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Soil Gases: The Missing Link in Accidents Involving Subsurface Structures?

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Introduction

Over the years, the cause(s) of many accidents that have occurred in subsurface structures in the infrastructure and in industry 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 involved was odorless and provided no warning. Rapid collapse of the victim occurred. In some situations, carbon dioxide (CO_2) and methane (CH_4) sometimes were present at elevated levels relative to the external atmosphere. 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 levels relative to the external atmosphere. H_2S, when detectable at time of investigation was present at low level.

A common thread in accidents in many of these situations was the presence of water. Liquid water or moisture is essential for microbiological activity involving organic material and for inorganic chemical reactions including corrosion and oxidation. 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 sulfide and other mercaptans, and ammonia and amines and carbon dioxide.

While undoubtedly conditions in subsurface structures at the time of entry reflect the influence of residual contents, additional influences are entirely possible. Piping that enters some structures can transport the atmosphere from a distant location. These situations include routes of intended conveyance, as in the case of sewers and underground electrical vaults linked together by piping and duct, but can also include routes of unintended conveyance where the structure is connected to a source or sink in another location by a single path.

The walls, floors and often the tops of subsurface structures are surrounded by fill. Sometimes the fill is native material and sometimes introduced material that meets some engineering requirement. These materials usually are porous to the migration of gases and vapors, as indicated by conditions known to develop in these structures, sometimes in real time.

This document focuses on the latter situations: conditions external to the space in the ground that surrounds the structure or in remote locations that can influence the atmosphere in the space, rather than residual contents or the external atmosphere.

Breathing Structures

Phenomena that have appeared in recent times include subsurface structures that act as lungs. They typically have a single connection to a source and/or sink, and 'inhale' atmospheric air and 'exhale' a contaminated or highly oxygen-deficient atmosphere.

Well Digging

A number of situations mentioned in the NIOSH report on confined spaces pertained to wells (NIOSH 1994). In a situation not contained in the NIOSH report, a father and son died in separate wells dug in sand. The men worked inside concrete culverts positioned vertically. The cause of death was an atmospheric hazard that was never identified.

These wells were dug through previously undisturbed soil, mainly sand. The locations of the wells were forested and reforested areas containing semi-mature trees, properties being the sites of recent construction of cottages and homes. The undisturbed soil and sand at the bottom of the well were potentially reactive with the oxygen in the airspace. An additional potential sink for oxygen in the airspace was diffusion through the concrete of the walls into the soil in response to a concentration gradient to supply respiration demands of roots and aerobic soil bacteria and other microorganisms.

Well Pit

This situation concerned a subsurface chamber located under the floor of a barn. It contained the well-head and pumping equipment and pressure tank for a drilled well. Such chambers are common in rural areas and protect the equipment from freezing during the winter. The well consisted of two pipes, one inside the other. The outer pipe terminated in the rock structure above the water table. The inner pipe penetrated into water-bearing rock further down.

The family had used the chamber as a 'root cellar' for storing vegetables over the winter and had entered without incident for 25 years. On the critical occasion, the daughter entered and collapsed and died. Her brother entered to rescue her and also collapsed and died. Their father, who attempted to rescue his children also collapsed, but survived.

The atmosphere in the chamber at the time of the accident was estimated to contain 91% nitrogen (N_2), 8.5% oxygen (O_2) and 0.6% CO_2. Investigation showed that the gasket that sealed the gap between the two pipes had failed. This enabled the atmosphere in the chamber fo become contiguous with the atmosphere between the two pipes and potentially that in the rock structure. The well structure literally was breathing.

These wells are called blowers and suckers by well-drillers. Blowers and suckers are well-known throughout North America. High pressure conditions force the atmosphere down the space between the two pipes into the rock structure. Under low pressure conditions, the atmosphere exhales through the space into the surroundings. In this case, the surrounding airspace was trapped in a confined space.

Other structures in which this situation can develop involve buildings located at ground level that surround the well head. Hence, the conditions reported here are likely not unique to subsurface chambers that are confined spaces. (Refer to the document on the uncharacterized workspace.)

