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# Underground Coal Gasification: An Overview of Groundwater Contamination Hazards and Mitigation Strategies

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## Preface

All energy production technologies produce environmental impacts, and create environmental risks. It is always difficult to weigh the benefits of additional energy production against the risks of that activity. Further, if a venture is approved, it is difficult to balance the trade-offs between environmental protection and costs. The main purpose of this report is to provide information and understanding so that these difficult decisions can be made as well as possible.

The hazard of groundwater contamination by underground coal gasification (UCG) operations is real and must be addressed seriously by all projects. In the past, some UCG projects have unacceptably contaminated groundwater resources, while others have been carried out safely. The goal of this work is to provide an understanding of specific contamination hazards and mitigation best practices. This report describes how UCG can work without contaminating groundwater. It also describes things that can go wrong. The underlying goal is to identity mitigation strategies and best practices to minimize groundwater risk.

The audience for this report is regulators, project developers, and stakeholders with a wide range of expertise in UCG. The emphasis is education and information, not prescription. The phenomena are too complex and the range of possible specifics are too wide for specific prescription. Each case will be unique and require detailed assessment and analyses, using this document to guide appropriate questions and critical review.

## **Summary**

Underground coal gasification is the *in situ* conversion of coal into an energy-rich product gas. It takes place deep underground, using chemical reactions to consume the coal and grow a cavity. Gas wells, drilled into the coal seam, inject reactant air, oxygen, and/or steam to sustain the reactions. Production wells then extract the product gas.

Preventing groundwater contamination during a UCG operation requires care at many steps. Key requirements include:

- Selecting a favorable site
- Analyzing failure modes
- Careful and conservative design, construction, and testing
- Conservative operations
- Quality-assurance and operational controls
- Monitoring, by a combination of measurements and modeling
- Early detection and correction of unwanted conditions or escaping gas
- Proper closure procedures
- Post-closure monitoring and management

During normal UCG operation contaminants are continually generated, destroyed, and removed, leaving only small amounts confined locally. The gas within parts of the UCG cavity during operations will contain many organic contaminants, including those formed by pyrolysis of the coal. These species will include aliphatic and, especially, aromatic hydrocarbons—including benzene, polyaromatic hydrocarbons, and phenols. In proper operation virtually all of this gas will be converted to a more benign composition, produced out of the ground within contained piping, and properly separated above ground.

At termination of a properly operated module, a small inventory of contaminant species will be present in the cavity and its walls and rubble zone. Post-burn module cleaning operations—such as nitrogen sweep, steam sweep, and/or gradual steam-producing water infiltration—can greatly reduce the local inventory of these contaminants. These post-burn cleaning operations—coined "Clean Cavern" by the Rocky Mountain 1 team—were demonstrated during the Rocky Mountain 1 test and are being evaluated in recent Australian UCG panels. Thus, a properly operated and cleaned UCG module will terminate with a small quantity of organic contaminants present in the immediate vicinity of the cavity.

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Transport of contaminants outside the local confinement zone is abnormal, either during operations or after closure. It will occur if there is an outward pressure gradient and a pathway for flow. Whatever the amount and distribution of residual contaminants, their impact is dependent on the proximity and value of nearby groundwater resources, and the transport barriers (or hydrologic gradients) between the contaminants and protected waters.

UCG should be avoided within some keep-out distance of a high-value ground water resource. Site-specific geomechanical and hydrologic studies, coupled to the UCG designs being considered, will be needed to set this keep-out distance as a function of various factors. Qualitatively, one wants to avoid having open pathways extend up into a valuable aquifer.

Over the years, the UCG community has improved in its understanding and approach to mitigating contamination risks. Some of the general approaches include the following:

- The operating pressure of the UCG cavity must be controlled below the surrounding water pressure at the highest gas-connected part of the cavity.
- The UCG production wells and their completion must be designed and constructed properly to maintain their integrity despite thermal and mechanical stresses.
- As with any industrial operation that produces waste-water, care must be taken to keep it from spilling at the surface.
- Careful geotechnical analysis must be carried out on the geomechanical behavior of the open (or rubble filled) cavity, possible extent of roof collapse, and likely fracture extents.
- In general, narrower cavities with larger pillars will increase subsidence protection, but at the expense of higher well-placement costs and reduced resource recovery.
- Monitoring of the operation, including indications of vertical cavity growth, is important.
- Rings of groundwater sampling wells can typically provide early detection of any problems close to the operation, while confirming far-field cleanliness in outer, regulatorycompliance rings.
- A method for detecting gas leakage to the formation can be used, as it may detect contamination-spreading conditions earlier and further away.
- A proper shutdown and follow-up procedure should be followed, along the lines of the Clean Cavern concept demonstrated at Rocky Mountain 1 and other subsequent field tests.

Careful analysis and understanding of likely failure modes will help prevent and minimize impacts. This document provides a general description of the relevant processes, potential failure modes, and practical mitigation strategies. It can guide critical review of project design and operations.

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## Chapter 1

## **Introduction to UCG**

This chapter is designed as an introduction to underground coal gasification (UCG) for the unfamiliar reader. We discuss the basic process, as well as its advantages and disadvantages with respect to more traditional coal extraction techniques. The chapter covers the key physical processes taking place, typical layouts for a modern UCG operation, and the major hazards that must be addressed. Later chapters will draw on this background material as we focus in more detail on groundwater-quality hazards and relevant mitigation techniques.

#### 1.1 What is UCG?

UCG is a coal recovery technique in which solid coal is converted *in situ* into a gaseous product known as synthesis gas (syngas). The basic reactions are the same as occur in a surface gasifier, but during UCG the coal seam itself is used to create a reaction chamber. This approach avoids many of the costs and challenges associated with mining the coal by more traditional means. The resulting product gas is quite flexible and can be used for a variety of downstream applications—e.g. for power generation, or as a feedstock for chemical products like hydrogen, methanol, ammonia, fertilizers, and synthetic natural gas. Like surface gasification, the  $CO_2$  in the product gas can efficiently be separated if desired for sequestration or beneficial use.

In its most basic configuration, two wells are drilled into the coal seam, one for injection and the other for production (Figure 1.1). Modern gasifiers often use a mixture of horizontal and vertical wells to create a linked system. The coal is then ignited, and an oxidant—some combination of air, pure oxygen, and steam—is introduced through the injection well. As the coal is consumed, a series of favorable reactions convert the solid fuel into syngas, which is then extracted through the downstream production well. In general air is injected when the product will be burned to make electricity or heat, and oxygen or oxygen plus steam is used when the product will be converted to higher-value chemicals or be stripped of its  $CO_2$ . By converting the coal *in situ*, UCG eliminates many challenges associated with mining, transporting, pulverizing, cleaning, and handling the coal and most of its ash residue.

A hundred or so experimental, pilot, and demonstration UCG operations all over the world over the past eighty years have shown it to be technically feasible, and the technology

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Fig. 1.1 Evolution of a typical UCG module.

has continued to improve. A large effort to improve and commercialize UCG in the United States in the 1970's and 1980's hit a commercial dead end with the drop in energy prices in the 1980's. Significant efforts towards commercial-scale development are going forward in their early stages in many parts of the world today, including Australia, South Africa, China, Canada, Indonesia, Pakistan, southern Africa, and Eastern Europe. Nonetheless, UCG is not as technologically mature or as far along the development and commercialization path as surface gasification.

Modern UCG is generally targeted at coal seams deeper than 200 or 300 meters. Two small pilot experiments were run below 1000 meters in Europe, and a recent field test in Alberta, Canada was deeper than 1400 meters, with plans to scale up there. Surface gasification most commonly runs at tens of atmospheres pressure. Higher pressures have thermodynamic and kinetic advantages, but technical challenges such as injecting coal and removing ash have limited most applications to 20-60 atmospheres. UCG typically operates somewhat below surrounding hydrostatic pressures. Thus a 1000 meter-deep seam may be gasified at about 90 atmospheres.

Several factors make UCG an appealing alternative to traditional mining techniques:

- It may potentially be applied to seams that are too deep, low grade, or thin to be economically mineable.
- It eliminates several of the major costs and worker hazards associated with mining, transport, and surface gasification.
- It has a light surface footprint, leading to smaller reclamation costs.
- During the gasification process, fly ash and many pollutants—e.g. SO<sub>x</sub>, NO<sub>x</sub>, mercury, particulates, and sulfur species—are either left entirely downhole or the produced volumes are much reduced.
- It has a small water demand.

• When combined with a combined cycle power plant, net CO<sub>2</sub> emissions are reduced in comparison to standard coal-fired generation.

There are also disadvantages that factor into project decision-making:

- While UCG is relatively old technology, limited field experiences implies that it is still an immature technology.
- Market costs (especially for natural gas) are volatile, making it challenging to predict future demand for UCG products.
- Operators have less control on gas quality, as compared to a surface gasifier. In fact, the key technical challenge is designing and operating the UCG module to achieve a stable, high-energy-content gas stream.
- Lack of familiarity with UCG can also increase the time necessary to get permits for a new operation. Public perception of new technologies also presents a social challenge.
- The gasification process excavates large underground cavities. Unlike a traditional mine, however, there is no opportunity to introduce artificial supports to control caving. As a result, additional care must be taken to avoid unwanted geomechanical deformations and significant surface subsidence.
- If not operated properly, there is the potential for an underground gasifier to contaminate groundwater. The keys to mitigating this risk are careful site selection and characterization, prudent operation, environmental monitoring, and proper post-operation closure procedures. While absolutely necessary, all of these procedures add additional cost.

The effective design of a UCG gasifier is a complex task, requiring a detailed understanding of the physical processes taking place in the subsurface. Further, large-scale commercial projects required significant attention to the surface process engineering in order to create an economically viable operation. Nevertheless, if done properly UCG can be an efficient, safe, and environmentally sound process. The widespread interest in UCG in many markets around the world is evidence of this appeal.

## 1.2 Major hazards

While UCG has several environmental benefits that make it appealing, there are also a variety of hazards that must be addressed. These impacts can be roughly divided into four categories:

- Surface disturbance: One key advantage of UCG is its relatively small surface footprint. This footprint is non-zero, however, and there will be surface impacts associated with the well pads, access roads, pipelines, and facilities.
- 2. *Geomechanical impacts:* As mentioned earlier, the UCG process excavates large underground cavities. As there is no opportunity to introduce artificial supports, the open cavity

will deform and possibly collapse. This can lead to surface subsidence, as well as deformation and fracturing of overlying strata. Any unexpected geomechanical movements can also damage well casings.

- 3. *Petrochemical hazards:* UCG, like many other petrochemical processes, produces waste and by-product streams at the surface that must be handled appropriately. If not contained properly, these streams could leak into the ground or nearby surface-water.
- 4. *Groundwater degradation:* The UCG process produces a variety of harmful compounds. These include BTEX compounds (benzene, toluene, ethylbenzene, and xylenes), phenols, and aromatics. Heavy metals may also be leached from residual coal ash left in the cavity. If a UCG site is not prudently operated, these contaminants could migrate away from the cavity and impact nearby groundwater. This work is primarily focused on this last category.

Of the four, the groundwater contamination issue is the greatest risk, and also the trickiest one to deal with. Historical experience with UCG includes a few cases in which serious groundwater contamination occurred [10] and many cases with small to no environmental impact [56]. The ultimate goal of this work is to identify those features of planning and operation that separate the successful operations from the unsuccessful ones.

The surface impacts of UCG are similar to other industrial operations. A pre-work survey of topsoil, vegetation, animal life, and surface water is often required at a prospective site. This survey can be used to identify any specific environmental hazards, as well as provide a baseline for the post-operation reclamation.

The geomechanical issues are nearly identical to those encountered with underground mines, and many of the same geotechnical design procedures apply. A major concern for UCG, however, is that geomechanical processes can open up leakage pathways into surrounding strata, and allow contaminants to migrate into overlying aquifers. As such, the geomechanical and groundwater risks are tightly linked.

Surface hazards associated with waste and by-product streams must also be addressed. While the containment and cleanup procedures used in UCG are similar to many other petrochemical operations, the composition of these streams is unique to UCG. This hazard is also closely related to the groundwater contamination hazard, as a surface spill could provide an easy pathway for contaminants to reach drinking water. Section 1.5 below discusses the composition of these waste and byproduct streams in more detail.

#### **1.3 Physical Processes**

Within an underground gasifier, a number of chemical, thermal, hydrologic, and mechanical processes interact simultaneously. Here, we briefly summarize the major processes at work.



Fig. 1.2 Cross-section of different layers in the wall zone (not to scale). The typical thickness from open cavity to saturated coal is 1–30 cm.

## **1.3.1 Gasification Reactions**

The basic UCG process converts solid coal into a gaseous product (syngas) containing hydrogen, methane, carbon monoxide, and carbon dioxide. The syngas has a high chemicalenergy content and can be used for power generation or as a feedstock for other chemical processes. The conversion works by reacting coal at high temperatures in an oxygencontrolled environment. By restricting the oxygen, full combustion is avoided. Instead, a limited quantity of fuel is allowed to combust in order to generate heat and volatile gases. These exothermic reactions then drive secondary, endothermic reactions that produce hydrogen, methane, and other species.

Most of these reactions take place in a thin zone near the cavity wall (Figure 1.2). The key stages are:

- 1. *Drying:* The coal in the seam begins saturated with water. As heat is generated within the cavity, a thermal front is created which dries the coal near the gasifier and generates steam. Because the cavity pressure is typically less than hydrostatic, a pressure gradient drives water influx from the far-field towards the cavity, which encounters the thermal front and also converts to steam. The volume of water influx is controlled by the permeability of the strata, local hydraulic head, and operating pressure of the cavity.
- 2. *Pyrolysis:* When the dry coal reaches 200–500° C, volatiles are released and the coal turns to char,

$$\label{eq:Coal} \begin{split} \text{Coal} & \rightarrow \text{Char} + \text{Ash} + \text{Hydrocarbons} \\ & + \text{CH}_4 + \text{H}_2 + \text{H}_2\text{O} + \text{CO} + \text{CO}_2 \end{split} \tag{1.1}$$

The pyrolysis occurs in a thin layer around the boundary of the cavity, just within the drying layer. The gaseous species are then free to migrate towards the open cavity, where they can participate in other reactions.

3. *Oxidation:* The volatile products and carbon-containing compounds in the char (C) react with injected oxygen,

$$\mathbf{C} + \mathbf{O}_2 \to \mathbf{CO}_2 \tag{1.2}$$

$$2C + O_2 \rightarrow 2CO \tag{1.3}$$

These exothermic reactions release the necessary heat to drive the other, endothermic processes. The oxidation reactions mostly occur within the cavity itself, as oxygen is consumed near the injection point. At the cavity wall, temperatures can reach 800–1200° C. Note that only a limited amount of oxygen is injected, just enough to produce the necessary heat and gases to drive the endothermic reactions. Steam may also be injected to provide additional water.

4. Gasification: The basic gasification reaction is

$$C + H_2 O \to H_2 + CO \tag{1.4}$$

which primarily occurs within the char layer at the cavity wall. The char gasification zone typically reaches  $500-1100^{\circ}$  C.

5. *Side reactions:* A number of side reactions also occur, depending on cavity conditions. These reactions can increase the methane and hydrogen content of the gas.

$$\mathrm{CO} + 3\mathrm{H}_2 \to \mathrm{CH}_4 + \mathrm{H}_2\mathrm{O} \tag{1.5}$$

$$C + 2H_2 \to CH_4 \tag{1.6}$$

$$C + CO_2 \to 2CO \tag{1.7}$$

$$\mathrm{CO} + \mathrm{H}_2\mathrm{O} \rightleftharpoons \mathrm{H}_2 + \mathrm{CO}_2 \tag{1.8}$$

The exact composition of the gas can be tuned (within limits) by controlling the oxygen/air feed rate, steam injection, gas pressure, and other operational aspects.

The gas flow within the cavity is quite complicated itself, involving reactive transport, turbulence, radiative heating, etc. Typically, a rubble zone also forms at the bottom of the cavity, further complicating the picture.

## 1.3.2 Hydrology

UCG gasifiers are always located in the saturated zone beneath the local water table. Because the cavity gas pressure is typically operated below hydrostatic pressure, water will flow into the cavity, convert to steam, and be consumed in the gasification reactions. If too much water flows in, however, the coal will extinguish and the cavity will flood. The rate of influx is controlled by the local permeability and the cavity gas pressure. Over time, the consumption of water will also lead to a decline in hydraulic head measurements in monitoring wells surrounding the cavity. A detailed understanding of the local hydrology is therefore essential for developing a good operation and monitoring plan.

If the cavity is operated below hydrostatic pressure, the water influx will tend to flush contaminants towards the cavity and minimize groundwater contamination risk. At the end of operation, the cavity can then be flushed to minimize contaminant migration after the wells are shut-in and the cavity floods.

Gas-quality can often be improved by operating at high-cavity pressures, so there is an economic incentive to operate the cavity as close to hydrostatic pressure as possible. A critical observation, however, is that if the cavity gas operating pressure ever exceeds hydrostatic, gas can be pushed *away* from the cavity and into the formation, setting up a risk for groundwater contamination. We will focus on this risk extensively in later chapters.

## **1.3.3 Geomechanics**

The UCG process excavates large, unsupported underground cavities. The mechanical properties of the coal and surrounding strata therefore play an important role. In general, there are two mechanical processes of interest: (1) thermal spallation and (2) large-scale caving.

As the coal and surrounding rock are heated, thermal expansion will induce stresses around the cavity perimeter. Heating these materials can also degrade their strength properties. As a result, thermal spallation can occur, with small pieces of rock and coal popping off the walls into the cavity. The rate of spallation is a key control on the cavity growth rate, as spallation can quickly open up new surface area for the gasification reactions.

If the cavity opening reaches a sufficient size, large-scale geomechanical failure can occur. If not designed for, this large-scale collapse can suspend operations, cause significant surface subsidence, and open up fracture pathways in the overburden. The presence of preexisting joints and faults can also complicate the picture. A detailed geologic characterization and careful geotechnical design are therefore pre-requisites for safe and efficient operation. It should also be noted that geomechanical deformations can impact permeability, and therefore it is often necessary to consider the coupled, hydromechanical behavior of the system.



Fig. 1.3 Section view of the CRIP process, reproduced from [51].



Fig. 1.4 Plan view of the linear and parallel CRIP designs.

## 1.4 Gasifier Designs

The design of a UCG gasifier can vary substantially between operators, and these specifics are often regarded as valuable intellectual property. There are a large number of possible configurations, depending mainly on:

- the layout of the injection and production wells;
- the casing/liner design for each well;
- the method used to pneumatically link wells;
- the ignition method;
- the method used to control the injection point;
- the degree to which roof caving is allowed;
- and site specific features such as coal seam thickness and dip.

It should also be born in mind that a commercial-scale operation requires an array of gasifiers, since an individual module can only produce a limited volume of coal. Typically one or more gasifiers operate at any given time, and new gasifiers are brought online as old ones retire. In between each gasifier, some volume of coal is left in place for containment and subsidence control purposes. The resulting extraction scheme can often resemble either a room-and-pillar mine or a longwall mine, and many of the same design principles apply.

Rather than describe the full spectrum of available gasifier designs, here we simply introduce two typical layouts: Linear CRIP and Parallel CRIP. These two designs illustrate many of the fundamental features shared by other methods.

## 1.4.1 Linear CRIP

The simplest example using a mixture of horizontal and vertical wells is the Linear Controlled Retracting Injection Point Design (or Linear CRIP). The CRIP idea was invented by LLNL in the 1980's, and tested in the Rocky Mountain I field trial [51]. The key advantage of CRIP is its ability to carefully control the injection point, and therefore maintain a steady, high-quality syngas stream. The section and plan geometry are illustrated in Figures 1.3 and 1.4.

First, a vertical production well is drilled to base of the target coal seam. Then, a directional injection well is drilled so that it passes horizontally through the seam and intersects the production well. The vertical sections of the well are cased and cemented to avoid gas leakage to overlying strata. The horizontal section in the coal seam only has a steel liner, for both mechanical stability and to control the location where reactions take place. The coal is then ignited at a point near the production well, and air or an oxygen/steam mixture is injected to sustain the reactions. Over time, coal is consumed locally and a cavity grows outward and upward. During this initial growth, the gas-quality is good, with a high BTU-content.

Eventually, however, the growing cavity reaches the top of the coal seam, and begins to expose the overburden rock. A significant portion of the energy content of the coal now goes to heating this roof rock and any rubble that falls into the cavity. The rate of coal consumption around the perimeter of the cavity is not sufficient to balance these losses, and gas-quality can noticeably decline at this point. This decline is an indication that a "CRIP maneuver" should be performed. The basic goal is to create a new injection point in virgin

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coal, further upstream from the burn front. To do so, a special tool is fed down the injection well. The tool basically consists of a torch on the end of a long coiled tubing. This tubing provides a fuel/air mix and also allows the operators to control the torch position downhole. For the maneuver, the tool is pushed down to a point several meters upstream of the burn front, where it is used to burn a hole through the steel liner and into the formation. The torch is then switched off, and the coiled tubing is retracted upstream—away from the high temperature zone—to prevent damage. The oxidant can now exit the liner further upstream.

As gasification proceeds a new cavity section forms, which then merges with the old cavity. Because this new section is surrounded by virgin coal, the gas quality is high and heat losses are minimized. Over time, however, the roof will again be reached and a second CRIP maneuver is required. The tool is again pushed forward to the desired location, the liner is burned, and then the tool is retracted. The whole process repeats up the length of the horizontal section, leading to a long channel of consumed coal.

A common challenge with this scheme (and most other UCG designs) is that either a well may become clogged or a tool may get stuck downhole. If the blockage cannot be removed, the module may have to be abandoned. Operator experience plays a big role in avoiding these snags. In the Rocky Mountain 1 test, the injection casing melted or ruptured occasionally [51]. Therefore, in addition to the intentional large pullbacks of the injection point, there were semi-continuous smaller pullbacks that tended to keep the injection point near the upstream cavity wall.

## 1.4.2 Parallel CRIP

Parallel CRIP is similar to Linear CRIP, but uses three wells instead of two (Figure 1.4). There are now two horizontal wells, which run parallel to one another for several hundred meters before turning inward to intersect a vertical well. One of the horizontal wells is used for production, while the other is used for injection. The vertical well is used to help link the system and for initial ignition. After this it is shut-in.

As gasification proceeds, the same CRIP procedure is used to slowly retract the injection point. In parallel CRIP, however, the flow of gas towards the production well creates a burn "face" that slowly recedes. In this way, a large panel of coal can be extracted in a controlled manner, much like the advancing face of a long wall mine. To give a sense of the lateral scale, a typical configuration might have the two horizontal wells offset from one another by  $\sim 25$  m, though this spacing can vary greatly depending on the project. This offset controls the panel width that is extracted. From a coal recovery point of view, larger extraction widths are appealing, but there are challenges to gasifying very large widths.

Also in analogy to a long wall mine, for wide cavities the surrounding rock may not be sufficiently strong to support the free span. As a result, caving can occur behind the advancing face, leading to gob (goaf) formation. This caving may be an intentional part of the design or an unintentional consequence of poor site characterization. A later chapter discusses this and related geomechanical issues in more detail, as they have significant bearing on water-quality impacts.

#### 1.4.3 Historical Development

Early UCG tests used a "linked vertical well" approach. In the simplest variation, two vertical wells are drilled and completed into the coal seam. A channel or highly permeable path is created between the wells. Linking techniques included drilling a horizontal borehole; performing a reverse burn; hydraulic and/or pneumatic fracturing; and explosive fracturing. These approaches were pioneered and developed in the former Soviet Union [90]. In the 1970's—making use of LLNL-translated Soviet reports—LLNL and the Laramie Energy Technology Center successfully deployed these techniques in the US.

CRIP, both linear and parallel, was pioneered by LLNL in the 1980's. The use of emerging horizontal well drilling technology was first made use of—at least in the West—in LLNL's third Hoe Creek field test [9, 22]. This test also demonstrated the utility of moving the injection point, an important component of CRIP. CRIP was conceived shortly after this and first demonstrated, in its linear mode, by LLNL in the Centralia series of field experiments [1]. In the final United States UCG technology demonstration of that era, LLNL convinced the rest of the leadership team of the Rocky Mountain 1 test to add a CRIP module alongside an already-planned linked vertical wells test [51]. This CRIP module demonstrated both linear CRIP and the early stages of parallel CRIP, with both discrete long retractions as well as (unintended) phases of continuous retractions.

In the 1990's, the European Union's El Tremedal test used linear CRIP [92]. In the 2000's, Carbon Energy's Bloodwood Creek first test demonstrated parallel CRIP over a longer time and larger scale than Rocky Mountain 1, in a configuration very similar to Rocky Mountain 1. More recently, Carbon Energy has run parallel CRIP in its second Bloodwood Creek test. It is believed that Linc's most recent demonstration UCG burns have been parallel CRIP. Both of these Australian sites are thought to have very strong overburden, possibly spanning 20 or more meters of width without collapse.

Each approach and its variations have proponents and detractors, and advantages and disadvantages in different situations. Approaches, such as linear and parallel CRIP, which utilize long horizontal wells, are generally thought to be appropriate for deep seams. Where overburden is not very strong, a narrow channel may be desired, and linear CRIP is well-suited to this. The cost of drilling and completing wells for linear CRIP is intermediate between linked vertical wells (lower cost, at least for shallower target coals) and parallel CRIP (higher cost).

## 1.5 Process waste and byproduct streams

The raw product gas coming out of the ground in the production well includes the expected gases ( $N_2$ , CO,  $H_2$ , CH<sub>4</sub>, and CO<sub>2</sub>) along with a significant amount of water. The water is

usually in vapor form, but could possibly be liquid mist or liquid slugs depending on local pressure, temperature, concentrations, and process details. There will usually also be small concentrations of a broad suite of hydrocarbons, organics, and heteroatom (N, S) species. These will exist as vapor and possibly liquid mist depending on temperature, pressure, and phase behavior. Some small concentrations of fine ash and/or char particulates are also likely.

Typically the first few stages of gas cleanup will involve particulate separation and/or condensation. These will produce side stream(s) of particulates and/or condensable liquid streams which may contain particulates. The liquid stream will likely contain an aqueous phase of water with dissolved organics and inorganics, an organic phase consisting of hydrocarbons and other organics, and possibly a sludge phase consisting of ash and/or char and/or very heavy tar particulates. Additional details can be found in Chapter 6.

The amount of water produced will depend on the coal, surrounding strata, and design and operating characteristics of both the module and the entire UCG project area over time. The possible range might be from 0.1 to more than 1.0 times the mass of coal gasified. If no other information is available, a multiplier of 0.4 is likely to be within a factor of two.

The organic liquid stream may be considered a waste product or it may be a valuable byproduct of the gasification, depending on markets and separation/purification opportunities and costs. The aqueous stream and the solid or sludge streams will most likely be waste streams requiring management, waste treatment, and effective controls to assure they are not released into the environment. Depending on the scale of the operation there may be holding tanks or ponds, and transportation for off-site treatment or on-site wastewater treatment and disposal.

It should be noted that the magnitude of the solid or sludge streams is expected to be much smaller than from conventional coal mining, beneficiation, processing (such as pulverizing), and combustion processes. With UCG, most of the inorganic mineral matter in the coal will stay underground. The wastewater and organic streams will be very similar to wastewater from surface coal gasification operations, especially those with lower heating rates, such as fixed or moving packed beds or fluidized beds. There is a significant experience base in dealing with these streams that should provide adequate guidance for proper handling and environmental protection during the storage and treatment operations. These streams are also generally similar to many wastewater and heavy residual organic streams in the petroleum production, refining, and petrochemical industries. Thus best practices in these industries provide an adequate level of knowledge and experience for safely storing and treating the streams. At small scales, this wastewater may be sent off for appropriate off-site treatment. At larger scales on-site treatment would likely be chosen.

An alternative to be considered is the re-injection of process wastewater into the process. Depending on details of the proposal, this might have the potential to reduce net water consumption. The contaminants could be consumed by the process and would be expected to remain in or near the cavity. The details of such a proposal would need to be evaluated carefully, however.

## Chapter 2

## Site Selection and Characterization

One of the most effective ways to prevent and minimize the groundwater contamination risk from UCG is by good site selection. A site with favorable characteristics relating to groundwater protection will tend to leave less contamination, have that contamination be more narrowly localized, have lower probabilities of further contamination transport, and produce less impact to people, agriculture, and valuable groundwater resources if there are problems.

The risk to the environment and groundwater depends on site characteristics, design, and operating characteristics. The risks at a site with non-optimal or even poor characteristics can be mitigated by conservative design and operation, though at some cost. The risks at a site with outstanding site characteristics can be made unacceptably high by overly aggressive and poor design and operation.

It is common for a project developer or coal owner to evaluate candidate coal fields against a large number of technical, geographic, economic, and environmental factors when determining which of several UCG opportunities looks best to pursue further, or when determining whether to go forward with a project at a specific site. Key criteria to be considered include coal properties, geologic setting, infrastructure, labor, available markets, and possible impacts.

In the following sections we describe those assessment factors which are relevant to protecting groundwater resources from contamination. In many aspects, technical UCG performance is closely coupled to mitigation of contamination risk. The discussion below therefore includes some technical performance aspects, but it is biased to emphasize environmental protection.

## 2.1 Overview of Site Characteristics

General site characteristics that affect the risk of groundwater contamination include:

- Regional structural geology
- Local coal seam geometry (thickness, depth, dip, lateral continuity)
- Hydrologic properties
- Geomechanical properties

• Coal rank, properties, and chemical attributes

The following sections describe each of these general characteristics in more detail, and their role in environmental hazards. These same properties also have an impact on process performance, and we also briefly describe these relationships. In some cases process performance and environmental protection favor the same characteristics, and in some cases they favor opposite characteristics. An understanding of these tradeoffs is important for evaluating various design decisions.

#### 2.2 Regional Structural Geology

## 2.2.1 Faults

An ideal UCG region would have no faults. But all things being equal, fewer, smaller faults are better for UCG than more, larger faults. UCG is possible in a faulted region, though certain aspects of the project will be more challenging.

Faults complicate projects in several ways. They make the geology and its structure more complex. The presence of faults can make it harder to identify and map coal seams. Seam elevations cannot be extrapolated far, even if dip angle and direction are known. As a result, a higher resolution mapping effort may be needed for site evaluation. Large seismic surveys may be needed for a candidate area, followed by expert interpretation.

