

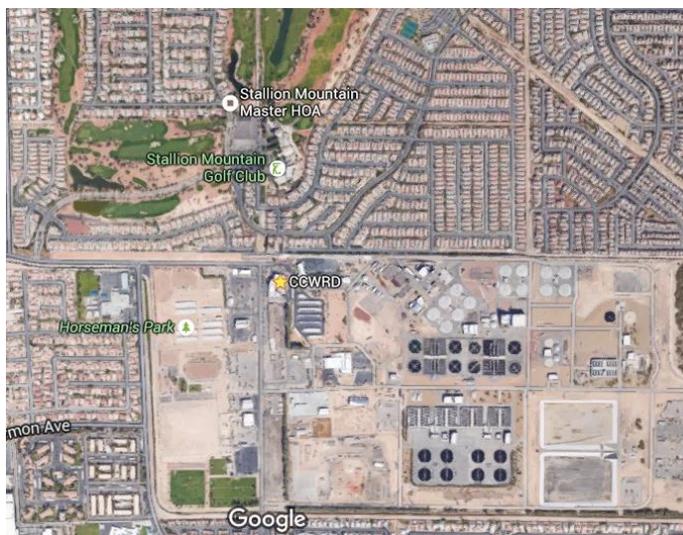
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Abstract

In the world of odor control, Hydrogen Sulfide (H₂S) dominates the conversation. There are a multitude of technologies to monitor and control Hydrogen Sulfide. But, many applications also contain low levels of other gases which can be a challenge to identify, quantify, and remove. Very little research has been conducted and even fewer control options have been commercialized to address these concerns. This paper will discuss many of those odors, where they often occur, what their characteristics are, and how to remove them. Additional discussion will be made in regard to standards for quantifying objectionable odors and specifying requirements for total odor reduction.

Wastewater odor controls systems have become standard features in new in the new collection and treatment projects. Urban encroachment has led to residential and commercial development on the doorsteps of treatment plants and lift stations. Where once wastewater odors were just a fact of life, neighbors no longer accept this status quo. Very expensive litigation is common from new neighbors of wastewater systems which have been previously in place for decades. An example below is the Clark County, LV Water Reclamation Division (Las Vegas). The neighborhoods adjacent to the facility were built in recent years. Many of the homes are within 150 ft from major odor sources. The development of this land resulted in millions of dollars of improvements to the facility to cover odor sources and treat the odors.



Various technologies are available to the wastewater professional to treat these odors. Most technologies concentrate on the removal of hydrogen sulfide (H₂S) as it is the predominant odor in the market. The concentration on removal of hydrogen sulfide has been sufficient in the past.

With urban encroachment and the public awareness of the public of the ability to control odors, sole concentration on hydrogen sulfide is expected to be insufficient.

There are two primary reasons why odor control installations have previously focused on hydrogen sulfide. The first is that hydrogen sulfide is the predominant odor in the wastewater environment. The second reason is that technology for the detection of hydrogen sulfide is far more available than other odors.

Hydrogen Sulfide levels in the wastewater industry are well documented and often even predictable.^{1) 2)} With few exceptions, hydrogen sulfide is the primary odor from processes with significant odor.

Hydrogen sulfide detection has been bolstered by other industries which have to deal with gas. Industries such as petroleum refining and paper production. In these areas, H₂S levels are a matter of health and safety as well as reliability of electronics. OSHA exposure levels are well defined for hydrogen sulfide as is the level required to protect industrial controls from corrosion of the gas³⁾. Because of this, many devices have been developed to measure H₂S. These device include stationary, portable, and even wearable devices which measure and alarm at determined H₂S levels.

There are far less available methods for detection and measurement of other odors. These gases are typically not found in toxic levels, so the need for monitoring of these gases for health and safety reasons is far less.

The “other” types of odors are typically grouped as follows:

- Ammonia, amines, and diamines – Nitrogen based molecules and derivatives which contain carbon chains.
- Mercaptans – a series of organic molecules which contain a carbon chain with a C-S-H ending.
- Sulfur-Organic Compounds – This family differs from the Mercaptans in that the S is captured between C molecules.
- Nitro-organics – Aromatic compounds with benzene bases
- Volatile Fatty Acids – Organic molecule with a COOH chain.