In some regions, homeowners use these exhalations for cooling in basements during summer months. Exhalation in some situations is powerful enough to propel small rocks from the well. The mechanism of oxygen removal from the atmosphere in the situation documented here is unknown.

Mine Tailings Reclamation
This situation involved a sampling shed that measures about 2 m by 2.5 m. The narrow wall contains a door of normal dimensions. The sampling shed contains a pit used to provide access to drainage for sampling that was located in the floor. The pit was created from ‘lock blocks' (large poured concrete blocks used to construct retaining walls and other structures. The pit is about 1.2 m deep. A culvert empties into one side of the pit and pipe located on the other side conveys the drainage to a water treatment plant.

The culvert collects drainage from a ditch located at the base of a pile of waste rock that had accumulated over the period of 50 years. The rock was waste from a mine that had operated for 100 years. During reclamation, the pile of rock was recontoured and the ditch filled-in with large rocks to enable continued collection of the drainage. The recontoured pile of rock was then covered by 1 m of clay soil.

The waste rock in the pile contains sulfides and carbonates. During its history, rain freely entered the pile and the atmosphere freely diffused into and from exposed surfaces. The purpose for the clay soil was to create a cap to prevent continuance of this process, meaning to stop production of acidic mine drainage.

Water sampling at the building prior to installation of the soil had occurred for five years without incident. On the critical occasion, an independent contractor entered the shed to obtain the water sample and perished. Three other people also died in this tragedy 36 hours later. (Refer to the article on the uncharacterized workspace for further discussion.)

Investigation showed that the atmosphere at the time of the accident contained an estimated 90% N_2, 8% CO_2 and 2% O_2. The CO2 was mineralogical in origin. The authors of the investigative report hypothesized that the sulfides in the rock reacted with O_2 to form sulfates, and that the acid produced in this process reacted with the carbonates to form CO_2. These reactions are well-known in hard-rock mining and influence decisions about mine ventilation.

Further investigation indicated that atmospheric air entered the pile of rock through the culvert and that the pile exhaled highly oxygen-deficient gas in a regular cycle. In other words, this structure also was breathing.

Cemetery
Today's cemeteries have changed the way in which burial occurs. Instead of digging a hole in the ground using the excavator attachment on the back of a front-end loader, inserting the coffin and refilling the hole, the sequence now is to scrape the sod from the top of a concrete vault, to remove the top and insert the coffin, and to replace the lid and the sod. The ‘cemetery' is actually a gigantic structure containing many rows of vaults. The vaults sit on coarse drain rock. The coarse drain rock surrounds perforated plastic piping. The piping leads to a pump station. Aerobic decay in the vault removes oxygen from the airspace. This, in turn, scavenges oxygen from the airspaces between the pieces of rock, from the airspaces of the drain piping and finally the airspace of the pump station.

In the example that prompted this story, there was 5.5% O_2 at the surface of the manhole, and 4.5% at the level of the pumps, 4 m down. Methane was undetectable. This situation indicates that an individual attempting to view the interior of the pump station from the surface could die without placing the face below the plane of the ground. (Refer to the article on the uncharacterized workspace for further comment.)

The opening and reclosing of vaults in various locations provides a mechanism for potential inhalation and exhalation. This structure also potentially breathes.

Subsurface Chambers and The Water Table

Poured and precast concrete is used in many subsurface structures that form the infrastructure. These structures can have either a concrete or a dirt floor. The concrete of the walls and floor generally is uncoated, and therefore porous. The absence of a coating on the concrete and absence of a concrete floor provide conditions for exchange of the atmosphere in the space with gases in the ground. This situation can lead to inward diffusion of gases from the ground and outward diffusion of oxygen, depending on conditions.

One such structure had experienced routine entry during a period of years. The critical occasion that led to a fatal accident was considered to be no different in concept from the others. Subsequent investigation led to consideration about the water table in the area. The water table had experienced a shift due to construction dewatering and a severe drought. Change in the level of the water table was believed in some manner to have had an influence on the atmosphere in the space. This space potentially experienced an inhalation-exhalation episode.

