Prevention of Groundwater Contamination from Underground Coal Gasification

3rd Underground Coal Gasification Network Workshop
IEA Clean Coal Centre

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Lawrence Livermore National Laboratory

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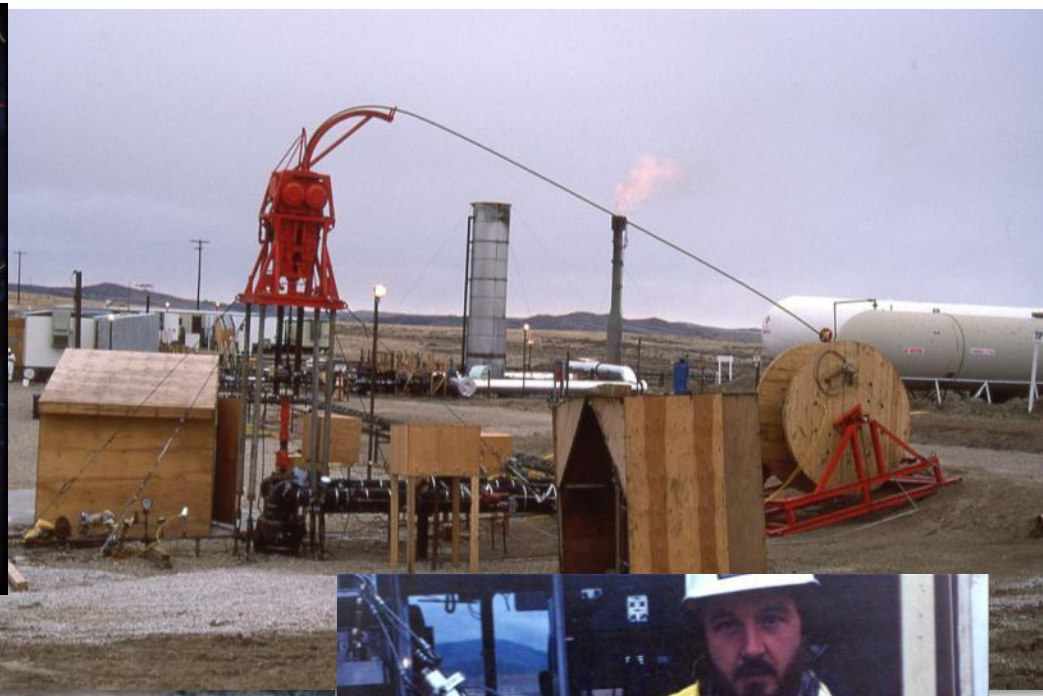
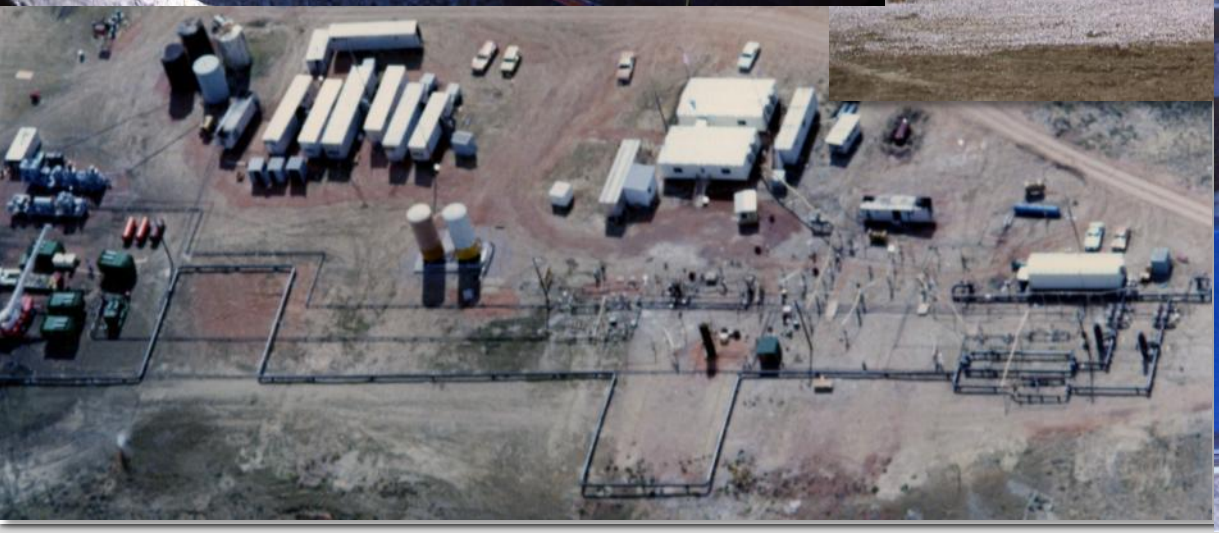
applying multidisciplinary science and technology to missions of national and global importance

- 3 km^2 main site + 30 km^2 remote test site
- Approximately 6,000 career employees
- Total gross square feet: ~7.4 million (677 facilities)

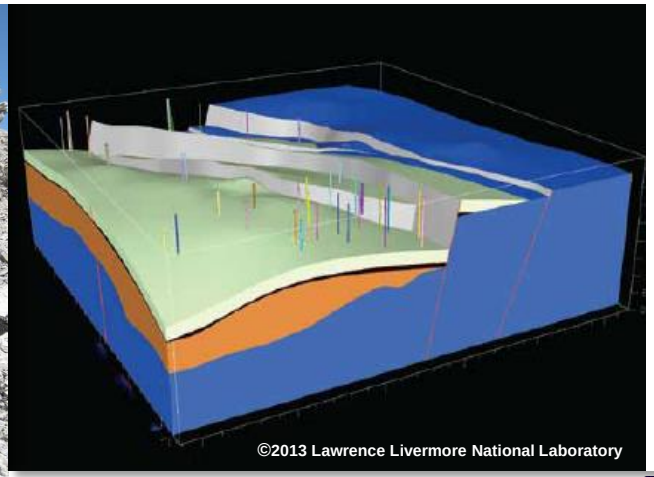
LLNL was a UCG leader in the 1970's and 1980's