Faults also make coal seams discontinuous in two planes. Discontinuities in the seam can constrain UCG panel size. For a large-scale UCG project operating for decades, mine-plan layouts may need to be adjusted accordingly. Faults can also affect hydrologic connectivity between UCG-affected strata and shallower strata. Faults can be harmful if they create direct paths for contaminant transport. On the other hand, faults can also create transport barriers by sealing a permeable formation against an impermeable one. It should be noted that experience with UCG in highly faulted regions is limited. As the body of knowledge develops, along with industry best practices, the impacts of faults on UCG will become clearer.

## 2.2.2 Folds

Coal surrounded by flat-lying stratigraphy is simpler to map and exploit. However, folds can provide advantages for UCG operations. For example, anticlines provide an opportunity for improved containment. Sites with predictable structures can also increase the chances of finding a target coal seam at a chosen depth and dip.

#### 2.3 Local Coal Seam Characteristics

#### 2.3.1 Thickness

From a process performance point of view, thicker seams are preferred over thinner seams for UCG. All things being equal, the amount of coal accessed per unit construction cost and per acre has at least a linear dependence on the thickness of the coal seam. This is because a UCG panel, with a given cost of well construction, will usually be expected to recover most of the coal seam thickness over some width. The maximum width obtainable will tend to increase with increasing seam thickness. Also, the ratios of coal gasified to some sources of heat loss (such as heating of roof and floor rocks) are roughly proportional to seam thickness (volume to surface-area ratio). Both theoretical curves and Former Soviet Union UCG data show product gas heating value diminishes strongly as seam thickness drops below 2 meters.

From an environmental protection point of view, there are few clear cut reasons to prefer thick vs. thin seams. The seam thickness does, however, play an important role in the geomechanical stability of the extraction plan, and will factor into the geotechnical design. For example, inter-module pillar strength usually depends on the height-to-width ratio, and so thicker seams will require proportionally wider pillars.

Because of the sedimentary characteristics of coal deposits, coal seams are rarely a simple seam of pure coal surrounded by thick zones of organic-free rock. Coal zones often have regions of variable ash, partings of inorganic or organic-rich rock, and thin interburden layers separating multiple coal seams.

It is often difficult to identify the exact bottom and top of the thickness of coal that will be consumed, and the experience base is small. It is a case-by-case judgment to be made based on heating values, ash content, organic content, panel width, overburden strength, and thicknesses of seams and interburdens. As an example, the Hoe Creek tests—conducted by LLNL in Wyoming from 1976-1979 [22]—focused on two adjacent coal seams, named Felix 1 and Felix 2. The process began in the lower Felix 2 seam, but eventually migrated to the upper Felix 1 seam when the interburden between the two spalled and/or collapsed. Felix 2 was eight meters thick, the interburden was five meters thick, and Felix 1 was three meters thick.

#### 2.3.2 Depth

The depth to the gasified coal seam presents a number of tradeoffs in terms of process performance and environmental protection. Factors favoring deeper gasifiers are mainly related to environmental protection, and include:

- Greater separation and isolation from drinking-water resources
- Smaller surface subsidence
- Lower probability of sink-hole formation

#### CHAPTER 2. SITE SELECTION AND CHARACTERIZATION

- Deeper rocks tend to have stronger mechanical properties
- Deeper rocks tend to have lower permeability
- Gasification must take place below the local water table to avoid risk of uncontrollable coal fires
- Deeper coals may be more mature, with a higher heating value and less moisture
- Deeper gasification may favor higher methane yields due to higher operating pressure
- The horizontal reach of directional wells is controlled by vertical depth.

Factors favoring shallow gasifiers are mainly cost-related, and include:

- Cheaper drilling costs for process and monitoring wells
- Cheaper gas compression and water-pumping costs
- Smaller intervention costs to fix wells or module problems
- · Lower production well pressures may reduce leakage risk
- Geotechnical design needs to support smaller lithostatic stresses
- Larger experience base with shallow UCG

While there is no optimal depth, modern UCG operations are considering seams between 100 and 1500 m depth. It is expected that in most cases the depth-related trade-offs will be optimized somewhere between 250 and 800 m, but understanding and experience around the world is evolving. In all cases, site-specific and design-specific information is more important than any fixed rule about depth.

## 2.3.3 Dip

Older conventional wisdom says that the optimum dip for the UCG process is about 5 to 25 degrees. Some dip is desirable to take advantage of the tendency of the UCG process to burn up-dip. For commercial-scale projects with gasifiers covering a large area, however, low dip angles may be more favorable. This simplifies management of the local hydrology and panel-panel interactions, by ensuring that all modules are operating at similar depths. For example, operations and interpretation of the Rocky Mountain 1 test [52] were significantly complicated because the two modules—in operation at the same time and in the same seam—were at different elevations and hence at different hydrostatic pressures. On the upside, in a dipping seam a more favorable operating depth can be found by simply moving a project laterally.

Experience with steeply dipping seams is limited—mostly tested in the Former Soviet Union. Looking at contaminant transport from a deep UCG operation to the surface, steeply dipping coal seams or other strata may provide a permeable path for bringing contaminants closer to the surface, and should be evaluated carefully.

#### 2.3.4 Lateral Continuity

UCG operations generally favor coal seams that are continuous for long distances, so that a regular panel layout can be established. In general, it is relatively easy to find sites with limited vertical permeability, but harder to find sites with limited lateral permeability.

From the point of view of contaminant transport, an ideal situation might be a lens of coal surrounded laterally as well as vertically by impermeable materials. Similarly, a coal block surrounded by offset, sealing faults may be effectively compartmentalized. The latter configuration is more questionable, however, depending on the vertical permeability of the faults and surrounding damage zones.

### 2.3.5 Multiple-Seam Extraction

A project may contemplate gasifying multiple coal seams that are separated vertically from each other by a significant distance. There is little-to-no prior experience, however, with multi-seam UCG extraction. This approach is higher risk since geomechanical interactions between modules at different depths must be considered. Careful analyses of both the geomechanics and the hydrology—in the context of affected rock structure—are essential. The ordering of the panel extraction (overmining vs. undermining) and vertical alignment of panels (aligned vs. offset) must be carefully considered.

### 2.4 Hydrologic Properties

From a process performance perspective, low permeability in the coal and rock is almost always preferred because of reduced water intrusion. There is usually more water influx into the cavity than is optimal, due to the combination of permeation through the coal, permeation through the adjacent strata, drying of surrounding rock, and drying of wet rock that falls into the cavity. These different sources usually supply more than enough water for the gasification chemistry. Too much liquid water coming in also wastes valuable energy in evaporation.

From a contaminant transport perspective, low permeability is also preferred. Low permeability strata can prevent contaminants from migrating large distances away from the cavity. Also, a lower influx rate of water into the cavity can reduce the volume of water produced—water that must ultimately be cleaned and disposed of.

In general, the goal of a hydrologic assessment is to determine the permeability and storativity properties of the coal seam and adjacent strata. Regional groundwater flow should also be measured, to determine if there are persistant hydrologic gradients that could carry contaminants away from the cavity. It is also important to remember that many sites experience significant seasonal variation, and these cyclic changes should be adequately characterized. The ideal configuration from a site selection point of view is a situation in which the target coal seam is separated from any drinking-water aquifers by low-permeability seals. Thick seals and multiple redundant seals can lower risk.

A good hydrologic model for the site is also essential for the design of the water sampling well array. If one wants to place wells in a configuration that can rapidly detect unwanted contaminant excursions, a solid understanding of the local site hydrology is essential.

#### 2.5 Geomechanical Properties

## 2.5.1 Disadvantages of Vertical Cavity Growth

The resistance of the surrounding strata to vertical cavity growth is a crucial characteristic of a good UCG site. Vertical growth of the cavity due to rock caving into the excavated coal volume is undesirable for three important reasons.

- 1. When rubble falls into the hot cavity, it is heated and its water content is evaporated. This both robs the process of energy and adds to the amount of water produced that must be cleaned and disposed of.
- 2. A taller vertical extent of the cavity means that the cavity must be operated at lower pressure in order to avoid exceeding the hydrostatic pressure threshold. A lower operating pressure results in a larger influx of water into the lower elevations of the cavity.
- 3. All things being equal, a larger cavity volume means greater subsidence potential at the surface, greater vertical extent of potentially fractured overburden above the cavity, and a larger volume of strained material surrounding the cavity.

Surface subsidence due to large extractions can be highly disruptive to surface infrastructure. Also, significant strains and fracturing around the cavity can enhance formation permeability and create unwanted contaminant leakage pathways.

#### 2.5.2 Mechanisms of Cavity Growth

The cavity can grow up into the surrounding rock formation by spalling, rock decomposition, or mechanical collapse. Here, spalling refers to the small-scale erosion of rock due to induced thermal stress. Rock decomposition refers to a physical disintegration of the rock due to thermal decomposition of its minerals. Mechanical collapse refers to the larger-scale failure of the walls of the cavity, after it can no longer withstand the modified stresses created by cavity extraction and pore pressure changes. Usually a combination of these mechanisms controls the cavity growth, though for a given lithology one or more processes may dominate. To minimize vertical expansion of the cavity the surrounding formation needs to be mechanically strong and resistant to spalling or decomposition processes.

#### 2.5.3 Spalling

Spalling has been observed when overburden cores are heated, due to thermally-induced stresses. The phenomena has been useful in describing the rate at which UCG roofs grow upward and the rate at which water from the affected rock enters the process. The rate at which the cavity advances vertically is an important parameter to measure during a pilot test at a given site. In the United States, spalling rate parameters have been obtained as fitted parameters during retrospective modeling of field tests. Spalling rates must be physically reasonable and consistent with known laboratory data. It is expected that models calibrated for a site would be predictive for other operations with similar geology.

Despite its importance, no standard assay has been developed for spalling parameters. This is an important research topic. It has proved difficult to study in the laboratory, and reliable correlations have not emerged. Qualitatively, we expect that spalling will be more likely in sedimentary rocks that exhibit some combination of brittleness, weakness, strength-weakening on drying, and low permeability. Shale is prone to spalling because it is fissile and easily splits along close parallel planes. Unconsolidated sands may often be prone to spalling, as the grains may simply slough off as they dry.

## 2.5.4 Decomposition

It is undesirable if the overburden rock physically disintegrates due to thermal decomposition of its constituent minerals. Individual strata should be assessed to determine if reactive minerals are present.

Calcining reactions of carbonates are one possibility to be aware of. Carbonates have the potential to significantly impact the energy balance, the yield of carbon dioxide, and the strength of rocks. Calcining reactions such as

$$CaCO_3 \to CaO + CO_2 \tag{2.1}$$

and analogous reactions occur at high temperatures and are endothermic. Because the  $CO_2$  occupies a significant volume of the carbonate molecule, in general the calcined form (e.g. CaO) is considerably less strong. UCG experience in the United States does not include carbonate rich sediments. However, experience and models for the huge dolomitic oil shale resources in the United States indicate the extent of these calcining reactions depends on both thermodynamics (temperature and carbon dioxide partial pressure) and mass- and heat-transfer and kinetics.

In addition to decomposition of carbonate minerals, dehydration of clay minerals should also be considered. Clay minerals in the ash and/or surrounding rock strata will dehydrate, but it is not certain if they will make the overburden weaker or stronger. Dehydration temperatures are typically a few hundred degrees Celsius at atmospheric pressure and presumably increase with pressure as water vaporization does. Clay dehydration is endothermic, with a heat of reaction similar to the heat of water evaporation. The proximate analysis of coal may already account for dehydration of clay minerals in the coal ash, but this needs thoughtful checking. For surrounding rock, it is important to know the total water, including pore water and bound water, typically in the form of hydrated clays. Total water in rock is best measured by a drying experiment in a Thermogravimetric Analysis (TGA) apparatus, making sure the temperature exceeds clay dehydration temperatures. Alternatively, an estimate of porosity may be used to obtain the pore water fraction, and mineralogy may be used to estimate the amount of water associated with clays.

#### 2.5.5 Mechanical Collapse

A mechanically-weak overburden will increase parasitic energy losses and increase the risk of environmental impacts. The mechanical quality of the coal and adjacent rocks are typically assessed using a combination of laboratory tests and field observations. A number of well established rock-quality rating systems are used in geotechnical practice (e.g. the Coal Mine Roof Rating [89]) and these assessments are equally useful for UCG design. Similarly, empirical correlations concerning pillar and roof strength are also useful in module design.

When mechanical collapse does occur, the rubblized rock takes up a larger volume due to bulking. If the collapsed volume is sufficiently large, bulked material may begin to transfer a portion of the overburden stress—analogously to gob formation in a longwall mine. Current UCG designs tend to favor smaller cavities that behave much like a room-and-pillar mine. In the future, however, there may be a move to higher extraction ratios, and designs that deliberately incorporate large-scale caving.

#### 2.6 Coal Rank, Properties, and Chemical Attributes

Coal rank has little direct effect on the groundwater contamination risk. Most of the UCG experience is with sub-bituminous coal and to a lesser extent, lignite. There is significantly less experience doing UCG on bituminous coals, and this relative lack of experience is a risk factor. Significant uncertainty also surrounds the use of bituminous coals that have significant swelling/agglomerating/plastic behavior upon heating.

Rank, proximate analysis, and ultimate analysis probably affect details of concentrations of the contaminants produced initially by pyrolysis, as well as gasification kinetics, etc. But the effect of these differences on the overall risk to groundwater is probably very small relative to most of the other factors.

High content of sulfur and nitrogen would tend to produce more heteroatomic compounds, many of which may be more hazardous than their hydrocarbon analogs. Most of the sulfur will come off as H<sub>2</sub>S and most of the nitrogen will come off as NH<sub>3</sub>, but minor organic species containing S and N can be hazardous. Favorable properties for UCG would tend to give the operator a more technical and economic project. This could afford the operator some latitude to make trade-offs if needed to provide additional environmental protection.

High concentrations of sodium and alkali metals as major species in the ash will make the ash more likely to fuse within UCG. This will affect the process somewhat. From an environmental point of view, it may slow and limit the leaching of trace species from the slag compared to separate fine particulates. Concentrations of toxic metals in the ash analysis make the ash a source term for leaching of these species after UCG, especially if UCG leaves warm and acidic waters.
# Chapter 3

# **Contaminant Behavior During Proper Operation**

In normal UCG operation, compounds that could contaminate groundwater are continuously generated, destroyed, and removed from the system along with the product gas. They are generated by pyrolysis and other reactions. They are destroyed (chemically converted to desired products or benign byproducts) by combustion, cracking, and coking. Some of remainder are condensed and then revolatilized later. The rest and the revolatilized species flow out of the system through the production well with the product gas to the surface.

When shutting down a module following the active gasification phase, a cleaning process using a combination of inert gas, steam, and/or water is used to sweep out most of the small localized inventory of contaminants. This leaves only a small quantity of contaminants, and these are generally non-mobile. These normal processes of contaminant generation, destruction, removal, and cleanup are described in the subsequent sections of this chapter.

Certain abnormal unwanted scenarios can happen if good practices are not followed. These can lead to transport of significant quantities of contaminants away from the process. This increases the probability and magnitude of contaminating valuable/protected groundwater. The key to avoiding these scenarios is to understand them.

#### 3.1 Generation of contaminants

This section describes the processes that generate compounds that could contaminate groundwater and the general chemical nature of these contaminants. Chapter 6 details the specific compounds produced by UCG, making use of data on the gas, organic, and aqueous streams produced by UCG tests.

There are essentially two types of contaminant produced by UCG, direct (or primary) and indirect (or secondary). Direct production of a suite of organic contaminants comes mainly from the pyrolytic decomposition of coal (pyrolysis) and subsequent reactions in the gasification process. In addition to the organics, contaminant species that are directly produced include hydrogen sulfide (H<sub>2</sub>S) and ammonia (NH<sub>3</sub>).

Contaminants are also produced indirectly, and often later in time. These occur because of increased temperature, changed pH, and/or other physical or chemical changes to the system. These factors can mobilize or increase concentrations of various contaminants.

If gas escapes from the UCG process it will contain direct and possibly indirect contaminants and these in turn can contaminate groundwater. The exact composition of the escaping process gas will depend on precisely where it escapes from. The UCG product stream can be analyzed at the surface and makes a good proxy for gas that might escape from the UCG process.

Many of the direct and indirect species are toxic, hazardous, or otherwise noxious and their contact with valuable or protected ground water is undesirable or unacceptable.

## 3.1.1 Direct generation of species by pyrolysis, partial oxidation, and gasification

# 3.1.1.1 Gas-phase products (the noncondensables)

UCG process gas will contain the major constituents of carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), hydrogen (H<sub>2</sub>), water (H<sub>2</sub>O), and methane (CH<sub>4</sub>) in concentrations of tens of percent by volume. In air-blown systems, nitrogen, (N<sub>2</sub>) can be up to more than half of the gas volume. In addition there will be lesser amounts, on the order of 1% or less, of light hydrocarbons, hydrogen sulfide (H<sub>2</sub>S), ammonia (NH<sub>3</sub>), and some trace species.

Pyrolysis and cracking reactions produce light hydrocarbons, ranging from ethane and ethylene compounds to volatile condensables such as hexane and toluene. The partitioning of volatile condensables between the gas condensed product streams will depend on the exact compositions and condenser details.

Hydrogen sulfide ( $H_2S$ ), is the dominant sulfur-containing product, as most of the coal sulfur is produced as  $H_2S$ . Ammonia ( $NH_3$ ) is the dominant nitrogen-containing gas species, as 50-60% of the coal nitrogen is produced as ammonia.

#### 3.1.1.2 Condensable organic species from pyrolysis and gasification

We designate as primary or direct contaminants the organic species produced by pyrolysis and other reactions in the hot process zone, as described in this section. Condensable organics from pyrolysis or gasification processes are a mixture of "light oils" and heavy organics that are sometimes collectively called "tars." We will call them condensable organics or "condensables," although other references variably use "oil" or "tar" to describe the entire organic phase.

Organic condensables are well known in the thermal coal processing industries. The early 20th century coal pyrolysis plants that produced "town gas" also produced condensable organics. Coal gasification plants also produce condensable organics and the literature on these tars will be generally relevant to UCG. Their amounts and composition depends on process details. In general, oxidative processes such as gasification produce more oxygenated polar species than inert purely pyrolytic processes. Coal gasifiers running at lower

temperatures and slower heating rates such as Lurgi, fixed bed, or moving packed bed gasifier are similar enough to UCG to expect some similarities in their condensable products.

A general introduction to pyrolysis and its resulting products, and gasification processes, is found in various chapters of Probstein and Hicks [93].

In UCG, coal adjacent to the hot cavity or in pieces within the hot cavity becomes heated. When coal is heated in the absence of an oxidant it pyrolyzes. Pyrolysis is the breaking of large molecules (coal) into smaller parts due to heat. Pyrolysis products include a solid char residue, and a suite of volatile organic species. The organics can include hydrocarbons and heteroatomic (containing other atoms besides C and H) organics. Some of these volatile products are gases under standard conditions and some are vapors at high temperatures that will condense to liquid or solid phase at lower temperatures.

Oxygen and other species capable of oxiding organics are present in the hot underground process environment. In addition to complete oxidation (forming  $CO_2$  and  $H_2O$ ) and gasification reactions (forming CO and  $H_2$ ), organics present may be partially oxidized or reacted to produce species such as organic acids, phenols, ketones and alcohols.

As a result of pyrolysis, partial oxidation, and other reactions, the gas within parts of the UCG cavity during operations will contain many organic species. Coal can be thought of as a highly aromatic macromolecule with aromatic and other ring structures linked by aliphatic groups (Aromatic means containing one or more benzene-like aromatic rings. Aliphatic means not aromatic). Because of the aromatic nature of coal, aromatic species are more plentiful than aliphatic species, at least in the larger molecules.

The UCG process gas will contain a huge number of individual compounds including hydrocarbons, and oxygen-, nitrogen-, and sulfur-containing compounds. These include small and large molecules (low or high molecular weight), reactive and stable species, volatile and nonvolatile compounds, and water soluble and water insoluble compounds, and strongly and weakly adsorbing compounds. The fate and transport of different species depends strongly on their various physical-chemical behaviors.

In general, species such as methane, ethane, and propane are gases at standard conditions and commonly, if simplistically, called noncondensables. These are not considered part of the organic condensables. They are generally considered to be valuable UCG products.

A fraction of organic compounds are readily condensed at ambient conditions. These include light organics and heavier tars. "Light oils" are generally considered to include those compounds with boiling points below 170° C. Condensable hydrocarbons may include low concentrations of small to medium aliphatics, and larger concentrations of small to large aromatics, hydroaromatics, and polycyclic aromatics. Oxygenated organics may include phenols, cresols, ketones, etc. Nitrogen- and sulfur-containing compounds may include pyridines, pyrroles, aniline, sulfides, mercaptans, etc. Most of the heteroatoms in the condensable organic phase are contained in ring compounds.

#### Table 3.1 Some condensable organic compounds typically present in UCG process gas.

#### Hydrocarbons

- Paraffinic (Saturated Aliphatic) Hydrocarbons, (C4 to C~12+ linear and ring)
- Olefinic (Unsaturated Aliphatic) Hydrocarbons, (C4 to C~12+ linear and ring)
- Single-ring Aromatic Hydrocarbons (Benzene, Toluene, Ethylbenzene, Xylene, ...)
- Double-ring Aromatic Hydrocarbons (Napthalene ...)
- Triple-ring (Anthracene, Phenanthrene, ...)
- Mixed Aromatic-Aliphatic Ring Structures (Tetralin, Fluorene, Indane ...)

Oxygen-containing organics

- Phenolics (aromatics with a hydroxyl group) such as (Phenol (C6H5(OH)), Dihydroxybenzenes (C6H4(OH)2)catechol, resourcinol, quinol), Trihydroxybenzenes including pyrogallol (C6H3(OH)3), Napthol (C10H7OH), Pyrogallol, Cresols, Xylenols,
- Furans (aromatic rings including a ring oxygen); e.g. di-benzofuran
- Ketones aliphatic linear (acetone, butanone) or ring (cyclopentanone), or alkylaromatic

Nitrogen-containing compounds

- Ammonia (NH3), probably simple aliphatic amines
- Nitrogen-containing heterocyclic organics (Pyridine (C5H5N) Pyrrole (C4NH5), Carbazols, Acridenes, Quinolines (C9H7N), ...
- Nitrogen-containing amines and aromatic amines, e.g. Aniline (C6H5NH2)

Sulfur-containing compounds

- Hydrogen sulfide (H2S) is the dominant gas species, with a little carbonyl sulfide and methyl mercaptan

 Sulfur-containing heterocyclic aromatics (aromatic ring structures with S in the ring), e.g. Thiophen, Benzothiophenes

In a UCG operation the raw product gas stream is condensed. This condensate has aqueous and organic fractions. Data on the composition of the organic fraction from UCG tests provide a good idea of the kinds of species that would be in the UCG process gas underground. The organic fraction of the Rocky Mountain 1 product condensate, designated in reports as "tar," had an estimated average molecular weight of 210 g/gmol and atomic ratios of  $C_1H_{1.32}O_{0.037}N_{0.014}S_{0.002}$ . Table 3.1 lists some typical organic compounds in UCG condensed organic product stream.

Most of the organic species found in UCG oil-phase liquids would be undesirable contaminants in groundwater. Some, such as benzene, are tightly regulated, and even very small concentrations are unacceptable in any aquifer of value. Liquids and tars from early 20th century coal "town gas" processes were often disposed of in places and ways that have required remediation in modern times. The body of more recent literature and practical knowledge associated with characterizing and remediating these sites may be useful in the UCG context.

# 3.1.1.3 Water-soluble organic species from pyrolysis and gasification

If hot UCG process gas were to mix well with groundwater underground, the water would pick up organics (and inorganics from its ash and inorganic gas species) and end up looking a lot like the aqueous condensate stream from a UCG operation. In a UCG operation the raw product gas stream is condensed. This condensate has aqueous and organic fractions. A bounding case of what contacted groundwater might look like is the aqueous phase of the UCG product gas condensate. This has been in intimate contact with the UCG product gas stream, including its noncondensible gases, condensable vapors, and some char and ash particulates. Data on the composition of the aqueous fraction from UCG tests provide a good idea of the kinds of species that might be expected in UCG-contaminated groundwater.

It should be noted that for most UCG contamination scenarios, UCG process gas flows through porous media and fractures underground. Contaminants would be deposited on the host rock and in the groundwater along the way in a "chromatographic" fashion. The higher boiling point, more water-soluble, and more readily sorbed species will leave the gas stream first, and thus be found closest to the leak origin. Similarly, lower boiling point, more water insoluble, and less readily sorbed species will stay in the gas phase longer and travel further. In other words, for most gas-escape contamination scenarios, not all of the species seen in product condensate will be found in one place underground. These species will be distributed spatially along the path of the leak.

The aqueous condensate product of a UCG operation is well contacted with the vapor and the organic condensate, and multicomponent phase equilibrium will be approached. Between the water phase and the vapor or organic liquid phases, the aqueous concentration of any species will tend to approach (approximately) the product of the species' neat water solubility times its mole fraction in the gas. In general, the more polar and smaller the compound the more soluble. Large hydrocarbons (e.g. anthracene) have very low water solubilities; heteroatomics organics such as phenols tend to have moderate solubilities; and highly polar species such as ammonia have relatively high solubilibies.

Chapter 6 presents analyses of the aqueous condensate with quantitation and a long list of compounds. As would be expected from their solubilities and high concentrations in the liquid product, phenolics such as phenol, cresols, xylenols are by far the most plentiful group of organics found in the water. At much lower concentrations, other groups found are nitrogen-containing organics, non-phenolic oxygen-containing organics, sulfur-containing organics, aromatic hydrocarbons, and aliphatic hydrocarbons. For all of the attention that benzene gets, the BTEX concentrations in the aqueous phase are only a few parts per million, despite being 2-5% of the oil-phase condensate. This is because of their low solubility.

In samples that have not had particulates (either solid or organic colloids) extensively separated, significant quantities of low-solubility multi-ring aromatics are present. It is likely that they exist dissolved within or sorbed onto colloid particles of tar and/or char that are suspended in the water phase.

# 3.1.1.4 Direct production of inorganic species

Pyrolysis and gasification produce inorganic species. These include carbon dioxide, ammonia, and hydrogen sulfide. Carbon dioxide (CO<sub>2</sub>) could be considered a groundwater contaminant because it and its ions (CO<sub>3</sub><sup>=</sup>, HCO<sub>3</sub><sup>-</sup>, etc.) affect water chemistry and pH. Ammonia (NH<sub>3</sub>) is a highly soluble contaminant and affects pH. Hydrogen sulfide (H<sub>2</sub>S) is noxious, toxic, and somewhat soluble in water (0.4% w/w at 20° C).

Pyrolysis and gasification also produce particulate mineral ash, often in colloidal particle sizes. These will be present within the cavity and also may travel through the formation with escaping process gas and contacted groundwater.

Organic solids such as char or colloidal particles of polyaromatics are also generated by the UCG process and may travel underground suspended in either gas or groundwater.

## 3.1.2 Generation of indirect contaminants by other physical chemical processes

We designate as indirect or secondary those contaminants that may be produced indirectly or later in time, typically by physical-chemical reactions and processes. These are described briefly in this section but are not considered further in this report.

Inorganic species, including unwanted contaminants, have sometimes been found at elevated concentrations. At Rocky Mountain 1, post-test sampling data show a  $1.25 \times$  increase in total dissolved solids near the process area and elevated boron within the cavity [52]. There are several general sources or mechanisms that could lead to higher inorganic concentrations:

- The consumption of coal will leave most of the ash minerals in the cavity, and a large fraction of these will be in the form of very fine particulates. Similarly, spalled/collapsed and heated roof rock particles and dust will also reduce particle size and increase fines. The residual fine coal ash and spalled rock dust increases surface area which will increase the rate of leaching of metals or other unwanted species into groundwater.
- Elevated aqueous temperatures will typically increase the solubility of metals as well as organics. Elevated temperatures will also change sorption equilibria of inorganics as well as organics. This will be local to areas of elevated water temperatures. If a bolus of warm water moves from the site, by buoyancy or gradients, it will carry with it the higher solute concentrations.
- Change in pH can increase the solubility of metals. Carbon dioxide from UCG may form carbonic acid and tend to decrease the pH. Ammonia from UCG will tend to increase the pH. Ammonia production averaged about 0.5% by volume of the total wet gas product flow rate in the Rocky Mountain 1 test [60, 46]. Some metals are more soluble at lower or higher pH.

- Changed oxidation state (typically more highly oxidized) of minerals and metals within the ash and rock may increase the solubility of some metals or the physical state of host minerals.
- Reduction in hydrostatic pressure will shift sorption equilibrium toward desorption of gases including CO<sup>-</sup>, methane, and radon. Lower pressures will also shift vapor-liquid partitioning toward vapor.
- Increased concentration and transport of radon has been observed at UCG sites in China. This is probably due primarily to hot temperatures, but secondarily may result from lower pressures. The radon measurements have correlated well enough to UCG geometry that it is being considered as a UCG monitoring/mapping tool in several Chinese tests.
- Large increases over background in concentrations of boron (substitutes for aluminum in minerals) were measured in the water sampled directly from a Rocky Mountain 1 cavity before pump treatment. Only very small or insignificant increases in boron were measured in a few in-seam sampling wells after the test, including locations that had been contacted by a gas "bubble" excursion during the test. It is possible that the very high temperatures within the process cavity caused the loss of some boron from ash minerals.

# 3.1.3 Inorganic and other water quality characteristics of condensate water

The UCG process and its gas can affect contacted groundwater in other ways besides dissolved organics. Analyses of the aqueous phase of the UCG product condensates are presented in Chapter 6. We have not compared these side-by-side to background groundwater quality data, but qualitative aspects may be called out. These include high total organic carbon, ammonia and amine nitrogen,  $CO_3^=$  in various forms, cyanide, thiocyanates, and possibly boron. The pH is also high.

# 3.2 Destruction of organics during operation

In proper operation, the UCG process gas is contained within the immediate cavity system and flows into the production well where it flows to the surface processing units. Containment of the process gas is very important. Within the contained process zone many organics are destroyed. Figure 3.1 illustrates the containment, flow, and some of these destruction processes.