Subterranean Geologic Processes

Subterranean processes not under the influence of human activity include volcanic processes and processes involving rainwater and groundwater.

Volcanic processes involve magma, the molten material in the central core of the earth (USGS 2010). The magma contains dissolved gases. Volcanic gases drive eruptions. Gases escape continuously from soil, volcanic vents (fumaroles) and hydrothermal systems. The most abundant volcanic gases are water vapor or steam (H_20), carbon dioxide ($C0_2$), about 1/150 that from human activity, and sulfur dioxide ($S0_2$). In addition, there are smaller amounts of hydrogen sulfide (H_2S), hydrogen (H_2), carbon monoxide (CO), hydrogen halides (HF, HCl, and HBr), helium (He), carbonyl sulfide (COS), carbon disulfide (CS_2), methane (CH_4), ammonia (NH_3), mercury (Hg) vapor, and organic compounds.

Gassy Volcanic Lakes

The situations described in previous sections refer to man-made structures conducive to expression of phenomena caused by subterranean gases. Gas production and entrapment also occur through natural phenomena. Lake Nyos, Lake Monoun and Lake Kivu in Africa are carbonated by seepage of CO_2 from deep rock strata (Anonymous 2011a). Carbon dioxide produced by geological activity deep in the rock follows pathways through natural fissures and escapes into the waters of these lakes. In other locations, this transfer occurs undetected into the atmosphere.

Lake Nyos in Cameroun is a deep lake located in the cone of an inactive volcano. CO_2 enters the water deep in the lake. Over a long period of time, a supersaturated solution of CO_2 forms in the water. This solution becomes about 5 times as concentrated as the CO_2 in a container of soda pop or beer. This situation is possible because of the shape and depth of the lake, temperature of the water and pressure exerted by upper levels of water on the lower level. Another factor was stratification and absence of mixing. Stratification and turbulent mixing normally occur in lakes as part of an annual cycle. The system illustrated by Lake Nyos becomes highly constrained and unstable.

At the critical moment, Lake Nyos literally burped as the gas rapidly evolved from solution to form bubbles in the water. The volume of water increased because of the sudden formation and rise and escape of gas. Over an estimated 20 seconds, the gas escaped from the surface of the lake and flowed down the cone of the mountain into the contours of the surrounding valleys. The CO_2 was at least 1.5 times as dense as the surrounding air (the normal ratio of density for the same temperature). Coming from the depth of the lake, the gas likely was colder and even more dense than the surrounding air due to the difference in temperature.

In this disaster, 1700 people and many animals perished.

Lake Kivu in East Africa contains methane from subterranean emissions as well as CO_2. Commercial recovery of the methane occurs.

Gassy Springs

Water issuing from certain springs is naturally carbonated. This occurs from contact with CO_2 seeping upward from deep sources and also from CO_2 produced through the action of acid on carbonates in rocks. Most rainwater contains dissolved CO_2. The CO_2 reacts with the water to form carbonic acid, H_2CO_3. Both of these pathways lead to carbonation. Decarbonation can occur in inopportune locations and at inopportune moments leading to unpredicted exposure to atmospheres enriched in CO_2.

Cave Gases

Caves are logical locations in which to anticipate the presence of gases. These situations occur when the cave is part of a system containing vents with penetration deep into the rock structure.

The gas of greatest concern in caves is CO_2 . An atmosphere in a cave containing >1% (>10,000 ppm) of CO_2 is called 'foul air' (Smith 1997). This hazard is most likely to develop in deep limestone caves having a relatively still atmosphere. CO_2 can enter the atmosphere of the cave by exhalation from groundwater and from exhalation from fissures leading to deep strata. Respiration by microorganisms, bats and other cave dwellers and visitors are additional sources. This situation affects 1% to 2% of caves in North America

The Oracle of Delphi is the most famous of the 'applications' of natural emissions from subsurface structures (Anonymous 2011b). The Greeks created a temple complex on the site as a means of legitimizing the properties of the Oracle as a means of predicting the future. The priestess would sit above a vent and allow herself to be intoxicated by emission of gases and vapors from deep geological faults. The original location of the oracle is no longer visible. Emissions in a cave located near the site include CH_4, ethanol vapor, and CO_2 . Hence, the emissions were capable of inducing a hypnotic (intoxicated) state in the priestess during which time she would mumble unintelligible comments which were interpreted as predictions of future events.

