NorthWest Occupational Health & Safety

H_2S, non-Newtonian Fluids and Froth Formation: A Deadly Combination

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Introduction

Over the years, the cause(s) of many accidents that occurred in the infrastructure, in industry and in agriculture involving atmospheric hazards has(have) defied identification during investigative assessment.

Typical of accidents that occurred in the infrastructure was that the workspaces were subsurface concrete structures (confined spaces) and that entries previous to the accident had occurred routinely, without incident. As determined subsequent to the accident, the atmosphere was odorless and provided no warning. Rapid collapse of the victim occurred. In some situations, carbon dioxide (CO_2) and methane (CH_4) were present at elevated level. Hydrogen sulfide (H_2S), when present at time of investigation, was not present at elevated levels. Water, but not wastewater sometimes was present.

In the situations that occurred in industry, sulphur-containing substances were known to be present in some situations. Previous entries were routine and had occurred without incident. The atmosphere at the time of the fatal accident usually provided no odor to serve as a warning, as determined afterward. The victim collapsed rapidly. CO_2 and CH_4 sometimes were present at elevated level. H_2S, when detectable at time of investigation, was present at low level.

Accidents involving unexplained causes have also occurred in agriculture. Typically, these accidents involved manure storage, handling, homogenizing, pumping, and spreading. Some occurred in typical confined spaces and others in barns and sheds and open environments. (Refer to the document on the uncharacterized workspace.) These accidents often involved multiple fatalities. The causative agent was not identified at time of accident, emergency response or follow-up investigation. The causative agent was attributed in coroners' reports typically to CH_4, CO_2, and oxygen deficiency.

A common thread in accidents occurring in many of these situations was microbiological activity involving organic material. Organic material can support growth of microorganisms, such as fungi and bacteria. Growth of microorganisms under aerobic conditions (presence of sufficient oxygen) leads to production of carbon dioxide. Growth under anaerobic conditions, as occurs under oxygen deficient conditions, leads to production of methane, hydrogen sulphide and other mercaptans, and ammonia and amines and carbon dioxide.

Beer-, Wine- and Cider-Making and Other Fermentation Processes
Beer, wine and ciders are fermented products. Beer, sparking wines and ciders embody a characteristic of the process: entrapment of carbon dioxide in the liquid due to formation of a froth on the surface during fermentation. The froth results from flotation of debris from the fruit or other source of flavor by bubbles of carbon dioxide produced during respiration.

Several recent accidents have occurred in operations involved in production of wine and apple cider.

Mushroom Composting
A fatal accident at a mushroom composting operation in which several workers died has provided a starting-point for identifying a plausible causative agent and mechanism in some of the situations mentioned above. The accident occurred during an attempt to unblock a pipe. The men were rapidly overcome by a lethal atmosphere. The causative agent was not identified or identifiable during subsequent investigation.

Follow-up investigation at another composting operation provided what appears to be an important clue. The outdoor surroundings of these operations normally are odorless because of an odor-entrapment and control system. The odor of H_2S suddenly appeared without warning in a large, outdoor area between the two large buildings in which composting occurs. There was no apparent activity to indicate the cause.

The source of the odor was a pump station. A pump station is a subsurface chamber containing pumps and associated piping and valves. Water collects from a source, in this case a large pit in which soaking of bales of straw was occurring to prepare them for composting. Water in the pump station was actively frothing (effervescing) during collection and pumping. The monitoring instrument indicated very high levels of H_2S in the airspace above the pump station. This was the only occasion during several visits to this composting operation during which an odor was detectable and the emission of gas measurable.

This water is known as ‘goody water’. The term, ‘goody’, refers to nutrients retained in the water from previous soakings. The farmer uses this water to soak the straw prior to composting. and collects and reuses it. The compost recipe contains gypsum (calcium sulfate), chicken manure and other ingredients. The appropriate bacteria in the environment, given appropriate nutrition, have the ability to convert sulfates to H_2S.

