Hydrogen Sulfide Issues at Coal Combustion Residual and Municipal Solid Waste Disposal Facilities

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BACKGROUND

Historically, coal combustion residuals (CCRs) have been stored in and/or disposed of in dedicated ponds and landfills. In the future, we anticipate that CCRs will also be placed in dedicated units that comply with the new U.S. Environmental Protection Agency (USEPA) design, construction, and operating regulations. In the interim, as old CCR units are being closed and new units are not yet available, industry professionals are increasingly interested in the co-disposal of CCR in existing municipal solid waste (MSW) landfills.

While the waste industry has limited experience with co-disposal of CCR and MSW, landfill operators have significant experience with the disposal of drywall (aka gypsum) and MSW. Under certain conditions, gypsum decomposition can generate problematic amounts of hydrogen sulfide. Similar conditions could occur if select CCR streams are co-disposed and co-mingled with MSW.

This paper discusses the conditions that contribute to hydrogen sulfide generation in an MSW landfill, health and odor concerns associated with hydrogen sulfide, and potential mitigation options.

Major CCR streams include bottom ash/slag, fly ash, and flue gas desulfurization (FGD) material. The physical and chemical properties of the CCRs are covered elsewhere. This paper focuses on concerns regarding hydrogen sulfide generation resulting from co-disposal of sulfate-containing CCRs with MSW. FGD, which is essentially calcium sulfate (aka gypsum, $CaSO_4 \cdot 2H_2O$), has a high sulfur content and presents the greatest concern for hydrogen sulfide generation.

HYROGEN SULFIDE CONCERNS

Hydrogen sulfide gas presents a series of significant issues and concerns, including:

- Health/toxicity issues
- Odor issues
- Equipment corrosion
- Air emissions/permitting issues

HEALTH/TOXICITY ISSUES

The primary exposure pathway for hydrogen sulfide is inhalation, because it is a gas under typical conditions. Lower concentration exposures can cause neurological and respiratory effects; irritation to the eyes, nose, or throat; fatigue, headaches, and nausea.

“Brief exposures to high concentrations of hydrogen sulfide (greater than 500 ppm) can cause a loss of consciousness. In most cases, the person appears to regain consciousness without any other effects. However, in many individuals, there may be permanent or long-term effects such as headaches, poor attention span, poor memory, and poor motor function.” (ATSDR ToxFAQs)

High concentrations and exposures can be lethal.

Various government agencies and organizations have established inhalation exposure standards, covering a multitude of acute and chronic exposure scenarios. Some of the more common standards include:

- OSHA Permissible Exposure Limits
  - 8-hour Time Weighted Average (TWA): Not Est.
  - Vacated (1993) 8-hr TWA: 10 ppm
  - Ceiling: 20 ppm
  - Peak (10 minutes): 50 ppm
- NIOSH Exposure Limits
  - Ceiling (10 minutes): 10 ppm
  - Immediately Dangerous to Life & Health (IDLH): 100 ppm
- ACGIH Exposure Limits (2015)
  - 8-hour Threshold Limit Value – TWA: Not Est.
  - Ceiling (no time limit): 10 ppm
- ATSDR Minimal Risk Levels for Inhalation
  - Acute (1 - 4 day exposure): 0.07 ppm
  - Intermediate (14 - 364 days exposure): 0.02 ppm
- USEPA Regional Screening Level (May 2016) – Long Term Exposure
  - Residential: 0.0014 ppm
  - Industrial: 0.0059 ppm
- NC Ambient Air Level (15A NCAC 02D.1104): 0.086 ppm

ODOR ISSUES

Hydrogen sulfide exhibits the characteristic sulfur odor of rotten eggs. The odor threshold in air is very low, reported in the range of 0.0005 to 0.3 ppm (ATSDR Toxicological Profile, December 2016). The very low odor threshold can result in complaints from facility workers and neighbors, even in situations where the hydrogen sulfide concentration may be below risk-based inhalation standards.

Exposure to hydrogen sulfide can lead to rapid olfactory fatigue or paralysis. With continuous low-level exposure, a person loses the ability to smell the gas even though it is still present. At high concentrations, this can happen very rapidly or even instantaneously. Therefore, odor is not a reliable indicator. (Reference: OSHA Fact Sheet).

In addition to hydrogen sulfide, the degradation of gypsum in an MSW landfill can also produce other smelly sulfur compounds including mercaptans and thiophene.

EQUIPMENT CORROSION

Hydrogen sulfide corrodes many materials commonly used to construct landfill gas (LFG) control systems; and can cause sulfide stress cracking in alloys, particularly at elevated temperatures. Moisture – which is ubiquitous in MSW landfills – increases corrosivity to metals. Hydrogen sulfide can be converted to sulfuric acid, which is highly corrosive. High hydrogen sulfide concentrations may require the use of corrosion resistant (and expensive) alloys and polymers for LFG system components. Sulfur compounds can poison selective catalytic reduction (SCR) catalysts in nitrogen oxide reduction systems.

AIR EMISSIONS/PERMITTING ISSUES

While hydrogen sulfide is neither a criteria pollutant nor a USEPA Hazardous Air Pollutant (HAP), it is regulated as an air toxic (aka Toxic Air Pollutant – TAP) under many state programs (e.g., NC). Reduced sulfur compounds also pose Prevention of Significant Deterioration (PSD) implications during the permitting stage. Combustion (e.g., flaring, internal combustion engine) converts hydrogen sulfide to sulfur dioxide, a criteria pollutant.