The majority of condensable organics that are produced are "destroyed" within the process. "Destroyed" means converted by reaction into species that are not hazardous. For example most of the benzene produced by pyrolysis is "destroyed" by oxidation to carbon dioxide and water, and larger organics are "destroyed" by coking reactions that convert them to nontransportable solid coke and gases such as hydrogen and methane.

Most of the pyrolysis products produced in the wall zone will be carried inward into the hot reactive cavity and rubble zones. The "carrier gas" is inward-flowing water vapor

#### CHAPTER 3. CONTAMINANT BEHAVIOR DURING PROPER OPERATION



Fig. 3.1 Organic compounds produced by pyrolysis and other reactions are contained and continually destroyed before flowing into the production well where they are removed from the underground system.

coming from the drying zone and the pyrolysis gas itself. These flow inward into the cavity because of the inward pressure gradient.

Combustion will be nearly instantaneous when injected oxygen mixes with pyrolysis organics and much of the pyrolysis organics are destroyed this way. There will be regions of low oxygen concentration where partial oxidation can convert compounds.

Just as gasification is done industrially on petroleum residuals and municipal waste, in addition to coal, gasification reactions will also consume heavy organics, converting them to CO and  $H_2$ .

Larger hydrocarbons and probably other organics will "crack" into smaller molecules at high temperature. These are the same reactions used industrially for cracking petroleum fractions into lighter components. The products from cracking of heavier organics are lighter hydrocarbons, gas (noncondensable hydrocarbons such as methane), and a small amount of solid nonvolatile nonmobile coke. It is thought that the high surface area and metal content of ash and rock dust in the process gas tends to facilitate UCG reactions, just as catalytic cracking or catalyzed water-gas shift reactions are done industrially.

Coking reactions will also eliminate organics. Coking of organics produces a larger fraction of solid immobile coke and some gas. This would be expected to take place further downstream at intermediate temperatures, including on organics condensed on surfaces at intermediate temperature.

In most UCG process arrangements, the process gas will flow through progressively less hot regions on its way to the inlet of the production well. The gas will cool along this path. As it cools, organic species will condense according to vapor-liquid phase equilibria (higher-boiling and more-concentrated species will condense first). Condensation will be onto solid surfaces, and into mist droplets. Some of the mist droplets will impinge onto and be retained on the rubble and wall surfaces, and some mist droplets will be carried up and out with the product gas. Most of the condensed organics on surfaces will be either consumed by the coking and gasification reactions described above, or be revolatilized later and carried out the production well.

As the UCG process continues and grows over the next hours, days, weeks, and months, places which were cool become hotter. Species that condensed at a location will later vaporize and be advected further downstream towards the production pipe. As the UCG process runs longer, the interior area of the exit channel through which most of the flow goes becomes hotter, the perimeter coal or rock will have a gentler temperature gradient, and more and more of the organics will reach the production pipe without recondensation.

As the UCG process grows the very hot reactive zones of the UCG process will advance through places where coke or condensed tar may remain. These organics will then be consumed by coking, cracking, gasification, and oxidation reactions.

Today's condensation zone is tomorrow's revolatilization zone, the next day's coking zone, the next day's gasification zone, and the next day's oxidation zone. These advancing processes will successively consume organics and move them forward towards the production well. This keeps the quantity of condensed organics low.

Only a fraction of the organics that are generated persist in the UCG process gas to the production well. Pyrolysis of coal typically yields about 15% of its dry ash-free mass as "liquids," [93, 11]. Coal tars and liquids typically comprise about 1-2% by weight of UCG product gas (46 gallons of liquid oil condensate per MSCF of product gas) [84]. The oil condensate yield from UCG on a coal basis has typically been about 2-4% of the dry ash-free coal (e.g. 2.5% of coal mass for Rocky Mountain 1; 2.9% of coal mass for Hanna IV; and 3% of coal mass for Hanna II Phase III [84, 11, 60]). These data suggest that roughly 80% of the coals condensable pyrolysis products are destroyed or trapped underground.

# 3.3 Containment and removal of contaminants during operation

UCG process gas and the chemicals in it will be contained within the cavity and its close confinement zone if pressure gradients are inward or there is no path or permeability for gas to escape. Best practice will choose a site with good (low) permeability barriers. It is essential to manage pressures so that the gradients driving flow are inward.

Given containment, process gases and the contaminants in them will flow into the production well and up to the surface.

A small inventory of contaminants that are left underground after regular operations are stopped can and should be reduced further by a proper shut-down cleaning operation.



Fig. 3.2 To help assure containment of UCG process gas, fluid flow must be inward everywhere over the surroundings of the cavity. Therefore, the pressure of the cavity—and any connected, gas-filled voids—must be kept below the pressure of the immediate, water-saturated surroundings at all locations.

# 3.3.1 Containment by pressure management

Process gas will tend to escape from the cavity and carry contamination out with it if there is an outward pressure gradient.

It is common to hear a simplistic description of the desired pressure management: "Operate the cavity below the surrounding hydrostatic pressure." This is imprecise, and can be misleading, because no location or time is specified for evaluating this rule. The formation fluid pressure varies with position, especially vertical position, around the cavity and with time. The hydrologic system surrounding UCG is dynamic and changing, not static.

The following formulations of the pressure rule come closer to being well posed and sufficient.

- Fluid flow must be inward everywhere over the surroundings of the cavity.
- The pressure of the cavity—and any connected, gas-filled voids—must always be kept below the pressure of the immediate water-saturated surroundings, especially at the highest reaches of the cavity.

In this report we often loosely use the term "pressure" to mean the potential to drive flow. In reality, all fluid drivers such as capillarity, buoyancy, density, and momentum must be properly accounted for, as this is a multiphase system. For the remainder of this discussion we will use pressure to simplify the presentation.

The importance of stating the inflow rule precisely will be seen in several scenarios described in Chapter 4. In particular, it is possible for the pressure gradient to go from inward to outward *without* the cavity pressure being increased or exceeding the initial far-field hydrostatic pressure. Figure 3.2 illustrates a few aspects of applying this rule to a UCG operation.

The critical point to evaluate the pressure rule is at the highest gas-filled point in the cavity, where the difference between the cavity pressure and formation pressure is likely to be greatest. This is not necessarily the top of the coal seam, because roof collapse and/or large open fractures may allow gas to travel further vertically.

Assuring proper pressure management requires coupling between field measurements of in-situ fluid pressures, estimates of the height of the cavity and open fractures above it, and a continually updated hydrologic model. Using Figure 3.2, an approximation of the pressure rule that conveys some of the important points to watch out for and which can be used for preliminary design estimates is:

$$P_{\text{threshold}} = P_{\text{initial, top of seam}} - \Delta P_{\text{drawdown}} - \Delta P_{\text{safety margin}} - \rho_w g(H_{\text{roof collapse}} + H_{\text{gas-filled fractures}})$$
(3.1)

Inward pressure gradients and fluid flow are expected if the gas pressure in the cavity is managed to be below the threshold value  $P_{\text{threshold}}$ . Note that this threshold can change with time due to changes in the drawdown  $\Delta P_{\text{drawdown}}$  and heights of roof collapse and fracturing,  $H_{\text{roof collapse}}$  and  $H_{\text{gas-filled fractures}}$ .

The estimated drawdown  $\Delta P_{\text{drawdown}}$ —i.e. the change in pressure from the initial state, because the cavity serves as a fluid sink—can be estimated by a combination of measurements and modeling. It is important to include a safety margin, however, to account for a variety of factors:

- Sudden fluctuations in cavity pressure
- Uncertainty in formation hydrology
- Uncertainty in cavity geometry

The pressure within the cavity will fluctuate around its controlled average pressure. This is due to the stochastic nature of the underground system and the process. Fluctuations in water permeation (e.g. the cavity wall reaches a set of natural fractures), or rates of drying of coal or rock (e.g. a fall of small wet rock pieces from the ceiling) could cause this. Temperature fluctuations (e.g. a volume of high oxygen concentration gas mixes with a volume of high fuel concentration gas) can also cause gas pressure spikes. Data from downhole pressure transducers can provide an estimate of the expected magnitude of pressure fluctuations.

It is crucial to know with confidence an upper bound on the maximum vertical extent of the cavity, as this is a key control on the pressure threshold. Fractures may also extend out or up from the cavity, providing additional gas pathways.

Many sketches of UCG cavities show the cavity staying within the coal seam. In all sizeable DOE-sponsored UCG field tests in both the Powder River Basin and Hanna Basin,



**Fig. 3.3** Cross-sections following the Hanna II and Hoe Creek II tests, based on operational monitoring data and post-burn coring. Note that the height of roof collapse above the coal seam is on the order of the seam thickness, and that for Hoe Creek it extended much higher than the roof of the lower seam where the burn was intended.

the cavity grew vertically far up into the roof rock. Figure 3.3 shows final cross-sections for the Hanna II (Hanna Basin) and Hoe Creek II (Powder River Basin) tests, along with the approximate heights of roof collapse. A detailed geotechnical analysis can guide likely-geometry estimates, and monitoring tools can be used to estimate cavity changes with time.

# 3.3.2 Possible shoulder of gas-saturated coal around upper cavity perimeter

It is possible that there may be a "shoulder" of unreacted coal around the cavity that is not saturated with water—i.e. some of its porosity is gas-filled. Figure 3.4 illustrates this situation. This shoulder would extend from the burned cavity outward some distance into the upper elevations of the coal seam. Its extent will depend on pressure and permeability details. This must be included in the design and operating plans and modeled using a two-phase (gas and water) flow model. Preliminary estimates of the shape of the water-saturated surface can be obtained using the Dupuit approximation (c.f. Bear and Verruijt [82]).

Having such a gas-saturated shoulder does not in itself constitute an escape of gas. But it must be recognized as possibly extending the process domain containment region in which process gas and its contaminants may exist. Having a low-permeability horizontal or anticline (concave downward) roof stratum to contain it is helpful. If the cavity pressure is maintained adequately low, flows will be inward.

## 3.3.3 Containment by selecting a site with permeability barriers

If the pressure gradients are not properly managed, process gas and the contaminants carried with it can still be contained if the surrounding formation has low permeability. This aspect of site selection provides additional assurance of containment. It is discussed in more detail in Chapter 4.



Fig. 3.4 Under some conditions of permeability and pressure history, a "shoulder" of unreacted coal may exist in the upper part of the coal seam, surrounding the cavity, that is unsaturated (some of porosity is filled with gas).

# 3.3.4 Continuous removal of contaminants during normal UCG operation

Given proper pressure operation or permeability barriers, no process gas should escape into the underground surroundings. In proper operation all of the gas and vapors and most of the aerosols and particulates will be transported from the deep contained cavity into the production well and flow through hard piping to the surface. At the surface, the contaminants can be properly separated from the gas using standard separation methods.

# 3.3.5 Contaminants left underground when oxidant injection is stopped

When it is time to stop injecting oxidant and terminate the cavity or module, an inventory of condensable organics will be present underground. These will be in the hot perimeter where pyrolysis has been taking place (and will continue to take place until it cools), in the hot pyrolyzing coal/char rubble, and especially in the cooler zones where partial condensation has occurred, such as the downstream reaches of the module. There may also be a small amount of gases and condensed organics in the unsaturated "shoulder" of unreacted coal around the upper perimeter of the coal-seam cavity.

The amount and location of the contaminants left underground will depend on many details. It is likely that some UCG approaches and scenarios leave fewer than others and/or leave more localized residuals. There is not enough experience or data to know. The best UCG process models available today are almost—but not quite—sophisticated enough to reliably make such predictions. This discussion could be informed by better modeling, incorporation of knowledge from relevant surface gasification and pyrolysis processes, and of course field experimentation. A review of proposed or competing designs and operational plans could include a qualitative assessment of the relative propensity for producing contaminants in the various locations in the cavity and surrounding it. But today this will be mostly conjecture. We are at the state today where all we know is there will be residual organics and that a post-burn protocol will help reduce them.

#### 3.4 Removal of more contaminants during module shutdown

The way the module is managed after oxidant injection is stopped will affect the final inventory and distribution of contaminants. Poor management will make things worse. Proper post-burn operations can make things better by removing some of the underground contaminant inventory.

The wells must not be closed. If the wells are closed, the hot coal that may be in the rubble or cavity walls would continue to pyrolyze until the heat dissipates enough to drop temperatures below 300° C. This would generate additional pyrolysis organics, adding to the inventory. The pyrolysis gases and vapors, together with steam generated by re-infiltrating water would raise the pressure in the cavity which would tend to drive the gas and liquids out away from the cavity into the surroundings.

A clean shutdown procedure will minimize additional pyrolysis and remove as much of the contaminant inventory as possible. Such an approach, dubbed "Clean Cavern," was demonstrated at the end of the Rocky Mountain 1 test, and variations of it have been used in field trials and demonstrations since then.

Proper post-burn module cleaning operations will manage pressures (to manage underground fluid flow) and use some combination of steam and/or nitrogen injection and/or gradual infiltration of groundwater to produce steam.

# 3.4.1 Rocky Mountain 1 and recent Australian procedures

The Final Technical Report for Rocky Mountain 1 [52] describes the shut down procedure as follows:

After the cavities were depressured following the test, steam was used to flush the cavities. The steam helped speed cavity cooling and sweep the remaining UCG product gas from the cavities and to the surface After steam flushing, the cavities were maintained at near atmospheric pressure. This allowed ground water and associated UCG-induced constituents to flow into the test cavities. The water cooled the cavity rubble and walls thereby reducing continued coal pyrolysis which is the source of volatile organics and water soluble inorganics ( $NH_3$  and  $H_2S$ ) most associated with UCG affected ground water. Once pyrolysis had stopped and the cavities had begun to cool, the production wells were left open and vented to the atmosphere to prevent pressure buildup in the reactors due to continuing steam generation.

| Vapor Pressure<br>MPa |
|-----------------------|
| 0.000612              |
| 0.00317               |
| 0.01235               |
| 0.0386                |
| 0.1014                |
| 0.4762                |
| 1.555                 |
| 3.976                 |
| 8.588                 |
| 16.529                |
| 22.064                |
|                       |

**Table 3.2** Steam saturation temperature as a function of pressure. Note that 0.1 MPa is approximately 1 bar which is approximately 10 meters of water column.

Two recent Australian UCG panels, by Linc and Carbon Energy, were being shut down in late 2013 without injecting fluids. Both simply depressurized to let groundwater infiltrate. Pyrolysis and production of flareable product gas continued over a time scale of months. The operating permits required demonstration of safe shutdowns with water monitoring. It will be very informative to discover the results, especially if any near-field data are made public.

# 3.4.2 Analysis, Discussion, and Recommendations

There has not been enough comparative testing or rigorous modeling to optimize this postburn shut-down cleaning process. That said, the following observations are helpful in arriving at an effective protocol.

The hottest regions underground may be  $1000^{\circ}$  C. These would contain little to no coal capable of further pyrolysis. The coal perimeter of the hot region of the cavity will probably have a sharp transition, over less than a meter, from hot char, to coal at pyrolysis temperatures, to the boiling point of water, to near-ambient. Pyrolysis will be very slow below  $300^{\circ}$  C and be relatively fast above  $400^{\circ}$  C. So one goal is to minimize the amount of coal above  $300^{\circ}$  C. Steam can do this. At pressures (depths) expected for UCG the temperature of saturated steam is below the pyrolysis quench temperature. Table 3.2 gives some values. Saturated steam will be below  $300^{\circ}$  C when the fluid pressure is below 860 meters of water, so this should work for UCG depths to roughly 1,000 meters.

Using water infiltration to make steam may work best if the water infiltration is slow. There are no data or models for this but the reasoning is as follows. If water infiltrates slowly into the hot coal perimeter, it will boil and the steam will sweep through the pyrolysis zone. This will provide two benefits. It will sweep out pyrolysis products into the open cavity and it will cool the coal to below pyrolysis temperature. This will let the hot steam evaporate and sweep out any condensed organics in the area before the cool liquid water condenses them completely. The rate of water infiltration would be controlled by managing cavity pressure. Rapidly dropping the cavity pressure will cause water to infiltrate fast. This will quench pyrolysis but also overcool the coal and rock and trap organics as liquids before being able to sweep them out as vapors. This may be especially true near the downstream side of the module, where there has been much condensation of organics.

To best clean the downstream region of condensed organics it would be desirable to have a long period where 200-300° C steam or nitrogen sweeps through regions that likely contain organics. This will evaporate the organics into the sweep stream so they get carried out the production well. Having regions that contain condensed or vapor organics stay open to gas flow longer is good.

Steam could be injected or water could be injected into the region of the module containing very hot ash and rubble to make the steam. The goal would be 200-300° C steam. Nitrogen could also be used, with some advantages and disadvantages. Any fluid injection at or below 300° C will tend to cool the cavity gas and hence the coal walls to below pyrolysis temperature but provide an opportunity for condensed and vapor organics to mix with the steam or nitrogen so they could be swept out.

At some point, there will be diminishing returns of contaminant production and/or the temperatures will have cooled enough and enough water will have flowed in for the cavity to be filled with water. Several cavity volumes of water will need to be pumped out and treated in the short term, followed by a longer period of pumping and treating to remove contaminants at a slow rate. During this, the pressure in and near the cavity should be maintained below surrounding hydrostatic pressure to continue to produce contaminants and keep them localized. After some time it is expected that the system is sufficiently cleaned to enter a long term monitoring and hydraulic control program.

# 3.4.3 Summary

Clean shutdown practices are available for UCG. Management of fluid flows and cavity pressures can be done so-as to remove most of the contaminant inventory, leaving less residual in a given volume. Shut down procedures, nicknamed "Clean Cavern," were demonstrated successfully after the Rocky Mountain 1 test and in field tests since then. It is difficult to know what the best post-burn procedure is, and doubtful that the Rocky Mountain protocol is optimum. Nonetheless, a post-burn protocol that uses some combination of groundwater infiltration and injection of steam (or water to produce steam) or nitrogen will be beneficial. The underlying goals are to cool coal below 300° C and sweep organics out.

# Chapter 4

# **Abnormal Transport of Contaminants**

The hot process gas and the coal and rock immediately bounding the cavity contain contaminants. Under normal operations, the gas and contaminants stay within the process domain. Most of the contaminants are continuously destroyed and removed out of the process domain with the product gas. Some are likely to be condensed in the downstream side of the process, to be revolatilized, coked, or cracked later and carried out with the product.

The process domain includes process wells and underground process volumes that are open to the geologic surroundings (cavity, process flow pathways such as reverse-burn links or previously burned voids and rubbles, and uncased or slotted boreholes) and process wells. For our purposes it also should contain any unsaturated shoulder of surroundings where the pores contain gas as well as water.

A significant amount of process gas, and the contaminant species it contains, will escape out of the process domain into the surroundings if there is both an outward pressure gradient to drive flow, and a permeable path or open channel that allows a significant rate of flow. This is unwanted and not consistent with proper operation at a good site. But it has happened before and can happen again if mistakes are made.

There are a number of possible scenarios or failure modes to consider. It is a main premise of this chapter that a critical analysis of possible failure modes will help prevent, detect early, and minimize impacts. This approach is far more helpful than dismissing failure modes "that would never happen."

Good pressure management, as described previously, will keep gradients and flows inward. Good site selection will help minimize permeable paths. But certain abnormal unwanted scenarios can happen if good practices are not followed.

There is a general rule for preventing process gas from escaping and spreading contaminants. It is often heard in its overly simplistic forms, "Operate the cavity below the surrounding hydrostatic pressure" or "Don't overpressure the cavity." A more accurate view of pressure management requirements was presented in the previous chapter. The importance of a nuanced view of pressure management will be seen from several scenarios described in this chapter.

Most of the contaminants are condensible and/or water soluble and will condense or dissolve out of the gas phase into liquid or solid phases upon cooling. As gas flows out

# CHAPTER 4. ABNORMAL TRANSPORT OF CONTAMINANTS

of the cavity, presumably through a fracture or high-permeability path or a high-mobility gas-saturated finger, it will cool by transferring its heat by conduction to the formation rock. Condensable contaminants will be deposited where the temperature drops. Because the volumetric heat capacity of rock is much greater than gas, the contaminants will go only a small fraction of the distance the gas travels. As more gas flows past, the length of the hot zone increases and the deposition of condensable contaminants will extend further and further. This is the major way contaminants are transported outside the immediate cavity area. The fact that noncondensable gases will travel much further than the condensable or soluble contaminants has two important results. First, it reduces the distance that contaminants are spread. Second, it provides an opportunity for early detection of problems, by monitoring for gas leaks before too many contaminants are transported too far.

Gas loss from the cavity has been a common experience in many past field tests. Depending on the details of where and when the gas loss occurs and where the gas goes, this is typically the dominant mechanism by which contaminants can be transported away from the cavity. Details of the situation will determine how much and where contamination is deposited. Large gas loss over a long time near protected aquifers will produce an unacceptable problem. Small gas losses over short times that are isolated from protected aquifers may produce a very small, localized, and "acceptable" level of contamination. For example, the Rocky Mountain 1 field test had some gas losses, but the environmental monitoring showed only low levels and localized transport of contaminants [51, 60, 56].

The following sections describe potential scenarios that could lead to unacceptable contamination. Understanding and analyzing these helps prevent them, allows them to be detected early, and can help minimize their impacts.

# 4.1 Transport and deposition of contaminants by escaping gas

## 4.1.1 Contaminants in the process gas

The process gas contains contaminants, though the relative concentrations vary from location to location within a process. For approximate descriptive purposes, it is reasonable to use typical product gas as the composition. In addition to the major expected gas species, it contains condensible and heavier organics and particulates, some of which are very undesirable contaminant species.

# 4.1.2 An outward pressure gradient and a permeable path will result in significant gas loss

As mentioned earlier, we often use "pressure" simplistically to mean the potential to drive flow. More strictly speaking we should use potential or head, where hydrostatic pressure is subtracted out, and account properly for capillarity. Where a gas phase is present, the full 2-phase flow equations, with relative permeability, etc. would describe the system.



(b) Finger flow



A scenario that has a combination of wrong-way (outward) pressure gradient to drive flow and a high-permeability pathway for flow will produce significant gas loss. The path of the escaping gas will be downgradient, with higher fluxes following steeper pressure gradients and more permeable (less resistive) flow paths.

Sometimes, as in upward fracturing and collapse of the cavity roof, one scenario can produce both problems together. Often the pressure situation is not directly coupled to the permeability situation. The discussion below is organized into situations that could produce an outward pressure gradient, and situations in which a permeable path for unwanted gas flow away from the process can exist.

#### 4.1.3 Escaping fingers of gas are more likely than broadly uniform outward flow

If an outward gradient of potential moves gas out away from the cavity, it is likely that the escaping gas will tend to finger, rather than advance in a broad uniform front. Figure 4.1 illustrates this qualitatively.

# CHAPTER 4. ABNORMAL TRANSPORT OF CONTAMINANTS

The path could initiate and become established due to the natural hydrogeological permeability field, pre-existing fractures or faults, and/or process-caused fractures or permeability changes. But even in a perfectly homogenous isotropic porous medium the front that divides a high-mobility (low viscosity) fluid displacing a low-mobility fluid is unstable with respect to fingering and will not stay planar. This fingering is reinforced by relative permeability concepts in which the gas-phase permeability increases as the gas-phase volume fraction increases.

Buoyancy also plays a role. Gas fingers and flow will tend to move preferentially up due to buoyancy and hydrostatics. The higher up the gas-filled finger goes, the lower the surrounding water pressure and hence the greater the pressure difference driving gas flow. A second-order factor is the decrease in gas density as pressures decrease at higher elevation, increasing the buoyancy of the gas relative to water.

After a period of gas fingering out, if the cavity pressure is reduced and water re-invades and pinches off the gas finger, the gas is unlikely to uniformly flow back inward, but would be pinched off leaving a bubble of high gas saturation out in the surroundings. This could move along with the surrounding water or might rise up by buoyancy.

These phenomena are complex. Detailed multi-phase flow modeling of hypothetical permeability fields, capillary parameters, and pressure histories are useful and informative. The exact behavior in a specific site under specific conditions will depend on all the relevant details and detailed analyses would be needed to assess the expected flow patterns.

# 4.1.4 Overview of contaminant transport and deposition in a finger of escaping gas

In this section we describe the phenomena of how and where the contaminants are deposited if there is a gas escape. We presume the escaping gas travels in a finger. The same principles and discussion applies if the front of outward flowing gas is broad.

During operation (as opposed to the years following shut-down) contaminants are primarily carried outward by escaping gas. Contaminant species do not move by themselves far from the cavity without the carrying gas because diffusion is slow. Outward transport in moving groundwater is also slow compared to how fast contaminants can be carried outward by escaping gas.

The distance and quantities of contaminants transported outward with the gas will be limited by at least five mechanisms. The mechanisms that remove contaminant species from the gas stream include (1) condensation, (2) dissolution into pore water, (3) dissolution into liquid or solid oil/tar phase materials, (4) adsorption onto solid organic and mineral surfaces, and (5) filtering and colloidal capture of particulates.

There will be a chromatographic nature to the separation of contaminant species from the carrier gas stream. The gas will cool rapidly because its heat capacity is much lower than the rock it is flowing through. Heavier (less volatile, higher boiling point) compounds will

be deposited sooner than lighter, more volatile compounds. Highly water-soluble species will dissolve out of the gas into pore water sooner than insoluble species.

Before the gas has traveled very far most of the condensable and soluble species will have left the gas phase into condensed phases. This has two important ramifications. First it greatly mitigates the amount and distance that contaminants are initially transported away from the cavity from a gas leak. Second, the far-travelling gas provides an opportunity for detecting contamination-producing gas leaks considerably sooner and/or further away than by looking only for contaminated groundwater.

# 4.1.5 The thermal front moves at a much lower velocity than the escaping gas

Process gases are hot when they escape, but they deposit their heat into the rocks along their path, cooling the gas and heating the rock. The heat capacity of gas is vastly lower than the heat capacity of rock on a volumetric basis. The hot gas will be cooled quickly by the cool surrounding rock. The black curves in Figure 4.2 illustrate the difference between the location of the thermal front or gradient and the front of flowing gas.

The figure is not to scale horizontally—a back-of-envelope calculation estimates the location of the thermal front to be 1/1000th of the distance that the escaping gas has advanced<sup>1</sup>. This relative difference will hold whether the gas flow pattern is finger-like or broad. Imperfect local thermal equilibrium will broaden the thermal front. Still we can conclude that the thermal front will probably move less than 1/100th as far from the cavity as the noncondensable gas will.

Flow of gas through fractures may broaden and advance this thermal front, but qualitatively the result will be similar. A back-of-envelope calculation for fracture flow suggests the thermal front would advance at 1/100th the gas front<sup>2</sup>.

If an operation the scale of Rocky Mountain 1, operating at a pressure of 40 bar, lost 1% of its gas production along a finger having  $10 \text{ m}^2$  cross-section and gas-filled porosity of 10%, the gas velocity and gas-front advancement rate would be about 45 meters per

<sup>&</sup>lt;sup>1</sup> Suppose a UCG operation sized like Rocky Mountain 1 ( $2 \text{ Nm}^3$ /day of gas production having average molecular weight of 22.5 g/mole) has 1% of its gas production escape along a finger or path that has a cross-section of 10 m<sup>2</sup> (finger diameter of 3.6 m). If the pressure is 40 bar and the porosity available for gas flow is 10%, the gas will travel outward at a velocity of 45 meters per day. If this leak persists for 10 days the finger of gas will have travelled 450 meters. A cubic meter of porous medium will contain 0.9 m<sup>3</sup> of rock with a mass of 2,520 kg and 0.1 m<sup>3</sup> of gas with a mass of 1.41 kg. The mass heat capacities of rock and UCG gas are about 1.1 and 1.5 kJ/kg K respectively. The heat capacities of the 0.9 m<sup>3</sup> of rock and the 0.1 m<sup>3</sup> of gas are, respectively 2,770 and 2.1 kJ/K. Because thermal diffusion times are fast relative to the timescale of the gas leak, an assumption of local thermal equilibrium is reasonable. The thermal front will travel less than 1/1000th as far as the gas front

<sup>&</sup>lt;sup>2</sup> Suppose the 1% escaping gas flows through 1-cm wide parallel fractures spaced every 1 m and the finger through which the gas moves has a cross-section of 100 m<sup>2</sup> (finger diameter of 11.3 m). This is a 1% porosity and in the example the gas and its front will travel at 40 m/day and move 400 meters in 10 days. The volume of gas in a 1-cm aperture fracture that is 1 meter wide and 1 meter deep is 0.01 m<sup>3</sup> and its heat capacity is 0.24 kJ/K. The volume of the rock within 0.45 cm of this fracture is 0.009 m<sup>3</sup> and its heat capacity is 27.7 kJ/K. If local thermal equilibrium can be assumed over a half centimeter of rock surrounding the fracture then the thermal front will advance at about 1/100th the rate of the gas front. The thermal diffusivity of sedimentary rock is such that 0.45 cm of thickness will approach thermal equilibrium in a few minutes, which is much faster than the time scale of the leak. By this calculation the thermal front would advance at 1/100th the gas front. Considering a thicker zone of rock adjacent to the fracture would have the front advance more slowly on average but be broadened significantly by lack of local thermal equilibrium.



**Fig. 4.2** Qualitative profiles of temperature and condensable species concentration after leaking gas has moved for short or long periods of time through a porous medium. For typical UCG situations, the thermal front will travel outward only 1/1000th or 1/100th as far as the gas front. Condensable species carried as vapor in the gas will be deposited onto cool rock after flowing past the thermal front. The qualitative nature of these profiles will be similar when the gas flows through fractures.

day. But the thermal front will advance only 0.45 to 45 meters in 10 days, and most of the condensable contaminants will condense near the thermal front. This is very good news in terms of the risk of a gas leak conveying the full load of process gas contaminants far from the process.

### 4.1.6 Condensable contaminants are deposited close to the cavity by condensation

Condensation will generally be the dominant mechanism of removing most contaminants from the flowing gas stream and this will be described first. Nearly all of the high-boiling compounds and the majority of the volatile compounds like benzene will be condensed very close to the cavity.

The condensable species will condense onto the cool surrounding rock. The heavy, highboiling point tars will tend to condense first, closest to the cavity. The light highly volatile compounds will condense as the gas cools further, somewhat further from the cavity. The cool gas, containing now only uncondensable species will continue flowing out through the formation.

