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# Non-Newtonian Fluids and Uncontrolled Emission of Toxic Gases: A Major Threat to Worker Safety

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## Abstract

This article explores the role of shear-thinning, pseudoplastic non-Newtonian fluids in the causation of fatal accidents involving hazardous atmospheres. Analysis of fatal accidents indicates an appreciable likelihood of occurrence in structures in the infrastructure. When subjected to a shear force, such as stirring, stored gas emits from these fluids. Depending on the gas, lethal concentrations can develop almost instantaneously. Upon cessation of the stress, the ambient condition restores rapidly. Chemical and physical processes that provide reservoirs for the storage of gases potentiate anaerobic respiration by microorganisms as the source of the gases stored in some non-Newtonian fluids. Hydrogen sulfide ($H_2S$) is the most toxic gas followed by carbon dioxide ($CO_2$) and ammonia ($NH_3$). Very limited methods are available for controlling exposure to gases emitted during the disturbance of these fluids. Control strategies must accommodate almost instantaneous high-level emissions. Disturbance under controlled conditions that isolates emissions from workers is a possible means to minimize the risk of exposure. Engineering design that incorporates suitable control devices into equipment and structures is critical to the success of this strategy. The Prevention through Design program created by the U.S. National Institute for Occupational Safety and Health is a formal initiative for coordinating an organized response to these challenges.

## Keywords

$CO_2$, $H_2S$, Confined Spaces, Fatal Events, Lethal Atmosphere, Infrastructures, Shear-Thinning, Pseudoplastic, Non-Newtonian Fluid, pH, Trapped Toxic Gas, Uncontrolled Rapid Emission

## 1. Introduction

Fluids are substances in which all elements no matter how small share common

characteristics [1]. Fluids deform continuously under the application of a shear force. That is, the application of a shear force is essential to produce the deformation. In the absence of the shear force, the deformation ceases and disappears. The application of shear forces can occur through translational, reciprocating, and rotational movement applied to the fluid. Rotation or agitation of a fluid induced by stirring by a mixer or the impeller of a pump is a common example of the application of a shear force. In liquids, resistance to deformation is primarily controlled by cohesive forces between and among molecules because of the close packing. Cohesive forces and hence the viscosity decrease with increasing temperature.

Fluids in which shear stress is directly proportional to the rate of deformation are classified as Newtonian fluids [1] [2]. Conversely, fluids in which the shear force is not directly proportional to the rate of deformation are classified as non-Newtonian fluids. Most non-Newtonian fluids are shear-thinning, pseudoplastic, meaning that the apparent viscosity decreases with increasing rate of deformation. The converse is also true. The viscosity restores once the shear force is removed.

The flow of non-Newtonian (non-linear) fluids occurs not only in nature, for example, mudslides and avalanches, but also in many industrial processes involving chemicals (polymers), biological materials (blood), food (honey, ketchup, yogurt), pharmaceutical and personal care items (shampoo, creams), etc. [3] [4]. In the case of shear-thinning, pseudoplastic non-Newtonian fluids, the more the fluid is sheared, the less viscous it becomes [4]. A good example is paint. Paint is very viscous when poured from the can or when picked up by a paintbrush since the shear rate is small. During application of the paint to the wall, the thin layer between the paintbrush and the wall is subjected to a large shear rate and becomes considerably less viscous.

Gas accumulation in non-Newtonian fluids is an important consideration in many industries, including chemical, biochemical, and food processing [5] [6] [7]. Considerable engineering attention is paid to the controlled removal of dissolved gas from solutions and mixtures of these fluids. Mechanically agitated vessels are commonly employed in these processes because they promote a high degree of contact between the phases. Mixing non-Newtonian fluids to expel gases in a controlled way involves variables including volumetric mass transfer coefficient, power consumption, gas holdup, bubble diameter, and cavern size.

Gas accumulation and desorption involving shear-thinning, pseudoplastic non-Newtonian fluids also occur under uncontrolled conditions. Uncontrolled release of gases from non-Newtonian fluids is an area of immense importance and concern particularly in regard to worker safety and potential and actual causation in serious and fatal industrial accidents. This concern is unrecognized and unreported in the literature.
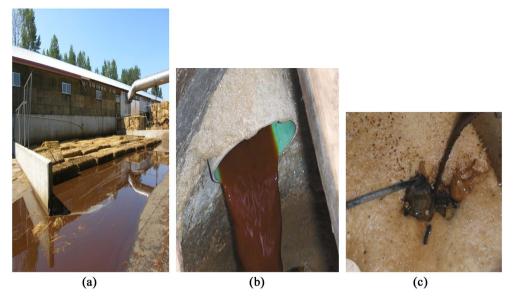
A recent article [8] provides one of the few sources of quantitative information concerning gas release within the context of this discussion. This article pertained to the unexpected release of hydrogen sulfide ($H_2S$) into the airspace

of a very large excavation during the removal of disturbed soil used for fill. $H_2S$ is readily recognizable at a very low level by the characteristic odor of rotten eggs. The literature contains no information concerning worker exposure to $H_2S$ in these situations. The source of the $H_2S$ was believed to be the anaerobic metabolism of sulfur-containing organic matter located along the former shoreline or material dumped onto the shoreline to raise the level of the ground prior to industrial development or prehistoric geologic processes.