While various sulfur removal technologies are available for retrofitting LFG systems, the capital and operation and maintenance (O&M) costs are generally high (typically high 6 or 7 figures), and can outweigh economic benefit from disposal of high-sulfur wastes.

With respect to landfill gas to energy systems (LFGTE), note that CCRs do not generate methane. Therefore, energy predictions based on MSW may overestimate the actual energy realized by LFGTE systems.

THE SEVEN CONDITIONS FOR CONVERSION OF SULFATES TO HYDROGEN SULFIDE

Hydrogen sulfide can be produced when all of the following conditions are present:

1. Liquid Water
2. Source of Soluble Sulfate
3. Sulfate-reducing Bacteria
4. Organic Material
5. Anoxic Environment
6. Appropriate pH Range
7. Appropriate Temperature Range

As described below, these conditions are likely to be present in an MSW co-disposal scenario, but will not typically all be present in a CCR disposal facility.

Condition 1 - Liquid Water. The biological conversion of sulfate to hydrogen sulfide occurs in the aqueous phase (i.e., free liquids must be present). While modern landfills are equipped with leachate collection systems, the presence of perched and discrete zones of saturation within the waste mass are relatively common. Nonetheless, proper design, maintenance, and operating of leachate control systems can reduce the presence of free liquids, thereby minimizing the potential for hydrogen sulfide generation. Low permeability confining layers (e.g., clay used for daily cover) may trap water in discrete pockets. Leachate recirculation (e.g., bioreactors) may exacerbate moisture problems that lead to hydrogen sulfide generation.

Condition 2 - Source of Soluble Sulfate. Gypsum, having the chemical formula $CaSO_4{\bullet}2H_2O$, is a good source of soluble sulfate. Gypsum sources include FGD and wallboard. Considering the high sulfur content in gypsum, small quantities can generate problematic amounts of hydrogen sulfide. Fly ash and bottom ash contain lower concentrations of sulfate, but with large volumes these waste streams still can represent a major source of soluble sulfate when co-disposed in an MSW landfill.

Condition 3 - Sulfate-reducing Bacteria. Primary sulfate reducing bacteria (SRB) include Desulfovibrio and Desulfotomaculum. These SRBs are believed to be commonly present in MSW landfills, and less commonly present in construction and demolition debris landfills. SRBs are not likely present in CCR monofills.

Condition 4 - Organic Material. SRBs use organic material as a food source to multiply and degrade sulfate hydrogen sulfide. Carbon is a source of energy for the bacteria. Typical MSW has a high organic content, and contains a wide variety of organic materials such as wood, paper, cardboard, food, vegetative waste, and fabrics.

Condition 5 - Anoxic Environment. SRBs thrive under anoxic (without oxygen) conditions. The presence of oxygen will stop bacteria growth and prevent hydrogen sulfide generation, but will not necessarily kill SRBs. Anoxic conditions are typical in

MSW landfills. While the injection of oxygen within the landfill may be an effective method of terminating SRB activity, it is NOT recommended as it can lead to other undesirable effects such as landfill fires.

Condition 6 - Appropriate pH Range. SRB reduction of sulfate to hydrogen sulfate is reportedly optimum within a pH range of about 7 to 8, and does not occur outside a pH range of about 4 to 9. The pH range within a typical MSW landfill falls within this activity range.

Condition 7 - Appropriate Temperature Range. SRB reproduction and hydrogen sulfide generation are reportedly optimum within a range of about 30°C to 38°C (86°F to 100°F). Many MSW landfills are within or a little above this optimum range. Studies of SRB in geologic environments found reduced activity above about 60°C (140°F), and no activity above about 80°C (176°F). Similarly, SRB activity ceases in freezing conditions (no free liquids).

Considering these seven conditions, most are beyond the practicable control of the landfill operator. However, there are few practicable measures that the landfill operator can implement to prevent or minimize hydrogen sulfide at MSW and CCR co-disposal sites. Potential measures include:

- **Segregation** of MSW and CCR, either using dedicated cells or dedicated disposal areas that are arranged such that the disposed materials, and any leachate generated through the materials, are not in contact.

- **Aggressive Moisture Control** via stringent operation and maintenance of leachate and storm water management systems.

Other issues to be addressed when considering co-disposal of MSW and CCR, which are beyond the reach of this paper, include geotechnical considerations (slope stability), dust control, leachate chemistry, impact on landfill gas generation and collection, and other operational issues. If a waste segregation approach is pursued to minimize hydrogen sulfide, the waste segregation design and operation plans should address these items.

CONCLUSION

When considering co-disposal of MSW and CCR, the old adage is particularly applicable – ***An Ounce of Prevention is Worth a Pound of Cure.*** Generation of hydrogen sulfide is a potential consequence of co-disposal, and can have negative impacts for both the landfill operator and waste generator. Measures aimed at minimizing hydrogen sulfide generation can be implemented, but must be evaluated with respect to current design and operating practices, and economic considerations. The waste industry and utility industry have an opportunity to learn as more co-disposal experience is gained, and to develop best practices for CCR management at MSW facilities.

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