If a plume of hot gas escapes from the cavity through the porous or fractured surroundings, the tars will tend to condense on the cooler adjacent surrounding rock before they have travelled far. The light condensables will then condense a bit further away and the noncondensables will keep on going. As more and more gas flows along the same path, the adjacent rock will become hot enough to re-vaporize the tars and deposit them where the light species had been, and the rock at that location will become hot enough that the light species will re-vaporize, get carried further, and condense further away. The longer this goes on and the more hot gas that flows along this path, the further away the tars and liquids and heat are transported. The noncondensable gas will just keep on going down the pressure gradient along high-permeability path. Condensable species are typically transported in vapor phase, carried by a leak of hot gas, and deposited into the formation by condensation according to their concentration, their vapor pressure at the local temperature, and the fluid pressure. Continued flow and heating of the hot gas through the contaminated zones will move the contaminants further away by successive re-vaporization and condensation.

In the hot regions of the process the gas phase contains the full suite of species present that have even the slightest amount of volatility. For a qualitative understanding of the transport, it is helpful to think of this continuum of species of volatility as consisting of a simpler mixture of three types of materials:

- High boiling point "tars" (aka: high molecular weight, heavy, low-volatility, ...; e.g. anthracene (C<sub>14</sub>H<sub>10</sub>, solid at room temperature, melts at 217C, boils at 354C); napthalene (C<sub>10</sub>H<sub>8</sub>, solid at room temperature, melts at 80C, boils at 218C); phenol (C<sub>6</sub>H<sub>6</sub>O, solid at room temperature, melts at 41C, boils at 182C); cresols (C<sub>7</sub>H<sub>8</sub>O, melts at about room temperature, boils at about 200C)
- "Light condensables" or "liquids" or "light oils" (aka: medium molecular weight, mediumvolatility, liquids; e.g. benzene (C<sub>6</sub>H<sub>6</sub>, liquid at room temperature, boils at 80C))
- "Noncondensable" gases (meaning gases at normal ambient conditions; e.g. O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, CO, H<sub>2</sub>, and the lightest hydrocarbons, CH<sub>4</sub>, C<sub>2</sub>'s )

Recall that higher system pressures will tend to make compounds condense at lower temperatures than their boiling point, but dilution with other species that are more volatile will tend to make compounds tend to condense at higher temperatures than their boiling point. A simple version of the quantitative relation that describes this is Raoult's Law:

$$x_i P_{vi}(T) = y_i P_T \tag{4.1}$$

where  $x_i$  is the mole fraction of species *i* in the condensed phase (the higher, the more tendency for a species to condense; the lower, the more tendency for a species to remain in the vapor phase),  $y_i$  is the mole fraction of the species in the vapor(gas) phase,  $P_T$  is the local total system pressure (absolute pressure), and  $P_{vi}$  is the vapor pressure of species *i* at the local system temperature. There is a readily-available (handbook) function for  $P_{vi}(T)$  for all common chemical species.

In the segment of the gas path closest to the cavity where the gas will cool and tars and liquids will condense, volatile hydrocarbons such as benzene will condense with and/or dissolve into the organic phase according to Raoult's law. The importance of this is to recognize that these organic-phase liquids and tars are a low-mobility reservoir of species such as benzene. The good news is that they will tend to be located close to the process domain unless the gas leak that transported them out of the process domain was very large and/or persistent.

# 4.1.7 Volatile contaminants at their dew point in gas are carried further from the cavity

A fraction of the condensable but volatile compounds such as benzene will not be condensed. A portion of these will stay in the gas phase beyond the condensation zone at concentrations fixed by their dew point.

We can estimate an upper bound of benzene that will stay in the gas phase, neglecting its dissolution into water or sorption onto solids. For an ambient rock temperature of 25C and a total pressure of 40 bar (roughly what might be expected for a UCG operation at 500 meters depth) the gas may hold up to about 0.1 mole percent of benzene plus 0.2 mole percent of similar organics<sup>3</sup>. As the gas travels further benzene and these compounds will be further scrubbed from the gas by dissolution into water and sorption onto solid surfaces.

# 4.1.8 Adsorption of organics onto solid surfaces will reduce the distance they are carried

After all the organics have condensed that can, the gas and its volatile organic vapors at their dew-point concentration will be moving at ambient temperature through the formation. In addition to condensation and solubilization, contaminants will also leave escaping gas because of adsorption. Species in the gas phase are driven toward phase equilibria to adsorb onto solid surfaces. The affinity of a species for a surface depends on the compound, the surface, the concentrations of other species competing for the sorption site, and other specifics. Following the rule of "like dissolves like," organic compounds will tend to adsorb onto organic surfaces. Coal would be expected to adsorb organics, though water and natural species may compete for sites. Sedimentary rock strata typically have an organic fraction, often essentially coal amongst a high fraction of mineral grains.

Adsorption will tend to reduce how far contaminants are spread during the initial gasescape phase of transport. Adsorption also will affect the transport of contaminants during clean-up and/or natural flows of water off site after a UCG operation.

<sup>&</sup>lt;sup>3</sup> After traveling a relatively small distance through the pores or fractures of the surrounding coal or rock, the temperature will reach the ambient surroundings temperature. The ambient surrounding temperature is estimated at 25C (near-surface ambient temperature of 10C plus 500 m of a 0.03 C/m geothermal gradient). By this point the less volatile organic tars and liquids, and most of the water will have condensed out. Most of the benzene and similarboiling compounds will also have condensed out, leaving only a small concentration of them in vapor phase. They will continue to condense until their dew point is reached. This dew-point calculation goes as follows. At 25C benzene has a vapor pressure of 0.13 bar. There are several other organics with similar vapor pressures. We will estimate that benzene comprises one third of them and their properties are the same as benzene. Raoults law simplifies to  $y_{\text{organic}} = x_{\text{organic}} P_{v,\text{organic}}(T)/P_T$  where  $x_{\text{organic}}$  is 1.0. At 25C and 40 bar, the result is  $y_{\text{organic}} = 0.0032$ . If benzene comprises one third of these organics, the gas can hold about 0.1 mole percent benzene (plus 0.2 mole percent of similar organics) without condensing more organics.

# 4.1.9 Dissolution of species into pore water will reduce the distance they are carried

In addition to condensation and adsorption, contaminants will also leave the highly mobile escaping gas by dissolving into less-mobile pore water. Species in the gas phase are driven toward phase equilibria to dissolve into tar/oil or water phases.

After all the organics have condensed that can, the gas and its volatile organic vapors at their dew-point concentration will be moving at ambient temperature through the formation. Because of capillarity, relative permeability, and inhomogeneity (high permeability channels of high gas fraction adjacent to low permeability zones that remain water saturated) there will still be a significant amount of pore water remaining and the gas will travel past this. As the gas flows by this water, a fraction of the benzene and similar compounds will be scrubbed out of the gas phase into the water. The approximate equilibrium relationship is similar to Raoult's law, but an extra term,  $\gamma_i$  the activity coefficient, is added to account for the nonideality of the organic-water solution.

$$x_i = y_i P_T \left(\frac{1}{\gamma_i} P_{vi}(T)\right) \tag{4.2}$$

This is commonly and more conveniently expressed as Henry's Law

$$C_i = y_i P_T H_i(T) \tag{4.3}$$

Where  $C_i$  is the molality of *i* (moles of *i* per kg of water),  $H_i(T)$  is the Henry's Law coefficient for species *i* in water at the temperature of interest (units of gmoles of *i* / (kg of water  $\times$  bar of partial pressure of *i*))<sup>4</sup>,  $y_i$  is the mole fraction of species *i* in the vapor (gas) phase, and  $P_T$  is the absolute total system pressure. For benzene at 25C, the Henry's coefficient is 0.18 gmoles benzene / ((bar of benzene)(kg of water))). If the 40 bar gas contains 0.1 mole percent benzene and 0.2 mole percent similar organics, water in equilibrium with it is expected to contain about 0.6 g benzene per kg water, and 1.2 g of similar organics per kg water. This estimate of 0.6 g benzene per kg water is independent of total system pressure.<sup>5</sup>

The capacity of pore water to strip out benzene from escaped gas is significant. A calculation suggests that the majority of the benzene will be stripped out in the closest (to the cavity) three-tenths of the length of the gas-escape path.<sup>6</sup> There is uncertainty in this calculation, mainly associated with the ratio of gas-filled to water-filled porosity along the finger,

$$mass_{B,g} = V_{pm}\phi_g P_T Y_B M W_B / TR$$

the mass of benzene in the water phase will be

<sup>&</sup>lt;sup>4</sup> Henry's law appears in many different forms with corresponding different values and units of the coefficient H. When looking up a value for H, care must be taken to determine its precise units and defining equation.

<sup>&</sup>lt;sup>5</sup> The dew point calculation of vapor mole fraction is inversely proportional to the total system pressure. The Henry's calculation of water mole fraction is proportional to the total system pressure. Thus the calculation of water mole fraction in equilibrium with gas containing benzene vapor at its dew point is independent of total pressure.

<sup>&</sup>lt;sup>6</sup> The following back-of-envelope calculation estimates that at 25C, a volume of porous medium containing 10% by volume gas and 5% by volume water will have at equilibrium approximately 30% of the benzene present in the gas phase and 70% of the benzene present in the water phase. In a porous medium volume,  $V_{pm}$ , the mass of benzene in the gas phase will be



Mass of benzene per volume of formation in gas, pore water, combined

**Fig. 4.3** Volatile vapors that are somewhat soluble in water, such as benzene, will be scrubbed from escaping gas by residual pore water. This figure shows reasonable qualitative profiles of benzene concentration (mass of benzene per volume of porous medium) in the escaping gas and pore water along the path of a hypothesized escaping finger of process gas at 40 bar and 25C containing 0.1 mole percent benzene, assuming gas-filled and water-filled porosities of 10% and 5%, respectively. For this case an assumption of local equilibrium would result in step-function curves that transition from the near-cavity values to zero at 30 percent of the finger length.

and a reasonable range of stripping lengths would be from a few hundredths of the finger length to three-quarters or more of the finger length. The front between benzene-rich and clean gas will be broad; i.e. the concentration profiles will be stretched out much smoother than a step function because of deviations from local equilibrium.<sup>7</sup> Figure 4.3 illustrates a reasonable profile of benzene concentration in the gas and pore water along the length of a finger of escaping gas. A sophisticated model with a detailed description of the flow and details of the porous medium would be needed to provide better estimates.

#### 4.2 Potential causes of outward pressure gradients

Gas loss from the cavity would be expected to occur if the gas-phase pressure in the cavity or gas-filled fractures above the cavity exceeds the pore water pressure surrounding the gasfilled volume. In this circumstance the local pressure gradient is outward and fluid (gas) may

 $\operatorname{mass}_{B,w} = V_{pm}\phi_w P_T Y_B \rho_w M W_B H_B(T)$ 

and the ratio of the mass of benzene in gas to the mass of benzene in water will be

$$\operatorname{mass}_{B,q}/\operatorname{mass}_{B,w} = (\phi_g/\phi_w)\rho_w TRH_B(T)$$

where  $\phi_g$  and  $\phi_w$  are the volume fractions of gas and water in the porous medium,  $P_T$  is the total system pressure,  $Y_B$  is the mole fraction of benzene in the gas phase,  $MW_B$  is the molecular weight of benzene, T is the temperature [K], R is the gas constant [m<sup>3</sup> bar/gmol K],  $\rho_w$  is the density of water, and  $H_B(T)$  is the Henry's constant for benzene at temperature T [gmol/kg bar]. The fraction of the benzene mass in the porous medium that is in the gas phase is

 $mass_{B,g}/mass_{B,total} = 1/(1 + mass_{B,g}/mass_{B,w}) = 0.31$ 

for the numerical values assumed in this calculation. If local equilibrium existed, the 31 percent of the gas finger length would contain all the benzene that was carried by the gas beyond the condensation region at its dew point, and the distal 69 percent of the finger would have no benzene. If the gas/water volume ratio was 0.01/0.14, the contaminated fraction of the finger would be 0.016. If the gas/water volume ratio was 0.14/0.01, the first 0.75 of the finger would be contaminated.

<sup>&</sup>lt;sup>7</sup> This is because diffusion through liquid in pores is slow and the real gas and liquid concentrations at any position will not actually reach local equilibrium.

flow outward. This outflow will transport contamination. The goal is to have everywhere in the cavity surroundings pore water permeating inward, maintaining water saturation.

The previous chapter described in detail what is required to have inward pressure gradients in the formation surrounding the cavity. For most of the time and place of a UCG operation, an outward pressure gradient from the cavity is an uncommon situation that can be avoided by conservative best practices. The probability of having both an outward gradient and a path for flow is the product of two unlikely probabilities. However, there are several scenarios that could result in outward gradients and/or permeable paths. A good way to minimize risk is to consider and analyze such scenarios so actions can be taken to minimize their probability and impact. Some scenarios that could result in outward pressure gradients are discussed in this section.

# 4.2.1 Pressure in the production well usually exceeds the surrounding water pressure

# Scenario of concern

The ascending production well is the one place in the system where there is an outward pressure gradient from the process domain (inside the pipe) to the surroundings. You no longer have the probability advantage of multiplying two unlikely events (overpressure and pathway). In this case only the leak-proof reliability of the pipe/casing/grout, and the low permeability of the formation prevent and reduce gas from escaping.

Over most of the vertical extent of the production pipe, the pressure of the product gas inside it will exceed the fluid pressure of the surrounding formations. This pressure difference is typically large. This is because the backpressure control that maintains the cavity gas at the desired pressure is located at the surface. The product gas at any location will be the cavity pressure minus two relatively minor quantities, the pressure drop from flow resistance between the cavity and the elevation of interest, and the weight of the product gas fluid column from the cavity to that point.

Over the upper portion of the pipe, where the surrounding formation fluid pressure is lower because of hydrostatics, the outward pressure gradient will be very strong. For a cavity operated at 40 bar, the pressure drop between the product gas in the pipe and the top of a shallow freshwater aquifer will be over 35 bar. Figure 4.4 illustrates this.

The risk of a leak from the production pipe is real. It happens sometimes in conventional petroleum and gas production from high-pressure reservoirs. Leaks of gas and fracturing fluid from poorly completed wells have been one of the problems in the emerging shale gas industry that have led to opposition.

# Mitigation

There is no practical way to avoid the product gas being higher pressure than the surroundings. A shallower and hence lower-pressure UCG operation would have a smaller outward



**Fig. 4.4** The pressure inside the production well decreases only slightly with decreasing depth. The water fluid pressure in the surroundings increases roughly linearly with depth below the pieziometric surface. For most of the upper portion of the production well, the product gas pressure exceeds the surroundings pressure. If there is a leak in the well, product gas will flow out into the formation.

pressure drop, but other factors will control the choice of depth. Operating a deep UCG cavity at near atmospheric pressure will usually cause undesirably high water influx. In theory a high-temperature back-pressure control valve could be placed at the bottom of the production pipe but this has two major disadvantages: first, the remoteness and high-temperature and structurally challenging environment would make this valve less reliable; and second, process energy and economic efficiency strongly favor keeping the product gas at high pressure.

In light of this concern, mitigation recommendations include:

- Assure the integrity of the pipe/casing/grout barrier throughout the duration of the operation by proper design, construction, and testing.
- Minimize the magnitude of a leak by detecting a leak promptly. This should include a gas material balance approach, gas sampling around, adjacent to, and above the well, and, less useful, groundwater sampling wells and piezometers in the formation around the production well.
- Minimize the magnitude of a leak by selecting a site where the production well is surrounded as much as possible by low-permeability formations.
- Minimize the impact by selecting a site where the production well is not in close transport proximity to valuable or protected groundwater.

# 4.2.2 Pressurizing other boreholes and wells with cavity gas

# Scenario of concern

This scenario is analogous to the pressurized production well. If the cavity gas intersects a borehole, monitoring well, or instrument well that is open at depth to the cavity gas but is capped or closed off near the surface, it will fill with process gas at the cavity pressure. At shallower depths this pressure will be greater than the fluid pressure in the surrounding formation. An outward pressure gradient exists between the borehole or well and the surroundings. If there were a leak in the well wall, process gas would escape into the surroundings.

This same situation applies if there is a gap between a process well grouting and the formation that allows process gas to flow up the gap. If the grout were properly sealed to the formation near the surface the gap would become pressurized and drive process gas out into the formation.

An auxilliary well could also break or becomes open to the cavity gas as the result of mechanical or thermal stresses near the cavity or in the mechanically-affected region around the cavity.

Here we consider how such boreholes and auxilliary wells could result in outward pressure differences at shallower depths. The consideration of them as pathways (e.g. if they are not capped but open at the top) is discussed later.

# Mitigation

These scenarios are tricky to mitigate as they generally involve trade-offs between the risk of pressurizing and gas escape from an auxilliary well and the value of the information the well is intended to provide. Locating instrument, piezometer, and sampling wells near where the cavity might intersect them involves a trade-off between the information they provide and this potential vector for contaminant transport. This additional hazard should be considered and mitigated when deciding to install auxilliary wells. Careful and creative engineering will help minimize the risk while maintaining the benefit of the wells.

Recommendations include:

- It is important to know the location of old and new boreholes and wells, and their casing/cement design.
- Assure that unneeded boreholes are properly cemented in, and that installed auxilliary and process wells are tightly grouted into the formation with no vertical continuous gaps.
- Whenever possible, close instrument wells at the bottom so that gas can not enter there.
- Design auxilliary wells to hold pressure without leaking, including resisting thermal stresses that may be encountered if gas flows up at a significant rate.
- This risk could be reduced by operating the cavity so it does not intersect auxilliary wells, but this has disadvantages and may be difficult to control.

- The decision to cap auxilliary wells or not should be evaluated. If the risk of a leak into shallow valuable groundwater can not be assured by the engineering of the well, having the well uncapped should be considered. A leak at the surface can be captured and treated, but a subsurface leak will produce contamination that will be difficult to treat.
- An approach should be considered wherein the main resistance to upward flow of gas is near the bottom of the instrument well, and the top be open. The resistance would greatly reduce the flow and the pressure drop would be taken deep so that the upper part of the well can be near atmospheric pressure. This might take the form of packing the well interior with sand, silt, or clay, or closing off the open interior of the well near the bottom, letting only the sampling tube or cables come through.

# 4.2.3 Pressure in the cavity becomes higher than intended

# Scenario of concern

All of the factors needed by the operator to set an appropriate cavity pressure may be known accurately. The operator may intend for the cavity to be at an appropriately low pressure, but for any one of a variety of reasons, the actual pressure in the cavity may be higher than intended. This can cause an outward pressure gradient that can lead to the escape of process gas out into the formation.

In any industrial activity things do not always go according to plan. UCG is a challenging operating environment. For most process variables there is a very wide dynamic range. Temperatures can range from sub-freezing at the surface to over 1000 or 1200° C in the hot zones, are variable in time, and the hot and cold zones move around in time. Pressures are very high, approaching the hydrostatic pressure of the coal seam, and vary with position and time. There is a very large dynamic range of flow rates, from full blast to full shut-off. The process gas is dusty, laden with condensable tars and liquids, and corrosive. Much of the operation takes place far underground where it is difficult to know precisely what is going on; process data are sparse, sometimes obtained indirectly, and more vulnerable to instrument error than conventional surface processes.

The following are potential causes of the actual cavity pressure exceeding the intended pressure.

- Partial or complete plugging of production well (or downstream of the wellhead) faster than controls (such as reducing the injection flow rate) can compensate
- Partial or complete plugging of the in-seam gas exit channel between the cavity and the production well faster than controls (such as reducing the injection flow rate) can compensate
- Equipment failure
  - Pressure transducers/gages misreading (reading lower than actual)

- Backpressure valve/controllers
- Flow controllers
- Injection (too fast)
- Production (too slow)
- Software/control system failure
  - Programming bug
  - Connections failed
  - Power outage
- Operator error
  - Miscommunication ("I said 15, not 50")
  - Wrong set point
  - Wrong valving
- Inadequate design inability of the system to control to the specified pressure
  - Multiple modules operating at different pressures and flow rates requires careful design and piping construction
    - For example, the Rocky Mountain 1 injection design was not able to independently control pressures and/or flows of the two modules because the two modules were at different elevations (and hence different surrounding pressures) and the oxygen and/or steam supplies were not independent [52].

# Mitigation

The operator must assure that the cavity pressure is actually what it is intended to be, and must have ways of quickly discovering when it is not and correcting the situation. Suggestions for doing this are found in the next chapter. Quality assurance aspects of measurements in the challenging UCG system, including cavity pressure, are discussed as well. The operator should always allow for uncertainties and a reasonable magnitude of errors.

# 4.2.4 Temporal fluctuations in cavity gas pressure become greater than expected

# Scenario of concern

Even if the average cavity pressure is controlled at a value that seems appropriate, the cavity gas pressure can fluctuate so that the high spikes produce a temporary outward pressure gradient. Temporal fluctuations in cavity gas pressure might be caused by any of the following:

• Exothermic reactions heat up cavity gas. For example, a change in flow paths causes a pocket of combustible gas to contact a pocket of injected oxygen. A 100K spike in

temperature from such an exotherm will temporarily increase the absolute cavity pressure by about 10% (100K change / 1000 K nominal temperature)

- Surge in gas production. For example, a large volume of warm coal falls into a zone filled with hot rocks and pyrolyzes. An in-cavity surge in gas production can only be caused by reactions with positive net molar production of gas, such as in pyrolysis.
- Other stochastic processes.

On average, a simple linear analysis would show that the gas may expand out into the formation temporarily but then flow back into the cavity with no net outward flow, much as a balloon being expanded and retracted. However two phenomena make such fluctuations a possible source of contaminant spreading.

Even if there is no net outward flow of gas when averaged over time, "huff and puff" gas motion in and out of the formation will transport contaminants outward in a ratchet effect. The ratchet effect may be due to either: dual-continuum fracture- flow with transverse diffusion into the matrix; or adsorption/dissolution on surfaces, pore water, etc. If the fluctuations are few, of short duration, and/or early in the cavity lifetime, it is likely that the contaminants will remain within the zone of coal that will be consumed later in the process.

If gas is pushed out into the porous medium, relative permeability factors and fingering front instabilities may make the subsequent retraction uneven. It is possible that fingers of gas-saturated porous media may persist after retraction phase, especially if they extend upwards.

# Mitigation

Recommendations include:

- Obtain and analyze data from previous field tests to determine typical and extreme degrees of pressure fluctuations.
- Analyze raw data taken at the surface to estimate the downhole fluctuations so that damping mechanisms are accounted for.
- Model potential sources of pressure fluctuations or excursions to estimate their magnitude.
- Set the cavity pressure conservatively to allow room for more fluctuations than expected.

# 4.2.5 Fluid pressure in the surroundings is lower than thought

# Scenario of concern

If the fluid pressure in the surroundings is lower than the operator thinks it is, or goes down faster than anticipated, a cavity pressure that seems reasonable may be too high and result in an outward pressure gradient. There are several possible ways in which the actual surrounding fluid pressure may be lower than thought.

An unlikely cause of this is errors in piezometer measurements or clerical errors.

A more likely cause is that the pressure in the surroundings changes, possibly through natural causes but likely as a direct result of the UCG operation. The pressure field in the surrounding formations will change during the course of operations. The cavity will tend to act as a large-diameter water well, with water flowing from the (initially) higher-pressure surroundings into the relatively lower-pressure cavity. Without injection of water into the surroundings, a decrease in pressure will diffuse outward with time from the cavity into the formation.

If there has been a large drawdown of the local pore water pressure near the cavity and the operator underestimates this drawdown and believes that the local surroundings are closer to the original hydrostatic pressure, there is a serious risk of the cavity pressure being set too high and driving flows outward. This situation was encountered in a recent Australian field trial. The cavity pressure was maintained very low for a long time for a practical operation reason. When the operator was able, they raised the cavity pressure back up to where it had been. Relative to the newly-established surrounding pressure field, the new cavity pressure was higher and fluids were pushed out away from the cavity.

# Mitigation

Recommendations include:

- It is imperative to know accurately at all times the fluid pressure field in the near field as well as the far field. The next chapter discusses a recommended approach for obtaining this information from a combination of modeling and measurements with frequent updating and iteration between them.
- Operations must allow for uncertainties in the measurements and models. These uncertainties can be accommodated by using an adequate margin for the cavity pressure.
- The operator may need to slowly, continually decrease the cavity pressure to maintain an adequate inward pressure gradient everywhere. Modeling can inform this possibility.
- To maintain an adequate inward pressure gradient the operator may consider having a ring of water injection wells that are outside the process zone, but inside what would otherwise be the cone of pressure depression. The purpose is to keep the surrounding pressure roughly at original hydrostatic level.

# 4.2.6 Cavity or connected gas-filled fractures extend vertically up higher than thought

# Scenario of concern

If the cavity or its gas-filled connected fractures extend upwards and the operator does not reduce the cavity pressure correspondingly, the cavity pressure will exceed the surrounding pressure at the higher parts of the cavity. This outward pressure gradient will tend to push process gas out into the upper surroundings. Figure 4.5 illustrates this qualitatively.



**Fig. 4.5** If the cavity and/or its connected gas-filled fractures grow upward vertically without the cavity pressure being reduced, it can reach an elevation where the cavity pressure is higher than the surrounding pressure. This will tend to push process gas out into the surroundings, carrying contaminants with it.

The pressure within the gas-filled open cavity, rubble zones of the cavity, and connected large-aperture fractures will be roughly the same at all locations. This is because the relatively low flow velocities and open flow paths will not generally cause a large pressure drop. For this discussion it is adequate to consider the cavity gas pressure to be approximately uniform over all the connected gas-filled volume.

In the surrounding water-saturated rock formations, the pressure field will initially be close to hydrostatic, with deviations from this due to the flow history. In general, the water pressure will decrease with decreasing depth according to a hydrostatic gradient. For discussion purposes an adequate round-numbers approximation is 1 bar of hydrostatic pressure for every 10 meters of water column.

The location at most risk of an outward pressure gradient is the top of the cavity and/or vertically-extending large-aperture fractures, where hydrostatics tend to make the water pressure in the surrounding formation lower than at the bottom of the cavity.

There are likely to be many fractures, both natural and cavity-induced, surrounding the cavity. In this context we are only concerned with those that are gas-filled and pneumatically connected with the cavity. Tight, water-filled, or unconnected fractures may affect the water permeability of the formation, but will not be filled with process gas at the cavity pressure. To be gas-filled, they must have a large-enough aperture to drain of water and fill with gas before more water from the surroundings can refill them.

Some possibilities of fractures that are connected to the cavity and large enough to fill with process gas include the following.

- Large-aperture fractures
- Voids bounding pendant blocks.
- The expanding cavity or its connected large-aperture voids could intersect a pre-existing fracture. Most such fractures will be tightly closed, but tensional stresses from the cavity could open them up.
- The expanding cavity or its large-aperture voids could intersect a structural fault. In most cases these will be tightly closed but sometimes they could have significant pre-existing large apertures for one reason or another. In either case tensional stresses from the cavity could open them up further.

# Mitigation

Recommendations include:

- The cavity pressure must be adjusted to stay below the surrounding pore water pressure in the surrounding formation, assuming the highest credible vertical extent of the cavity and its connected large-aperture or gas-filled fractures.
- This requires being able to know or estimate where the top of the cavity and its open fractures are, and what the uncertainty of this is. The next chapter provides recommendations for doing this.
- The prescribed cavity pressure must allow for uncertainties in the location of the top of the cavity or open fractures.

#### 4.3 Gas-filled zones or outward gas flow despite inward water flow

It is possible for proper operation to maintain an inward gradient of water pressure in the surroundings. This will result in inward flow of water. The much lower density of the gas phase can produce scenarios in which gas, in zones of low water saturation (where gas occupies pore space) could exist. In some circumstances this could lead to outward gas flow over or through water-saturated regions.

# 4.3.1 Gas-saturated shoulder in the upper coal seam surrounding the cavity

# Scenario of concern

As mentioned earlier, there may be a shoulder around the upper cavity where the surrounding coal drains of water and pores contain gas. Consider a permeable horizontal coal seam with impermeable surrounding strata. The coal seam will be a confined aquifer. The cavity will be the analog of a screened pumped well. With inward pressure gradients and flow, there can be a shoulder surrounding the cavity, above which the coal is not water saturated

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**Fig. 4.6** An unsaturated should (pink shading) may extend some distance away from the cavity in the upper portion of a coal seam acting as a confined aquifer. The unsaturated pore space in this shoulder will be UCG process gas.

and pores will contain cavity gas. Figure 4.6 illustrates this. A Dupuit analysis [82] gives an approximate shape of the surface at which the water pressure equals the cavity pressure and below which the coal will be water saturated.

If the roof remains impermeable and the structure is anticlinal, horizontal, or low dip, the gas shoulder will be finite in extent. It is expected that there will be a small flow of gas inward in this region, due to water vapor produced from the moist coal behind (outward from) the pyrolysis zone. Process gas or pyrolysis gas may diffuse some distance into this region. If the cavity gas pressure is suddenly increased, it will push process gas outward into this region. If cavity gas pressure is suddenly decreased, water may flow into the hot parts of this region and make considerable steam which might affect flows in the unsaturated region. This is complicated. It must be looked at closely because under some circumstances it poses a risk of spreading contamination and/or gas escape.

# Mitigation

The phenomena of a shoulder of unsaturation is complicated. It must be analyzed and understood because under some circumstances it poses a risk of spreading contamination and/or gas escape.

A good two-phase flow porous medium model, ideally with heat transfer and water vaporization phenomena included, can be used to understand under what conditions of pressure history this shoulder might pose a gas-escape or contamination problem.

The cavity pressure should be controlled without rapid or large changes. The least risk of problems seems to be if the profiles of water saturation, temperature, pyrolysis, pressure in this shoulder region stay constant with respect to the open cavity boundary; i.e. move outward at the same rate as the cavity wall growth rate.


Fig. 4.7 In a dipping seam, the unsaturated shoulder will extend further up-dip. In some circumstances, this could become a pathway for buoyant gas to escape.

# 4.3.2 Gas-saturated shoulder in a dipping coal seam may let gas escape

# Scenario of concern

In a dipping coal seam, it may be possible that this shoulder of unsaturated pore space extends a long distance in the up-dip direction, as illustrated in Figure 4.7. If this happens, gas could flow up away from the process area even though water is flowing down into the cavity.