Levels of $H_2S$ detected by a Jerome 631-X (an instrument of high sensitivity) ranged from 1 ppb (part per billion) to 25 ppb in 1-min samples during various activities [8]. This situation provided important information concerning the emission of $H_2S$ under two semi-repeatable conditions, namely background activity and excursions. Levels increased from zero when activity began and decreased to zero when activity ceased. Unpredicted excursions peaking at 2500 ppb superimposed onto background levels immediately followed the exposure of material containing trapped $H_2S$. Material containing trapped $H_2S$ typically was either very wet or wet enough to show plastic behavior. Excursion levels rose abruptly, peaked, and decreased rapidly to the background. Excursions occurred once per day and lasted about 10 min.

These emissions share characteristics of shear-thinning, pseudoplastic non-Newtonian fluids as described above [2] [4]. A very conservative estimation of exposure during this work compared to the 8-hour Threshold Limit Value-Time-Weighted Average (TLV-TWA) of 1 part per million (1 ppm = 1000 ppb) suggested that it was considerably less than the lowest level of regulatory concern and that work under these conditions could proceed without overexposure to $H_2S$. (The 8-hour TLV-TWA published by the American Conference of Governmental Industrial Hygienists is used in many jurisdictions as a regulatory Exposure Limit [9].)

An unpublished investigation performed by the author provides additional quantitative information. This event involved unexpected and unpredicted emission of $H_2S$ from a pump station (A pump station is an in-ground chamber containing one or more pumps which drains water from a defined source). This pump station has a large open top located just above ground level. The liquid involved was used in the production of compost for growing mushrooms. This liquid contained water, gypsum ($CaSO_4$) from recycled drywall, chicken manure, and possibly other undisclosed ingredients.

Prior to the start of this event, there was no odor or bubbling in the water (Figure 1(a)). The odor of $H_2S$ suddenly appeared without warning in the large, outdoor area between the two large buildings in which composting occurs. There was no apparent activity to indicate the cause. There was no evidence of emission from the water in the soaking pit. The source of the odor was the pump station. Water entering the pump station was the same brown color as the water in the soaking pit (Figure 1(b)). Operation of the pump caused bubbling and the formation of a beige-colored foam (Figure 1(c)).

**Figure 1.** (a) It shows the soaking pit containing bales of straw and brown "goody" water. Notice the absence of bubbling on the surface of the liquid. (b) It shows entry of brown liquid from the green drain pipe into the pump chamber and the presence of beige-colored foam. (c) It highlights the role of rotation of the impeller of the pump in formation of the beige-colored foam. The beige-colored foam contains the $H_2S$. $H_2S$ escapes into the chamber following breakage of the bubbles.

The rapidly increasing level of $H_2S$ (~200 ppm) on the monitoring instrument in the environment adjacent to the pump station forced rapid evacuation from the area. This was the only occasion during several visits to this composting operation during which an odor was detectable by nose and emission of gas detectable by the monitoring instrument.

Emission of $H_2S$ occurred only during the drainage of goody water from the soaking pit and operation of the pump in the pump station. Subsequent to the shutdown of the pump, emission ceased. That is, the emission was related solely to the operation of the pump.

The observations reported above are consistent with the behavior of shear-thinning, pseudoplastic non-Newtonian fluids as described previously [1-7]. The concern expressed in the limited example [8] for which quantitative data exist has wide repercussions in industry. This concern reflects the design and operation of industrial equipment and structures employed in this type of service. Knowledge about this phenomenon is essential for designers and practitioners in other disciplines of engineering because design is the first link in the chain that influences the conditions of work. This concern is particularly important in the emerging areas of "green" and "sustainable" design where there is an emphasis on the storage and reuse of drainage water and heat recovery from wastewater.

The focus of this Review is to:
- identify serious and fatal events caused by uncontrolled release of gas(es) from non-Newtonian fluids in structures in the infrastructure;
- identify and discuss potentiating mechanisms involved in these releases;
- alert designers in particular those involved in design of "green" and "sus-

tainable" structures about implication of choices made in design;

- identify and discuss precautionary measures for minimizing the occurrence of these events.

## 2. Shear-Thinning, Pseudoplastic, Non-Newtonian Fluids in Fatal Accidents

### 2.1. Historical Records and Studies

The U.S. Occupational Safety and Health Administration (OSHA) and National Institute for Occupational Safety and Health (NIOSH) published several studies that provided summaries of fatal accidents that occurred in confined spaces [10]-[15]. Confined spaces are workspaces that pose elevated risks compared to "normal" workspaces because of atmospheric and other hazards [16]. McManus and Haddad [17] reported on a technique to deconstruct these summaries in order to extract to the extent possible additional information. McManus [18] summarized the results from this analysis.