Table 1 describes many of the odorous compounds and provides information about concentration where these odors can be detected and be recognized. It should be noted that many of these compounds have extremely low detection thresholds and very offensive odor characteristics.

| Table 1 | | | | |
|---|---|---------------------------------------|---|-------------------------|
| Odorous Compounds Associated with Wastewater Treatment | | | | |
| Compound Name | Formula | Detection Threshold ppm, (v/v) | Recognition threshold, ppm (v/v) | Odor description |
| Acetaldehyde | CH ₃ CHO | 0.067 | 0.21 | Pungent, fruity |
| Allyl mercaptan | CH ₂ :CHCH ₂ SH | 0.0001 | 0.0015 | Disagreeable, garlic |
| Ammonia | NH ₃ | 17 | 37 | Pungent, irritating |
| Amyl Mercaptan | CH ₃ (CH ₂) ₄ SH | 0.0003 | - | Unpleasant, putrid |
| Benzyl mercaptan | C ₆ H ₅ CH ₂ SH | 0.0002 | 0.0026 | Unpleasant, strong |
| n-Butyl amine | CH ₃ (CH ₂) ₃ NH ₂ | 0.08 | 1.8 | Sour, Ammonia |
| Cadaverine | H ₂ N(CH ₂) ₅ NH ₂ | - | - | Putrid, decaying fish |
| Chlorine | Cl ₂ | 0.08 | 0.31 | Pungent, suffocating |
| Chlorophenol | Cl C ₆ H ₅ O | - | - | Medicinal, phenolic |
| Crotyl Mercaptan | CH ₃ CH:CHCH ₂ SH | 0.0077 | - | Skunk-like |
| Dibutyl amine | (C ₄ H ₉) ₂ NH | 0.016 | - | Fishy |
| Diisopropyl amine | (C ₃ H ₇) ₂ NH | 0.13 | 0.38 | Fishy |
| Dimethyl amine | (CH ₃) ₂ NH | 0.34 | - | Putrid, fishy |
| Dimethyl sulfide | (CH ₃) ₂ S | 0.001 | 0.001 | Decayed cabbage |
| Diphenyl sulfide | (C ₆ H ₅) ₂ S | 0.0001 | 0.0021 | Unpleasant |
| Ethyl amine | C ₂ H ₅ NH ₂ | 0.27 | 1.7 | Ammonia like |
| Ethyl mercaptan | C ₂ H ₅ SH | 0.0003 | 0.001 | Decayed cabbage |
| Hydrogen sulfide | H ₂ S | 0.0005 | 0.0047 | Rotten eggs |
| Indole | C ₆ H ₄ (CH) ₂ NH | 0.0001 | - | Fecal, nauseating |
| Methyl amine | CH ₃ NH ₂ | 4.7 | - | Putrid, fishy |
| Methyl mercaptan | CH ₃ SH | 0.0005 | 0.001 | Rotten cabbage |
| Ozone | O ₃ | 0.5 | - | Pungent, irritating |
| Phenyl mercaptan | C ₆ H ₅ SH | 0.0003 | 0.0015 | Putrid, garlic |
| Propyl mercaptan | C ₃ H ₇ SH | 0.0005 | 0.02 | Unpleasant |
| Putrescine | NH ₂ (CH ₂) ₄ NH ₂ | - | - | Putrid, nauseating |
| Pyridine | C ₅ H ₅ N | 0.66 | 0.74 | Pungent, irritating |
| Skatole | C ₉ H ₉ N | 2.7 | 0.05 | Fecal, nauseating |
| Sulfur dioxide | SO ₂ | 0.0001 | 4.4 | Pungent, irritating |
| Tert-Butyl Mercaptan | (CH ₃) ₃ CSH | - | - | Skunk, unpleasant |
| Thiocresol | CH ₃ C ₆ H ₄ SH | 0.0001 | - | Skunky, irritating |
| Trimethyl amine | (CH ₃) ₃ N | 0.0004 | - | Pungent, fishy |
| Carbon disulfide | CS ₂ | 3.65 | - | Disagreeable, sweet |
| Isobutyl mercaptan | C ₄ H ₁₀ S | 0.0020 | - | - |
| Diethyl sulfide | C ₄ H ₁₀ S | 0.0047 | - | Foul, garlicky |

(WEF MOP No. 22 1979, 1995)

Odor control methods typically rely on some type of chemical reaction. Hydrogen sulfide, as an acid, readily reduces in acid/base reactions. Furthermore, it can be oxidized. "Wet" type scrubbers typically utilize one or more of these compounds to neutralize H₂S. Biological scrubbers typically have acidophilic bacteria which consume H₂S and convert it to non-volatile compounds. Traditional activated carbon adsorption systems utilized highly porous carbon to capture H₂S utilizing carbon molecular bonds referred to as van der Waals forces. Chemisorptive adsorbents utilize these forces along with a chemical reaction to convert H₂S to nonvolatile compounds.