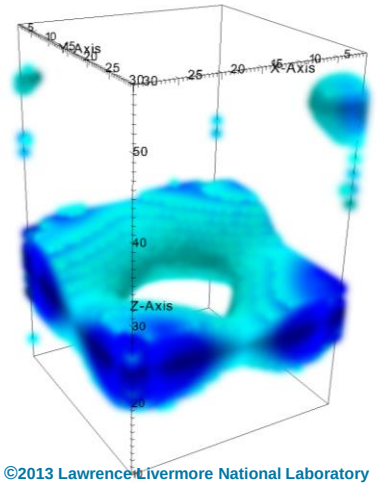


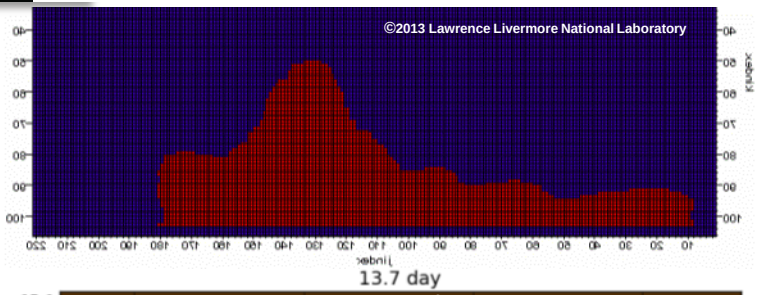


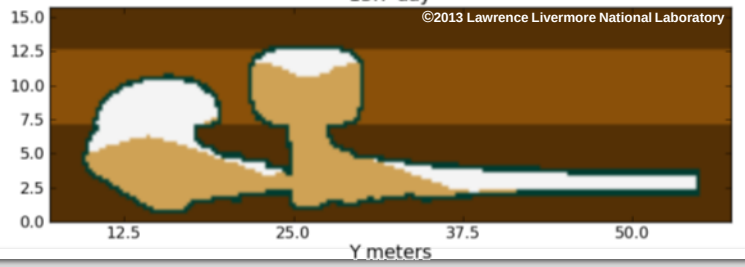
We continue with state-of-art analyses and practical support for today's UCG projects

- Multidisciplinary team of about 20
- Site Selection
- Site Characterization
- Design
- Modeling & Simulation
- Environmental Analyses
- Critical Reviews
- Process engineering and economics
- Monitoring
- Program planning









UCG has four impact categories:

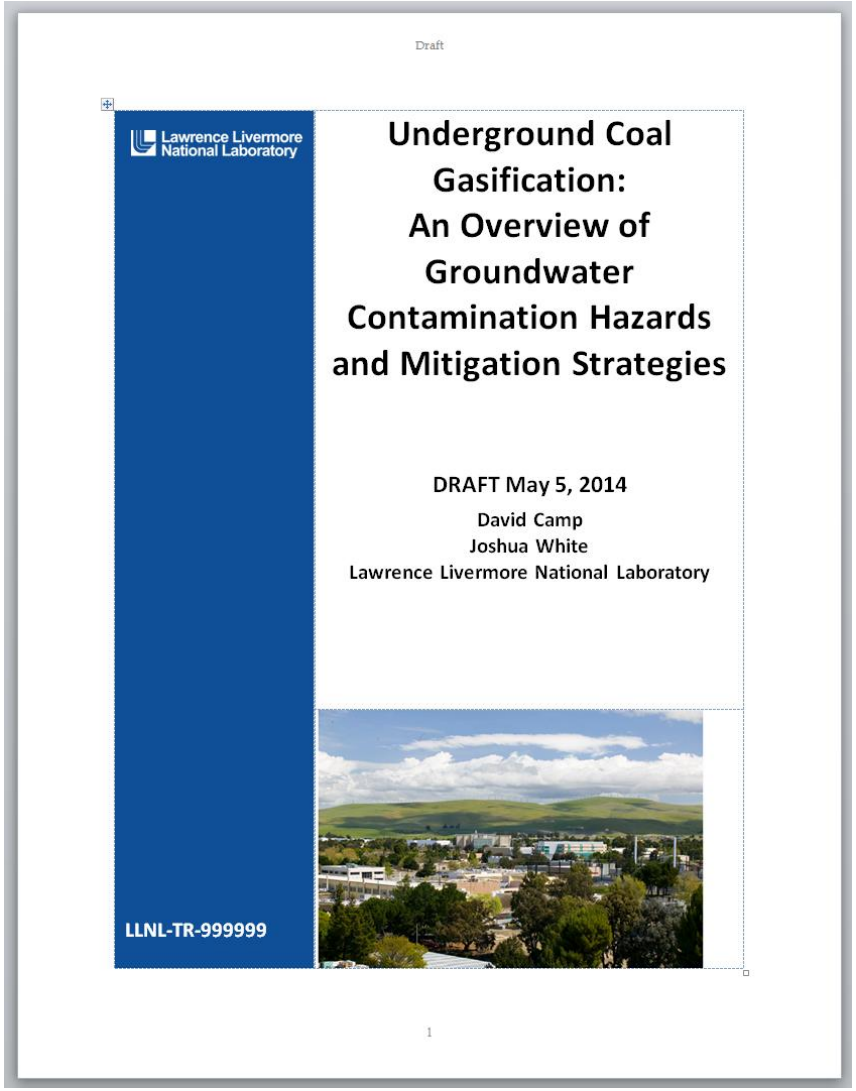
- Conventional petrochemical industrial hazards
- Surface disturbance
- Subsidence and geomechanical changes
- Groundwater contamination

Groundwater contamination arguably poses the biggest risk, and important aspects are unique to UCG

We are writing a report summarizing the risks and prevention of groundwater contamination from UCG

- Sponsored by U.S. Department of Interior, Office of Surface Mining and Reclamation

- Thanks also to Clean Air Task Force, a nongovernmental organization, for early funding of LLNL's current program in UCG, including its potential environmental advantages and challenges


Draft

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

DRAFT May 5, 2014

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LLNL-TR-999999

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UCG can be done clean or dirty. It depends on where and how it is done.

