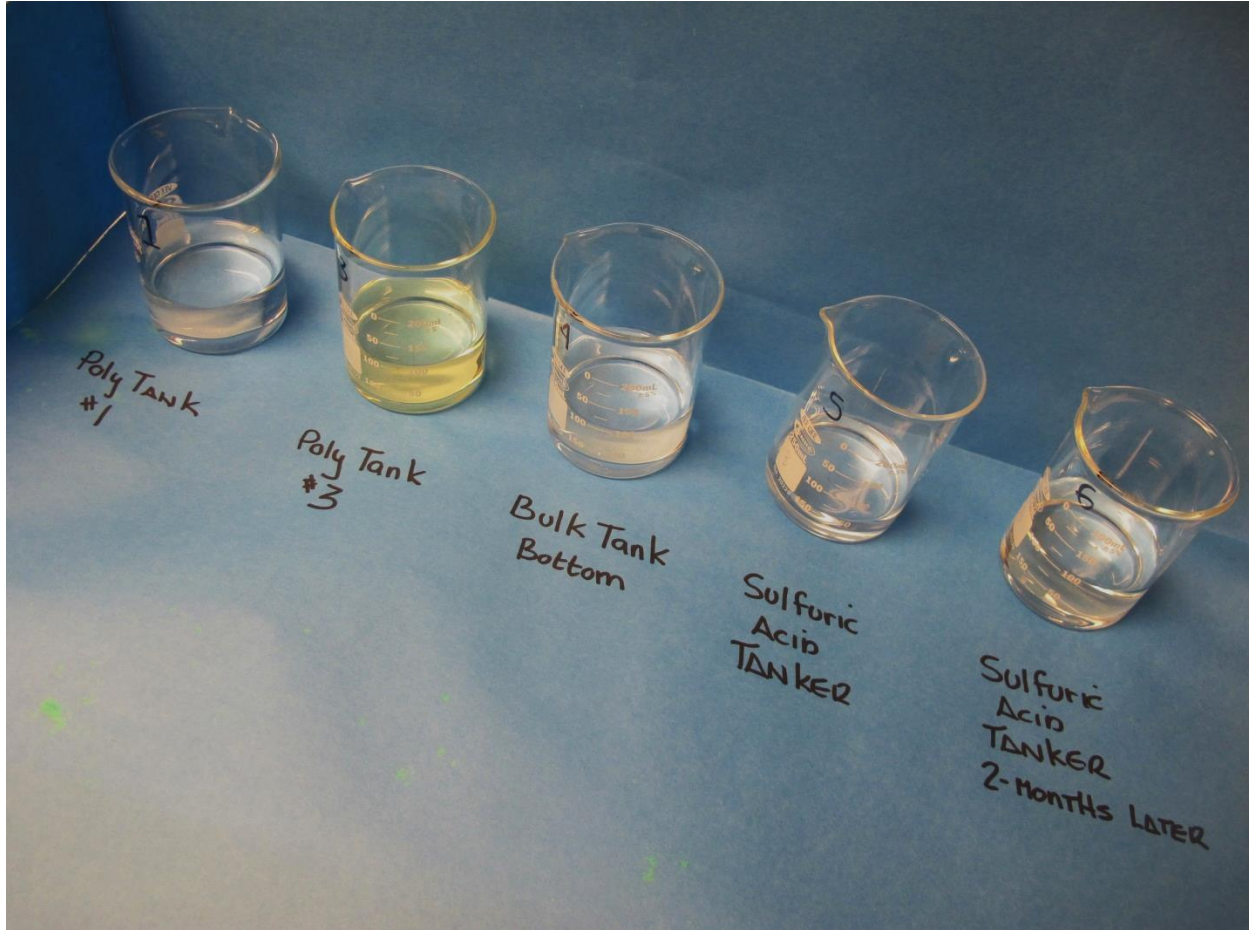
Figure 1

Figure 1 shows the FTIR spectral comparison of the evaporate solids found in both Item 1 and 4.



Photograph 1

The photograph shows sub-samples of the subject samples.



Photograph 2
The photograph shows sub-samples of the subject samples.



Photograph 3
The photograph shows sub-samples of the subject samples