#### Mitigation

Choosing a site with horizontal or low dip angle is the simplest way to avoid this risk. The structure should be known well enough to assure that a small local dip angle is not the bottom of a syncline or adjacent to an upward fold.

A high-quality two-phase unsaturated flow model of the site using a reasonable range of geologic structure, material properties and operating conditions can provide information about the expected extent of shoulder and gas escape possiblilities.

If gas escape appears likely, either a lower-dipping or anticlinal site must be selected, or the cavity must be operated at sufficiently low pressure so as to avoid this phenomena.

Careful and steady control of the cavity pressure will help minimize any risk that gas and contaminants will spread by this mechanism.

# 4.3.3 Can gas finger upward against a downward pressure gradient?

#### Scenario of concern

In this section we discuss a mechanism by which process gas might escape upward in plumes or fingers, despite a downward gradient in the pore water pressure within the over-



Fig. 4.8 Downward pressure gradient causes downward flow of groundwater into the cavity roof, with upward-flowing fingers of gas caused by buoyant instability.

burden. At this time, further analysis and research is required to know if this mechanism is real and important or if it can be dismissed. Here we will simply describe qualitatively the possible mechanism.

The question here is what happens at the roof and near-field overburden of a gas-filled cavity when the gas pressure in the cavity is below the water pressure in the adjacent roof rock and the water pressure gradient within the overburden is downward. The downward water pressure gradient will cause a downward flow of groundwater through the overburden into the cavity. This sounds fine.

Conceivably, it is possible for a buoyant instability to cause fingers of gas to flow upward (while fingers of water flow downward), even though the water-saturated pressure gradient is downward. This possibility is illustrated in Figure 4.8. The behavior depends on whether or not the front where advancing water meets the cavity gas is stable.

If this situation is unstable, plumes or fingers of gas may flow upward. If the site has high permeability overburden or insufficiently thick low permeability overburden, this mechanism could transport gas (and hence contaminants) upward towards high-value ground water.

From a macroscopic point of view, the argument for instability is that the system potential energy may be reduced if a volume of gas ends up high in the formation and that volume of liquid ends up low in the formation.

# Mitigation

The simplest way to minimize this risk is to choose a site where the coal seam is overlain by low permeability formation(s) that will not be compromised by cavity operations. Good conservative practice would be to assume buoyant fingers of gas are possible. The magnitude of gas and contaminants they could transport will be proportional to the gas permeability of the overburden formation.



Fig. 4.9 Potential permeable pathways for escape of UCG process gas into the surroundings. Note that outward flow of escaping gas is only expected if there is an outward pressure gradient, or possibly a buoyantly driven flow.

### 4.4 Permeable paths for gas and contaminant escape

Previous sections discussed several scenarios that could lead to an outward pressure gradient from the process domain. An outward pressure gradient has the potential to drive process gas out in the formation, transporting contaminants with it. For much gas to go far, however, there has to be a permeable path for it. This section describes a number of possible pathways—some natural, some produced by the UCG operation, and some a combination of these. Figure 4.9 illustrates some of the possible permeable pathways for process gas to escape and transport contaminants. These include the natural permeability field, the UCGaffected permeability field, faults, abandoned boreholes and wells, UCG instrument and process wells, and the production well if it should leak.

In this section, we are describing primarily the initial transport of gas and contaminants out away from the process into the surroundings during the process. Once such a leak and transport have occurred, additional transport, typically by aqueous advection will occur over longer time scales.

# 4.4.1 Proximity to valuable/protected groundwater

### Scenario of concern

If the UCG process domain (cavity and production well) is in close transport proximity to valuable and/or protected groundwater, then even a small escape of process gas for a short time could produce unacceptable consequences of contamination.

# Mitigation

Other things being equal, if the potential contaminant sources were far from valuable or protected groundwaters, then an outward pressure gradient and permeable path would not result in much risk to those protected groundwaters.

Ideally the UCG operation would be far and hydrologically isolated from any groundwater of value. Modeling, as described in the next chapter, can help with judging how far away is adequate.

# 4.4.2 The natural permeability field and vertical connectivity

# Scenario of concern

The permeability field around and especially above the UCG operation strongly affects the amount of gas escape and contaminant transport to protected groundwater that would occur if outward pressure gradients were allowed.

In a perfect site the target coal seam would be overlain by a very thick, strong, and impermeable formation. Ideal sites are challenging to find, unfortunately. Potential features of concern include:

- High permeability strata
- Permeable strata with a high dip angle
- Discontinuous or penetrated low permeability barrier strata
  - Taper out
  - Lenses
  - Stream channel cuts
  - Collapsed or fractured barriers resulting from the growing UCG cavity
- Overly thin low-permeability barrier strata above the coal seam
- Transmissive faults

In most sedimentary formations there will be a distribution of permeabilities, generally tending to be continuous in the bedding plane and changing frequently perpendicular to this plane. Path(s) for lateral transport will typically exist in some of the strata such as sandstones and sometimes the coal seam itself. Other strata will have low permeabilities such as siltstones and claystones. Where these are continuous and reliably thick they provide a barrier to gas escape and contaminant transport.

Optimistic reliance on a low-permeability stratum above the target coal seam as a barrier is a concern if that stratum is not thick enough. To count on it as a barrier it must be thicker than the highest credible upward growth of the cavity and any cavity induced fractures. For example, in the Hoe Creek series of tests, the burn was expected to be confined to a thick lower seam by a 5-meter overlying claystone caprock. This caprock spalled and/or collapsed into the cavity early in the test and an overlying 3-meter seam was also gasified [35, 21, 34].

Vertical permeable pathways are of greater concern than laterally permeable pathways. Vertical connectivity or highly permeable vertical paths allow contaminants to be carried by escaping gas past barrier strata to higher permeable strata and closer to the surface where valuable and/or protected groundwater is more likely. Several possible deviations from layer-cake stratigraphy can provide vertical connectivity that far exceeds what would be predicted for a layer-cake.

Faults are possible pathways. Sometimes faults are relatively impermeable or sealing, and sometimes their fractured nature gives them higher permeability than the surroundings, making them transmissive. A transmissive fault provides an avenue for high rates of gas and contaminant transport away from the process. Such transport would often be preferentially up due to gas buoyancy. Unless there is confidence that a fault is not transmissive, it is best to keep UCG cavities and likely regions of local contamination away from known faults. It is hoped that major faults will be known and mapped. But it must be recognized that unknown faults exist due to inherent limitations in characterizing the subsurface.

Sometimes low permeability barrier strata taper out and disappear, allowing high permeability strata to connect. This is illustrated on the right-hand side of Figure 4.9 where the clay/silt layer that separates the coal seam from the saline sand disappears. Contaminants in the lower stratum (coal) can then flow directly into the upper permeable stratum (saline sand). Sometimes a characterization borehole can intersect a discontinuous lens of low-permeability material and be mis-interpreted as a broad stratum.

Layer-cake deposits are sometimes cut by streams or other erosional processes. When this happens a low-permeability barrier stratum can be cut out and permeable stream gravels left in place. Widely spaced characterization boreholes often do not find these infrequent stream channels. The thicker the barrier layers the less likely that a stream will have cut a channel through it.

Updipping permeable strata, even if layer-cake, provide a pathway for escaping process gas, and later flowing groundwater, to flow closer to the surface, where it is more sensitive to contamination impacts. At the first steeply-dipping Rawlins, Wyoming UCG test run by Gulf Oil [81, 87] process gas was observed in the gas-analysis trailer, creating an industrial health and safety problem from carbon monoxide and probably other gases. This was attributed not to a leaky pipe, but to process gas flowing up the dipping coal seam, which happened to reach the surface below this trailer.

# Mitigation

The ideal mitigation is to select a site with all favorable attributes and no unfavorable attributes. In general, if all of the surroundings had very low permeability to gas flow, including and especially vertical connectivity, then an outward pressure gradient would not result

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| Favorable attributes  | Unfavorable attributes  |
|---|---|
| Valuable/protected groundwater is nonexistent or only shallow                   | Valuable/protected groundwater extends down to the UCG cavity                   |
| Thick robust low-permeability strata above the cavity                           | No or only thin or undependable low-permeability strata above the cavity        |
| Low dip angle   | High dip angle  |
| Anticline structure   | Syncline structure  |
| No/few/small fractures, joints, or transmissive faults                          | Frequent/large fractures, joints, and transmissive faults                       |
| No old boreholes or mapped and properly closed boreholes                        | Unmapped or improperly closed boreholes   |
| Strong rock supports an economically-wide cavity with minimal vertical collapse | Weak rock results in excessive vertical collapse for an economical cavity width |

 Table 4.1 Some favorable and unfavorable attributes of a UCG site relating to pathways for contaminant transport.

 No site will be perfect, and engineering controls will be needed to assure acceptable cleanliness.

in much gas leakage or contaminant escape nor transport distance. The previous chapter on site selection has emphasized this point. Table 4.1 and the discussion that re-iterates some of these points.

It is expected that one of the mitigating aspects of a proposed site for UCG will be one or more low-permeability strata between the operation and any shallow fresh aquifer of value. The thicker the impermeable strata the better. This is most important in the overburden above the target coal seam, where a thick flow barrier should extend significantly above the highest credible height of cavity and open fracture growth.

The UCG operation would ideally be very far and hydrologically isolated from groundwater of value. Occasional impermeable strata will greatly reduce vertical transport, or vertical transport to a permeable strata. These can be an effective barrier between a potentially contaminated near-process environment and valuable near-surface groundwaters. A lack of breaks in such impermeable strata is important for them to act effectively as barriers to transport.

A proposed site should be adequately characterized. This is best done by a combination of logged boreholes and seismic reflection surveys. It is important that these map and characterize all the strata between the surface and the target coal seam. For geotechnical analysis, data concerning some depth into the underburden is also necessary.

Old exploration boreholes are often inadequate because they typically pay little attention to non-target strata and only sample, accurately delineate, and describe the coal seams. The spatial frequency of characterization boreholes must be dictated by how dynamic the structure is and the likelihood of infrequent features such as faults or stream channels.

Seismic reflection surveys are useful for mapping formations and strata in between widely-spaced characterization boreholes. Seismic surveys, especially 3D surveys, will be far better than boreholes at finding small-and medium-sized faults than scattered boreholes.

Of course, fault visibility is usually determined by whether they create substantial offset in reflecting horizons, so there is a lower limit to the size of faults that may be resolved.

UCG operations should be located far enough from known sizable faults that might be transmissive to assure that the cavity does not intersect them nor any zone of likely local contamination.

Two-phase flow and transport modeling of hypothetical overpressure scenarios should be performed. These would postulate possible durations and magnitudes of outward pressure gradient, at possible locations on the process domain perimeter. The models would then estimate the spatial extent of possible contamination events given the hydrogeology of the strata and structure of the site.

### 4.4.3 Failure of production well casing/connections

### Scenario of concern

The pressure in the product gas well will be roughly the cavity pressure. This is higher than the fluid pressure in the surrounding formations over much of its vertical length. In the shallower portion of the well the outward pressure difference will be large.

A breach of containment would lead to a large leak of raw product gas and outward transport of contaminants into likely sensitive shallow surroundings. The shallower depths that the production well runs through will typically be more sensitive to contamination because of their proximity to the surface and probability of containing fresh water.

The barriers to escape are the product pipe itself, any surrounding annular pipes and casing, the exterior grout between the casing and the formation, and the resistance to gas flow of the surrounding formation itself.

The risk of a leak from the production well is a major concern for a UCG operation. It happens occasionally in conventional petroleum and gas production from high-pressure reservoirs. Leaks of gas and fracturing fluid from poorly completed wells have been one of the problems in the emerging shale gas industry that have led to opposition. UCG is still on the industrial learning curve and even though some successes have been achieved, it is fair to say that the design, construction, and inspection of UCG production wells is not yet industrially mature.

The details of the production well are typically closely held proprietary information. This in itself presents a challenge to managing the risk of well failure. The less peer review and sharing of successes and failures, the higher the risk that the design and implementation will not be optimal.

There will be a casing to provide strength and mechanical separation from the surrounding material. The product gas may flow up directly within the casing, as in a simple well, or it may be contained in its own product gas pipe located within the casing. Multiple pipes/tubes and/or annuli may exist to provide separate paths for different fluids (such as water injection for cooling), wiring and cabling for monitoring diagnostics, insulation, strength, redundancy of containment, etc.

There will be grout or cement between the outside of the casing and the inside of the borehole. This grout must provide: a seal against vertical fluid flow up and down the borehole outside the casing; mechanical support backing the casing; sealing of casing joint gaps; and a barrier between the potentially hot casing and the wet surrounding formation (fast boiling of formation water coming in contact with a hot casing would tend to cause local high stream pressures).

Thermal stresses, especially many large changes in temperature, present an engineering challenge. The changes or cycling can weaken components and/or create voids in the surrounding grout. The well materials and design need to withstand high temperatures and accommodate expansion and contraction cycles. This includes the piping and the surrounding grout.

In addition to the thermal stresses, the production well may also be exposed to mechanical stresses and strains associated with the deformation and/or collapse of the cavity(ies). These stresses could shear a well or produce a leak, depending on subsurface movement and the production well placement.

Some of the gases in the product gas may be corrosive. Corrosion may create leaks or weak spots in pipe/casing that was good to start with. The product gas will contain particulates and condensable water, oil, and tars, and these have the potential to plug the line or downstream valves, increasing pressures.

#### Mitigation

The design, review, construction, inspection, and testing of the production well must be done in the context of the risk of a large groundwater contamination event at shallow depths if the high-pressure product gas leaks out underground. The well must provide containment despite the expected thermal and mechanical stresses and variability that the well will experience.

The design of the production well should be reviewed critically by experts.

There must be rigorous quality assurance of the well construction activities, with inspections of key features and installation steps.

There must be rigorous standard well testing. This can follow from existing practice in oil and gas production operations. Note, however, standard tests have not been designed to address the additional challenges presented by the high and changing temperatures that can be experienced in UCG production wells.

In addition to standard cold testing, there must be rigorous testing under realistic conditions of temperature and changes in temperature. These should be done before gasification starts, during the early phases of gasification, and/or possibly periodically throughout the life of the operation. Tests might consist of no-flow pressure leak-off tests, tracer tests, mass balance results etc. They must address high temperature and low temperature, high pressure and low pressure, and cycled temperatures and pressures. There is no standard for such testing and it will need to be developed by the industry.

Thermal stresses on the production well could be reduced by controlling the temperature of the product gas flowing through it. While one efficiency goal of UCG systems is to have the product gas arrive at the entrance to the production well at temperatures just above the local water boiling point (giving up its heat to preheat coal that will be gasified next) this is not reliably achievable. Active temperature control can be achieved by spraying water in the bottom of the well at rates that produce the desired product temperature. But this decreases the process thermal efficiency. Such a control system could be put in place to manage excessively high excursions in product gas temperature that would put the well integrity at risk.

Early detection of leaks from the production well will allow operators to take corrective actions quickly and limit the magnitude and extent of any gas escape and contamination event. There are several opportunities for early detection of leaks from the production well based on mass balances, gas detection, and gas sampling. Another indicator of production well leakage that could potentially be monitored would be an increase in temperature in the annuli of the production well, on its perimeter or in its immediate surroundings; thermocouples could monitor this.

# 4.4.4 Vertical connectivity up open boreholes or wells, or ruptured wells

#### Scenario of concern

The open interior of open boreholes and wells can provide a highly conductive vertical pathway. Abandoned production or characterization boreholes that were not properly cemented in, and UCG project piezometer, sampling, instrument and process wells can be intersected by the expanding cavity. Gas escaping the process due to some other problem could intersect these outside of the cavity.

Uncased, ungrouted open boreholes, such as from old exploration activity would be a large vertical conduit for gas and contaminant flow. Any intersection between the cavity or an escaping plume of gas and an open borehole will immediately fill the borehole with gas that will bubble/flow up with little resistance.

There are two scenarios of entry points for process gas into the open pipes of these wells. The wells could be intentionally open or slotted at the bottom or specific intervals. Even if they are entirely closed, they could be ruptured by mechanical strains or collapse events associated with the growing cavity. If the opening or breach is in contact with the open cavity, its gas-filled fractures, or an otherwise escaping volume of gas, then gas can flow into the open well.

There are three possibilities to consider for what will happen when a source of process gas at cavity pressure contacts an opening in these pipes:

- If the well is not capped at the surface, gas will flow up the well and out into the atmosphere. This will hopefully be quickly noticed at the surface. Surface leaks of process gas happened during the Rocky Mountain 1 test with wells that were inadequately capped.
- If the well is capped and the well does not leak, it will fill with gas, reach the cavity gas pressure, and sit there without harm. There is the industrial risk, however, of pressurized gas in a pipe.
- If the well is capped and there is an imperfect seal in the well or pipe, pressurized process gas will leak out into the surrounding formation. Thermal or mechanical stresses could weaken the pipe or its joints/couplings. The pressure difference driving such a leak is greatest where it is shallow because the surrounding hydrostatic pressure is less. This is analogous to a leak in the production well. Auxilliary wells are not though of as process gas production wells, however, and are likely to not receive the same amount of attention in design and construction as the production well. They may not have been designed to hold gas pressure. Carelessness or cost-savings is a concern for leaky wells if this groundwater contamination risk is not recognized.

## Mitigation

No open vertical boreholes should be allowed near a UCG process.

Historical records for the area expected to see UCG pressure effects should be searched carefully. There should be assurance that old boreholes were really cemented in. Clues pointing to unrecorded boreholes should be pursued to closure.

Auxilliary wells near the cavity must be designed, reviewed, constructed, and inspected with awareness that they may become open to high pressure process gas near the bottom and are a possible pathway for shallow contamination if they leak. Caps and joints/fittings must be leakproof even when stressed by warm gas, changing pressures or mechanical stresses.

One technical option to consider for instrumentation wells that are not needed for fluid flow is to fill them around the cables with material that will restrict gas flow, such as sand or foam. Activated carbon might be considered which would also adsorb enough organic contaminants to prevent contamination from a small leak.

Early detection of gas flow up the inside of an open well, or escaping out from a well to the formation should be considered. This would allow operators to take corrective actions quickly and limit the magnitude and extent of any gas escape and contamination event.

#### 4.4.5 Vertical connectivity along the outside of poorly grouted wells and boreholes

#### Scenario of concern

The exterior of poorly grouted boreholes and wells can provide a permeable vertical pathway. Gaps, loose material, or grout fractures can occur between the formation and the exterior of the grout, or between the grout and the casing. These may provide a much higher permeability vertical pathway than the surrounding native formation, especially in lowpermeability strata.

Old boreholes from previous exploration, characterization, production, or monitoring are typically required to be cemented upon abandonment. Cased wells, such as for production of water, oil or gas, or monitoring of groundwater will be grouted on the outside, between the casing and the formation. Modern UCG project wells for piezometers, sampling, instruments, or process flows will be present at a UCG site in close proximity to the cavity or potential gas escape paths. These will be grouted on the outside but may have imperfect seals between the casing and grout or between the grout and formation. This leakage path has been studied extensively in the context of  $CO_2$  sequestration, due to the buoyant nature of supercritical and gas-phase  $CO_2$  and potentially for thermally-induced stresses.

A leak of process gas up to the surface along the outside of the casing of the production well was observed at the first Rawlins UCG field test [87].

### Mitigation

The design, review, and construction of the exterior grouting of all boreholes and wells must be done in the context that this can provide a vertical pathway for contaminant transport. The borehole or well may come in contact with high-pressure process gas during operation, or contaminated groundwater in the years after operation. The grouting must not have or allow significant vertically-continuous gaps, delaminations, or fractures, despite the expected thermal and mechanical stresses and variability that the well will experience.

The design, prescribed materials, and grouting method should be reviewed critically by experts, in light of the stresses and temperatures that could reasonably be expected if the bottom of the well contacts pressurized process gas.

There must be rigorous quality assurance of the well construction activities, with inspections of key features and installation steps.

There must be sufficient inspection or logging done to identify at least major gaps in the grouting.

Methods for early detection of gas transport up the outside of wells should be considered. This would allow operators to take corrective actions quickly and limit the magnitude and extent of any gas escape and contamination event.

# 4.4.6 Cavity and its fractures grow higher than expected into a high-permeability stratum

# Scenario of concern

A favorable site will have a thick zone of low permeability located above the coal seam. This will be expected to keep any leaks or contamination from being transported through it. A good design and operating plan will plan that the cavity and its connected gas-filled voids do not penetrate through this low-permeability stratum.

If the cavity or its gas-connected voids extend higher than expected, going through the low-permeability zone into an upper high-permeability zone, then any outward pressure gradient or buoyant instability finger will be able to transport gas and contaminants away from the process through the now-connnected high-permeability stratum. The Hoe Creek III test is a relevant example where the upward growth of the cavity extended much higher than expected.

A detailed geotechnical assessment is necessary to determine cavity stability and the likely extent of any collapse zones. When multiple panels are to be extracted, inter-cavity interactions must be considered in the geomechanical response. Also note that there is often significant uncertainty in the final cavity geometry, and the geotechnical design should be sufficiently robust to account for significant deviations in cavity size, shape, and location.

# Mitigation

- Site selection (thickness of impermeable overburden layer) and UCG design (aspects that affect cavity height) should allow a generous amount of uncertainty in the vertical growth of the cavity.
- A conservative geotechnical design should be used to avoid unwanted cavity collapse.
- Any indications of an unexpected roof collapse should be treated seriously, with a halt in operations to evaluate the situation.

# 4.4.7 Cavity geometry is different than expected and intersects a permeable pathway

# Scenario of concern

The cavity may grow further outward than expected in a lateral direction. It could then intersect a permeable pathway that the planned geometry was going to avoid.

#### Mitigation

- The mine plan for the location of cavities must allow for the uncertainties of cavity position. Cavities cannot be controlled precisely.
- It is important to monitor the location and geometry of the cavities as they grow. Unfortunately, the cavity geometry and location can only be crudely measured with low-cost techniques.



Fig. 4.10 Illustration of failure modes associated with room-and-pillar mine plans. Similar modes may occur for UCG cavities.

# 4.4.8 Increase in permeability of surroundings by mechanical stress changes and fracturing

# Scenario of concern

Stress changes due to the cavity excavation can alter the permeability of the surrounding formation. Pre-existing fractures can be reactivated, or new fractures created. Bedding planes may delaminate. Faults may be reactivated. If significant cavity collapse occurs, large scale changes may take place.

The stresses and potential for fracturing are not only confined to the ceiling or overburden. Sidewalls and floor rock will also be stressed and may yield. Side walls providing pillar support carry high loads and can partially crush or fracture. Figure 4.10 illustrates several deformation mechanisms that have been observed for room-and-pillar mines, which are relevant for UCG operations as well. If cavity geometries are relatively wide, complete collapse may occur and a gob (goaf) region form, in exact analogy to a traditional longwall mine (Figure 4.11). In this case, fracturing and deformation can extend many times the seam height into the overburden, and significant surface deformations be observed.

The Hoe Creek III UCG field test is the most well-known example where geomechanical changes resulting from cavity excavation produced profound changes in the permeability field. Figure 4.12 is a photograph taken of a sinkhole that opened up soon after the test concluded. The two coal seams gasified were between 129 and 182 feet (39.3-55.5 m) below the surface.



Not to scale

Modified after Peng and Chiang, 1984

Fig. 4.11 Typical geomechanical behavior of a longwall mine. Similar zones of collapse, fracturing, and deformation could occur for wide UCG cavity geometries.



Fig. 4.12 The chimney-collapse sinkhole above the Hoe Creek III field test illustrates that UCG cavities can produce significant geomechanical disruptions.

# Mitigation

- A thorough geomechanical analysis must be done on any proposed mine plan. Its outputs should highlight any region where large permeability changes are expected.
- These analyses should include sensitivity to significant variations in the geometry (size, shape, location) of the UCG cavities. This is because UCG cavity geometry can not be precisely controlled nor known. Pillar widths are especially sensitive to the geometry and



Fig. 4.13 Combinations of possible outward pressure gradients that can push process gas away from the process domain, and permeable paths along which the process gas easily flow.

location. Cavity growth and location will also be affected by the existence of an adjacent cavity, whether it is operating or shut down. This cross-talk may make cavities tend to grow closer to a previous cavity because of lower pressure or less water in the coal near the old cavity, etc.

- There is very little UCG experience with multiple-cavity or large mine-plan operations. The uncertainties associated with cavity and pillar geometries and locations must be covered by the analyses and factored into decision making.
- An iterative feedback loop must take place between proposed mine plans, geomechanical analyses, permeability field estimations, and judgements about the adequacy of barrier strata.
- A conservative mine design will best protect groundwater resources. Unfortunately, a conservative scheme will also reduce the recovery efficiency of the site. Pilot tests and early cavities should be particularly conservative in their design. As more information is gathered about the field, and greater confidence is gained in the geomechanical behavior of the site, larger recovery ratios can be planned.

# 4.5 Combinations of outward pressure gradient and permeable paths

To convey much escaping gas and its contaminants far away from the process domain it takes a combination of driving force and path. Certain permeable pathways are in play for certain causes of outward pressure gradients, and vice-versa. Figure 4.13 illustrates pairs or combinations of outward pressure gradients and permeable escape paths that would typically act together to produce a significant escape of process gas. Note that here, as in the entire chapter, we are considering an episode of escaping gas during process operation, not the long-term hydrogeologic transport of contaminants after UCG shut-down.

# 4.6 Highest-risk scenarios

In our judgement, two scenarios appear to pose the highest risk:

- Leak from the production well into shallow surroundings: A leak from the production well to outside the casing and/or grout will create a very large outward pressure gradient and persist until the leak is noticed. The permeability of the formation will be whatever it is locally, but the leak will be along the production borehole which itself is a potential path for vertical connectivity if it was imperfectly grouted. The leak could carry contaminants much closer to the surface than the UCG cavity.
- 2. *Higher than expected vertical growth of the cavity*: A high risk of contamination is posed if the cavity and/or its gas-filled connected fractures extend vertically above assumed maximum height that was used to set the maximum allowable cavity pressure. This scenario will produce an outward pressure gradient that will persist until the leak is noticed, and it will reduce the thickness and effectiveness of any planned low-permeability barriers.

# 4.7 Scenarios not yet identified

This report has attempted to list and describe all the scenarios that might cause unacceptably large escape of process gas and its contaminants. It would be nave, however, to think that all problematic scenarios have been identified. UCG has not moved far along the industrial maturity learning curve, and it is likely that as time progresses mistakes will be made and lessons learned.

# Chapter 5

# **Risk Mitigation Recommendations**

We can never eliminate risk. We can only try and reduce it to acceptable levels. Consideration of things that could go wrong and their worst cases will help to reduce their likelihood and the magnitude of their impact.

Many specific mitigation measures were mentioned in the previous chapter, following each specific scenario of concern. Here we discuss in more detail some of the most common, important and cross-cutting mitigations—i.e. those strategies that help with multiple scenarios.

Underground coal gasification is still a relatively immature technology. There is limited experience with it. It takes place in a natural, stochastic environment that is difficult to characterize and monitor precisely. There have been cases of groundwater contamination caused by UCG. It is therefore important that current and future UCG operations adopt conservative practices. These may add costs and reduce profits from the early operations, but the reduction in risk seems worth it for the protection of groundwater resources and the long-term success of the industry.

The previous chapter described potential scenarios that could lead to unacceptable contamination. Understanding and analyzing these scenarios helps figure out how to prevent them, detected them early, and/or minimize their impacts.

In considering a proposed operation, it is important to ask questions such as:

- 1. What would happen if ...?
- 2. How do we assure that ...?
- 3. How do we know what ...?

The previous chapter provided a start towards this process. Its many scenarios of concern and corresponding mitigation measures should be reviewed. A focused critical analysis of any specific proposed project is important.

A risk assessment is a formal methodology to identify and quantify the damage that could result from various scenarios. It typically involves three components:

- 1. Identify scenarios that could lead to damage (the scenario of concern)
- 2. Determine the likelihood of a given scenario occuring (the hazard)
- 3. Determine the damage that would result from a given scenario occuring (the impact)

A good risk assessment can then drive management decisions to minimize risk. Note that there are two components to good management: (1) putting controls in place to minimize the likelihood of unwanted events occurring, and (2) putting controls in place to minimize damage *even if* an unwanted event should occur.

This chapter is broken into several sections, providing risk management recommendations on topics such as site selection, design and operations, monitoring, and modeling. Each recommendation is intended to help mitigate risk, either by lowering the likelihood of an unwanted event, or minimizing the damage that could result.

# 5.1 Site selection recommendations

Perhaps no mitigation is more important than choosing to operate in a location that makes groundwater protection easier and more assured. Chapter 2 covered this topic in detail. It is clear that an ideal site would have:

- · Target coal seam far below any valuable or protected groundwater
- Thick, impermeable strata between the mechanically affected zone (target coal seam and collapse/fracture zone above) and shallower aquifers
- No vertical connectivity through the low-permeability barriers
- Low dip angle, so that a permeable coal seam does not provide a permeable path to the surface
- Competent rock and coal that provides mechanical support and resists spalling/collapse
- Few faults, especially large faults and/or transmissive ones

# 5.2 Design and operations recommendations

# 5.2.1 Allow for uncertainties

UCG is not yet industrially mature, and deep geologic systems are inherently complex and difficult to monitor. Until industrial practice at large scale suggests otherwise, planning and precautions should be conservative and allow for a generous range of uncertainty.

### 5.2.2 Use conservative and robust mine plans

Given that one of the greatest risks is excessively tall cavity growth, planning for relatively small cavities and large, conservative pillars will decrease risk. For UCG, a large challenge is that the cavity geometry cannot be precisely predicted beforehand, and so the geomechanical design should be robust even if cavity size and shape is somewhat different than expected. This is especially true if there are multiple cavities or multiple seams being extracted. It is important to carefully monitor cavity geometry, and be on the look out for any signs of unexpected collapse or other geomechanical deformations.

# 5.2.3 Use a conservative strategy for managing cavity pressure

Cavity pressure must be managed to maintain an inward pressure gradient outside of the entire perimeter at all times. A well-thought-out strategy for doing this must be in place. It must be backed by high quality modeling that has addressed plausible scenarios for gas leakage. The desired cavity pressure is not a fixed value. It changes with time and depends on past pressure history, the history of any pumping, geometric changes in the cavity and fractures, and other factors.