Emission of H_2S occurred only during drainage of water from the soaking pit and operation of the pump in the pump station. Prior to the operation, the emission was not occurring. Subsequent to shutdown of the pump after dispersal of the gas, the emission no longer occurred. That is, the emission was related to the action of pumping. This counters the logical presumption that emission of gas would occur continuously, albeit at much lower rate from the entire surface of the water in the soaking pit, and that rapid release could not occur, unless another mechanism was operative. The expectation was that detection of H_2S during soaking in an open pit should occur, since the nose is extremely sensitive to low levels.

This situation paralleled emission of H_2S described in anecdotal reports. These reports have indicated transient presence of quantities of H_2S detectable by instruments during movement through sludges in drainage structures and in marshes and swampy environments. Reports also have indicated emission of transient detectable quantities during excavation at sites known to contain buried vegetation, wood and garbage. Transience means brevity in time.

Manure Handling and Processing
There are parallels between mushroom composting and manure handling. Manure is the waste produced by farm animals. Farm animals produce manure in all locations, indoor and outdoor, in which they spend their lives. Manure handling is one of the major considerations and concerns in the operation of every farm

in which animal husbandry occurs.

In modern dairy farms, manure handling is a mechanized process. Mechanical scrapers remove the manure from the stalls in the barn in which the animals spend much of their time. The mechanical scrapers move the material along the floor to a drop point where it falls into a chamber located partly or completely under the barn. This equipment moves very slowly so as not to injure the animals. The subfloor chamber may contain mechanical scraping equipment for moving the manure to a central collecting point where it is transported in piping to settling and storage structures.

Manure contains bedding material, as well as undigested solids. Bedding material includes sand, sawdust, planer chips, chipped wood, or possibly straw. The manure handling system contains size reducing equipment to enable transport to storage structures. This equipment includes specifically installed equipment, as well as propeller-type units powered by the power take-off unit on the tractor. Blockage of equipment and piping in the manure transport system is a well-recognized, never-ending problem.

At this time, farmers in most jurisdictions do not process manure, but store solid fractions in piles located on open ground and in sub-grade settling pits, and liquid fractions in concrete and steel tanks, and concrete and dug-out pits, depending on the specific configuration of the manure-handling system.

Manure storage is conducive to aerobic and anaerobic microbial processes. These processes employ bacteria already present in the waste, and bacteria, yeasts and other microorganisms characteristic of the process The latter bacteria may differ from those in the waste, depending on growth conditions. Digestion is incomplete in both types of process. This leaves behind a large volume of sludge requiring disposal.

Manure provides considerable economic value to farmers, as well as creating considerable obligations and potential and real problems. Manure has greatest economic value when undiluted by other sources of water, namely surface run-off from rain and snow, groundwater, and water from farm-related activities, such as operation of the milk parlor and floor cleaning. The farmer's perspective is that the extra water increases the energy, and hence, the economic cost of distributing the manure on the fields. The increased volume and ability to cover greater area are not considered beneficial in this discussion.

Storage of manure on dairy farms occurs for up to one year. Storage structures include open-topped concrete and steel tanks and earthen dug-outs, as well as enclosed structures, such as the under-barn structure mentioned above.

Material that is not mechanically mixed tends to separate into three discrete layers: froth, foam or scum on the surface, a watery layer and sludge that settles to the bottom of the structure. The surface layer develops as a result of emission of gases, mainly carbon dioxide, during anaerobic digestion in the watery layer and the sludge. Anaerobic digestion occurs until the temperature in the liquid decreases to about 6° C. The crust is beneficial to the process. It reduces odor due to emission and the loss of ammonia nitrogen and other gases from the liquid layer and may also provide insulation to prolong bacterial action during cold weather..

During the spring, the farmer deposits liquid manure on the fields. This is a departure from the more traditional spreading of solid manure. Liquid handling is less labor-intensive. In preparation for this activity, the farmer uses mechanical equipment, often powered by the power take-off on the tractor to agitate the material. The farmer then pumps the homogenized material into the tank of a liquid manure spreader. This equipment distributes the liquid through a boom that drags along the ground.