One of the important findings from this analysis [18] was the occurrence of fatal events involving hazardous atmospheres not having identifiable cause(s). Conditions had restored to normal soon after the accident at the time of discovery of the deceased. These situations occurred in confined spaces in the subsurface municipal infrastructure and in infrastructure in industry and agriculture. Investigators historically and into the present have been unable to discover the cause of these events despite today having considerably better instruments.

Some of the structures in which these events occurred were fully enclosed while others were open at the top. Open-topped structures are commonly found in agriculture. Enclosed structures typically are entered through manhole covers and hatches. Some manhole covers possess no opening to the atmosphere while some possess one opening and some, two or more openings. Some structures are networked together while others are isolated.

Common to all structures in outdoor locations was accumulation of water and organic materials [18]. Relevant indoor structures in animal husbandry also fit this description. Accumulation of water and organic materials in outdoor structures occurs through gaps in incompletely closed covers and openings used for inserting tools used for removal.

Organic material included leaves and fragments of leaves, dusts produced by processing facilities, insects and spiders and possibly small animals [18]. Microorganisms including bacteria and fungi (yeasts and molds) can populate these structures. Bacteria, yeasts and some fungi grow in wet areas. Molds grow on surfaces having a range of moisture.

Analysis performed by McManus [18] on accident summaries provided in historic reports [10]-[15] [18] indicated that events in the municipal infrastructure typically occurred in subsurface concrete structures and that previous entries had occurred routinely, without incident. As determined subsequent to the event, the atmosphere typically 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 when present at time of investigation, was not present at elevated levels. Water, but not wastewater sometimes was present.

In the events that occurred in industry, sulfur-containing substances were known to be present in some situations [18]. Previous entries were routine and had occurred without incident. The atmosphere at the time of the fatal event 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.

Events occurring in agriculture typically involved manure storage, handling, homogenizing, pumping, and spreading [19] [20]. Some occurred in typical confined spaces and others in barns and sheds and open environments. These events often involved multiple fatalities. The causative agent was not identified at time of accident, emergency response or follow-up investigation. The causative agent was variously attributed in coroners' reports without confirmatory proof to $CH_4$, $CO_2$, and oxygen deficiency.

OSHA maintains a database containing summaries of fatal events [21]. These are searchable according to type of work location. Review of recent documents and summaries of fatal events in comparison to historic ones and the work of McManus [18] indicates the ongoing repetition of fatal events that occur in almost the same manner under the same circumstances despite the effort expended by regulators, employers, workers and worker representatives, and practitioners in occupational health and safety to prevent their reoccurrence. Some of these events show characteristics of involvement of non-Newtonian fluids.

## 2.2. Natural Processes and Shear-Thinning, Pseudoplastic Non-Newtonian Fluids

Several processes exploited in industry offer possible assistance in addressing the questions posed in the Introduction. Practitioners engaged in commercial application of a process have the advantage sometimes of centuries of background knowledge and experience. This information could include controlled studies; revelations gained through happenstance; experience concerning practical application and optimization of the process; hazardous conditions created by it; and methods of control.

### 2.2.1. Emission of $CO_2$: Beer-, Wine-, Cider-Making, and Other Fermentation Processes

Beer, wine and ciders are produced through fermentation of sugars by yeast, a type of eucaryotic microorganism [22]. Sugars do not contain sulfur. As a result, fermentation is not a major source of $H_2S$.

Beer, sparkling wines and ciders share a common characteristic namely entrapment of $CO_2$ in the product during fermentation. Personal experience in winemaking shows that this entrapment begins during primary fermentation

and results in formation of froth on the surface of the liquid, a watery intermediate layer, and a settled layer of debris on the bottom of the container. The froth contains debris from the fruit. Emission of gas from this system is not evident in the absence of disturbance.

Agitation rapidly destroys the foam and causes vigorous bubbling in the liquid. This disturbance rapidly liberates $CO_2$ trapped in the foam and the watery layer. Following cessation of stirring, the surface calms rapidly and obvious emission of gas ceases. This suggests that emission of gas is initiated and controlled by the stress applied by stirring and causes an almost instantaneous major change in the status quo.

The history of fermentation contains numerous episodes of fatal events [23] [24] [25] that chronicle the outcome of uncontrolled emission of $CO_2$ from substances involved in fermentation. One event involved partial entry of a worker through an access hatch located near the top of a secondary fermentation tank during sample-taking. The victim leaned into the opening while dangling a container and was overcome by emissions from the surface of the liquid trapped in the airspace of the tank. Another event occurred inside a drained fermentation tank following entry for removal of residues remaining from secondary fermentation. The worker was shoveling the residues into a bucket to be lifted through the access opening and was overcome by emissions during disturbance of this material.

Undocumented anecdotes have reported on other events. In one situation at a winery, birds flying in the roof space of a production building died suddenly. The birds were overcome by emissions from open tanks involved in primary fermentation.