# 5.2.4 Implement a robust quality assurance program

UCG operations are difficult and performed in a challenging environment. The system is dirty, dusty, hot, aqueous, organic, corrosive, with often unsteady conditions, wide turn-down ratios and ranges of possible flows, pressures, temperatures etc.

Mistakes can be costly. An immature industry cannot afford a groundwater contamination event that results from someone forgetting to do something right, or hiring unqualified subcontractors. The public is highly skeptical of new energy technologies, as recent experience in many industries has demonstrated.

Robust quality assurance processes are essential and can mitigate many failure modes. Quality assurance programs should address all aspects of operation: design, procurement, construction, installation, control strategy and software, hardware, operations, training, and communications. Sloppiness and corner cutting increases the risk of groundwater contamination.

Hardware must be robust and accommodate the wide ranges of temperature, pressure, and flow rates, and the dusty, tarry, corrosive gas composition. Control systems must handle variable operations, wide dynamic ranges, and unexpected events such as flow blockages. The design and operations must have a way of quickly detecting a plugging event or unwanted closing of the backpressure valve, and there must be a response plan in place. These procedures should be practiced to ensure that they can be executed quickly.

Trained operators should be on-site, with necessary expertise in close communication. Clear procedures for handling emergencies should be defined. Human error must be minimized by a robust quality assurance program, training, methodical operations, and frequent close communication between technicians, monitoring and modeling analysts, and senior process experts.

#### 5.2.5 Minimize residual contamination from normal operations

UCG will leave some amount of contaminants within and close to the cavity during operations. The chosen operations strategy can effect the production / destruction rate of these contaminants. This idea should be given consideration, but unfortunately the current extent

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of experience and the state of modeling are not adequate to provide definitive guidance on this aspect.

# Process selection and optimization

It is likely that some set of operating conditions may tend to leave more or less contamination behind. This sort of process optimization will take place as the experience base grows—if detailed data are obtained from good comparative studies, and modeling capabilities grow. At this time, qualitative arguments about the advantages and disadvantages of candidate approaches have some value, but more empirical experience is needed.

#### Proper Module Shutdown Procedures

Good module shut-down procedures can remove contaminants and minimize the amount and distribution left behind. "Clean cavern" procedures were previously described. Again, more empirical experience and sophisticated modeling studies will provide clearer guidance on an optimum shut-down protocol.

# 5.3 Hydromechanical monitoring and modeling recommendations

# 5.3.1 Geometry of the cavity and any open fractures

It is crucial to have a good estimate of the cavity geometry and location at any given time during the operations. Unfortunately, cavity geometry and location cannot be precisely predicted or controlled. Further, low-cost monitoring techniques can only provide crude estimates of the cavity geometry. These uncertainties must be factored into the operations plan.

#### General Approach

An important mitigation is simply to recognize the importance of knowing the cavity's top height, geometry, and location, and devote resources to this accordingly. Plans for cavity size and geometry, or mine plans for multiple cavity operations, must allow for the impossibility of controlling and knowing the cavity geometry precisely. There is no perfect way to monitor cavity height, geometry, and location. Inexpensive, accurate, precise, proven, and robust methods do not exist yet. An important industry goal should be to develop, test, calibrate, demonstrate, and make robust for industrial practice a suite of methods to do this.

The best way to monitor will be by integrating information from a combination of multiple different measurements and modeling. At this time the selection of monitoring methods will require a trade-off between the benefits of better monitoring by more-expensive and redundant methods, and the cost and practicality of the methods. The trade-off will need to factor in the size scale of the operation, the extent of experience with the site and proposed type of operation, the physical aspects of the site, the environmental sensitivity of the site, and the conservatism or aggressiveness of the proposed operation.

# Geomechanical modeling

Geomechanical modeling of the system is needed to provide predictions in the early phases of a project, and as a framework for interpreting and interpolating measurement observations. The geomechanical model should be capable of estimating, for a given amount and geometry of coal excavation:

- For a single cavity or room-and-pillar mine plan (i.e. only small-scale yielding and roof collapse)
  - the expected extent of open cavity, as well as extent of damage around the cavity
  - the location of any surrounding compression arches or zones
  - stress and deformation in the near- and far-field.
  - location and extent of any inter-cavity pillar yielding.
- For long-wall mine plans (i.e. deliberate large-scale collapse)
  - The geometry of open cavity versus collapsed gob/goaf
  - The vertical extent of zones of caving, fracture, and substantial deformation.
- The initial geomechanical model could make use of the following information for calibration and validation purposes
  - Geomechanical behavior of mines and/or excavations in the same formations.
  - Geomechanical site characterization data, including: recovered core, core mechanical tests, well-bore logging to obtain geomechanical properties and characterization, *in situ* stress measurements or indicators, hydrogeologic characterization, etc.

The geomechanical modeling should address stochastic and uncertain characteristics of UCG and the subsurface. It should analyze sensitivities and a range of possibilities. Modeling results should communicate probabilities, at least qualitatively, including most-likely and worst-plausible results.

Geomechanical modeling should continue during the operations as well. Frequent updating of the model during operations, making use of new observational knowledge, will allow much more precise estimates and provide a useful framework for interpreting monitoring observations.

# Geomechanical monitoring

A variety of methods are available that provide direct or indirect information relating to the cavity geometry and its mechanical behavior. These include:

• Temperature measurements in monitoring wells

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- Formation fluid pressure measurements in monitoring wells
- Detection of gas in the formation (as opposed to water saturation)
- Downhole tilt-meters or strain gages
- Downhole failure anchors
- Time domain resistivity (TDR) measurements on available conductors such as well casings or interior pipes, or dedicated cables
- Seismic reflection imaging (2D, 3D, and 4D; surface and borehole)
- Microseismic measurements
- Channeled in-stratum seismic methods
- Electrical resistance tomography (surface and downhole)
- Subsidence surveys (conventional, GPS, InSAR)
- High frequency electromagnetic tomography (HFEM)<sup>1</sup>
- Noble/geo-radiological gas concentrations at surface or in subsurface<sup>2</sup>
- Electroseismic surveys
- Other novel methods

Many of these are not simple direct measurements. They require method-specific processing to interpret the data and produce estimates of cavity height and geometry. The time-delay associated with this processing should be factored into operational procedures.

As familiarity with a given site increases—i.e. after a series of pilot and demonstration tests—more confidence about the cavity and fracture growth can be obtained with fewer, less-intense, less-expensive measurement methods. Thus pilot tests may employ a kitchensink strategy, while commercial operations can have a streamlined monitoring program.

# 5.3.2 Hydrology

One of the best mitigation measures for preventing groundwater contamination is for a UCG operator to always know accurately the underground fluid pressure field, phases (liquid or gas), and flow field surrounding the operation.

# General Approach

The best approach to estimating pressure and flow fields is to combine measurements with modeling. Iteration between the flow model and all relevant data will arrive at the best possible interpretation and knowledge of the subsurface.

The model should be updated and truth-matched against measured pressure fields, operating pressures, and water balances at least once per week; daily during dynamic periods. Given a reasonable match between model and observations up to some recent time, the model can be updated a week later with actual operating conditions for that week, and

<sup>&</sup>lt;sup>1</sup> Successful for pilots in the US program (Stephens, 1981) but likely too expensive for industry practice

<sup>&</sup>lt;sup>2</sup> Radon measurements were employed in several Chinese tests

inputs such as expected cavity growth and any pumping etc. The model can predict water production expected over the past week and what pieziometric pressure fields would be. Large deviations between the predictions and observations would be cause for further investigations.

There should be frequent close communication between the hands-on operators and instrumentation specialists, the senior process experts, and the modelers. Discussion of interesting, surprising, inconsistent, or anomalous measurements or predictions is a productive way to discover that something is not as it should be.

Relevant data include measurements of the cavity pressure, in-situ fluid pressures, water production rates from process and auxilliary wells, and the geometry of the cavity and open fractures above it.

In both measurements and modeling, especially-close attention must be paid to the top of the cavity and fractures, including their upward extension by spalling, collapse, and fracturing. This is the region at highest risk of gas escape.

### Hydrologic modeling

A well-resolved underground flow model for the site is essential. This hydrologic model must support 2-phase unsaturated flow of both water and gas, accounting for capillarity. The model needs to be 3-dimensional because the UCG system is 3-dimensional, and the locations of pieziometers, process and instrument wells, and geological structure are 3-dimensional. A dual-permeability model (fracture and matrix) is advantageous but its necessity depends on the details. A coupled thermal component is useful, especially for buoyant water flows. The model must realize an adequate level of important geological structures such as dips, multiple strata, faults, etc. The model must accommodate the evolving geometry of the cavity and potential changes in the porosity and permeability fields. Many commercial and academic software packages are available that handle most of the relevant physics. Often, however, model quality comes down to the experience of the modeler rather than the software tool itself.

One of the main reasons the model must be 2-phase and account for unsaturation and capillarity is to provide information on the expected extent of any gas-saturated shoulders in the upper part of the coal seam surrounding the cavity. Tracking the pressures, phase compositions, and flows in this zone is important.

# Hydrologic monitoring

Useful monitoring and characterization data include

- Geologic characterization data
- · Initial pressure field, from pieziometers and sampling wells
- Initial permeability field, from core measurements and pump tests

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- Cavity geometry and geomechanical damage zones.
- Injection and/or pumping data from all wells
- Cavity pressure as a function of time, usually inferred from wellhead measurements.
- Subsurface fluid pressure measurements
- Water balance on the UCG system:
  - Material balances give total water influx
  - Process model and information on the cavity growth give water influx due to coal consumption, coal drying, rock drying
  - Water influx by permeation estimated by difference between these
- Downhole measurement/observation of formation gas content (fraction of porosity occupied by gas instead of water) at strategic locations in the surroundings.

### 5.4 Gas leak detection recommendations

Discovering leaks of process gas out of the containment zone may be the easiest and quickest way to detect potential contamination situations before contaminants are transported far. Early detection of leaks will allow operators to take corrective actions quickly and limit the magnitude and extent of any gas escape and contamination event.

The previous chapter described how escaping gas is likely to travel faster and further than most of the contaminants. Briefly, this is because most of the contaminants condense, dissolve, or adsorb, while the gas keeps going. Gas is also much more mobile and dispersive and diffusive than groundwater; i.e. it mixes and distributes better. Thus detection of gas leaks may be more likely than detecting groundwater contamination directly. Gas detection can be made outside of where the contaminants will have spread at a given time.

# General Approach

There are three basic approaches to discovering that gas may be escaping from the process into the surroundings:

- Mass balances on the process can indicate that gas is missing
- Detection of the presence of a gas phase where water saturation was expected
- Sampling of gas underground or from locations coupled to underground

Information from these approaches can be combined with all other information about the operation to interpret the observations and judge if a potential contamination situation has been discovered and what should be done.

There is a downside to the "more monitoring is better" view. Besides their extra cost, wells—including instrument and sampling wells—are a potential pathway for upward contaminant transport. This tradeoff must be considered.

### Mass balance on the process, including tracer recovery

A set of total and elemental mass balances on the process can provide an indication of gas loss. These are nontrivial, usually involve differences of large and imperfectly measured quantities, and often involve assumptions or estimates of things unknown. A good discussion of this approach is found in [60]. While mass balances are difficult, they are typically done as part of routine process monitoring and interpretation. Changes in the balances that indicate gas leakage should raise a red flag.

A more direct measure of gas loss can be obtained by periodically doing a tracer test. A known quantity of tracer compound can be injected into the injection gas, and its production rate measured and integrated. In principle, what goes in must come out and if less comes out than was injected there may be a gas loss. While it sounds simple, challenges with this approach include:

- Imperfect measurement of the quantity of tracer injected
- Imperfect measurement of the concentration of tracer in the produced gas
- Imperfect measurement of the flow rate of produced gas
- Imperfect conservation of the tracer due to sorption, dissolution, reaction, etc.
- A long tail of the produced tracer curve due to mixing producing a distribution of residence time in the gas phase, diffusion into pores of rock, coal, char, etc.

Even if the mass balance on the tracer is imperfect, changes over time may indicate gas loss. It is recommended that mass balance and tracer tests be evaluated during research, pilot, and demonstration phases. If they are well behaved, they could be informative and cost-effective indications of possible gas loss.

# Detecting the presence of gas

Most of the subsurface surrounding a UCG operation and below the pieziometric surface will have its pore volume saturated with water. If an escaping plume or finger of gas passes by, the pore water in the rock partially or mostly will be displaced by gas. An observation that a water-saturated location has become partly or mostly gas saturated is a clue that gas has invaded this area, possibly along its route of escaping further.

### Sampling gas

Underground gas can be sampled and then monitored or analyzed. This includes sampling of surface gas or gas within the headspace or annulus of a well. The sampling can be done periodically or continuously. Pore gas can be sampled directly from the unsaturated zone. The technology and art of collecting soil vapor samples has been well developed for environmental remediation applications. Gas sampling in the water-saturated zone presents a larger challenge.

# Analysis

The analysis of sampled gas could be a traditional laboratory analysis of a batch collected sample. Or it could be a continuous real-time detection of one or a few analytes by a detector. For example soil gas could be flowed past inexpensive, industrially mature carbon monoxide, ammonia, and/or hydrogen sulfide detectors.

Noncondensable gas constituents of the process gas include nitrogen (N<sub>2</sub>, in air-blown gasifiers), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), hydrogen (H<sub>2</sub>), water (H<sub>2</sub>O), and methane (CH<sub>4</sub>) in concentrations of several to tens of percent by volume, lesser amounts of other gases such as ammonia (NH<sub>3</sub>) and hydrogen sulfide (H<sub>2</sub>S), and vapors of volatile condensable species.

Detection of escaping gas plumes or fingers by gas sampling will be most successful if it analyzes for those components that are:

- high in concentration,
- conserved (not prone to adsorption or dissolution into solid surfaces or pore water),
- have low natural background and are unique to UCG
- are inexpensive to detect or analyze quickly

A later chapter assesses these characteristics and suggests that the following may be good candidates as gas sample analytes:

- · carbon monoxide and/or hydrogen
- · ammonia and/or hydrogen sulfide
- benzene or combined BTEX
- acetone
- napthalene,
- phenol or total phenolics,
- pyridine, and
- total organic carbon.

One or a few of these may be selected for frequent or continuous gas sample monitoring or sample analysis. Additional analytes will help with interpretation but it would be unduly expensive to analyze for them without cause. If the primary analytes are detected above background a gas sample can be analyzed in more detail to help judge if the gas came from the UCG operation or not, and possibly additional useful details to aid interpretation.

# Sampling locations

Escaped process gas should be detected or sampled at locations along anticipated paths where it is most likely to be found (Figure 5.1).

Escaping gas will be less dense than surrounding water, so will tend to rise. It will also tend to flow along paths of high permeability and large pore size (low capillarity). This



Fig. 5.1 Potential gas detection and sampling points. Chosen locations should emphasize places that are most likely to have escaped process gas passing by.

knowledge, combined with the various escape scenarios contemplated in the previous chapter, will lead to good location choices.

The natural composition of gas in unsaturated formations at the site must be measured before UCG operations start. This includes its spatial variability, and possibly temporal variability. Without knowing what is naturally occurring in the background it is more difficult to interpret measurements.

Head-space gas above (in equilibrium with) background samples of groundwater must be included in the background gas analyses. During operation, if a gas zone were to occur underground and be sampled, we would want to know if that gas contains UCG-created products or if it is just gas that picked up species from natural groundwater.

# 5.5 Groundwater monitoring recommendations

Monitoring groundwater around an industrial activity for contamination has become a common endeavor. It has been much studied and much practiced. Its application to UCG is relatively straightforward and has been done already for many test and demonstration projects. Thus we will not go into great detail on this topic. Specific compounds to look for around a UCG operation are discussed in greater detail in the next chapter.

There are two important limitations to groundwater sampling at any significant stand-off distance (more than a few tens of meters) from a UCG operation:

- By the time you get a "hit" you may already have a problem. Because of the condensation of most contaminant species from a plume of escaping gas, the extent of groundwater contamination may be much less than the distance the gas travels.
- A negative result does not prove there is no contamination. It may be a low-probability event if a finger of contamination passes through a given groundwater sampling station

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or not. If a finger or plume of contamination misses a station, it may be weeks, months, or years before mixing, diffusion, or cross-wise advection brings the contaminants to a sampling station.

Because of these two limitations, groundwater sampling should be combined with other monitoring techniques. For example, we advocate evaluating and using gas sampling more than has been typically done in the past, as an approach that offers the potential of much quicker detection of contamination-producing events.

# Baseline sampling is crucial

A thorough baseline of groundwater composition must be done. Without it, any future results can be inconclusive. The baseline sampling must include many samples and analyses of the reduced set of contaminants (see next chapter) and an adequate number of analyses of the full set of potential contaminants. It must define spatial and temporal variability. It must establish the likelihood and magnitude of false positives from sampling or analysis artifacts. The next chapter discusses many naturally occuring species that it is important not to confuse with operational contamination.

# A three-zone concept for early detection and corrective actions

Groundwater monitoring wells are sometimes installed with the goal of proving that there is no contamination. We believe that the more important goal should be early identification of unwanted situations or the beginnings of a contamination event, so that corrective actions can be taken as soon as possible.

The concept of groundwater monitoring "rings" is well established. But the sampling locations need to provide vertical coverage in addition to horizontal. "Shells" may be a better term than rings. Details of the site hydrogeology and the proposed operation will affect the exact placement decisions. Modeling should be done to assess how well a proposed monitoring array would detect hypothetical contamination events.

In general, a sampling well will be more likely to be in the path of escaping contaminants if it is in the top part of a permeable zone, below a layer of low permeability. Bouyancy of escaping gas and the warmer water that occupies rock warmed by previous gas is expected to cause contaminated water to rise, other things being equal.

We suggest dividing the UCG operation and its surroundings into the following three zones:

- Inner (near-cavity) zone where contaminants are expected. Observation of contaminants in this zone provides important early information, but do not indicate any abnormal migration has occurred.
- Middle zone for rapid detection of unexpected or infrequent small contamination events. This detection shows that contaminants have escaped the near-cavity containment zone.

This is really when and where a problem can be detected early. This provides an opportunity for aggressive correction action.

• Outer (compliance) zone, intended to be free of contamination, but still monitored for detection.

The inner zone includes the cavity, module, or adjacent modules and a surrounding volume where it is expected to have significant or detectable quantities of polluting chemical species present. Exactly how far the inner zone extends laterally and vertically depends on all the details of the site and proposed operation, but might be roughly 10 meters around the perimeter of a given cavity. The vertical extent will depend on the expected dimensions of roof collapse and geomechanical damage.

In the middle zone contamination is not expected if the operation goes entirely as planned, but it could be imagined that certain unwanted scenarios could have escaping gas pass into here and could bring small amounts of contamination here. The outer boundary of this middle zone are located such that if a small amount of contamination found its way into this zone, there would still be no expected impact on public health, safety, resources, or valuable/protected groundwater. Exactly where in space the outer envelope of this middle zone is placed again depends on all the details of the site and proposed operation. As a starting point for discussion of a single cavity module, this outer zone might extend roughly 30 meters around the cavity perimeter. Vertically it might extend to the nearest permeable layer not expected to be affected by operations.

The observance of a gas leak or contamination in this middle zone is a sign that something is not going as expected. This provides an opportunity to understand the situation and take actions so it will not happen further, and possibly reverse it. Ideally such measurements would be shared with the regulators, a reasonable time agreed upon to come up with adjustments, and an adjustment plan approved. Observation of contaminants in this middle zone should not trigger findings of noncompliance. The boundaries of this zone are such that the public's interest in protecting groundwater are still not at risk. The boundaries should be close in enough to allow early detection and correction of issues without creating a compliance crisis.

The outer zone is anywhere outside of the middle zone. This is the compliance zone. Monitoring should be done within this zone to provide detection of gas escape and possible contamination events, and to document compliance and lack of contamination. Limits of contaminants above background in this zone should be very tight. There could be agreed upon responses to detections of issues in this zone that still encourage honest communication and protection of the public; small limited excursion could receive minor penalties and large, enduring excursions could result in a major noncompliance finding.

# Chapter 6

# **Compositions and monitoring analytes**

#### 6.1 Composition of UCG-product streams

Analyses of UCG products provide information on the chemical species that would be present underground that could contaminate groundwater. The whole product stream contains gases, vapors, and some liquid/tar aerosols and solid particulates. The product stream is typically put through a condenser and separator to produce a gas stream, an organic liquid stream, and an aqueous stream.

The composition of the organic liquid stream provides the best information about what species would be left underground in condensed organic phase as tars and liquids. The composition of the aqueous stream provides information about what species would likely be found dissolved or suspended in UCG-contaminated groundwater. And the composition of the gas stream provides information about what species might travel furthest underground in gas phase and be observable by gas monitoring.

Because of chromatographic fractionation during underground flow and transport, samples at any one location underground will likely have only a subset of the compounds that are present in the UCG product stream.

A previous chapter described how the compounds are generated underground by UCG. It provided a general description of the types of compounds. This section provides more detail on the species and concentrations that have been measured.

### 6.1.1 Gas-phase products of UCG (the noncondensables)

UCG process gas will contain the major consituents of carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), hydrogen (H<sub>2</sub>), water (H<sub>2</sub>O), and methane (CH<sub>4</sub>) in concentrations of tens of percent by volume. In air-blown systems, nitrogen, (N<sub>2</sub>) can be up to more than half of the gas volume. In addition there will be lesser amounts of other gases and vapors of volatile condensable species.

Barbour et al. [46] report analyses of light hydrocarbons in the gas stream downstream from the condenser for the Rocky Mountain One UCG test. They sampled and analyzed both the Extended Linked Well (ELW) and Controlled Retractable Injection Point (CRIP)

|                |         |         |         | Time, ga | Time, gasification days |        |        |         |         |        |
|----------------|---------|---------|---------|----------|-------------------------|--------|--------|---------|---------|--------|
|                | 23      | 24      | 45      | 51       | 65                      | 66     | 67     | 78      | 79      | 94     |
| Methane        | 124290  | 105437  | 102735  | 90225    | 79344                   | 72555  | 72831  | 100979  | 94123   | 62284  |
| Ethylene       | 413     | 394     | 254     | 216      | 268                     | 423    | 357    | 293     | 374     | 139    |
| Ethane         | 9734    | 7875    | 6484    | 5267     | 4653                    | 4254   | 4020   | 8127    | 7059    | 3592   |
| Propylene      | 362     | 337     | 257     | 197      | 326                     | 352    | 307    | 273     | 433     | 103    |
| Propane        | 1720    | 1504    | 1342    | 1021     | 832                     | 804    | 735    | 1000    | 1214    | 868    |
| i-Butane       | 148     | 134     | 121     | 88       | 78                      | 78     | 69     | 91      | 117     | 52     |
| t-Butene       | 145     | 134     | 108     | 74       | 76                      | 83     | 72     | 63      | 102     | 49     |
| n-Butane       | 149     | 196     | 235     | 176      | 128                     | 132    | 122    | 150     | 177     | 36     |
| Trans-2-butene | <25     | <25     | <25     | <25      | <25                     | <25    | <25    | <25     | <25     | <25    |
| 1-Pentene      | 58      | 53      | 108     | 46       | <25                     | <25    | <25    | <25     | <25     | <25    |
| n-Pentane      | 91      | 75      | 86      | 63       | <25                     | 45     | <25    | 45      | 51      | 60     |
| 1-Hexene       | <25     | <25     | <25     | <25      | <25                     | <25    | <25    | <25     | <25     | <25    |
| n-Hexane       | 49      | 42      | 51      | 51       | <25                     | 51     | <25    | <25     | <25     | <25    |
| Benzene        | 622     | 703     | 1177    | 762      | 501                     | 579    | 457    | 1032    | 898     | 714    |
| n-Hepane       | <25     | <25     | 39      | 39       | <25                     | <25    | <25    | <25     | <25     | <25    |
| Toluene        | 130     | 131     | 235     | 134      | 46                      | 66     | 50     | 89      | 63      | 67     |
| n-Octane       | <25     | <25     | <25     | <25      | <25                     | <25    | <25    | <25     | <25     | <25    |
| Total          | 137,911 | 117,015 | 113,232 | 98,359   | 86,252                  | 79,422 | 79,021 | 112,142 | 104,611 | 67,964 |

 Table 6.1 Analysis of hydrocarbons in the gas stream downstream of the condenser for Rocky Mountain One, CRIP module. Reproduced from Barbour et al. [46]. Unit is ppmv.

**Table 6.2** Gaseous sulfur analysis of product gas from the CRIP module of the Rocky Mountain One UCG test. Reproduced from Barbour et al. [46]. Unit is ppmv.

|                  | -    |      |      | Time, ga | Time, gasification days |      |      |  |  |
|------------------|------|------|------|----------|-------------------------|------|------|--|--|
|                  | 23   | 24   | 45   | 51       | 65                      | 66   | 79   |  |  |
| Hydrogen Sulfide | 2515 | 2460 | 4220 | 5405     | 7453                    | 6908 | 4970 |  |  |
| Carbonyl Sulfide | 9    | 8    | 8    | 13       | 32                      | 29   | 16   |  |  |
| Methyl mercaptan | 12   | 12   | 10   | 14       | 23                      | 34   | <1   |  |  |
| Ethyl mercaptan  | <1   | <1   | <1   | <1       | <1                      | <1   | <1   |  |  |
| Carbon Disulfide | <1   | <1   | <1   | 6        | <1                      | <1   | <1   |  |  |
| Propyl mercaptan | <1   | <1   | <1   | <1       | <1                      | <1   | <1   |  |  |
| Thiophene        | <1   | <1   | <1   | <1       | <1                      | <1   | <1   |  |  |

module. Results are similar and only the CRIP results are reproduced here in Table 6.1. In terms of moles, there is far more methane than the other light hydrocarbons combined.

Hydrogen sulfide  $(H_2S)$  is the dominant sulfur-containing product, as most of the coal sulfur is produced as  $H_2S$ . Data from Barbour et al. (1988b) for gaseous sulfur species are reproduced here in Table 6.2. Hydrogen sulfide is by far the largest fraction.

Ammonia (NH<sub>3</sub>) is the dominant nitrogen-containing gas species. In the Rocky Mountain One test, 50-60% of the coal nitrogen was produced as NH<sub>3</sub> and the ammonia concentration

| SAMPLE                  | TOTAL<br>HYDRO-<br>CARBONS | TOTAL<br>PHENOLICS | NITROGEN<br>Compounds | OXYGEN<br>COMPOUNDS<br>(-PHENOLS) | SULFUR<br>Compounds | TOTAL<br>ORGANICS | ALKYL<br>BENZENES | PNA<br>2 RINGS | PNA<br>3 RINGS | PNA H<br>>4 RINGS | ALIPHATIC<br>YDROCARBONS |
|-------------------------|----------------------------|--------------------|-----------------------|-----------------------------------|---------------------|-------------------|-------------------|----------------|----------------|-------------------|--------------------------|
| SAMPLE 22-<br>Total PPM | -1<br>192,400              | 561,500            | 8,230                 | 6,200                             | 590                 | 768,900           | 37,300            | 85,500         | 15,800         | 2,900             | 50,800                   |
| SAMPLE 28-<br>Total PPM | 1<br>208,200               | 414,000            | 13,600                | 10,200                            | 1,200               | 647,100           | 21,100            | 122,200        | 27,000         | 3,600             | 34,300                   |
| SAMPLE 30-<br>Total PPM | 1<br>197,200               | 552,400            | 7,400                 | 8,500                             | 1,100               | 766,600           | 18,400            | 115,000        | 31,000         | 3,600             | 29,200                   |
| SAMPLE 32-<br>TOTAL PPM | 1<br>102,100               | 372,500            | 11,400                | 6,900                             | 980                 | 573,800           | 13,000            | 113,400        | 25,800         | 4,100             | 25,800                   |
| SAMPLE 34-<br>Total PPM | 1<br>150,500               | 298,200            | 5,300                 | 9,500                             | 910                 | 464,400           | 10,500            | 83,100         | 28,000         | 4,200             | 24,800                   |
| SAMPLE 36-<br>Total PPM | 1<br>118,000               | 498,900            | 5,600                 | 5,500                             | 590                 | 628,600           | 7,700             | 64,200         | 18,800         | 3,800             | 23,400                   |

**Table 6.3** Analyses, binned into chemical groups, of the oil phase of the product condensate from the Hanna IV UCG test. Reproduced from Humenick and Mattox [85].

in the product gas averaged about 0.5% by volume of the total wet gas product [59, 46, 94]. Barbour et al.'s attempts to measure ammonia and nitrogen species in the product gas of Rocky Mountain One were unsuccessful.

#### 6.1.2 Organic-phase products from UCG (condensable organics)

Condensable organics from pyrolysis or gasification processes are a mixture of "light oils" and heavy organics or "tars." We will call them condensable organics or "condensables." There have been a few studies in which UCG product condensate has been analyzed. These illustrate the plethora of species present and illustrate some of the major groups of compounds present.

The organic fraction of the Rocky Mountain One product condensate was analyzed by Barbour et al. [46, 47]. The mixture had atomic ratios of  $C_1H_{1.32}O_{0.037}N_{0.014}S_{0.002}$ . Barbour et al. used a simulated distillation method to estimated an average molecular weight based on alkane boiling point equivalence of 210 g/gmo. Such process experiment reports of "tar" includes all light and heavy organics that were actually condensed by the condenser system under the conditions in place and separable from water.