Agitation is the technique employed to homogenize the contents of the storage structure. The process of homogenization must destroy the crust and mix into suspension, a large part of the bottom sludge. The surface crust can become highly resistant to destruction. A tractor PTO-powered propeller is the common agitator because it moves a greater volume of water per minute for a given horsepower. Positioning the propeller slightly below the surface at a shallow angle will direct the flow into the crust. Directing flow along the sides of the structure is more effective than directing flow to the middle. Only deep agitation can suspend bottom sludge. Agitating deeply in one location for more than a few minutes can rupture the bottom seal and cause the lagoon to leak to groundwater.

Achieving thorough mixing may require agitation from more than one location. The contents are ready for pump-out when they swirl and move around. Maintaining the suspension of solids during pump-out may necessitate constant agitation.

When all of the mystique about manure is stripped away, what is processed in a manure storage structure in which anaerobic digestion is occurring reflects what is fed to it. This comment applies also to the ‘goody’ water used in mushroom composting. Goody water contains remnants from chicken manure and gypsum contained in the recipe.

Manure contains proteins, carbohydrates and fats and oils. Urea also may be present as an excretory product in the manure. However, urea decomposes rapidly to form ammonia. Proteins are composed of amino acids, which in turn are composed of molecular structures containing carbon, hydrogen, nitrogen, and some oxygen and sulphur. Carbohydrates contain carbon, hydrogen, and oxygen. Fats and oils contain carbon, hydrogen, and oxygen. Urea contains carbon, hydrogen, oxygen, and nitrogen.

Hence, proteins and urea are almost exclusively the source of the odorous compounds containing nitrogen detected at various stages of anaerobic digestion. Proteins are almost exclusively the source of H_2S and other odorous compounds containing sulphur.

Non-Newtonian Fluids and Entrapment of Gases

As mentioned previously, solids settle to the bottom of the liquid and form a sludge. This happens with the mash in beverage production, the material in the goody water and with components in manure.

Liquid manure is known in the agricultural engineering literature as a pseudo-plastic, shear-thinning, non-Newtonian fluid. This characteristic may have significant importance to understanding the mechanism of accidents that have occurred on dairy farms involving manure, and possibly the mushroom composting operation and the sources of emission reported earlier.

Viscosity of non-Newtonian fluids is related to applied stress.In technical terms, the relation between the shear stress and the strain rate in a Newtonian fluid is linear and passes through the origin (0,0 on a graph) (Anonymous 2010). The slope of the line is the coefficient of viscosity, a constant value. In a non-Newtonian fluid, the relation between the shear stress and the strain rate is a curve that lies above or below the line of the linear relationship, depending on the properties of the fluid. This curve can even be time-dependent. Hence, viscosity of non-Newtonian fluids is not a constant value.

Many polymer solutions and molten polymers are non-Newtonian fluids, as are many common substances, such as ketchup, paint, blood and shampoo. Paint and catsup are also examples of shear-thinning, non-Newtonian fluids. They require application of force before they begin to flow. When first handled, the paint in a can is very stiff and resists stirring. Gradually the paint loosens and is able to be stirred with little effort and is ready for application. The stress of stirring causes the paint to change from being thick like honey to flowable like water. When applied, the shear created by the brush or roller thins the paint and enables easy coverage of the surface. The viscosity restores and prevents drips and runs. The paint formulator wants the paint to flow readily off the brush or roller when applied to the surface, but not to drip excessively.

Entrapment of gases in sludges of various origins creates an unstable, constrained system. The action of homogenizing the manure prior to pumping for distribution onto the fields creates tremendous turbulence with the accompanying release of gases in solution or adsorbed or trapped in some manner in the material. These gases have caused fatalities during manure disturbance and handling, similar in concept to the situation that occurred at the mushroom composting operation.

The phenomenon of entrapment of gases and the need to allow escape of trapped gases from manure at various stages in manure storage and handling are well-known to farmers involved in animal husbandry and readily acknowledged in the agricultural health and safety literature.