### 2.2.2. Low-Level Emission of $H_2S$

Relevant examples of low-level emission of $H_2S$ of possible importance for explaining the mechanism involved in fatal events exist in anecdotal reports passed verbally from person to person. These episodes are transient, infrequent, and short in duration.

One common example of low-level emission of $H_2S$ occurs during walking through wet swampy areas containing still (stagnant) water. Anecdotal reports indicate that no odor is present until the area is disturbed by stepping through the water onto the bottom. The action of pressing the foot into the bottom material and lifting the foot and repeating this action is sufficient to release $H_2S$ trapped in the sludge under the water. The odor of $H_2S$ ceases rapidly when walking stops. Emission of $H_2S$ in wetlands is well-documented [26] [27] in environmental studies. However, these studies do not quantitate exposure of investigators to $H_2S$.

### 2.2.3. Lethal Emission of H2S: Mushroom Composting

A fatal event at a mushroom composting operation in which several workers died [28] has provided a starting-point for identifying a plausible causative agent

and mechanism in some of the situations mentioned in previous discussion. The event occurred during an attempt to unblock a pipe in a facility that manufactured compost for growing mushrooms. The victims were rapidly overcome by a lethal atmosphere. The causative agent was $H_2S$. The mechanism of emission was not identified during subsequent investigation. No measurement of $H_2S$ levels occurred.

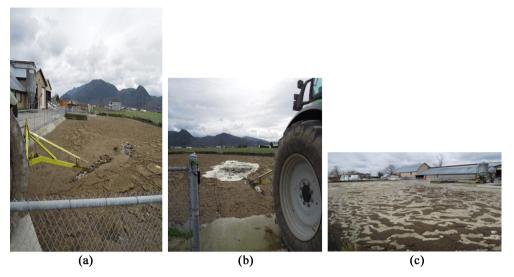### 2.2.4. Lethal Emission of H2S: Manure Handling and Processing

There are parallels between mushroom composting and manure handling. Manure handling has caused many fatal events and has prompted considerable investigative research [29] [30] [31]. 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. Manure storage involves structures in the infrastructure of the farm. Research to date has focused on laboratory-scale study and area measurements in buildings but not situations involving massive, rapid emission of $H_2S$.

The following information reflects experience gained by the author of this article from visits to dairy farms. 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 storage is conducive to aerobic and anaerobic microbial processes [22]. These processes employ bacteria already present in the waste, and bacteria, yeasts and other micro-organisms 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 and solid material requiring disposal. This material has economic value as fertilizer.

Material that is not mechanically mixed tends to separate into three discrete layers: froth, foam or scum on the surface; a watery layer in the middle; and sludge that settles to the bottom of the storage structure. The surface layer develops as a result of emission of gases, mainly $CO_2$, during anaerobic digestion in the watery layer and the sludge.

During the spring, the farmer uses mechanical equipment, often powered by the power take-off on the tractor to agitate the material in the storage structure (Figure 2). Agitation homogenizes 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

|     |     |     |
| --- | --- | --- |
| (a) | (b) | (c) |

**Figure 2.** (a) It shows the manure storage pond at the beginning of the agitation procedure. Notice the brown hardened crust on the surface. There was no odor detectable by nose. (b) It shows the beginning of agitation and the beginning of formation of beige-colored froth. (c) It shows the dispersion of froth and the remains of the crust near the end of the procedure.

destruction. A tractor PTO-powered propeller is the common agitator because it moves a greater volume of water per minute for a given amount of engine power.

Positioning the propeller slightly below the surface at a shallow angle directs the flow into the crust. 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. 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.

The monitoring instrument in the southeast corner of the structure visible in **Figure 2(a)** indicated 7 ppm of $H_2S$ during homogenization. The foam visible in **Figure 2(b)** and **Figure 2(c)** was very similar in appearance and color with that in **Figure 1(c)**. Monitoring performed during agitation of manure in a considerably smaller structure located outdoors in an area partly enclosed by walls indicated 12 ppm of $H_2S$ during the procedure.

### 2.2.5. Work in Sewers

There are many examples of work situations in sewers in which serious and fatal accidents have occurred. One example of low-level emission of $H_2S$ for which monitoring data is available is an anecdote concerning removal of gravel from the inside of a culvert used to channel surface drainage to the ocean. This occurred near a former fish processing plant. Surface water from the plant was known to have entered the drainage collection system. The workers reported that there was no odor when they entered the culvert to begin the work and that the odor developed almost immediately following the start of disturbance of the gravel. This emission caused the $H_2S$ sensor in the instrument that they were carrying to sound the alarm. The workers stopped work immediately after the alarm sounded and vacated the space. The set-point for the alarm was 10 ppm.

Had the workers continued to work, without respecting the alarm, their exposure would have been considerably higher and not predictable given the information provided.

A second example highlights the extreme nature to which these situations can extend. A crew was removing debris from an in-service sewer line for installation of a cured-in-place interior liner [32]. The sewer line measured 0.6 m wide by 1.5 m high and 183 m long. The sewer line contained 0.3 to 0.6 m of untreated sewage that had stood inactive for about 10 days prior to entry of the cleaning crew of two workers through a manhole at the downstream end of the section. The workers walked upstream toward an open access pit where other workers were preparing for installation of the liner. When the cleaning crew called for help, five co-workers attempted to rescue them. They also were overcome.