- During normal UCG operation contaminants are continually generated, destroyed, and removed, leaving only small amounts confined locally

- Transport of contaminants outside the confinement zone is abnormal. It occurs when you have both

  <u>Outward pressure gradient</u>*, and <u>A path for flow</u>**

* "Pressure" must properly account for gravity head and gas buoyancy.
** See later discussion of buoyancy fingering.

Analyzing and addressing failure modes helps prevent, detect early, and minimize impacts

- "What would happen if …?"
- "How do we assure that …?"
- "How do we know what …?"
- …

"Direct" or "primary," and "indirect" or "secondary" contaminants from UCG

- "Primary" contaminants are created directly by the gasification process
- "Secondary" contaminants are created indirectly and often later in time
  - Solubility of metals increased by higher temperatures, lower pH (CO_2), or more oxidized ash and rock minerals
  - Desorption of gases (radon, …) from higher T, lower P
  - Residual fine coal ash and spalled rock dust increases surface area for leaching of metals

This talk will consider only the organic "primary" contaminants

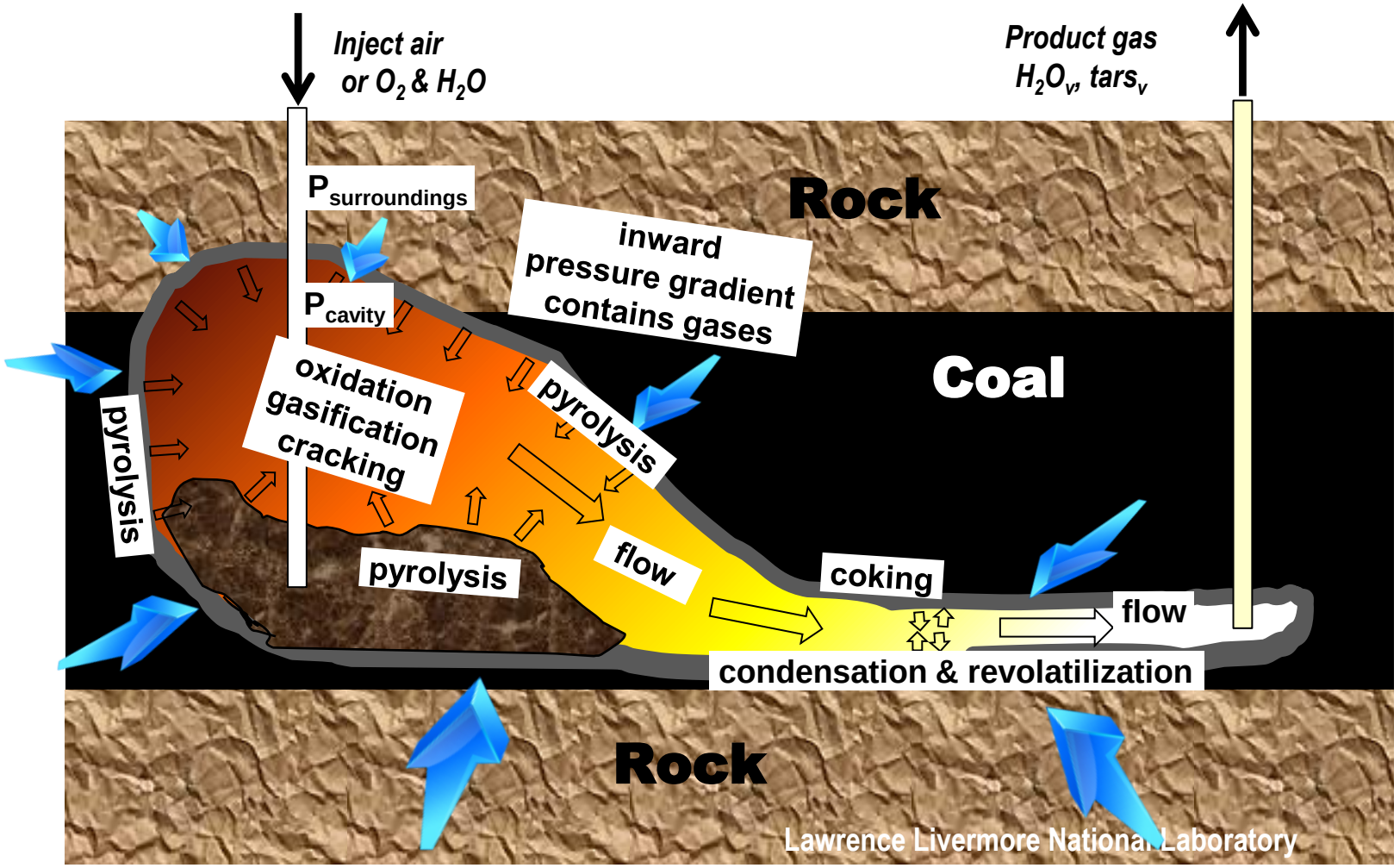
Contaminants are continually generated by pyrolysis and partial oxidation

Condensable organics from coal pyrolysis or gasification are often collectively called "tars"

- Hydrocarbons, typically aromatic
  - Benzene, toluene, napthalene, anthracene, …
- Alcohols and organic acids, typically aromatic
  - Phenols, cresols, benzoic acid, …
- Some N- and S- containing compounds, typically aromatic
  - Pyridine, ammonia, amines, …, sulfides, …
- Wide range of volatility and solubility