Froth Formation and Entrapment of Gases in Liquids

Froth formation results from anaerobic respiration by bacteria and yeasts and production mainly of CO_2. The CO_2 forms bubbles. The bubbles rise to the surface, bringing with them debris. A crust of pulp and other remnants of fruit and plant products used in the recipe forms on the surface. This crust forms a constraining layer to the effusion of carbon dioxide and other gases from the liquid below. In the presence of a constraining layer, the gas remains trapped in the liquid, thus forming an unstable, constrained system

The force exerted on the surface by the froth can pressurize the gas in the liquid underneath to about one atmosphere of pressure (100 kPa or 14.7 lb/in^2). As anyone who has opened a bottle of sparkling wine soon learns, this represents an unstable system. Gas evolves rapidly from the liquid during the depressurization that accompanies opening the bottle. This is also true for beer and carbonated soft drinks.

Together these features can create a highly unstable constrained system, as reflected by common experience and open discussion in the agricultural literature. This system can release gas to the atmosphere from the exposed liquid when the crust is broken and from the sludge when the viscosity decreases following application of a shear force such as movement of feet or a struggling animal. The system can rapidly return to the *status quo* once the gas depletes from the exposed liquid and the viscosity rebuilds in the sludge.

Causative Agent

Taken together, the accidents summarized in the Introduction indicate rapid collapse of individuals exposed to a highly toxic, rapid-acting, transient atmospheric agent. This agent was able to kill one or more individuals during these accidents and was present in open areas, buildings and confined spaces. (Refer to the article on uncharacterized workspaces.) Previous discussion indicates a possible link to non-Newtonian fluids and release triggered by strenuous disturbance due to agitation or other disruptive action.

Investigators and coroners' reports have attributed causality for accidents involving manure to various gases, including oxygen deficiency, CH_4, and CO_2. Yet, the attributed causes are not consistent with physical properties and physiological actions of the gases mentioned.

Oxygen deficiency is a major concern in the occupational setting and a topic of discussion in many standards and regulations. Typically, the following Table 1 or a similar version which, appears in publications, summarizes the effects of acute exposure to oxygen-deficient atmospheres as commonly reported based on concentration and partial pressure.

Table 1
Effects of Acute Exposure to Oxygen Deficient Atmosphere

	Atmospheric Oxygen (dry air, sea level)	
Effect	**Concentration** %	**Pressure** mm Hg
no symptoms	16 to 20.9	122 to 159
increased heart and breathing rate, some incoordination, increased breathing volume, impaired attention and thinking	16	122

abnormal fatigue upon exertion, emotional upset, faulty coordination, impaired judgment	14	106
very poor judgment and coordination, impaired respiration that may cause permanent heart damage, nausea and vomiting	12	91
nausea, vomiting, lethargic movements, perhaps unconsciousness, inability to perform vigorous movement or loss of all movement, unconsciousness followed by death	< 10	< 76
convulsions, shortness of breath, cardiac standstill, spasmatic breathing, death in minutes	< 6	< 46
unconsciousness after one or two breaths	< 4	< 30

Oxygen deficiency develops only in limited ways. One of these is dilution or displacement by other gases. This could occur following rapid effusion of gas from the manure. This mechanism is rapid and reflects a massive change in the *status quo*, as would occur during mixing to create a homogeneous mixture in preparation for pumping and distribution on the fields. Oxygen deficiency under this condition could develop only where enclosure by boundary surfaces is present in order to contain the atmosphere.The air space above the manure in open dugouts exposed to normal atmospheric conditions of wind can contain normal atmospheric levels of oxygen. This may not be the case in deep structures with high straight walls.

Respiration by microorganisms, both aerobic and anaerobic is a very slow process. Development of an oxygen-deficient atmosphere during aerobic respiration depends on enclosure and quiescence and the absence of ventilation, especially natural air flow caused by wind and thermal buoyancy. An oxygen-deficient atmosphere is easily prevented and just as easily relieved in structures that are open to natural air flows, such as the wind.

Methane, mentioned in coroners' reports as a possible causative agent, is considerably less dense than air and would tend to escape from enclosed chambers through vents. Until recently, methane was regarded as a simple asphyxiant. As such, the killer in such accidents would be oxygen-deficiency, as testing would have indicated, had this been the case.