Radon

Radon (Rn) is present in some caves, some mines and in subsurface structures and sometimes above-ground structures. Radon is present only where radium (Ra) is also present in subsurface and exposed rock. Radon is formed by the radiolytic decay of the nucleus of Ra atoms. Ra is immobilized in soil and rock. Rn is an inert gas and therefore chemically unreactive. Rn can diffuse from the point of generation and is transported in water, pore spaces and fractures in soil. Radon can enter an airspace by diffusion through the surfaces of structures, and by exhalation, especially following highly turbulent use of water in showers, cooking, and cleaning in dishwashers and clothes washers.

The process of radiolytic decay of the nucleus of radioactive atoms is random and not predictable for an individual atom. All radon atoms are radioactive and therefore have a probability of experiencing radiolytic decay. Radon includes three types of radioactive atoms called isotopes. The longest lived isotope, ^{222}Rn has a half-life, $t_{½}$,of 3.8 days, meaning that in 3.8 days half of the atoms of ^{222}Rn have decayed to form other substances, themselves radioactive.

Subterranean Microbiological Processes

Microbiological processes are important contributors to soil gases, and possibly to processes that occur deep underground (Brock and Madigan 1991). This discussion focuses on microbiological activity depending on conditions and nutrients available for various reasons in soils, versus organic materials introduced from the surface into a subsurface structure.

Soils are subdivided by characteristic activities into horizons (layers). The O horizon contains undecomposed plant and animal materials. The A horizon comprises surface soil. Where the organic content is high, the soil in the A horizon is dark in color. High organic content brings a high level of microbial activity. The B horizon is the subsoil. The B horizon contains some organic matter and exhibits microbial activity. The C horizon contains the soil base and exhibits little microbial activity.

Soils are a mixture of mineral particles, organic matter, roots and microorganisms. Particles in well-drained soils have large spaces between them. This enables rapid drainage to occur. Water adsorbs to particles and forms sheets or films. When air readily penetrates, the O_2 level is high. Little water or gas penetration occurs in poorly drained soils. Available O_2 is quickly consumed by microorganisms. This produces anaerobic conditions.

Almost all of the microorganisms in the soil are attached to particles. Aerobic and anaerobic microorganisms can live side by side on soil particles due to the varying level of O_2. Greatest activity occurs around roots, as would be expected. Microbial processes include nitrogen fixation into nitrates and aerobic respiration involving oxygen present in soil spaces. Aerobic respiration consumes O_2 with resultant production of CO_2 .

Aerobic respiration in soils with resultant consumption of oxygen creates a sink and provides a mechanism for creation of oxygen-deficient conditions in the airspace of subsurface structures through diffusion through porous concrete surfaces in walls and floors.

Water is key to growth in surface soil. Availability of water creates feast or famine conditions for the microorganisms. Coincident availability of nutrients creates rapid growth and resulting competition and collaboration for nutrient resources by microorganisms. Under collaborative conditions, where nutrients are scarce, growth continues to occur, although considerably more slowly than occurs at optimum conditions.

Microbiological activity deep in rock was hypothesized as a possible cause of the oxygen-deficient condition involving the drilled well, discussed earlier. Fungi and bacteria are known to colonize rock structures far below the surface (at least 300 m), hence, the interest in the potential for life on Mars following discovery of water in the rock. Nutrient availability is the key to growth.

A biofilm forms near intake of water wells deep in the rock. A biofilm is a large colony of bacteria, fungi and other microorganisms that cooperate and collaborate for mutual survival.