These must be kept out of valuable/protected groundwater

The organic compounds are contained and continually destroyed and removed



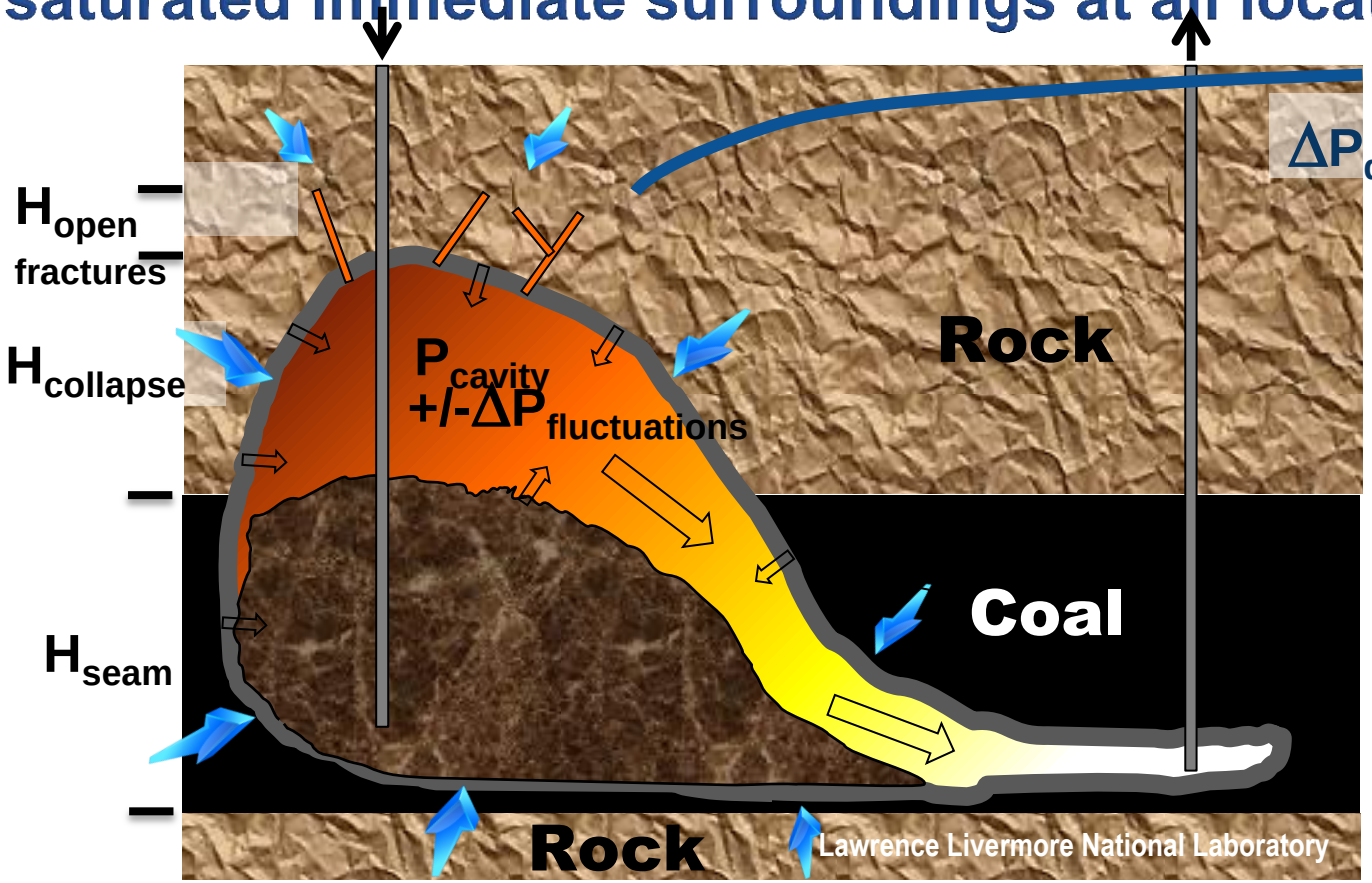
The organic compounds are contained and continually destroyed and removed

- Inward pressure gradient means inward water permeation and containment of process gas
- Combustion, cracking, coking, …convert a fraction of the organics to uncondensable gases and solid immobile coke
- The remainder flows with product gas up the production pipe
  - Coal “tars” comprise ~1-2% of product gas or 2-4% of coal
- Some of the high-boiling species condense in the downstream perimeter of the cavity/channel
- These are re-volatilized and/or coked the next week as the process advances

Containment

~~"Operate below hydrostatic pressure"~~ *Too simplistic!*

The pressure* of the cavity and its connected gas-filled voids must be kept below the pressure of the water-saturated immediate surroundings at all locations



* By "pressure" we more precisely mean "total pressure" or "potential" which have hydrostatics properly accounted for