Carbon dioxide is about 1.5 times as dense as air at the same temperature. CO_2 could accumulate in enclosed structures for this reason. CO_2 is a product of human and animal respiration and is tolerated at concentrations considerably above normal atmospheric levels. CO_2 acts as a respiratory stimulant at elevated levels. At concentrations at which CO_2 poisoning would occur, oxygen deficiency would also occur because dilution of the atmosphere would accompany carbon dioxide poisoning as a cause of death at high levels.

Gases and vapours dissolve in water and either remain intact, as in the case of methane, or react chemically with water to form an acid and an anion.

Given the opportunity, gas molecules dissolved in water establish an equilibrium with gas molecules in the air in the space above the liquid at a particular pressure. To illustrate, hydrogen sulfide exists in water as molecules in equilibrium with H_2S molecules in air and also reacts with water to form hydrosulfide (HS^-) ions, as described in the following equation:

$$H_2S_{(\text{gas in air})} \leftrightarrow H_2S_{(\text{gas in liquid})} \leftrightarrow H^+ + HS^-$$

Hydrosulfide ions can further react with water to form sulfide ions (S_2^-). At pH = 7, half of the sulfide in the water is present as H_2S molecules and half as hydrosulfide ions. Lowering the pH to 5 converts all of the hydrosulfide ions to H_2S molecules. The presence of greater numbers of H_2S molecules in the water displaces the equilibrium with the result that there are more H_2S molecules in the air above the water. The following equation describes this equilibrium.

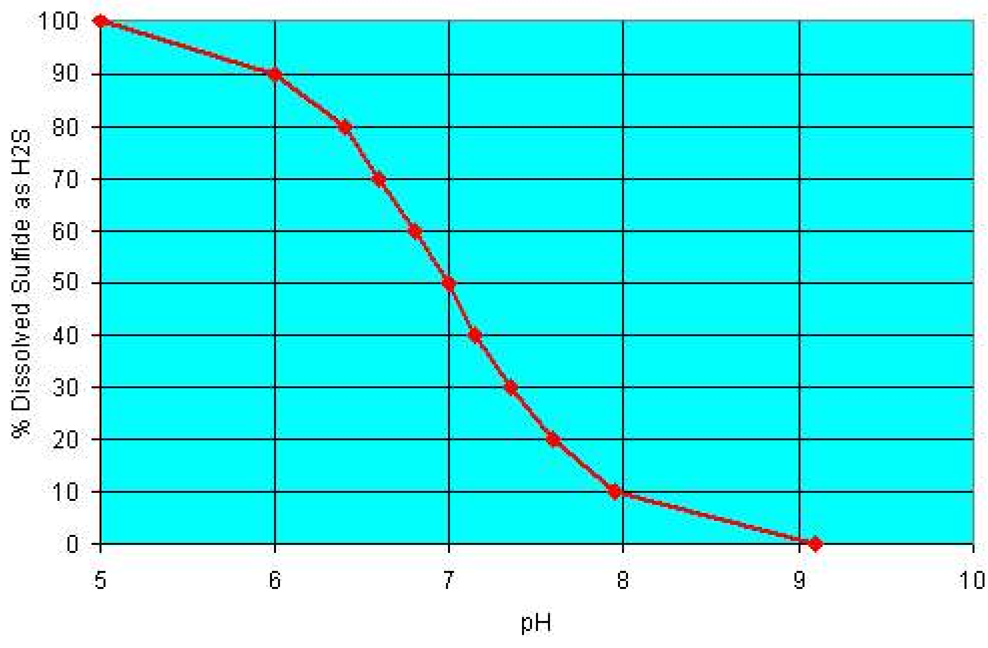
$$pH = pK_A + \log\frac{[A^-]}{[HA]}$$

pH is a measure of the acidity of alkalinity of the liquid.
pK_A is a value measured for the substance. Reference textbooks contain tables of pKA values.
HA is the molecular form, in this example, H_2S.
A- is the ionized form, in this example, HS^-.