The processes above are not always effective with the other odorous compounds mentioned above. Methods have been investigated to capture these odors. These methods involve the use of alternate chemisorptive methods utilizing different types of reactions which are effective to target the removal of these gases. This paper will explore these methods.

The premise behind the research of this paper is that no one process can effectively and permanently remove all odors since these odors have very different chemical properties. Two methods were explored in this regard. This first method involves creating layers of chemisorptive adsorbent media. The first layer, in order of contact with the odorous air stream, is a "catalytic" metal oxide carbon. This chemisorbant has proven to be an effective hydrogen sulfide removal agent. The second layer is a mixture of virgin activated carbon and permanganate impregnated alumina. This two-step approach is expected to act as a "roughing" and "polishing" manner to remove the majority of odor first and then capture any remaining odor from there.

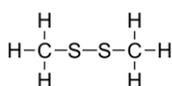
The second method involves combining three types of adsorbents in a blended, homogenous adsorbent bed. These adsorbents include permanganate impregnated alumina, virgin activated carbon, and a new product composed of an activated alumina substrate impregnated with Ferric ion also referred to as Iron (3+) or Fe³⁺.

Permanganate impregnated alumina has been used in odor control for more than a decade. Permanganate (typically potassium permanganate or sodium permanganate) is a strong oxidant. Activated alumina (Al₂O₃) is a highly porous inorganic substrate which can be used as an adsorbent reaction site. When permanganate is put into solution with water and placed on the alumina, it creates a readily reactive chemisorbant. Because permanganate is a strong oxidizer, those odors when can be oxidized will react with the permanganate. An example of the reaction is below:



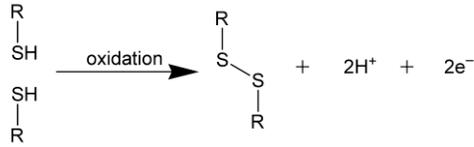
The resultant reactants are solid, do not have any odor, and are bound inside the activated alumina. It should be noted that while permanganate is a strong oxidizer, not all odors are easily oxidized. For instance mercaptans, reduced sulfur-organic, and nitro organic odors have strong double bonds which are not readily broken in an oxidizing reaction.

The oxidizing reaction can occur under special conditions such as acid environments. One concern in regard to the use of permanganates is the possibility to oxidize (under the right conditions) a mercaptan to a reduced sulfur compound as in the reaction below. This has been theorized as source for the especially difficult odor dimethyl disulfide which could be formed by the oxidation of methyl mercaptan.



Methyl Mercaptan

Dimethyl Disulfide



Virgin activated carbon has been used in wastewater odor control applications for many decades. The product works using the van der Waals forces mentioned above to hold the odorous gases inside the carbon. These weak molecular bonds are greatest among molecules with higher molecular weight. Volatile organic compounds with high molecular weight are most strongly held in the activated carbon. Lower molecular weight compounds are less likely to be captured in activated carbon. Furthermore, lower molecular weight odors can be desorbed from the activated carbon if displaced by larger molecules or under a change in temperature, pressure, or humidity. Further uncertainty exists because there are many different types of activated carbon which have different adsorption capabilities and restrictions. These are the primary reason why virgin activated carbon is less often used in wastewater odor control applications. The theory behind using it in this research is that it is a very broad acting agent. If used after a H₂S adsorbent and in conjunction with a permanganate impregnated alumina, it may serve to capture the odors not captured by the permanganate impregnated alumina.

The second experiment involves the use of a triple blend of adsorbents on one homogenous bed. The blend utilizes the activated carbon and the permanganate impregnated alumina. The third adsorbent is produced using activated alumina which has been impregnated with iron in the form of iron (III), also referred to as Fe³⁺.