** See also the later discussion of possible buoyancy fingering

An approximation of the pressure rule

$P_{cavity\ operating\ pressure} =$

$P_{initial/farfield\ hydrostatic\ pressure\ at\ top\ of\ seam}$

$- \Delta P_{estimated\ drawdown\ (t)}$

$- \rho g H_{roof\ collapse\ (t)}$

$- \rho g H_{gas\text{-}filled\ fractures\ (t)}$

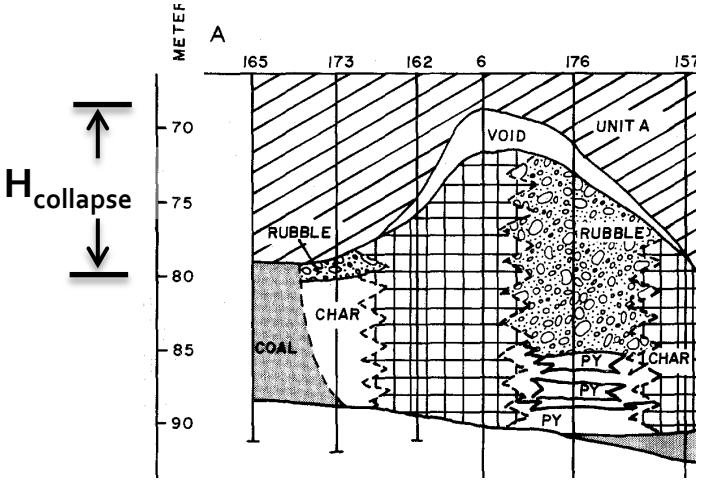
$- \Delta P_{fluctuations}$

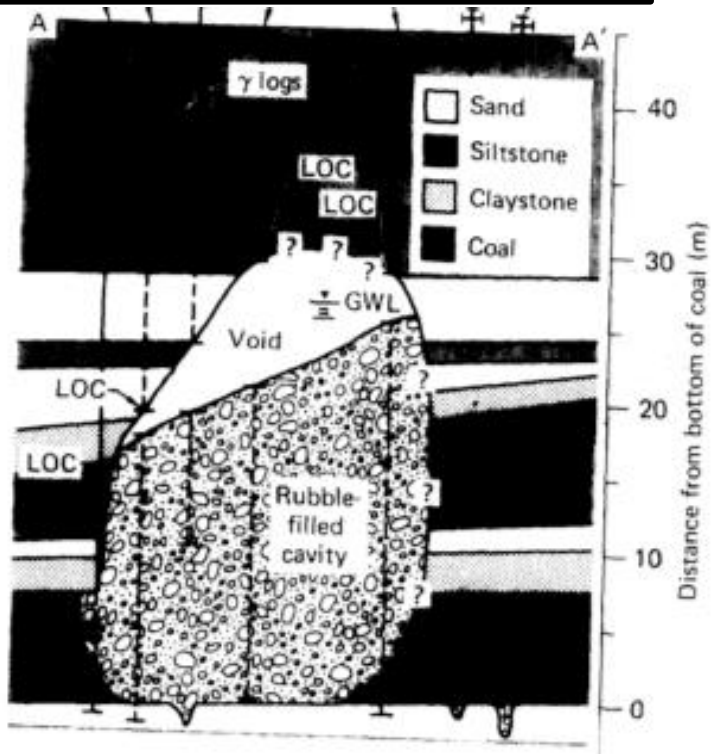
$- \Delta P_{margin}$

Actual operation must be informed by a live (updated) unsaturated hydrology model and data or conservative estimates on the cavity and fracture height

Post-burn cavity cross-sections for the Hanna II and Hoe Creek II tests

The collapsed cavity often extends up much higher than the coal seam





$H_{collapse}$ based on top of upper seam

$H_{collapse}$ based on top of intended seam

The small inventory of contaminants is decreased by shutdown cleaning

- "Clean Cavern" shutdown practices were pioneered at Rocky Mountain 1

- Management of fluid flows and cavity pressure stop pyrolysis and remove contaminant inventory
  - Pressure reduction to allow venting of gases
  - Steam (and/or N_2) injection
  - Water permeation influx cools perimeter and makes steam
  - Produced waste water must be disposed of
  - Cavity will fill with water and cool

Contaminants remaining locally after module shut-down can be managed

- Prevent the small residual inventory from unwanted transport
  - slow/periodic pumping
  - managed hydraulic containment
  - sorption will retard transport of most species
- Long-term monitoring to assure levels stay low

Risk Assessment

- We can never eliminate risk. We can only try and reduce it to acceptable levels and be prepared for the worst.

		Likelihood				
		1.#Rare	2.#Unlikely	3.#Possible	4.#Likely	5.#Almost#Certain
Consequence	Response					
1.#None	None	1	2	3	4	5
2.#Minor#degradation	Simple#corrective# actions,#selfE correcting	2	4	6	8	10
3.#Moderate# degradation	Moderate# remediation	3	6	9	12	15
4.#Major#degradation	Major#remediation	4	8	12	16	20
5.#Catastrophic	Remediation#nE effective	5	10	15	20	25

Scenario	Likelihood4x4 Consequence	Comments	Safeguards	Monitoring
Legacy#wellbore# leakage	1#x#3#=#3	No#known#legacy# wellbores#but#ite		Periodic#waterE quality#sampling
Wellbore#leakage	2#x#3#=#6		QA/QP#program	Integrity#testing,# NearEwell#sampling
Cavity#collapse	1#x#4#=#4		Strong#caprock	Subsidence#surveys,# Geophones
Fault#leakage	1#x#3#=#3	No#faults#above# seismic#resolution	Redundant#seals,# Large#aquifer# separation	Continuous#above# zone#pressure# sampling
Hydrostatic#pressure# threshold#exceeded	3#x#2#=#6	Result#of#poor# estimate#or#operator# error	SafetyEmargin#on# design#threshold,# Operator#training	NearEcavity#pressure# monitoring

- Multiple factors play in to a risk assessment.
  - Land-use; water-bodies
  - Sensitive areas
  - Populated areas
  - Seismically-active areas
  - Well density; mines
  - Aquifer status; overburden vulnerability

Groundwater contamination scenarios

Process gas containing contaminants will escape when there are outward pressure gradients and a permeable path for gas flow

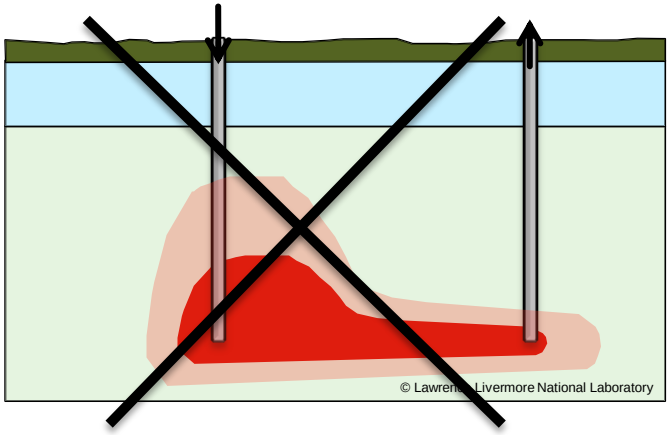
This is unwanted and abnormal, but possible if mistakes are made