Humenick and Mattox [85] analyzed the oil- and aqueous-phases of the condensate stream from the Hanna IV UCG test. In the oil phase they identified over two hundred individual compounds, and these compounds amounted to about 60% of the oil—the other 40% being a combination of quantitation error and other compounds not identified or quantified. They found an average total production rate of the organic phase to be about 2.9% of the mass of the coal consumed, with a concentration in the product gas averaging 46 gallons of organic per million standard cubic feet of product gas. They binned the organic compounds found in the condensate oil phase to simplify the presentation. Their table is reproduced here as Table 6.3. It shows that by far the two biggest fractions are phenolics and either unidentified compounds or quantification error (1,000,000 minus Total Organics

**Table 6.4** Relative concentrations of selected compounds in the tar (organic) fraction of condensate from the ELWand CRIP modules of the Rocky Mountain 1 UCG test. Reproduced from Barbour et al. [47]. Unit is area percent.

|                    |     | Time, gasification days |     |     |     |     |     |     |     |  |  |  |
|--------------------|-----|-------------------------|-----|-----|-----|-----|-----|-----|-----|--|--|--|
| -                  | 17  | 24                      | 28  | 31  | 35  | 38  | 42  | 48  | 57  |  |  |  |
| Benzene            | 0.3 | 0.4                     | 0.3 | 0.7 | 0.7 | 0.4 | 0.6 | 0.4 | 0.1 |  |  |  |
| Toluene            | 0.8 | 1.0                     | 0.8 | 1.9 | 1.5 | 1.1 | 1.2 | 0.9 | 0.4 |  |  |  |
| Xylenes            | 1.9 | 2.2                     | 1.8 | 3.3 | 2.8 | 2.4 | 2.2 | 2.2 | 1.3 |  |  |  |
| Naphthalene        | 4.8 | 5.4                     | 5.0 | 4.9 | 5.3 | 5.1 | 6.0 | 8.1 | 7.1 |  |  |  |
| Methylnaphthalenes | 4.1 | 4.2                     | 4.0 | 3.7 | 4.1 | 4.2 | 4.2 | 5.3 | 4.9 |  |  |  |
| Anthracene         | 1.7 | 1.9                     | 2.1 | 1.4 | 1.5 | 1.8 | 1.9 | 2.8 | 2.4 |  |  |  |
| Phenol             | 2.6 | 2.5                     | 1.5 | 1.4 | 1.7 | 1.6 | 1.2 | 1.1 | 0.9 |  |  |  |
| Tricyclic A        | 3.9 | 2.8                     | 3.4 | 2.4 | 2.7 | 2.5 | 2.1 | 3.1 | 4.0 |  |  |  |
| Tricyclic B        | 4.9 | 3.2                     | 3.9 | 3.2 | 3.6 | 3.2 | 2.6 | 2.9 | 3.4 |  |  |  |

(a) Extended Linked Well Module

|                    |                         |     | (b)  | CRIP Mo | dule |     |      |     |      |  |  |  |
|--------------------|-------------------------|-----|------|---------|------|-----|------|-----|------|--|--|--|
|                    | Time, gasification days |     |      |         |      |     |      |     |      |  |  |  |
|                    | 16                      | 18  | 20   | 25      | 30   | 33  | 37   | 42  | 46   |  |  |  |
| Benzene            | 1.0                     | 0.6 | 1.4  | 1.1     | 1.3  | 1.3 | 1.0  | 1.1 | 1.1  |  |  |  |
| Toluene            | 1.7                     | 1.2 | 1.9  | 1.7     | 1.6  | 1.8 | 1.0  | 1.2 | 1.2  |  |  |  |
| Xylenes            | 2.8                     | 2.2 | 2.9  | 1.5     | 2.7  | 2.8 | 1.8  | 2.1 | 2.1  |  |  |  |
| Naphthalene        | 6.9                     | 6.8 | 10.6 | 8.4     | 10.1 | 9.8 | 12.3 | 9.7 | 11.9 |  |  |  |
| Methylnaphthalenes | 3.8                     | 3.8 | 4.8  | 4.3     | 4.6  | 4.6 | 4.6  | 4.1 | 4.3  |  |  |  |
| Anthracene         | 2.0                     | 2.0 | 1.5  | 2.6     | 2.5  | 2.3 | 1.9  | 3.1 | 3.4  |  |  |  |
| Pheno1             | 5.2                     | 3.4 | 7.2  | 2.4     | 3.9  | 4.2 | 3.0  | 3.4 | 2.5  |  |  |  |
| Tricyclic A        | 2.0                     | 2.8 | 1.7  | 2.7     | 1.8  | 1.6 | 2.4  | 1.5 | 1.7  |  |  |  |
| Tricyclic B        | 2.7                     | 3.2 | 2.5  | 3.1     | 2.0  | 1.6 | 2.4  | 1.6 | 1.9  |  |  |  |

| (c) | CRIP | Module, | continued |
|-----|------|---------|-----------|
|-----|------|---------|-----------|

|                    |      | Time, gasification days |      |      |      |      |      |      |      |  |  |
|--------------------|------|-------------------------|------|------|------|------|------|------|------|--|--|
| -                  | 50   | 55                      | 61   | 65   | 68   | 75   | 81   | 87   | 92   |  |  |
| Benzene            | 0.7  | 0.8                     | 0.8  | 0.6  | 0.3  | 1.1  | 0.7  | 0.6  | 0.5  |  |  |
| Toluene            | 0.9  | 1.1                     | 1.2  | 0.8  | 0.7  | 1.2  | 1.1  | 1.0  | 0.9  |  |  |
| Xylenes            | 1.7  | 1.9                     | 2.0  | 1.9  | 1.8  | 2.1  | 2.2  | 2.0  | 1.9  |  |  |
| Naphthalene        | 10.2 | 10.7                    | 12.3 | 12.4 | 10.3 | 13.0 | 14.4 | 12.9 | 16.0 |  |  |
| Methylnaphthalenes | 4.5  | 5.2                     | 5.2  | 5.3  | 5.4  | 5.0  | 5.7  | 5.7  | 6.1  |  |  |
| Anthracene         | 3.4  | 2.7                     | 3.0  | 3.1  | 3.2  | 2.3  | 2.7  | 2.8  | 3.3  |  |  |
| Phenol             | 1.1  | 2.8                     | 2.6  | 1.1  | 2.0  | 2.6  | 3.3  | 3.0  | 1.2  |  |  |
| Tricyclic A        | 2.2  | 2.0                     | 2.1  | 2.6  | 1.9  | 1.7  | 1.2  | 1.2  | 1.5  |  |  |
| Tricyclic B        | 2.5  | 2.3                     | 2.6  | 3.1  | 2.3  | 1.9  | 1.6  | 1.5  | 1.7  |  |  |
| Tricyclic B        | 2.5  | 2.3                     | 2.6  | 3.1  | 2.3  | 1.9  | 1.6  | 1.5  | 1.7  |  |  |

ppm). Other organic categories, in descending order of prevalence are: multi-ring aromatic hydrocarbons, aliphatic hydrocarbons, alkyl benzenes, non-phenolic oxygen compounds, nitrogen compounds, and sulfur compounds.

Barbour et al. [47] analyzed the organic "tar" fraction of condensate from both modules of the Rocky Mountain 1 test. Reported compounds and compositions were qualitatively similar, but only a handful of representative compounds were analyzed for and the quantitation was by relative peak area. Their results are shown here in Table 6.4. Compared to Humenick and Mattox, they show relatively more napthalene, less phenol, and a higher ratio of saturated to aromatic compounds. This paper provides references to several other studies of UCG organic condensate product.

The chemical complexity of the organic liquid fraction is illustrated by the detailed analysis results presented in the appendices of Humenick and Mattox [85], not reproduced here. The broader body of literature on pyrolysis products and gasification tars contains additional analyses and lists of compounds that might be expected from UCG. Also the literature on characterizing and remediating sites contaminated by coal liquids may be useful in the UCG context.

# 6.1.3 Aqueous-phase products (water-soluble species)

Data on the composition of the aqueous fraction from UCG tests provide a good idea of the kinds of species that could be found in UCG-contaminated groundwater.

It should be noted here that for most UCG contamination scenarios, UCG process gas flows through porous media and fractures underground. Contaminants would be deposited in the groundwater along the way in a "chromatographic" fashion, with the highest boiling point and most water-soluble and most readily sorbed species leaving the gas stream first (and thus being found closest to the leak origin) and the lowest boiling point, most water insoluble, and least readily sorbed species staying in the gas phase longest and traveling further. In other words, not all of the species seen in product condensate will be found in one place underground in most gas-escape contamination scenarios—these species will be distributed spatially along the path of the leak. A fingerprint of UCG-contaminated groundwater from one location will not be expected to match a fingerprint of the aqueous UCG product stream; the former will be a subset of species with concentrations determined by underground transport processes.

# Organic analyses of aqueous condensate

Humenick and Mattox (1982) analyzed the organic components in the aqueous phase of the condensate from the Hanna IV UCG test. As with the oil phase, there were hundreds of species. Binned into chemical groups, the GC-MS analytical results for medium to large organics are summarized in Table 6.5.

| SAMPLE                                | TOTAL<br>HYDRO-<br>CARBONS | TOTAL<br>PHENOLICS | NITROGEN<br>COMPOUNDS | OXYGEN<br>COMPOUNDS<br>(-PHENOLS) | SULFUR<br>Compounds | TOTAL<br>ORGANICS | ALKYL<br>BENZENES | PNA<br>2 RINGS | PNA<br>3 RINGS | PNA<br>>4 RING | ALIPHATIC<br>HYDROCARBONS<br>S |
|---------------------------------------|----------------------------|--------------------|-----------------------|-----------------------------------|---------------------|-------------------|-------------------|----------------|----------------|----------------|--------------------------------|
| SAMPLE 22-<br>TOTAL PPM<br>% OF TOTAL | -2<br>76<br>L 0.           | 10,200<br>7 94.3   | 359<br>3.3            | 154<br>1.4                        | 31<br>0.3           | 10,900<br>100.0   | 11<br>0.1         | 43<br>0.4      | 10<br>0.1      | 1              | 10<br>0.1                      |
| SAMPLE 28-<br>TOTAL PPM<br>% OF TOTAL | -2<br>26<br>0.1            | 8,820<br>3 97.2    | 162<br>1.8            | 39<br>0.4                         | 27<br>0.3           | 9,080<br>100.0    | 2.                | 14<br>0.2      | 5<br>0.1       | 1              | 3                              |
| SAMPLE 30-<br>TOTAL PPM<br>% OF TOTAL | -2<br>41<br>0.             | 8,550<br>5 95.8    | 215<br>2.4            | 60<br>0.7                         | 61<br>0.7           | 8,968<br>100.0    | 3                 | 25<br>0.3      | 8<br>0.1       | 1              | _4                             |
| SAMPLE 32-<br>TOTAL PPM<br>% OF TOTAL | -2<br>159<br>2.            | 7,240<br>0 92.5    | 291<br>3.6            | 67<br>0.8                         | 71<br>0.9           | 7,980<br>100.0    | 7<br>0.3          | 110<br>1 1.4   | 24<br>0.3      | 3              | 15<br>0.2                      |
| SAMPLE 34-<br>TOTAL PPM<br>% OF TOTAL | -2<br>34<br>0.5            | 3,780<br>9 96.5    | 89<br>2.3             | 15<br>0.4                         |                     | 3,952<br>100.0    | 1                 | 18<br>0.5      | 9<br>0.2       | 2              | 4<br>0.1                       |
| SAMPLE 36-<br>TOTAL PPM<br>% OF TOTAL | -2 2                       | 6,980<br>98.6      | 80<br>1.1             | 20<br>0.3                         |                     | 7,084<br>100.0    |                   | 1              | ::             |                | 1                              |

**Table 6.5** Analyses, binned into chemical groups, of the aqueous phase of the product condensate from the Hanna IV UCG test. Reproduced from Humenick and Mattox [85].

As would be expected from their solubilities and high concentrations in the liquid product, phenolics such as phenol and cresols are by far the most plentiful group of organics found in the water. At much lower concentrations, other groups found, in descending order of concentration, are: nitrogen-containing organics, non-phenolic oxygen-containing organics, sulfur-containing organics, aromatic hydrocarbons, and aliphatic hydrocarbons.

The analysis details show that by far the most plentiful organics in the aqueous condensate are phenol, the cresols, the xylenols, and the ethyl phenols (BTEX compounds with an -OH on one of the ring carbons), with 2-ring alcohols (napthol and indanol) also present in sizable concentrations. Pyridine, methyl pyridine, pyrrole (all aromatics with a ring nitrogen), and aniline (benzene with an -NH2 on one of the ring carbons) are the most plentiful nitrogen compounds. Nonphenolic oxygenated compounds in significant concentrations include various cyclic ketones. Alkyl benzenes (mainly BTEX) are found in the aqueous condensate at only a few parts per million, despite being 2–5% of the oil-phase condensate. This is because of their low solubility.

Species are sometimes found in UCG product condensate water at concentrations that are significantly higher than expected from their solubilities. This is notable in Table 6.5 for the multi-ring aromatic hydrocarbons. It is likely that they exist dissolved within or sorbed onto colloid particles of tar and/or char that are suspended in the water phase.

Barbour et al. [47] analyzed the aqueous fraction of the condensates from both modules of the Rocky Mountain 1 test. Their results are shown in Table 6.6.

Phenol is by far the most prevalent UCG-generated species in the aqueous product. Benzene is the most concentrated light hydrocarbon. Acetone is a volatile soluble species that is seen in moderate concentrations. Of the nitrogen-containing compounds, pyridine, pyrrole, and analine, and their alkyl relatives are all found in significant concentrations in the aqueous product.
**Table 6.6** Organics found in the aqueous phase of the product condensate from the ELW and CRIP modules of the Rocky Mountain One UCG test. Reproduced from Barbour et al. [47]

|                     | Sampling Time, gasification day |                          |              |  |  |
|---------------------|---------------------------------|--------------------------|--------------|--|--|
|                     | 23                              | 45                       | 52           |  |  |
|                     |                                 |                          | 1.1          |  |  |
| Acetone             | 160                             | 120                      | 88           |  |  |
| 2-Butanone          | 59                              | 52                       | 36           |  |  |
| Benzene             | 13                              | 18                       | 23           |  |  |
| Toluene             | 17                              | 11                       | 9            |  |  |
| Ethylbenzene        | 7                               | <ul> <li>*1.1</li> </ul> |              |  |  |
| Xylenes             | 28                              | 7                        | 7            |  |  |
| Phenol              | 3100                            | 1200                     | 1100         |  |  |
| 2-Methylphenol      | 900                             | 340                      | 340          |  |  |
| 4-Methylphenol      | 2200                            | 890                      | 800          |  |  |
| 2,4-Dimethylphenol  | 260                             | 130                      | 170          |  |  |
| Naphthalene         | 39                              | 14                       | 21           |  |  |
| 2-Methylnaphthalene | 15                              | 6                        | 5            |  |  |
| Acenaphthene        | 3                               | 1                        | 1            |  |  |
| Dibenzofuran        | 3                               | 1 .                      | 1            |  |  |
| Fluorene            | 5                               | 2                        | 2            |  |  |
| Phenanthrene        | 11                              | 3                        | 5            |  |  |
| Anthracene          | 3                               | · 1                      | 1            |  |  |
| Fluoranthene        | 2                               | *                        | 1 1 1 1 A    |  |  |
| Pyrene              | 2                               | * . * .                  | - <b>1</b> - |  |  |
| Acenaphthylene      | •                               | <1                       | • • •        |  |  |

(a) ELW module product water sample, mg/L

\* -- Compound below 1ppm detection limit

(b) CRIP module product water sample, mg/L

|                     | Sampling Time, gasification day |             |       |   |      |      |     |
|---------------------|---------------------------------|-------------|-------|---|------|------|-----|
|                     | 23                              | 45          | 52    | 64  | 65   | 79   | 95  |
|                     |                                 | 1. 1. M. A. | 1.1.1 | 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 -<br>1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 -<br>1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - |      |      |     |
| Acetone             | 130                             | 120         | 50    | 110   | 95   | 63   | 62  |
| 2-Butanone          | 45                              | 40          | 22    | 48  | 40   | 21   | 20  |
| Benzene             | 90                              | 32          | 8     | 60  | 29   | 11   | 13  |
| Toluene             | 100                             | 7           | 7     | 59  | 21   | 3    | 6   |
| Ethylbenzene        | 25                              |             |       | 18  | 7    | ¥.   | 2   |
| Xylenes             | 120                             | •           | 10    | 86  | 34   | 3    | 8   |
| Phenol              | 3300                            | 5500        | 540   | 1600  | 1600 | 1000 | 420 |
| 2-Methylphenol      | 650                             | 1500        | 180   | 440   | 430  | 490  | 160 |
| 4-Methylphenol      | 1600                            | 4000        | 450   | 1000  | 1000 | 1100 | 330 |
| 2,4-Dimethylphenol  | 180                             | 370         | 140   | 190   | 180  | 150  | 140 |
| Naphthalene         | 40                              | 12          | 27    | 75  | 36   | 80   | 77  |
| 2-Methylnaphthalene | 14                              | 3           | 14    | 25  | 12   | 12   | 36  |
| Acenaphthene        | 3                               | *           | 2     | 9   | 4    | 5    | 10  |
| Dibenzofuran        | 3                               | *           | 3     | 5   | 2    | 3    | 8   |
| Fluorene            | 5                               | 1           | 5     | 10  | 4    | 5    | 16  |
| Phenanthrene        | 9                               | 3           | 11    | 18  | 8    | 8    | 23  |
| Anthracene          | 2                               | 1           | 3     | 4   | 2    | 2    | 6   |
| Fluoranthene        | 2                               | 1           | 2     | 5   | 2    | 1    | 6   |
| Pyrene              | 1                               | 1.          | 2     | 4   | 1    | 1    | 4   |
| Acenaphthylene      | •                               | •           | * -   | * 1.1   | •    | •    | * . |

\* -- Compound below 1ppm detection limit

(c) Minor organic compounds in product waters, mg/L

|                           | Productio | Production System and Day |         |  |  |  |
|---------------------------|-----------|---------------------------|---------|--|--|--|
|                           | ELW-45    | CRIP-23                   | CRIP-79 |  |  |  |
| Methylpyridines           | 32.7      | 36.6                      | 38      |  |  |  |
| Methylpyrroles            | 12.5      | 12.8                      | 13      |  |  |  |
| C <sub>2</sub> -Pyridines | 14.4      | 8.2                       | 14      |  |  |  |
| C2-Benzenes               | 18.1      | 17.7                      | 5.3     |  |  |  |
| C2-Pyrroles               | 4.7       | 3.4                       | 4.3     |  |  |  |
| C <sub>2</sub> -Benzenes  | 29.3      | 17.3                      | 4.6     |  |  |  |
| Anilline                  |           | 91                        |         |  |  |  |
| Methylaniline             | 28        | 35                        | 36      |  |  |  |
| C <sub>2</sub> -Phenols   | 206       | 132.0                     | 90.3    |  |  |  |
| C <sub>2</sub> -Phenols   | 35.5      | 20.6                      | 14.0    |  |  |  |
| Co-Naphthalenes           | 27.4      | 18.0                      | 11.5    |  |  |  |

#### CHAPTER 6. COMPOSITIONS AND MONITORING ANALYTES

| Compound class | Average concentration (mg/L) |
|----------------|------------------------------|
| Phenolics      | 576                          |
| BTEX           | 0.04                         |
| PAHs           | 1.4                          |

 Table 6.7
 Average concentrations of grouped species in condensate (presumed to be the aqueous condensate) from a UCG trial on hard coal in Poland. From Smolinski et al. [95].

A more recent paper by Smolinski et al. [95] reported analysis results for the condensate from a UCG trial on hard (high-rank) coal in Poland. It is not clear whether the analyzed stream was aqueous-phase condensate, oil-phase condensate, or combined. From the reported results and units we presume it was the aqueous stream following a not-very efficient condension (low BTEX) and a not-very efficient colloids/solids separation (high PAH). Average results are presented in Table 6.7. Data on individual compounds and their time dependence are available in the paper.

The chemical complexity of the aqueous liquid fraction is illustrated by the detailed analysis results presented in appendices of Humenick and Mattox [85], not reproduced here.

#### Inorganic analyses of UCG aqueous condensate

The UCG process and its gas can affect contacted groundwater in other ways besides dissolved organics. An extreme bounding case of what contacted groundwater might look like is the aqueous phase of the UCG product gas condensate. This has been in intimate contact with the UCG product gas stream, including its noncondensible gases, condensable vapors, and some char and ash particulates.

Humenick and Mattox [85] also performed a conventional analysis of the aqueous phase of the UCG product condensate from the Hanna IV test. Table 6.8 shows the result.

It is notable that the simple measurement of Total Organic Carbon in the standard water analysis is roughly consistent with the sum of the concentrations of organic species measured individually by extraction-GC-MS.

It is unfortunate they did not report a similar analysis of natural background groundwater at the site. A comparison would be useful. Without knowing background, results that appear notable are high organics, high amine nitrogen, high amounts of  $CO_2$  in various forms, high boron, high cyanide and thiocyanates.

Barbour et al. analyzed the aqueous fraction of the condensate from the ELW and CRIP modules of the Rocky Mountain 1 UCG test. Tables 6.9 and 6.10 show these results. We note that the Barbours pH and TOC values were similar to Humenick and Mattox, but Barbours ammonia values were 2-10 times larger, and boron values were 1/10 of those reported by Humenick and Mattox. High concentrations of the bicarbonate ion are found in the aqueous phase of UCG condensate.

|                                    | SAMPLE NUMBER |           |             |             |          |         |
|------------------------------------|---------------|-----------|-------------|-------------|----------|---------|
|                                    | 22-2          | 28-2      | 30-2        | 32-2        | 34-2     | 36-2    |
| PARAMETER                          |               | CONCENTRA | ATIONS IN r | ng/1 EXCEPT | AS NOTED |         |
| Na                                 | 8.1           | 1.6       | 9.8         | 3.3         | 1.3      | 6.7     |
| K                                  | 1.5           | <1        | 9.2         | 3.7         | <1       | <1      |
| Ca                                 | 4.6           |           |             | INI         |          |         |
| Mg                                 | 17 000        | 42 000    | 20 000      | 22 000      | 11 000   | 8 600   |
| nco <sub>3</sub>                   | 26,000        | 18 000    | 22,000      | 14 000      | 650      | 1 200   |
| ALKALINITY<br>(CaCO <sub>3</sub> ) | 57,300        | 66,000    | 59,000      | 42,000      | 9,710    | 9,070   |
| SO4                                | 170           | 319       | 30          | 12          | 71       | 290     |
| C1                                 | 1,300         | 590       | 1,100       | 290         | 190      | 38      |
| F                                  | 30            | 15        | 7.5         | 6./         | 0.28     | 2.8     |
| NU <sub>3</sub> -N                 | 1 200         | 6,000^    | 850^        | 2 400       | 380^     | 1,200^  |
| NH3-N                              | 1,300         | 2,900     | 2,400       | 2,400       | 1,500    | 3,800   |
| DB (INTTS                          | 1,000         | 91        | 1,400       | 9 1         | 8.6      | 2,020   |
| CONDUCTIVITY,<br>UNITS             | 53,000        | 52,000    | 51,000      | 54,000      | 14,000   | 13,000  |
| COD                                | 33,000        | 14,000    | 15,000      | 21,000      | 7,700    | 1,700 - |
| TOC                                | 9,061         | 6,300     | 6,400       | 5,300       | 2,290    | 4,707   |
| TIC                                | 8,389         | 9,200     | 8,300       | 6,000       | 1,813    | 1,659   |
| OIL & GREASE                       | 121           | 108       | 171         | 184         | 266      | 180     |
| Ba                                 | <0.5          | <0.5      | <0.5        | <0.5        | <0.5     | <1      |
| Cd                                 | <0.05         | <0.1      | <0.1        | <0.1        | <0.1     | <0.2    |
| Cr                                 | 0.2           | 0.12      | 0.14        | 0.18        | <0.1     | <0.1    |
| PD                                 | <0.1          | <0.1      | <0.1<br>_   | <0.1        | <0.1     | <0.1    |
| AU                                 | 1 4           | TNT       | INT         | INT         | <0.5     | <0.1    |
| As                                 | INT           | INT       | INT         | INT         | INT      | INT     |
| B                                  | 5             | 11        | 9           | 12          | 2.7      | 10      |
| Cu                                 | 0.07          | <0.1      | <0.1        | <0.1        | <0.1     | 0.5     |
| CN                                 | INT           | 14        | 20          | 2,500*      | 1.8      | INT     |
| Fe                                 | 11            | 0.1       | 0.2         | 0.6         | 1.8      | 4.1     |
| Mn                                 | <0.1          | <0.1      | <0.1        | 0.2         | 0.1      | <0.1    |
| Ni                                 | 0.1           | <0.1      | <0.1        | 0.1         | <0.1     | <0.2    |
| Se                                 | INT           | INT       | INT         | INT         | <0.01    | 0.27    |
| ILIRATHIONATE-                     | 5 270         | 12        | 110         | 440         | <0.1     | <0.1    |
| THIOCH CATE-C                      | 390           | 30        | 160         | 100         | 140      | 10      |
|                                    |               | 390       | 100         |             | 140      | 41      |
| 7n                                 | 1010          | <01       | <0.1        | <0.1        | 0 52     | 0 11    |
| Ha                                 | INT U.US      | INT       | INT         | INT         | INT      | INT     |
|                                    | 2.00          | •         |             |             | 2        |         |

Table 6.8 Inorganic analyses of UCG product condensate aqueous phase from the Hanna IV test. Reproduced from Humenick and Mattox [85].

INT = INTERFERENCE
\* = Probable Error, see text

## 6.2 Naturally occurring organic species

Pore water of some coals sometimes contain organic compounds naturally. Surrounding strata often contain lesser amounts of coal and kerogen; they are not considered coal because their ratio of organic to inorganic material is too low to be economic. The organic compounds produced naturally from coal and kerogen may derive from microbial or lowtemperature breakdown, or be residual from ancient thermal maturation processes that were interupted. There will be some similarities between these natural organics and organics produced by the UCG process.

Table 6.9 Water quality analyses for Rocky Mountain One aqueous condensate samples. Reproduced from Barbour et al. [47].

| Components            | Sampling Time, gasification day |       |       |  |  |
|-----------------------|---------------------------------|-------|-------|--|--|
| and Properites        | 23                              | 45    | 52    |  |  |
|                       |                                 |       |       |  |  |
| Calcium               | .41                             | 1.46  | .19   |  |  |
| Magnesium             | .19                             | .14   | .05   |  |  |
| Sodium                | 3.68                            | 2.56  | <1    |  |  |
| Potassium             | <10                             | <10   | <10   |  |  |
| Ammonia               | 15400                           | 10900 | 4370  |  |  |
| Carbonate             | 2740                            | 798   | 138   |  |  |
| Bicarbonate           | 44800                           | 22900 | 7991  |  |  |
| Sulfate               | 320                             | 200   | 160   |  |  |
| Sulfide               | 890                             | 970   | 370   |  |  |
| Chloride              | 1100                            | 1600  | 570   |  |  |
| Nitrate               | *                               | *     | *     |  |  |
| Fluoride              | • •                             | *     | *     |  |  |
| Cyanide               |                                 | 1.1   | .44   |  |  |
| Thiocyanate           | *                               | *     | *     |  |  |
| Alkalinity            | 49800                           | 35600 | 13400 |  |  |
| Conductivity, mmho/cm | 52.6                            | 42.4  | 20    |  |  |
| pH                    | 9.0                             | 8.6   | 8.3   |  |  |
| TSS                   | 197                             | 400   | 60    |  |  |
| TDS                   | 1600                            | 1110  | 610   |  |  |
| COD                   | 22300                           | 24000 | 8900  |  |  |
| TOC                   | 7500                            | 6600  | 819   |  |  |
| Phenois               | 3200                            | 2680  | 819   |  |  |

(a) ELW module, mg/L

\* -- Analysis could not be determined because of interferences

# (b) CRIP module, mg/L

| Components            |       | Sampling Time, gasification day |             |       |       |              |       |
|-----------------------|-------|---------------------------------|-------------|-------|-------|--------------|-------|
| and Properties        | 23    | 45                              | 52          | 64    | 65    | 79           | 95    |
|                       |       | 11.00                           |             |       |       |              |       |
| Calcium               | .64   | 1.36                            | .24         | 1.57  | .96   | .06          | .02   |
| Magnesium             | .42   | .11                             | .06         | .12   | .09   | .03          | .08   |
| Sodium                | 3.34  | 4.3                             | <1          | 1.6   | 1.56  | <.5          | 1.0   |
| Potassium             | <10   | <10                             | <10         | <10   | <10   | <5           | <5    |
| Ammonia               | 37800 | 18000                           | 10540       | 12860 | 12200 | 20570        | 10670 |
| Carbonate             | 2740  | 1956                            | 570         | 840   | 582   | 2190         | 660   |
| Bicarbonate           | 44040 | 33550                           | 20070       | 19700 | 17690 | 27790        | 14520 |
| Sulfate               | 170   | 130                             | 230         | 130   | 140   | • • •        | . * S |
| Sulfide               | 850   | 600                             | 300         | 430   | 430   | 530          | 370   |
| Chloride              | 830   | 1000                            | 500         | 700   | 690   | 990          | 510   |
| Nitrate               |       |                                 |             | • •   |       | •            |       |
| Fluoride              |       | *                               | *           | •     | * -   | * . <u>.</u> |       |
| Cyanide               | 1.0   | .3                              | > <b>.1</b> | .5    | .4    | 1.4          | .3    |
| Thiocyanate           | * .   |                                 | •           | •     | *     |              |       |
| Alkalinity            | 78100 | 58300                           | 33800       | 33600 | 30000 | 49200        | 24900 |
| Conductivity, mmho/cm | 86.7  | 61.4                            | 39          | 46.7  | 43.3  | 55           | 35    |
| pH                    | 8.8   | 8.8                             | 8.5         | 8.7   | 8.6   | 8.9          | 8.7   |
| TSS                   | 157   | 380                             | 160         | 140   | 140   | 16           | 220   |
| TDS                   | 1440  | 1450                            | 1400        | 914   | 970   | 630          | 610   |
| COD                   | 25100 | 23000                           | 16000       | 20300 | 16900 | 14200        | 14000 |
| TOC                   | 7700  | 11300                           | 12700       |       |       | 4400         | 4100  |
| Phenois               | 4800  | 3200                            | 2070        | 2950  | 2540  | 2660         | 2370  |

 Table 6.10
 Trace metals analyses for Rocky Mountain One aqueous condensate samples from the ELW and CRIP modules. Reproduced from Barbour et al. [47].