The value of pk_A for H_2S is 7.0. At this pH, the concentration of A^- equals the concentration of HA because the log term is zero. (The log of 1 is zero). At this pH, half of the dissolved sulphide is present as H_2S molecules. The following Figure 1 illustrates the concept.

This situation also applies to ammonia and other amines that are gases, and to carbon dioxide. The pH of manure ranges from 6.5 to 7.2 during the stable period of anaerobic digestion. As a result, the equilibrium shifts toward molecular H_2S.

Figure 1
H_2S Molecule – HS^- Ion Equilibrium



Since the manure is the source of the H_2S molecules in the liquid, this also is the source of the H_2S molecules in the air. The ability of H_2S to accumulate in the air depends on many factors, including quiescence and the presence or absence of natural or mechanical ventilation, the extent of enclosure of the chamber, temperature, viscosity of the liquid and the presence of a constraining layer on the surface.

The measured value that describes the relative distribution of molecules between the atmosphere and the liquid is the Henry's constant, the air-to-liquid partition coefficient. This value is a ratio of the concentration of gas in the air to the concentration of gas in the liquid. Henry's constant depends on a number of factors, including temperature and pH of the liquid. Similar considerations apply to other gases and vapors generated from substances present in the manure.

Table 2 summarizes the values for the most important and prevalent substances. A large value of the Henry constant indicates the insolubility of the gas in water, as is the case with methane. Separating the water-reaction component from the molecular-solubility component of gases that react with water may not be possible. These data also indicate that ammonia preferentially remains in the water.

Table 2
Properties of Gases

Substance	pK_A	Henry' Constant	IDLH	$LC_{(50,\ 4\ h)}$
hydrogen sulfide	7	5.5	100 ppm	337 to 444 ppm
carbon dioxide	6.4	16.5	40,000 ppm	100,000 ppm
ammonia	9.2	0.03	300 ppm	2420 ppm
methane	not applicable	374	not available	not available

Hydrogen sulfide is an extremely dangerous gas compared to the others mentioned in Table 2. The IDLH (Immediately Dangerous to Life and Health) and $LC_{(50,\ 4h)}$ (Lethal Concentration to 50% at 4 hours) are considerably lower than the values for the other gases. While at low concentration, H_2S has the readily recognizable odor of rotten eggs, olfactory paralysis can occur rapidly such that no odor is detectable. This can occur at concentrations in excess of 100 ppm (parts per million, a unit of concentration). Rapid collapse can occur after one or two breaths at concentrations exceeding 500 ppm. H_2S paralyzes the respiratory center in the brain and the victim is unable to breathe.

This information suggests that an episode involving a toxic exposure to H_2S can occur very quickly and involve a small quantity of gas emitted from a small area of surface. This reality also suggests that the episode could affect more than one person, including would-be rescuers. As well, the atmosphere could disperse rapidly before responders equipped appropriately to effect rescue could arrive on the scene.

Discussion

This article has provided information available from several sectors about the manner in which fatal accidents involving hazardous atmospheric conditions have occurred. The causative agent in these accidents defied detection in follow-up investigations. This situation is consistent with rapid evolution of relatively small quantities of gas from an unstable, constrained system. This can occur following puncture of a crust of material floating on a liquid and release pressurized gas, and/or through disturbance of sludge under the liquid. This can result from the action of footsteps or by operation of a tractor-driven pump attempting to break the crust and to homogenize the contents (crust, watery layer and sludge) in a manure storage structure.

References

Anonymous: Non-Newtonian Fluids. San Francisco: Wikimedia Foundation Inc., 2010. [website]

McManus, N.: Safety and Health in Confined Spaces. Boca Raton, FL: Lewis Publishers, 1999.

McManus, N.: The Confined Space Training Program, Worker Handbook. North Vancouver, BC: Training by Design, Inc., 2004.

NIOSH: Worker Deaths in Confined Spaces (DHHS/PHS/CDC/NIOSH Pub. No. 94-103). Cincinnati, OH: National Institute for Occupational Safety and Health, 1994.