Microorganisms that live in soil and rock have evolved many metabolic pathways for survival, including some that seemingly contradict each other. This enables cooperative, collaborative relationships between microorganisms to utilize the energy content in available nutrients.

aerobic respiration:
$(CH_2O)_n + nO_2 \rightarrow nCO_2 + nH_2O$

methane oxidation:
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

hydrogen formation:
glucose + $4H_2O \rightarrow 2CH_3COO^- + 2HCO_3^- + 4H^+ + 4H_2$
glucose + $2H_2O \rightarrow C_4H_7O_2^- + 2HCO_3^- + 3H^+ + 2H_2$
butyrate + $2H_2O \rightarrow 2CH_3COO^- + H^+ + H_2$
propionate + $3H_2O \rightarrow CH_3COO^- + HCO_3^- + H^+ + H_2$

hydrogen oxidation:
$H_2 + 2HCO_3^- + H^+ \rightarrow CH_3COO^- + 4H_2O$

methane formation (methanogens only):
$H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O$
acetate + $H_2O \rightarrow CH_4 + HCO_3^- + H^+$
$H_2 + CO_2 \rightarrow CH_4 + 2H_2O$

iron oxidation:
$Fe^{2+} + 0.25O_2 + 2OH^- + 0.5H_2O \rightarrow Fe(OH)_3$

sulfide oxidation:
$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+$

acid mine drainage (iron pyrite):
$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H+$

sulfate reduction:
acetate + $SO_4^{2-} + 3H^+ \rightarrow 2CO_2 + H_2S + 2H_2O$
other electron donors: H_2, lactate, pyruvate, ethanol, etc.

nitrite oxidation:
$2NO_2^- + O_2 \rightarrow 2NO_3^-$

nitrate reduction:
$NO_3^- + H_2 \rightarrow NO_2^- + H_2O$
$2NO_2^- + 3H_2 + 2H^+ \rightarrow N_2 + 4H_2O$

Mine Gases

Mining is another possible source of gaseous emissions. Mining exposes minerals to the atmosphere in the airspace of the tunnel and provides a path of escape for emissions. Sulfide-containing rock exposed to air reacts with oxygen to form sulfates according to the following reaction that creates acid mine drainage (iron pyrite):

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$

This reaction removes oxygen from the atmosphere of the mine and is well-known to miners of sulfide-containing ore. The product of the reaction is acidic and is capable of reacting with carbonates in the following reaction:

$$CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$$

This reaction produces carbon dioxide. Production of CO_2 can accompany depletion of oxygen. This reaction is well-known to miners of sulfide-containing ores.

Some deposits of coal are the source of methane. Methane can enter the airspace of the mine by diffusion from exposed seams. This situation has caused numerous fires and explosions. Methane from coal also can seep into the atmosphere through cracks and fissures.

Methane seepage from the ground occurs in areas where coal is not present. This reflects production by geologic processes, such as volcanic activity, versus the biological processes that lead to formation of coal.

Blasting using dynamite and other explosives is the source of a number of gases, including CO, CO_2, NO, and NO_2. Explosion of coal dust also produces hydrogen These gases are well-known in mining. Miners use ventilation to remove these gases from the work area.

Considerably less well-known is the ability of the gases to migrate through rock and soil to distant locations. This became evident in a fatal accident that occurred in a subsurface structure (Anonymous 2002). The use of instruments for routine testing during work in subsurface confined spaces would have indicated accumulation of CO. Subsequent investigation revealed that blasting at a separate nearby work location was the source of the CO. The gases migrated through fractures in the rock, diffused through the concrete and entered the airspace of the structure.

Other Gases and Vapors

Surface soils can contain numerous gases and vapors. Most common sources result from disposal of organic chemical products into the ground, burial of vegetable and animal matter in garbage dumps, the filling-in of swamps and marshes, spillage and leakage from pipelines and tanks, and natural sources of petroleum located at or near the surface of the ground.

These circumstances are the source of CH_4 and ethane (C_2H_6) produced by anaerobic decay of organic matter in soil. Sulfur-containing substances are the source of H_2S and mercaptans, and nitrogen-containing substances are the source of ammonia (NH_3) and amines. Emission of CH_4 from such sites is a well-known phenomenon. Building codes require collection and venting systems under structures built in these locations. Occasional reports indicate the presence of high-level emissions from former industrial sites, such that monitoring during excavation is essential to prevent fire and explosion.

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