Identical adsorption units were setup at the same pumping station. One unit was filled with a 18" deep layer of H₂S catalytic carbon followed by an 18" layer of the blended permanganate impregnated alumina with activated carbon. The second unit was filled with a 36" deep bed of the triple blend media. The systems were balanced so that they were pulling equal levels of odorous air through the adsorbent beds. The systems were allowed to operate for three days in order to let the systems come to equilibrium.

The photo below shows a similar setup as used during this test.



Preliminary results

The inlet and both system outlets were tested with and odor panel for determination of odor threshold by dynamic olfactometry using EN13725. The results are below.

| | | | ASTM E679 & EN13725 | |
|---|-----------|---------------------|--------------------------------|-----------------------|
| # | Field No. | Sample Description | Detection Threshold | Recognition Threshold |
| 1 | 1 | Inlet | 9,300 | 6,100 |
| 2 | 2 | Outlet Dual Layer | 230 | 110 |
| 3 | 3 | Outlet Triple Blend | 40 | 25 |
| 4 | | | | |

The initial conclusion is that both methods work very well but that the Triple Blend has more improved results.

Further testing was performed to determine the effectiveness at removing particular odors. The results below are from the inlet to the two units. As can be observed, the odors from the station were hydrogen sulfide, carbonyl sulfide, methyl mercaptan, and dimethyl sulfide.

| CAS # | Compound | Result $\mu\text{g}/\text{m}^3$ | MRL $\mu\text{g}/\text{m}^3$ | Result ppbV | MRL ppbV |
|-----------|-----------------------|------------------------------------|---------------------------------|----------------|-------------|
| 7783-06-4 | Hydrogen Sulfide | 11,000 | 7.0 | 8,200 | 5.0 |
| 463-58-1 | Carbonyl Sulfide | 120 | 12 | 50 | 5.0 |
| 74-93-1 | Methyl Mercaptan | 2,900 | 9.8 | 1,500 | 5.0 |
| 75-08-1 | Ethyl Mercaptan | ND | 13 | ND | 5.0 |
| 75-18-3 | Dimethyl Sulfide | 1,300 | 13 | 500 | 5.0 |
| 75-15-0 | Carbon Disulfide | ND | 7.8 | ND | 2.5 |
| 75-33-2 | Isopropyl Mercaptan | ND | 16 | ND | 5.0 |
| 75-66-1 | tert-Butyl Mercaptan | ND | 18 | ND | 5.0 |
| 107-03-9 | n-Propyl Mercaptan | ND | 16 | ND | 5.0 |
| 624-89-5 | Ethyl Methyl Sulfide | ND | 16 | ND | 5.0 |
| 110-02-1 | Thiophene | ND | 17 | ND | 5.0 |
| 513-44-0 | Isobutyl Mercaptan | ND | 18 | ND | 5.0 |
| 352-93-2 | Diethyl Sulfide | ND | 18 | ND | 5.0 |
| 109-79-5 | n-Butyl Mercaptan | ND | 18 | ND | 5.0 |
| 624-92-0 | Dimethyl Disulfide | ND | 9.6 | ND | 2.5 |
| 616-44-4 | 3-Methylthiophene | ND | 20 | ND | 5.0 |
| 110-01-0 | Tetrahydrothiophene | ND | 18 | ND | 5.0 |
| 638-02-8 | 2,5-Dimethylthiophene | ND | 23 | ND | 5.0 |
| 872-55-9 | 2-Ethylthiophene | ND | 23 | ND | 5.0 |
| 110-81-6 | Diethyl Disulfide | ND | 12 | ND | 2.5 |

The results below are from the outlet of the dual layer unit. The only detected results were 29 ppb of Carbonyl Sulfide.