|            | Sampling |      |      |
|------------|----------|------|------|
|            | 23       | 45   | 52   |
|            |          |      |      |
| Silver     | <.02     | .03  | <.02 |
| Aluminum   | 17.5     | 6.4  | 1.7  |
| Arsenic    | <.2      | <.2  | <.2  |
| Boron      | .25      | 1.5  | 1.37 |
| Barium     | <.02     | <.02 | <.02 |
| Beryllium  | <.02     | <.02 | <.02 |
| Bismuth    | <.2      | <.2  | <.2  |
| Cadmium    | <.02     | <.02 | <.02 |
| Cobalt     | <.02     | <.02 | <.02 |
| Chromium   | .05      | <.02 | .05  |
| Copper     | .04      | .05  | <.02 |
| Iron       | 1.99     | .22  | .25  |
| Mercury    | <1       | <1   | <1   |
| Lithium    | <.02     | <.02 | <.02 |
| Manganese  | .04      | <.01 | <.01 |
| Molybdenum | <.02     | <.02 | <.02 |
| Nickel     | <.02     | <.02 | <.02 |
| Phosphorus | <2       | <2   | <2   |
| Lead       | <.1      | .18  | <.1  |
| Antimony   | <.2      | <.2  | <.2  |
| Selenium   | .53      | .65  | .94  |
| Silicon    | 1.09     | 1.17 | .30  |
| Thorium    | <.1      | .15  | <.1  |
| Strontium  | <.01     | <.01 | <.01 |
| Vanadium   | .02      | .03  | <.02 |
| Zinc       | .06      | .07  | <.02 |

| (a) | ELW | module, | mg/L |
|-----|-----|---------|------|
|-----|-----|---------|------|

| (b) | CRIP | module, | mg/L |
|-----|------|---------|------|
|-----|------|---------|------|

|            | ·    | Sampling Time, gasification day |      |      |      |      |      |
|------------|------|---------------------------------|------|------|------|------|------|
|            | 23   | 45                              | 52   | 64   | 65   | 79   | 95   |
|            |      |                                 |      |      |      |      |      |
| Silver     | <.02 | .03                             | <.02 | .02  | .06  | <.01 | <.01 |
| Aluminum   | 48.2 | 7.6                             | 5.88 | 1.7  | 1.6  | 1.17 | .81  |
| Arsenic    | <.2  | <.2                             | <.2  | <.2  | <.2  | <.1  | <.1  |
| Boron      | .07  | .15                             | .23  | .21  | .20  | .09  | .08  |
| Barium     | <.02 | <.02                            | <.02 | <.02 | <.02 | <.01 | <.01 |
| Beryllium  | <.02 | <.02                            | <.02 | <.02 | <.02 | <.01 | <.01 |
| Bismuth    | <.2  | <.2                             | <.2  | <.2  | <.2  | <.1  | <.1  |
| Cadmium    | <.01 | <.02                            | <.02 | .03  | <.02 | <.01 | <.01 |
| Cobalt     | <.01 | <.02                            | <.02 | <.02 | <.02 | <.01 | <.01 |
| Chromium   | .18  | .03                             | .02  | <.02 | <.02 | <.01 | <.01 |
| Copper     | <.01 | .05                             | <.02 | .04  | .05  | <.01 | <.01 |
| Iron       | 1.34 | 1.19                            | .17  | .27  | .19  | .08  | .53  |
| Mercury    | <1   | <1                              | <1   | <1   | <1   | <1   | <1   |
| Lithium    | <.02 | <.01                            | <.02 | <.02 | <.02 | <.01 | <.01 |
| Manganese  | .05  | .020                            | <.01 | .02  | .02  | <.01 | .02  |
| Molybdenum | <.02 | <.02                            | <.02 | <.02 | <.02 | <.01 | <.01 |
| Nickel     | .03  | <.02                            | <.02 | <.02 | .04  | <.01 | .01  |
| Phosphorus | <2   | <2                              | <2   | <2   | <2   | <1   | <1   |
| Lead       | <.1  | .18                             | <.1  | .12  | .25  | <.1  | <.1  |
| Antimony   | <.2  | <.2                             | <.2  | <.2  | .24  | <.1  | <.1  |
| Selenium   | .42  | -44                             | .36  | .26  | .29  | .13  | .21  |
| Silicon    | .65  | 1.1                             | .51  | .25  | <.2  | <.1  | <.1  |
| Thorium    | <.1  | .11                             | <.1  | .11  | .24  | <.1  | <.1  |
| Strontium  | <.01 | <.01                            | <.01 | <.01 | <.01 | <.01 | <.01 |
| Vanadium   | .02  | .03                             | <.02 | .03  | .05  | <.01 | <.01 |
| Zinc       | <.02 | .05                             | <.02 | .05  | .04  | .01  | .02  |

\* Mercury analysis by cold vapor atomic adsorption was approximately 7 ug/L

Other natural processes create organic compounds that find their way into groundwater. These include contemporary and geologically-recent decomposition of vegetable matter. This can produce complex organics such as from humic acids in streams, ponds, swamps, and muskeg (typically indicated by brown color and/or foaming tendencies). In some areas peat is being produced or has been produced and waters in and traveling through will contain organics.

Recent and ancient natural coal fires will produce a suite of products very similar to undergound coal gasification. Recent and ancient forest fires will also produce organics including compounds from incomplete combustion of lignins and resin-containing matter. There is much similarity between wood tars and coal tars. Natural transport processes (gas flow for coal fires and water flows for all materials) can move these natural organics.

The point here is that finding organics in groundwater near a UCG operation is not proof that UCG caused the contamination. A thorough set of pre-UCG baseline background water sampling data at the site is very important. This must be done near and surrounding the UCG operation, both laterally and across many strata, extending up to freshwater aquifers. Depending on the site's hydrogeology, this background sampling may need to cover multiple seasons and/or years. Screening analyses can look for total organic carbon and a small number of UCG-produced analytes (e.g. benzene, phenol, ammonia) to determine the general magnitude and variability of natural organics, including some expected UCG indicator species near the site.

Where significant organics are seen, a subset of samples should be analyzed for a large number of analytes, or "fingerprinted" to determine typical compositions of natural organics. A thorough background will facilitate interpretation of groundwater analyses done after the UCG operation has started. For example in the recent Queensland issues with the Cougar Kingaroy operation, it appears that a few water samples were reported positive for one or two compunds that might be associated with UCG, and this generated much debate and differences of opinion as to whether these might have been natural, or might have been introduced during the sampling, or might have been analytical anomolies. The absence of thorough baseline data made it difficult to arrive at confident conclusions.

#### 6.3 A reduced set of groundwater and subsurface gas sampling analytes

UCG produces hundreds to thousands of individual compounds that might be found in water or gas monitoring samples. Analyzing for all these would be very expensive. A simple analysis suite may be adequate to indicate that UCG contaminants have spread and how they have spread. The suite should cover major components that represent different transport and fate pathways—i.e. differences in volatility and water solubility at the least. Conceptually one might think about analyzing for six species: water soluble and water insoluble compounds that are uncondensable, condensable but volatile, and nonvolatile. In addition, a simple integrated analysis of Total Organic Carbon would be cheap and highly informative.

|                 | Volatility           | Low water solubility  | High water solubility                     |  |
|-----------------|----------------------|---|---|--|
| Groundwater     | Uncondensable        | СО  | NH3 and/or H2S                            |  |
| samples         | Volatile condensable | Benzene or<br>sum BTEX  | Acetone<br>Pyridine                       |  |
|                 | Low volatile         | Napthalene,<br>Phenanthrene, or total<br>polyaromatic<br>hydrocarbons | Phenol or<br>total phenolics;<br>aniline  |  |
|                 | Integrated           | Total Organic Carbon  |   |  |
|                 | Inorganic            |   | рН  |  |
|                 | Inorganic            |   | Conductivity                              |  |
|                 | Inorganic            |   | Sum all CO3 ions                          |  |
|                 | Inorganic            |   | NH3                                       |  |
|                 | Inorganic            |   | Boron                                     |  |
| Underground gas | Uncondensable        | CO and/or H2  | NH3 and/or H2S                            |  |
| samples         | Volatile condensable | Benzene or<br>sum BTEX  | Acetone                                   |  |
|                 | Low volatile         | Napthalene  | Phenol or total<br>phenolics;<br>pyridine |  |
|                 | Integrated           | Total Organic Carbon  |   |  |
|                 |                      |   |   |  |

 Table 6.11
 A suggested set of screening analytes. The nitrogen-containing organics do not cover any additional space of volatility and solubility, but broaden the set chemically.

A simple inexpensive set of screening analytes could be run to monitor for any worrisome changes or concentrations. Samples that produce interesting screening results could then be analyzed in more detail to understand better what is there and what might be happening underground. Table 6.11 illustrates an economical approach to screening analytes.

Favorable qualities for an analyte include being present in high concentrations in UCG materials but not in nature, and being easy and/or inexpensive to analyze for. It is useful to cover a distribution of properties to address various modes of transport. If there were an escape of UCG process gas, the low volatile compounds will condense closer to the hot UCG source than the volatile condensables, and the uncondensables will go further through ambient temperature surroundings. Highly water soluble compounds will be stripped out into

groundwater faster than insoluble compounds. Compounds that are soluble can be transported distances by groundwater flow. Compounds that are not very soluble in water will not have a large mass transported far by water flow.

Total organic carbon is easy to measure in both groundwater and gas samples. An increase above background is not proof of UCG effect but is indicative enough to warrant further investigation. It may turn out that screening only for TOC is adequate to detect UCG effects.

Benzene and phenol would be present in significant quantities in any conceivable UCG contamination event. Benzene represents a highly volatile, sparingly soluble species that would be transported by hot escaping gas. Phenol represents a medium-low volatility but fairly soluble species that would be transported further in detectable quantities by water flow. It is possible that analysis for total BTEX or total phenolics may be less expensive and more sensitive than a single component analysis.

Carbon monoxide would be an excellent UCG-indicative analyte for gas samples. It is conserved (uncondensable and not very water soluble (28 ppmw at 20C)), not present in nature, present in UCG gas at the 10-20% by volume range, and easy/inexpensive to analyze for, possibly even by using simple household CO detectors or derivatives of that technology. It does have enough solubility in water to likely provide an indication that UCG gas has flowed past. If there were a good analysis for dissolved CO this would make sense.

Hydrogen would be an alternative or additional analyte to consider alongside of carbon monoxide. Carbon dioxide is not as good an indicator because it is present naturally in high and variable concentrations, is part of both inorganic and biological and fossil natural cycles, and has complicated aqueous chemistry. Thus a  $CO_2$  or  $CO_3$  ion signal is open to interpretation. Ammonia is present in the gas at concentrations of about 1%. Because of its solubility in water it will tend to get stripped out. In some concentrations it will travel with the gas for some distance. Its presence in water would indicate a UCG effect because it usually has a low natural abundance.

Hydrogen sulfide will also travel with the gas, is incondensable, and easy to detect, at least in gas phase. It is soluble in water (3900 ppmw at 20C) and would roughly be expected to behave like ammonia.

#### **Chapter 7**

# Fate, transport, and remediation of residual contaminants

#### 7.1 Prevention is better than remediation

If large quantities of contaminants are left underground far outside the containment zone it will be infeasible or very expensive to remediate. Planning and operations must contain contaminants within the localized process area and minimize their quantity.

The amount and distribution of contaminants that may acceptably be left within the process area at the end of operation will depend on the details of the site and the operation. The longer-term removal and containment goals will also depend on the details of the site and distribution of contaminants. These need to be considered and decided before starting operations.

#### 7.2 Management of residual contaminants is needed

There will be some quantity of compounds remaining after a module or operation is shut down that could contaminate groundwater. In a well-run operation at a favorable site, the quantity of compounds will be fairly low and their presence will be confined to a tight volume in and around the immediate cavity. Under less-than-perfect conditions, there will be more residual spread over a wider volume.

Management of the residual must be planned for. Assuming modest quantities left in a localized area, the goals are to prevent this residual inventory from spreading and to monitor to assure that levels stay low and confined.

The cavity shutdown phase can be considered over after temperatures have cooled below the steam saturation temperature and the cavity and porosity around it are filled with liquid water. We consider this to be the beginning of the post shutdown management period.

We recommend slow and/or periodic pumping of water out to the surface from the center of the zone containing the highest concentrations of worrisome species. This will probably be at the production well entrance, or somewhat upstream (from the reference of the UCG operation) from this point. This pumping has two beneficial effects. It removes contaminants from the subsurface. It also reduces the fluid pressure there which creates inward pressure gradients and provides hydraulic containment. The pumped water will need to be treated at the surface. It is possible that the separated compounds may have value, but most likely there will be a net cost to do this. The concentrations of representative species in the produced water should be monitored as a function of time and the cumulative water production. The same reduced set of species could be tracked as suggested in the previous chapter.

The project hydrologic model should continue to be updated in this post-operations period. The model should be adjusted/calibrated to fit the observed concentrations, flow rates, and measured pressure field. Such a calibrated model would be the best tool for planning the future pumping schedule and judging when to stop or switch to a less frequent pumping schedule. The model must include fate and transport of the important compounds, and natural and managed regional and local natural hydrological pressures and pumpings that affect flow.

#### 7.3 Partitioning properties of the contaminants and rocks

How readily a species is removed by pumping, or how it might spread away from the area, will depend on the volatility, solubility, sorption, and reactive properties of the species in the environment it is in. A useful flow and transport model needs to include these factors for a set of representative compounds.

Solubility and volatility were discussed briefly in previous chapters, and are fairly easy to obtain data for. Sorption depends on both the compound and the substrate. In general, organics will adsorb quite strongly onto substrates with high organic content, such as coal and organic-rich rock.

Some compounds may be reactively converted to other, possibly less hazardous, compounds underground. The reactions can be chemical or biologically mediated. In both cases, especially for bioremediation, the rate limitation will be the rate of transport of reactants such as oxygen to the concentrated contaminant zones. Rates measured in surface reactors where reactants are not depleted tend to strongly overestimate underground reaction rates.

Another factor that must be represented well by models is the spreading of contaminants by oscillating flow. Contaminants diffuse and adsorb. Flow in porous media is often through conductive fractures surrounded by relatively stagnant porous volume into which contaminants can diffuse. An inward and outward flow, with no net transport of water, will spread contaminants. Once species have diffused onto the dead pore volume and/or sorbed it takes much longer contact with clean water to desorb them. Thus, any huff-and-puff or oscillatory flow (e.g. barometric pumping) will spread contaminants. Transport models that have dual permeability (fracture and matrix) are very helpful in representing such transport.

## 7.4 Natural and engineered flow and thermal effects

The underground fluid flows will be affected by both the natural hydrologic system, the UCG-related pumping and pressure management, other man-made drivers outside the UCG

system, and post-burn groundwater management operations. Also, the removal of coal and the geomechanics of the UCG operation will likely have changed the permeability, porosity, and storativity fields. These must all be incorporated into the post-burn subsurface flow and transport model.

Most UCG projects will require a year to a decade of active pressure management such that groundwater flows into the UCG production wells and not away from the area. Depending on the natural gradients, this could be done by a simple water production well, or be enhanced by a ring or a wall of injection wells surrounding and/or downstream of the UCG water production well(s).

The possibility of buoyancy-driven flow must be evaluated. Liquid water as warm as 200 C or more can exist at the pressures underground. This warm water will be less dense and could potentially drive flow or convection flows. If this is shown to be important, the long-term flow models must include thermal buoyancy effects and the cool-off time frame expected.

#### 7.5 Long term monitoring

During and following the active pumping and water management operations, there needs to be a groundwater sampling and monitoring operation in place. Periodic samples must be pulled from the central UCG zone and good locations downgradient. Placement of these would be based on natural gradients, permeability field, and higher-risk portions of the system. Collection of samples and their interpretation should be guided by models to properly account for typically-observed time-dependence of sampling operations. For example, if high initial concentrations are followed by a tail-off, which does one believe: the initial high concentrations or the tail due to pulling clean water in from a clean zone.

Again, all possible species need not be analyzed for. An abbreviated set of representative analytes, such as proposed in the previous chapter, should adequately provide enough information to validate containment and/or calibrate models.

#### 7.6 Remediation options and comments

Remediation is difficult, time-consuming, and expensive. There are no magically good options. It is by far easiest, cheapest, and best if the UCG project is operated well in a good site, where an acceptable level of risk could be achieved by either doing nothing or by hydrologic confinement. If the quantity and/or spatial distribution of contaminants left by the UCG operation is unacceptable, then a remediation action will need to be considered and its costs and prospects will need to be compared to the costs and prospects of no or lesser action.

In this section we discuss some of the possible approaches to remediation that might be considered if a UCG operation left too many hazardous organics underground. Since the Superfund era, there have been great advances in remediation of spills of hazardous organic materials into the subsurface, especially gasoline and other petroleum based organics. We note that the cleanup efforts at the Hoe Creek site in Wyoming and the Williams site are well documented and, for those interested, it would be very informative to review these in detail (e.g. [10]).

Briefly, at Hoe Creek, benzene was considered to be the driving contaminant. The first plan was to pump a volume of water out that exceeded by many times the volume of water that contained benzene in it. Once all the benzene-containing water was pumped out, the hope was benzene would disappear. Of course, it did not work that way because there were large reservoirs of benzene underground, including neat light hydrocarbon oil phases, benzene dissolved into immobile tars, benzene sorbed onto solid mineral and organic phases of the rock, and benzene in all these phases and in water solution located in stagnant pore volume that did not participate much in flow. Thus, when benzene-laden water was pumped out and clean water flowed into those active pore- and fracture-volumes, benzene came out of its reservoirs into the clean water, and sampling showed this rebound. After the futility of this approach was recognized, hopes were placed on bio-remediation. This was slow because of the reasons stated above. After many years, concentrations were deemed low enough that active remediation was stopped and a monitoring regime started.

Hydrologic confinement with aggressive pumping and treating of water is one approach to remediation. This works when there are no holding-reservoirs for the contaminant (tar or liquid phases, sorption onto mineral or organic solids), when most or all of the pore volume participates in flow (no "dead" pore volumes), and when the contaminant partitions to the water phase enough that its reservoirs get depleted. The problems of using this approach for UCG were discussed above for the Hoe Creek example.

The ubiquitous remediations of gasoline and petroleum at filling stations have strong similarities to BTEX-related UCG contamination. But the environment is very different. Filling stations are shallow and often unsaturated. They would be expected to be much cheaper to extract vapor from and bio-remediate. Vapor extraction was popular for a while and showed promising results, but often a large "rebound" occurred after vapor extraction stopped because benzene was emerging from its sorption and oil-phase reservoirs. Our understanding is the practical solution to most petroleum spills is to simply dig them up to stop the further source and then give up or contain the water plume.

Another option to consider is steam flooding. As with an oil-field enhanced recovery by steam flood, a remediation analog can sometimes be used. LLNL demonstrated this technology on its own gasoline spill, and then used it to clean up at least one other industrial spill. This has the potential of greatly speeding up the remediation and removing more contaminants than other approaches, especially contaminants that are not mobile nor water soluble, such as tars. Its disadvantages would be expense and lack of experience. The severely-affected hydrogeology/cavities/rubble associated with UCG would be a challenge that this approach has not faced before.

Microbial action occurs naturally underground. This is especially true near the surface in unsaturated conditions, but has been found deeper and in water-saturated sediments under certain conditions. An example is near natural petroleum seeps, where bacterial populations have adapted and found oxygen donor species to promote reactions. It would be reasonable to expect that after some time, natural microbial populations would slowly react some of the UCG contaminants, especially as they found their way closer to the oxygenated surface zone. The rates and assurance of this being adequate are the challenge.

Engineered bioremediation can be considered. It is usually possible to find a consortium of bacteria that can be effective at reacting contaminants. The bacteria are either a proprietary culture that has been developed, or are selectively found and concentrated from samples at the contamination site of interest. They generally work very well in vitro and in well-stirred large pilot-scale reactors with good supply of nutrients and removal of biomass (dead microbes). This approach is often much less effective in practice in the field. The big set of challenges are related to transport limitations: getting microbes, co-nutrients, and oxygen or other electron donors in contact with the contaminants and getting waste products out. This is difficult for several reasons. The contaminants often have diffused into tight zones of the matrix, and the flowing treatment fluid will go right past in the higher permeability pathways. A second challenge is plugging of pores and flow pathways by the bacteria.

In conclusion, remediation of an unacceptably contaminated UCG site would be expensive, slow, and incomplete. Clearly it should be viewed as an option of last resort. Clean operation at a confined site where it would be acceptable to leave a small volume of contaminants is by far the preferred approach.

## Chapter 8

# **Hazard Screening Checklist**

Quantitative risk assessments can be difficult and time-consuming. In the early stages of a project, detailed assessments are often unnecessary and overly expensive. In many cases one just wants a high-level screening to quickly identify hazards. For example, an operator may want an easy way to compare alternative sites and designs in terms of their hazard potential. Similarly, a regulator may want a strategy to assess a new permit application and pinpoint those areas that deserve additional scrutiny.

Here, we describe a simple checklist approach that can be used as a screening tool. The checklist given below consists of 65 basic questions about different aspects of proposed project. Any *Yes* answer indicates that a hazard exists that should be more carefully considered. Any *Unknown* answer indicates that there is insufficient information available to make a judgement about the hazard, and additional characterization efforts should be undertaken.

All of the questions in the checklist are deliberatively qualitative, and are not meant as a substitute for a more rigorous assessment. Rather, the questions are designed as a guide to help the analyst consider the full spectrum of things that can go wrong. At its best, this approach may identify an important hazard that had not previously been considered, or an overlooked flaw in the current design.

The total number of *Yes* and *Unknown* answers is irrelevant, as each hazard should be considered on an individual basis. Not all hazards are equally important, nor are all of the hazards strictly technical in nature. For example, the checklist includes a few public perception hazards. Also, just because a hazard exists does not imply that proper mitigation cannot be put in place to reduce risk. For example, one of the questions asks if the geotechnical design has a high extraction ratio. Clearly a reasonably high extraction ratio is a goal of any UCG project in order to be economic. The intent of the question is merely to suggest that high-extraction ratio projects are inherently riskier in terms of their geomechanical behavior than, say, a single-module pilot test. Even if the answer to this question is *Yes*, the engineering team may be able to show (quantitatively) that the design is not overly aggressive and that little risk exists of geomechanical failure.

The current questionnaire is designed so that every question is answered with Yes, No, or Unknown. Many of the questions could be re-phrased on some sort of scale—e.g. Low Risk, Medium Risk, or High Risk. One can also imagine a system in which numerical weights

are assigned to each question so that an overall score can be computed. The risk for alternative sites and designs could then be compared based on this score. While these are entirely valid alternatives, here we stick with the simpler true-false-unknown format. A *Yes* answer is somewhat less subjective than a *Yes but low risk* answer, unless there is already a quantitative risk assessment available to back up the assertion.

It is difficult to design a checklist that is appropriate for every project, and some questions may simply not apply to a given site. In these cases, it is often best to consider the intent—rather than the wording—of the question. There may be a related hazard that is not captured here. At the end of each section, it is also useful to spend a few minutes considering if any additional hazards have been overlooked.

Finally, this evaluation clearly requires a certain level of honesty and self-criticism to be useful. It is therefore most appropriate as an internal tool to be used by an operator or regulator for their own purposes, rather than as a formal regulatory evaluation.

| 1.  | Experience and Capabiliities                                   | Yes | Unknown |
|-----|--|-----|---------|
| 1.1 | This is the operator's first UCG project.                      |     |         |
| 1.2 | This is the operator's first UCG project at the proposed scale |     |         |
|     | (e.g. demonstration or commercial scale).                      |     |         |
| 1.3 | One or more service companies or sub-contractors have never    |     |         |
|     | worked on a UCG project.                                       |     |         |
| 1.4 | One or more service companies or sub-contractors have never    |     |         |
|     | worked on a UCG project at the proposed scale.                 |     |         |
| 1.5 | The relevant regulators have never permitted a UCG project.    |     |         |
| 1.6 | The relevant regulators have never permitted a UCG project at  |     |         |
|     | the proposed scale.  |     |         |
| 1.7 | The operator does not have the financial and technical re-     |     |         |
|     | sources to respond to unexpected events and emergencies.       |     |         |
| 1.8 | The local public is unfamiliar with UCG.                       |     |         |
| 1.9 | The local public is unfamiliar with the proposed project.      |     |         |
|     |  |     |         |
| 2.  | Project Location   | Yes | Unknown |
| 2.1 | The site is near surface water (streams, lakes, etc.).         |     |         |
| 2.2 | The site is near sensitive or protected plantlife.             |     |         |
| 2.3 | The site is near sensitive or protected wildlife.              |     |         |

 $\square$ 

#### Hazard Screening Checklist

2.4

2.5

The site is near protected or sacred lands.

The site is near high-value infrastructure.

| 2.6  | The site is near populated areas.   |  |
|------|---|--|
| 2.7  | Additional traffic to and from the site could create a public nuisance.                   |  |
| 2.8  | Additional noise, odors, or other industrial impacts could cre-<br>ate a public nuisance. |  |
| 2.9  | The site has limited evacuation routes.   |  |
| 2.10 | It is challenging to bring in emergency equipment and person-<br>nel to the site.         |  |
| 2.11 | The region is seismically active.   |  |
| 2.12 | Extreme weather could impact site operations.   |  |

| 3.  | Pre-existing Site Conditions                                     | Yes | Unknown |
|-----|--|-----|---------|
| 3.1 | Pre-existing wells can be found near the site.                   |     |         |
| 3.2 | Design and casing status of pre-existing wells is uncertain.     |     |         |
| 3.3 | Abandoned wells may be poorly plugged.                           |     |         |
| 3.4 | Pre-existing wells penetrate to protected aquifers.              |     |         |
| 3.5 | Pre-existing wells penetrate to target formation.                |     |         |
| 3.6 | Surface or underground mines are nearby.                         |     |         |
| 3.7 | Injection or extraction processes have taken place near the site |     |         |
|     | (e.g. coal bed methane, water production, hydraulic fracturing,  |     |         |
|     | oil and gas operations, etc.).                                   |     |         |
| 3.8 | The site contains buried pipelines, gaslines, or powerlines.     |     |         |
|     |  |     |         |
| 4.  | Hydrology and Geochemistry                                       | Yes | Unknown |

| 4.1 | The stratigraphic column contains drinking water and/or pro-<br>tected aquifers.                |  |
|-----|---|--|
| 4.2 | Aquifers and coal formations are not separated by reliable, low-permeability seals.             |  |
| 4.3 | There is significant regional groundwater flow through the for-<br>mation and/or nearby strata. |  |
| 4.4 | Coal and/or adjacent units have high permeability, in either the lateral or vertical direction. |  |
| 4.5 | Coal and/or adjacent units contain permeable fractures and joints.                              |  |
| 4.6 | Coal and/or adjacent units contain non-sealing faults.  |  |
| 4.7 | Baseline hydrology (with temporal fluctuations) is unavail-<br>able.                            |  |

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| 4.8  | Baseline water-quality (with temporal fluctuations) is unavail-<br>able.                                    |     |         |
|------|---|-----|---------|
| 4.9  | Adsorption properties are unavailable.  |     |         |
|      |   |     |         |
| 5.   | Geomechanics  | Yes | Unknown |
| 5.1  | Subsidence could impact surface infrastructure.   |     |         |
| 5.2  | Subsidence could impact sub-surface aquifers.   |     |         |
| 5.3  | Target formation has a weak Coal Mine Roof Rating relative to cavity dimensions.                            |     |         |
| 5.4  | Target formation contains weak or gouge-filled joints.  |     |         |
| 5.5  | Target formation contains faults.   |     |         |
| 5.6  | Adjacent rocks exhibits significant strength-degradation when heated.                                       |     |         |
| 5.7  | Zone of fracturing might breach a sealing unit.   |     |         |
|      |   |     |         |
| 6.   | Proposed Design   | Yes | Unknown |
| 6.1  | Geotechnical design has a high extraction ratio.  |     |         |
| 6.2  | Geotechnical design includes multi-seam extraction.   |     |         |
| 6.3  | Geotechnical design allows for yielding of inter-module pil-<br>lars.                                       |     |         |
| 6.4  | Geotechical design allows for significant roof-caving.  |     |         |
| 6.5  | Geotechnical design is sensitive to precise cavity geometry and/or location.                                |     |         |
| 6.6  | Deformations could damage well casing or cement.  |     |         |
| 6.7  | Thermal stresses could damage well casing or cement.  |     |         |
| 6.8  | Water-sparge or essential cooling systems are not redundant.  |     |         |
| 6.9  | Explosive gas mixtures could occur in a single well.  |     |         |
| 6.10 | A stuck tool or clogged well could create an explosion hazard.  |     |         |
|      |   |     |         |
| 7.   | Operation and Monitoring Plan   | Yes | Unknown |
| 7.1  | Gas pressure could exceed lowest hydrostatic pressure at cav-<br>ity walls.                                 |     |         |
| 7.2  | Cavity pressure thresholds do not have an adequate safety mar-<br>gin to account for pressure fluctuations. |     |         |
| 7.3  |   |     |         |

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| 7.4                     | An unexpected change in cavity size, shape, and location could go undetected.   |     |         |
|-------------------------|---|-----|---------|
| 7.5                     | Significant gas losses could go undetected.   |     |         |
| 7.6                     | Water well density and sampling frequency is insufficient to  |     |         |
|                         | detect water-quality degradation quickly.   |     |         |
| 7.7                     | Water-sampling regimen has weak quality controls.   |     |         |
|                         |   |     |         |
|                         |   |     |         |
| 8.                      | Closure and Reclamation Plan  | Yes | Unknown |
| 8.<br>8.1               | Closure and Reclamation Plan<br>Drinking-water degradation could occur if cavity-flushing is<br>incomplete or ineffective.  | Yes |         |
| 8.<br>8.1<br>8.2        | Closure and Reclamation Plan Drinking-water degradation could occur if cavity-flushing is incomplete or ineffective. Well shut-in procedures insufficient to prevent vertical trans- port along wellbores.  | Yes |         |
| 8.<br>8.1<br>8.2<br>8.3 | Closure and Reclamation Plan Drinking-water degradation could occur if cavity-flushing is incomplete or ineffective. Well shut-in procedures insufficient to prevent vertical trans- port along wellbores. Post-operation monitoring effort insufficient to measure long- term water quality. | Yes | Unknown |

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References are organized into six groups, based on test location: (1) Centralia, Washington; (2) Hoe Creek, Wyoming; (3) Rocky Mountain One and Hanna Basin, Wyoming; (4) Alberta, Canada; (5) Queensland, Australia; and (6) Additional References

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