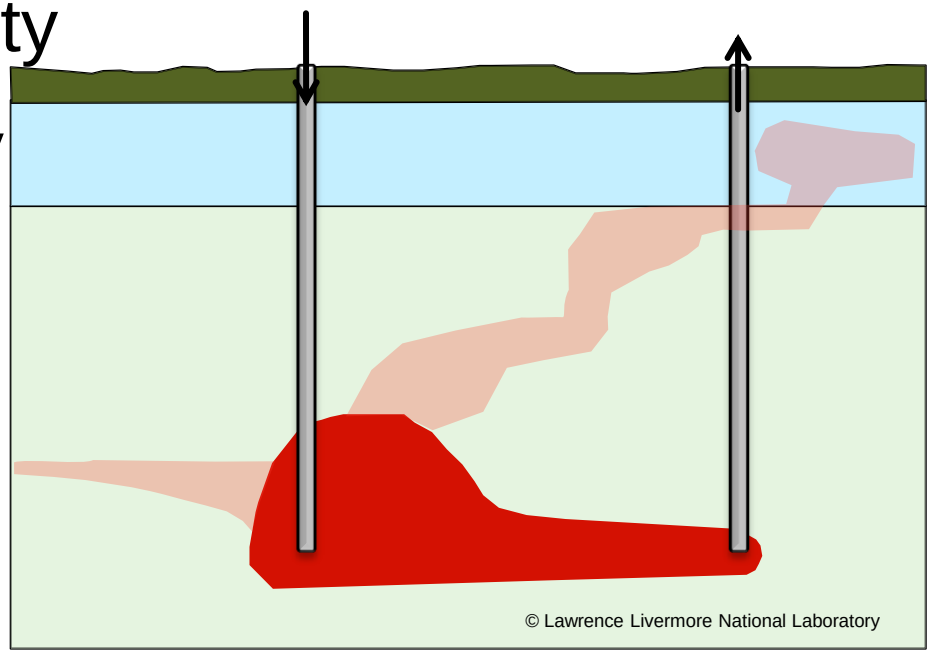
Not all gas escape scenarios are equal

- The amount and location of escaped contaminants depends on:
  - magnitude of the outward pressure gradient
  - duration of the outward pressure gradient
  - the permeability field or flow paths
- The impact to valuable/protected groundwater is prevented or minimized when escaped contaminants are:
  - Small in quantity
  - Deposited near the process containment zone
  - A large distance from the groundwater
  - With barriers to further transport towards the groundwater

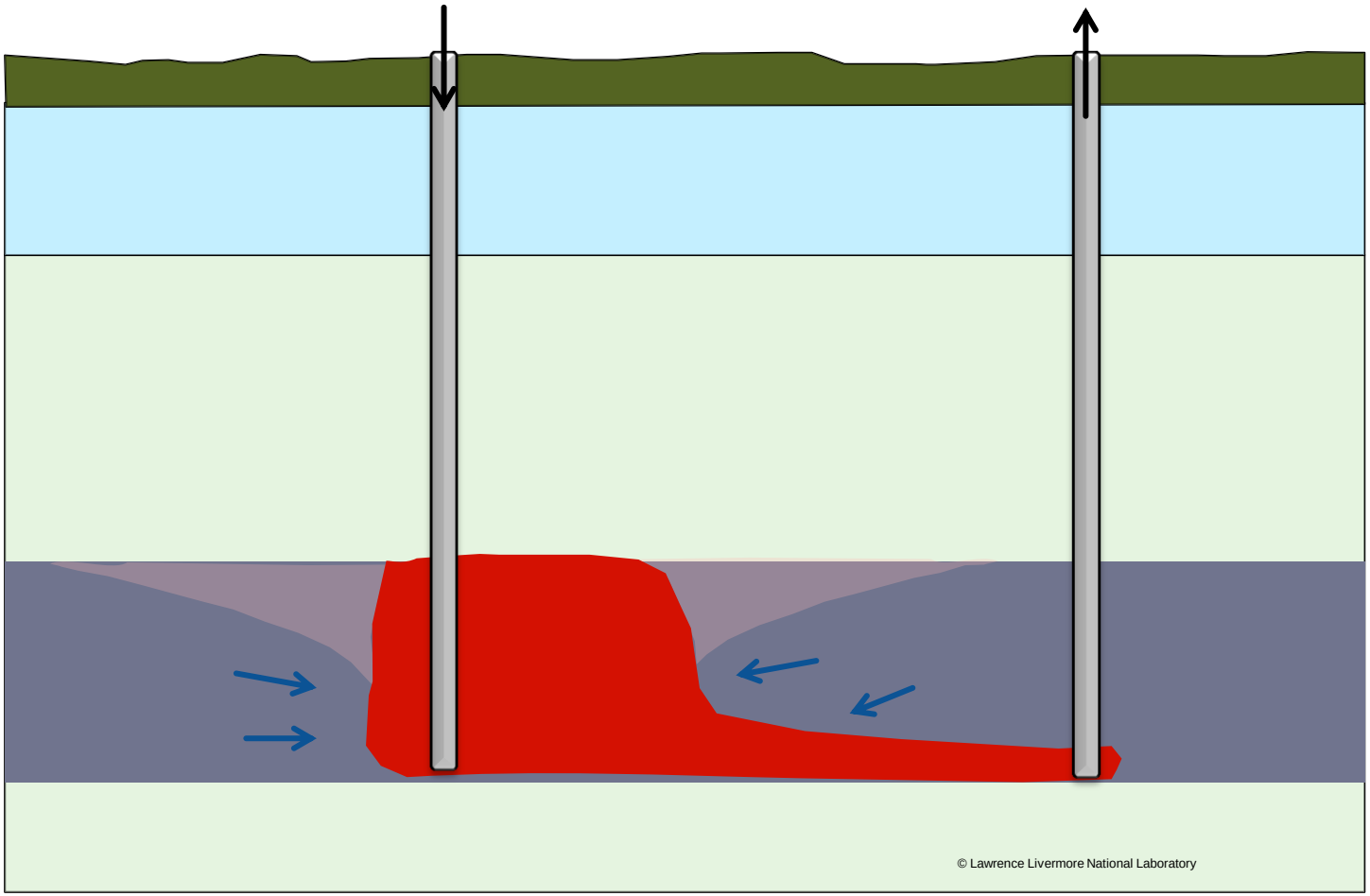
Escaping gas will tend to finger, not advance in a broad front