| CAS # | Compound | Result µg/m ³ | MRL µg/m ³ | Result ppbV | MRL ppbV |
|-----------|-----------------------|-----------------------------|--------------------------|----------------|-------------|
| 7783-06-4 | Hydrogen Sulfide | ND | 7.0 | ND | 5.0 |
| 463-58-1 | Carbonyl Sulfide | 71 | 12 | 29 | 5.0 |
| 74-93-1 | Methyl Mercaptan | ND | 9.8 | ND | 5.0 |
| 75-08-1 | Ethyl Mercaptan | ND | 13 | ND | 5.0 |
| 75-18-3 | Dimethyl Sulfide | ND | 13 | ND | 5.0 |
| 75-15-0 | Carbon Disulfide | ND | 7.8 | ND | 2.5 |
| 75-33-2 | Isopropyl Mercaptan | ND | 16 | ND | 5.0 |
| 75-66-1 | tert-Butyl Mercaptan | ND | 18 | ND | 5.0 |
| 107-03-9 | n-Propyl Mercaptan | ND | 16 | ND | 5.0 |
| 624-89-5 | Ethyl Methyl Sulfide | ND | 16 | ND | 5.0 |
| 110-02-1 | Thiophene | ND | 17 | ND | 5.0 |
| 513-44-0 | Isobutyl Mercaptan | ND | 18 | ND | 5.0 |
| 352-93-2 | Diethyl Sulfide | ND | 18 | ND | 5.0 |
| 109-79-5 | n-Butyl Mercaptan | ND | 18 | ND | 5.0 |
| 624-92-0 | Dimethyl Disulfide | ND | 9.6 | ND | 2.5 |
| 616-44-4 | 3-Methylthiophene | ND | 20 | ND | 5.0 |
| 110-01-0 | Tetrahydrothiophene | ND | 18 | ND | 5.0 |
| 638-02-8 | 2,5-Dimethylthiophene | ND | 23 | ND | 5.0 |
| 872-55-9 | 2-Ethylthiophene | ND | 23 | ND | 5.0 |
| 110-81-6 | Diethyl Disulfide | ND | 12 | ND | 2.5 |

The results below are from the triple blend system. These are the most improved results, with only a low level of carbon disulfide remaining in the outlet air.

| CAS # | Compound | Result $\mu\text{g}/\text{m}^3$ | MRL $\mu\text{g}/\text{m}^3$ | Result ppbV | MRL ppbV |
|-----------|-----------------------|------------------------------------|---------------------------------|----------------|-------------|
| 7783-06-4 | Hydrogen Sulfide | ND | 7.0 | ND | 5.0 |
| 463-58-1 | Carbonyl Sulfide | ND | 12 | ND | 5.0 |
| 74-93-1 | Methyl Mercaptan | ND | 9.8 | ND | 5.0 |
| 75-08-1 | Ethyl Mercaptan | ND | 13 | ND | 5.0 |
| 75-18-3 | Dimethyl Sulfide | ND | 13 | ND | 5.0 |
| 75-15-0 | Carbon Disulfide | 14 | 7.8 | 4.6 | 2.5 |
| 75-33-2 | Isopropyl Mercaptan | ND | 16 | ND | 5.0 |
| 75-66-1 | tert-Butyl Mercaptan | ND | 18 | ND | 5.0 |
| 107-03-9 | n-Propyl Mercaptan | ND | 16 | ND | 5.0 |
| 624-89-5 | Ethyl Methyl Sulfide | ND | 16 | ND | 5.0 |
| 110-02-1 | Thiophene | ND | 17 | ND | 5.0 |
| 513-44-0 | Isobutyl Mercaptan | ND | 18 | ND | 5.0 |
| 352-93-2 | Diethyl Sulfide | ND | 18 | ND | 5.0 |
| 109-79-5 | n-Butyl Mercaptan | ND | 18 | ND | 5.0 |
| 624-92-0 | Dimethyl Disulfide | ND | 9.6 | ND | 2.5 |
| 616-44-4 | 3-Methylthiophene | ND | 20 | ND | 5.0 |
| 110-01-0 | Tetrahydrothiophene | ND | 18 | ND | 5.0 |
| 638-02-8 | 2,5-Dimethylthiophene | ND | 23 | ND | 5.0 |
| 872-55-9 | 2-Ethylthiophene | ND | 23 | ND | 5.0 |
| 110-81-6 | Diethyl Disulfide | ND | 12 | ND | 2.5 |

The conclusion from this initial work is that both dual layer and triple blend methods of capturing odor are very effective. Further testing is required in applications where other odors are present than those observed here. Furthermore, additional testing could be conducted with each of individual odors with single adsorbents in order to determine the effectiveness of each adsorbent for each odor.

References

[1] Chester M. Morton, P.E., Scott Tudman., "Methods For Estimating Odor Emissions," *Proceedings of the Odors and Toxic Air Emissions 2002*, Water Environment Federation

[2] Design of Municipal Wastewater Treatment Plants: WEF Manual of Practice No. 8 ASCE Manuals and Reports on Engineering Practice No. 76, Fifth Edition