Emergency personnel from the local fire department entered the access pit after donning Self-Contained Breathing Apparatus (SCBAs). They lifted the seven workers out of the pit with the aid of a nearby mobile crane. The two workers walking in the pipe were found face down in the sewage and had drowned. None of the workers was wearing a respirator nor were air monitoring and ventilation occurring. The cause of the accident was attributed to release into the airspace of $H_2S$ likely provoked by disturbance of settled material as the men walked along the line and removed debris.

## 3. Potentiating Factors

### 3.1. Solution Effects

Gases and vapors dissolve in water and either remain intact or react chemically with water or something dissolved in water to form an acid and one or more anions. Methane remains intact and does not react with water or with substances commonly dissolved in water. The inability to react with water limits the solubility of $CH_4$.

Given the opportunity, gas molecules dissolved in water establish equilibrium with gas molecules in the air when in an enclosed airspace at a particular temperature and pressure. The solubility of gases that behave like methane is limited to the equilibrium that establishes between gas molecules dissolved in water and gas molecules in the airspace above the water (Equation (1)).

$$CH_{(4,\text{gas in air})} \leftrightarrow CH_{(4,\text{gas in water})} \tag{1}$$

$CH_4$ molecules dissolved in the water constitute the reservoir available to emit into the air above the water should conditions for dissolving become less favorable. The ratio of the two concentrations is the Henry's Law constant [33] (Refer to Table 2 for the Henry's Law Constant and further discussion concerning the potential role of methane in fatal accidents).

### 3.2. Role of Reservoirs

The situation with $H_2S$ is considerably more complex. As with $CH_4$, $H_2S$ molecules partition between the air and the water as non-ionized individual mole-

cules. This property is extremely important in the phenomenon of re-emission of $H_2S$ molecules into the air. Unlike $CH_4$, $H_2S$ reacts with water to form hydrosulfide ($HS^-$) ions, as described in Equation 2. Hydrosulfide ions can further react with water to form sulfide ions ($S^{2-}$) (Refer to Table 2 for the Henry's Law Constant and further discussion).

$$H_2S_{(gas\ in\ air)} \leftrightarrow H_2S_{(gas\ in\ water)} \leftrightarrow H^+ + HS^- \leftrightarrow H^+ + S^{2-} \tag{2}$$

Equation (2) introduces the concept of reservoirs. To illustrate their importance, introduction of $H_2S$ into the air above the liquid will shift the equilibrium toward more $H_2S$ dissolved in the liquid. Similarly, introduction of $H_2S$ gas into the liquid will shift the equilibrium toward more $H_2S$ emitting into the airspace above the liquid and ionization. The $S^{2-}$ ion and $HS^-$ ion are reservoirs capable of rapid generation of $H_2S$ molecules given appropriate change in conditions.

### 3.3. Role of pH

The second important mechanism concerns the role of pH. Acidifying the solution (lowering the pH) will shift the equilibrium toward formation of more $H_2S$ molecules dissolved in the liquid. This, in turn, promotes emission of $H_2S$ molecules into the airspace above the liquid. This situation occurred in a pulp mill following misconnection of an acid line from a delivery truck to a tank containing a solution of NaSH [34]. Raising the pH will shift the equilibrium toward formation of $HS^-$ and $S^{2-}$ ions.

The situation involving $CO_2$ is more complex than that of $H_2S$. $CO_2$ molecules exist in the air and can exist dissolved in water (Equation (3) and Equation (4)).

$$CO_{2(gas\ in\ air)} \leftrightarrow CO_{2(gas\ in\ water)} \tag{3}$$

$$H_2O + CO_{2(gas\ in\ water)} \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \tag{4}$$

$CO_2$ gas in liquid reacts with $H_2O$ to form $H_2CO_3$. $H_2CO_3$ then forms $HCO_3^-$ ions. $HCO_3^-$ ions then form $CO_3^{2-}$ ions. Acidifying the water can lead to rapid production of $CO_2$ gas molecules in the water and emission of gas molecules from the water into the air (Refer to Table 2 for the Henry's Law Constant and further discussion).

An extremely useful tool for visualizing the situation is the Henderson-Hasselbalch equation taught in chemistry courses and provided in Equation 5 [35]. All that is needed to produce a graph from Equation 5 is the value of $pK_A$. $pK_A$ for a given acid is available from chemistry reference sources [36]. The value of $[A^-]/[HA]$ is arbitrary. The fraction is directly convertible to percent ionization.

$$pH = pK_A + \log\left([A^-]/[HA]\right) \tag{5}$$

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 $pK_A$ values [36]. HA is the molecular form, in this example, $H_2S$. $A^-$ is the ionized form, in this example, $HS^-$ or $S^{2-}$.