- Natural heterogeneity
- Mobility ratio instability
- Relative permeability

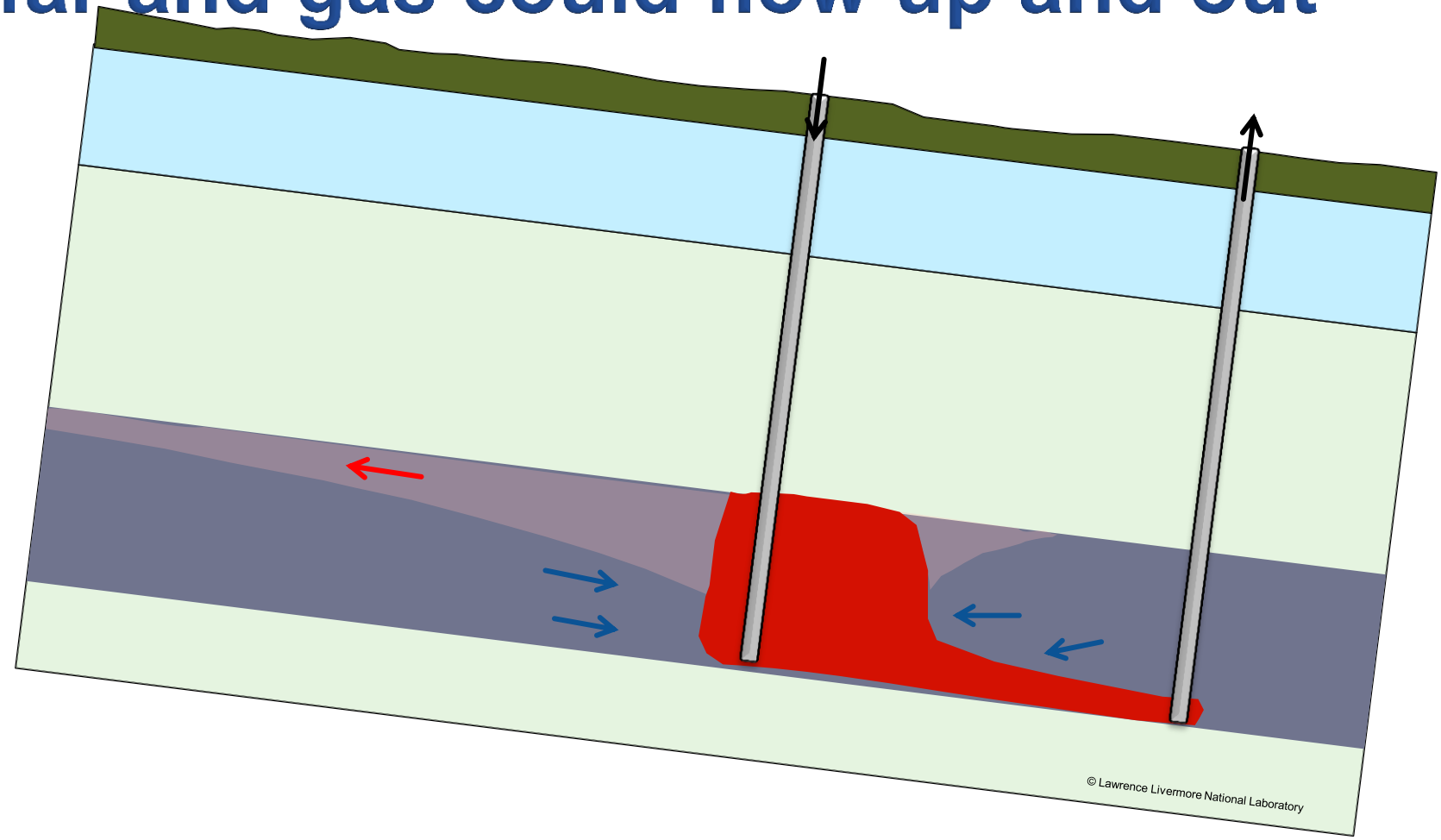




An unsaturated shoulder is likely to be present (depending on details)