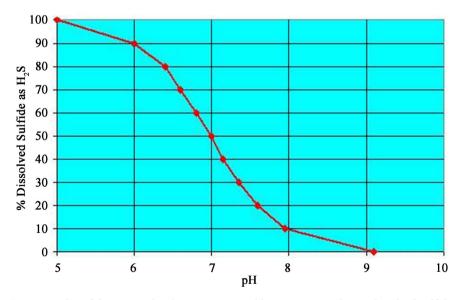The value of $pk_{A1}$ for the first anion from $H_2S$ is 7.0. At pH = 7, half of the sul-

fide in the water is present as $H_2S$ molecules and half as hydrosulfide ions (Figure 3). At this pH, the concentration of $A^-$ equals the concentration of HA because the logarithmic term is zero. (The log of 1 is zero). 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 $H_2S$ molecules emit from the water into the airspace above the water.

This situation also applies to $CO_2$, and ammonia and other amines that are gases or readily evaporated liquids. The amine form of the molecule is uncharged and able to create the equilibrium in the airspace above the liquid with molecules in solution. (Refer to Table 2 for the Henry's Law Constant for ammonia and further discussion.) Amines and ammonia also react with water in a manner that is pH-dependent. Amines and ammonia absorb $H^+$ ions from the water to form the ammonium ion. The ammonium form of an amine is often odorless and considerably more soluble in water than the molecular form because of the positive charge. $pK_A$ values for ammonia and amines are larger than for $H_2S$ and $CO_2$ (Refer to Table 2 for the $pK_A$ values and further discussion).

## 4. Causative Agent(s) in Fatal Atmospheric Events

Taken together, the events summarized in previous discussion indicated 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 events and was present in open areas, buildings and confined spaces [18].

Oxygen deficiency is a major concern in the occupational setting as a cause of death and a topic of discussion in many standards and regulations. Typically, the following Table 1 or a similar version which appears in publications summarizes



**Figure 3.** Plot of the $H_2S$ molecule—$HS^-$ ion equilibrium expressed as % dissolved sulfide as $H_2S$ versus pH. This graph visualizes the relationship between pH and $H_2S$ molecules. As pH decreases, the % of sulfide present as $H_2S$ molecules increases.

**Table 1.** Effects of acute exposure to an oxygen-deficient atmosphere.

| Effect | Atmospheric Oxygen (dry air, sea level) | |
| --- | --- | --- |
| | Concentration % | Pressure mm Hg |
| no symptoms | 16 to 20.9 | 122 to 159 |
| increased heart and breathing rate, some lack of coordination, 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 |

the effects of acute exposure to oxygen-deficient atmospheres as commonly reported based on concentration and partial pressure [18].

At sufficiently low concentration, effects of oxygen deficiency occur rapidly in as little as a few seconds. In order for oxygen deficiency to cause mortality in a manner consistent with the scenarios discussed previously, the concentration must decrease rapidly. Oxygen deficiency develops only in limited ways consistent with these situations. Two of these are dilution or displacement by other gases. This would necessitate emission of enormous quantities of the other gas. Another situation involves rapid removal of oxygen from the atmosphere by chemical reaction or by adsorption (a physical process).

As suggested in the scenarios discussed previously, this would necessitate rapid diminution of the concentration atmospheric oxygen. None of the scenarios discussed previously is consistent with these requirements.

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.

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. Methane is regarded as a simple asphyxiant for which there is no assigned regulatory Exposure Limit [9]. As such, the killer in such accidents would be oxygen-deficiency, as testing would have indicated, had this been the case. Oxygen deficiency caused by methane would necessitate major release and entrapment by boundary surfaces of the structure in which this occurs.

Respiration by microorganisms, both aerobic and anaerobic is a very slow process [22]. 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.

The pH of manure ranges from 8 to 12 with an average of 7.3 during the stable period of anaerobic digestion [37] [38]. **Table 2** lists $pK_A$ values for various gases of interest in this discussion. The shift in pH over time has an impact on the equilibrium between nonionized and ionized forms of molecular gases in solution and in the airspace above the liquid. This affects the odor of the gases and vapors in the airspace above the liquid and the ease of emission following disturbance. High pH favors ionized forms of $H_2S$ and non-ionized forms of amines and ammonia.

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 [33]. 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.

A large Henry's constant [33] as in the case of methane (**Table 2**) indicates the low solubility of the gas in the liquid. A very small Henry's constant as in the case of ammonia indicates high solubility of the gas in the liquid. For methane to be a causative agent in fatal events, large-scale, rapid displacement from the liquid into the airspace must occur in order to lower the concentration of oxygen sufficiently to become oxygen-deficient. Investigators and coroners' reports have attributed causality for accidents involving manure to various gases, including oxygen deficiency and $CH_4$. The attributed causes are not consistent with physical properties and physiological actions of the gases mentioned.

Carbon dioxide is about 1.5 times as dense as air at the same temperature based on molecular weight. $CO_2$ could accumulate in enclosed structures for this reason [39]. $CO_2$ 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

**Table 2.** Properties of gases potentially involved in causation of fatal events.

| Substance | $pK_A$ [36] | Henry's Constant [33] | IDLH [40] | LC$_{(1, 0.5 h)}$ [41] |
|---|---|---|---|---|
| hydrogen sulfide | 7 ($pK_{A1}$) 12 ($pK_{A2}$) | 5.5 | 100 ppm | 508 ppm |
| carbon dioxide | 6.4 | 16.5 | 40,000 ppm | 68,766 ppm |
| ammonia | 9.2 | 0.03 | 300 ppm | 3550 ppm |
| methane | not applicable | 374 | not available | not available |

atmosphere would accompany carbon dioxide poisoning as a cause of death at high levels.

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 [33]. 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 also provides values for IDLH (Immediately Dangerous to Life and Health) [40] and $LC_{(1, 0.5\,h)}$ (Lethal Concentration to 1% in 0.5 hours) [41].

The US National Institute for Occupational Safety and Health (NIOSH) created the concept of IDLH (Immediately Dangerous to Life or Health) to express their concern about the level at which a hazardous atmosphere poses a serious risk of causing death [40]. Acute or short-term exposures to high concentrations of some airborne chemicals have the ability to quickly overwhelm workers, resulting in a wide spectrum of undesirable health outcomes that may include irritation of the eyes and respiratory tract, severe irreversible health effects, impairment of the ability to escape from the exposure environment, and, in extreme cases, death.

NIOSH indicates that IDLH values were established to ensure that the worker can escape from a given contaminated environment in the event of failure of the respiratory protection equipment and to indicate a maximum level above which only a highly reliable breathing apparatus, providing maximum worker protection, is permitted. IDLH is not a usual working condition. IDLH requires a high level of respiratory protection and possibly chemical protective clothing in order to be able to work safely.

$LC_{(1, 0.5h)}$ refers to the lethal concentration to 1% of a group of animals projected to a duration of exposure of 0.5 hours [41]. $LC_{(1, 0.5\,h)}$ is stated in risk assessment documents prepared by the Health and Safety Executive (HSE) in the UK and by other regulators. HSE reports these values under the label, SLOT (Specified Level of Toxicity). The SLOT approach described by Turner and

Fairhurst [42] involves extrapolation to humans of the most relevant toxicity data available. In its usual application, the estimated dose is termed SLOT Dangerous Toxic Load (or SLOT DTL).

IDLH and $LC_{(1, 0.5h)}$ reflect estimates of toxicity for different purposes by independent groups. The values reported in **Table 2** are useful for comparison of relative toxicity between individual substances.

Hydrogen sulfide is an extremely dangerous gas compared to the others mentioned in **Table 2**. The IDLH (Immediately Dangerous to Life and Health) [40] and $LC_{(1, 0.5h)}$ (Lethal Concentration to 1% at 0.5 hours) [41] 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 [43]. This can occur at concentrations in excess of 100 ppm. 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 can 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. This supposition reflects information summarized by McManus [18] supplemented by discussion presented here concerning the behavior of shear-thinning, pseudoplastic non-Newtonian fluids.

## 5. Role of Design in Control of Emission of Toxic Gases from Non-Newtonian Fluids

This article has presented considerable information concerning shear-thinning, pseudoplastic non-Newtonian fluids and their potential role in causation of fatal accidents. This linkage occurs for the following reasons:

- ability of these fluids to trap gases and to release them suddenly and rapidly during provocation;
- inability to predict magnitude of emissions;
- high toxicity of gases involved in emissions ($H_2S$, $NH_3$, $CO_2$);
- rapid restoration of ambient conditions once disturbance ceases;
- absence of linkage between ambient concentration and peak concentration.

Insight gained from this analysis suggests that investigators have failed to identify the mechanism and agent(s) of causation of these accidents and underestimated the frequency of their occurrence.

Regulators worldwide have addressed these accidents through requirements applicable at time of entry into structures regulated as confined spaces. Confined spaces are structures into which entry for the purpose of performing work normally does not occur [17]. These workspaces pose elevated levels of risk.

This approach operates on the premise that only the owner of the equipment

or structure or employer of workers who must enter and work in them has responsibility for conditions created by choices made during design. This responsibility also extends to design. Engineering design influences the conditions of work, yet the literature contains no information concerning obligations imposed on engineering designers to reduce to the extent possible the risk of accessing, entering, and working in these structures and to provide external and internal structures such as access platforms of sufficient size to minimize the risk of emergency response.

The starting points for such considerations are the portal(s) for entering the equipment or structure and the means of accessing them. While design codes may limit characteristics of the portal(s), designers likely have some freedom with regard to the means of accessing them. This concern applies in particular to portals located above grade outdoors or the floor in a building. Safety of emergency responders demands access platforms that accommodate three to four people.

The points raised above further highlight this concern especially in regard to the changes occurring because of emphasis on "green" and "sustainable" engineering as mentioned previously. This is occurring because of the adoption of unusual measures that can increase the risk of work in these structures. These measures include capture and storage of rainwater for reuse and recovery of heat from wastewater. These types of water all contain organic matter on which anaerobic respiration can occur when trapped in sludges under the water level. Maintenance activities involving this equipment and structures are subject to hazardous conditions created through the action of shear forces on shear-thinning, pseudoplastic non-Newtonian fluids containing entrapped highly toxic gases.

An important consideration in this situation is the limited means to control exposure to hazardous gases during these emissions. To illustrate, successful design of ventilation systems depends on knowledge of expected conditions. This requirement has considerable practical importance in the design of ventilation systems in areas such as manure pits. A fatal atmosphere can arise on slight provocation of non-Newtonian fluids containing $CO_2$ and/or $NH_3$ and/or $H_2S$ [28]. Emission of unpredictable magnitude occurs without warning.

Designers reasonably ask whether to design for the ambient condition versus the anticipated maximum concentration. The ventilation system must maintain air quality at and above the level of the liquid so that the worker breathes air of acceptable quality at all times. Failure to do this would subject the worker to risk of intoxication, fall, and drowning. Given the previous considerations and rapid action of $H_2S$ and/or $CO_2$ and/or $NH_3$, a ventilation system in these circumstances seems to be impractical as a means of control.

This concern extends to respiratory protection. As mentioned in the previous section, NIOSH [40] and other agencies mandate the use of SCBAs during work in atmospheres posing unquantifiable inhalation hazard. This choice of respirator introduces additional complexity regarding emergency response.

A possible means to overcome this problem is to wash the interior of the

equipment or structure in high-pressure jets of water to expel the toxic gas from the fluid. This concept is implemented most efficiently and safely when the means to do so are incorporated by design into the equipment of structure.

Robotic high-pressure water jetting equipment has been available in the marketplace for at least 30 years [18]. Success of this technique and its variants depends on isolation of the emissions from workers and discharge to atmosphere or a destructive or capturing agent in a manner that maintains the isolation from workers. This approach seems feasible. Design of the equipment and/or the structure in which water jetting will occur must include consideration for mounting this equipment, and collection and controlled discharge of the mist and gas(s) emitted during its operation.

Responsive design can considerably reduce the risks of this type of work. One organized response to address this situation is the Prevention through Design (PtD) initiative created by NIOSH [44]. Prevention through Design seeks to 'design-out' a variety of hazards across industries. NIOSH indicates that one of the best ways to prevent occupational injuries, illnesses, and fatalities is to eliminate hazards and minimize risks early in the design or re-design process, and to incorporate methods of safe design into all phases of hazard and risk mitigation. Prevention through Design addresses occupational safety and health needs by eliminating hazards and minimizing risks to workers throughout the life cycle of work premises, tools, equipment, machinery, substances, and work processes including their construction, manufacture, use, maintenance, and ultimate disposal or re-use.

## 6. Conclusions

This article introduces and discusses the properties of shear-thinning, pseudoplastic non-Newtonian fluids. These fluids form highly constrained systems related to the storage of highly toxic gases ($H_2S$, $CO_2$, and $NH_3$, among others) and unexpected release into the air during the application of a shear force. This characteristic can change atmospheric conditions from ambient to potentially lethal almost instantaneously. Conditions return to ambient rapidly following cessation of the shear force. Investigation of fatal atmospheric events occurring in confined spaces indicates that, in some cases, the causative agent had disappeared prior to the time of investigation and was otherwise not identifiable.

Well-known chemical and physical processes not widely appreciated or considered in this context contribute to the severity of the situation. A chemical reaction between water and the hazardous gas or vapor can considerably increase the quantity available for emission into the air through the creation of reservoir(s) of anions or cations. Conversion of the ionic reservoir through a change in pH to the molecular form can rapidly exceed the solubility of the gas molecules in the water. The more viscous form of a shear-thinning, pseudo-plastic non-Newtonian fluid can store considerably more molecules of gas than the less viscous form subjected to the shear force.

The uncontrolled release of toxic gas(es) during disturbance of shear-thinning, pseudoplastic non-Newtonian fluids poses an extremely serious technical problem concerning the safety of workers of all occupations potentially involved with them because of limited options for control and protection.

This situation begs participation from all disciplines involved in the construction, operation, and maintenance of equipment and structures involved in processing shear-thinning, pseudoplastic non-Newtonian fluids starting with engineering design. Engineering design influences and potentially controls the conditions of work experienced by workers in other occupations. Engineering design that responds to the challenge discussed in this article has the potential to considerably reduce the risk of work. This is especially important in the areas of "green" and "sustainable" engineering related to the collection, storage and handling of fluids containing organic matter capable of participating in anaerobic digestion.

The Prevention through Design initiative sponsored by NIOSH provides a framework for organized response. Realization of the existence of such highly hazardous systems provides the critical piece of information needed to initiate measures to gain control over these environments. Gaining control to minimize risk necessitates a fundamental change in design, operation, servicing, and maintenance involving measures that address the nature of the formation of these systems.

## Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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