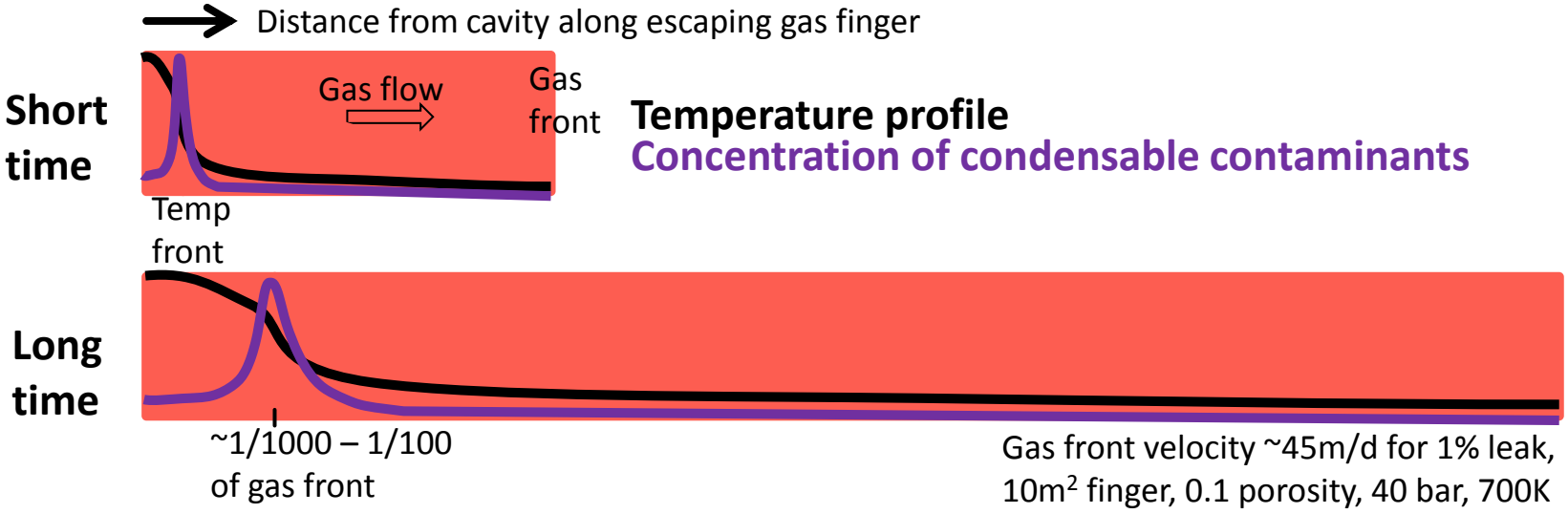


With a dipping seam, this unsaturated "shoulder" can extend far and gas could flow up and out



Escaping gas will travel much further than where condensation will deposit the contaminants

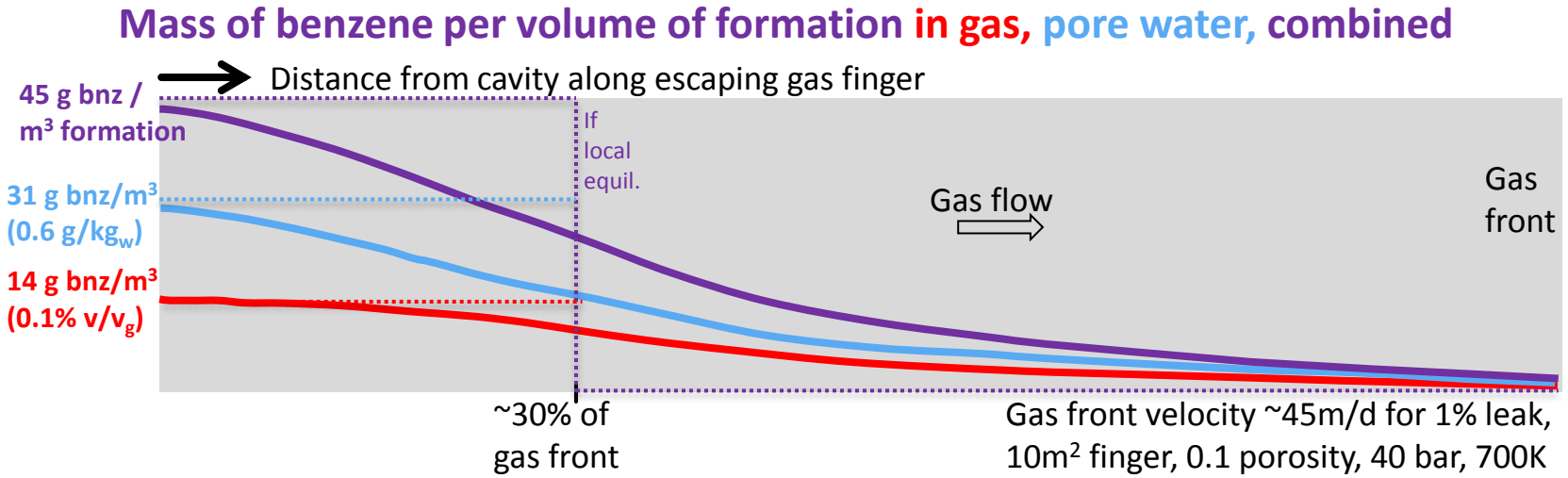
- Huge difference in volumetric heat capacity between rock and gas → temperature front advances slowly
- Organics will condense when they contact cool rock



This is beneficial two ways:
Contaminants condense close to the cavity.
Fast-traveling gas provides an opportunity for early detection.

Volatile compounds will be carried away at their dew point by escaping gas until adsorption and dissolution into pore water strips them out

- Estimate 0.1%v/v benzene in gas + 0.2% similar organics at 25°C and 40 bar
- Equilibrium water has 0.6 g bnz/kg + 1.2g/kg similar orgnc
- Adsorption is harder to estimate (not in this graph)



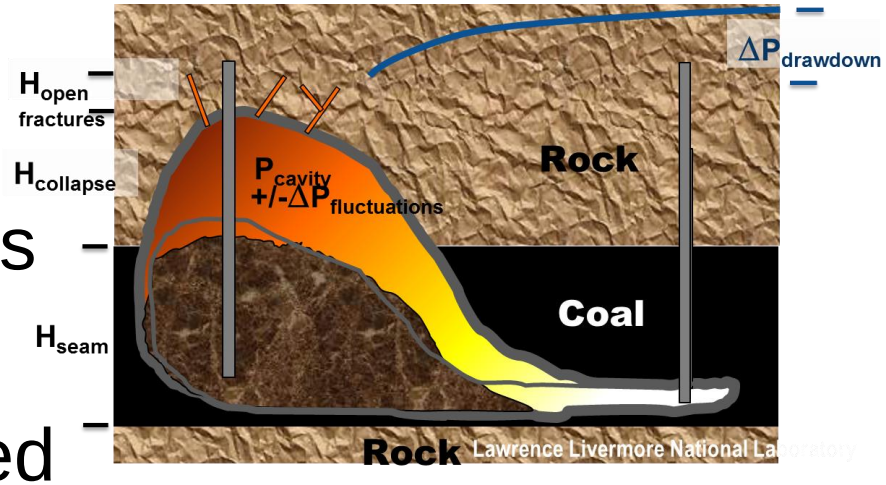
Compounds like benzene can be carried away from the cavity a significant fraction of the distance the escaping gas travels.

Details for previous concentration curves

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 45 bar and 25°C 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.

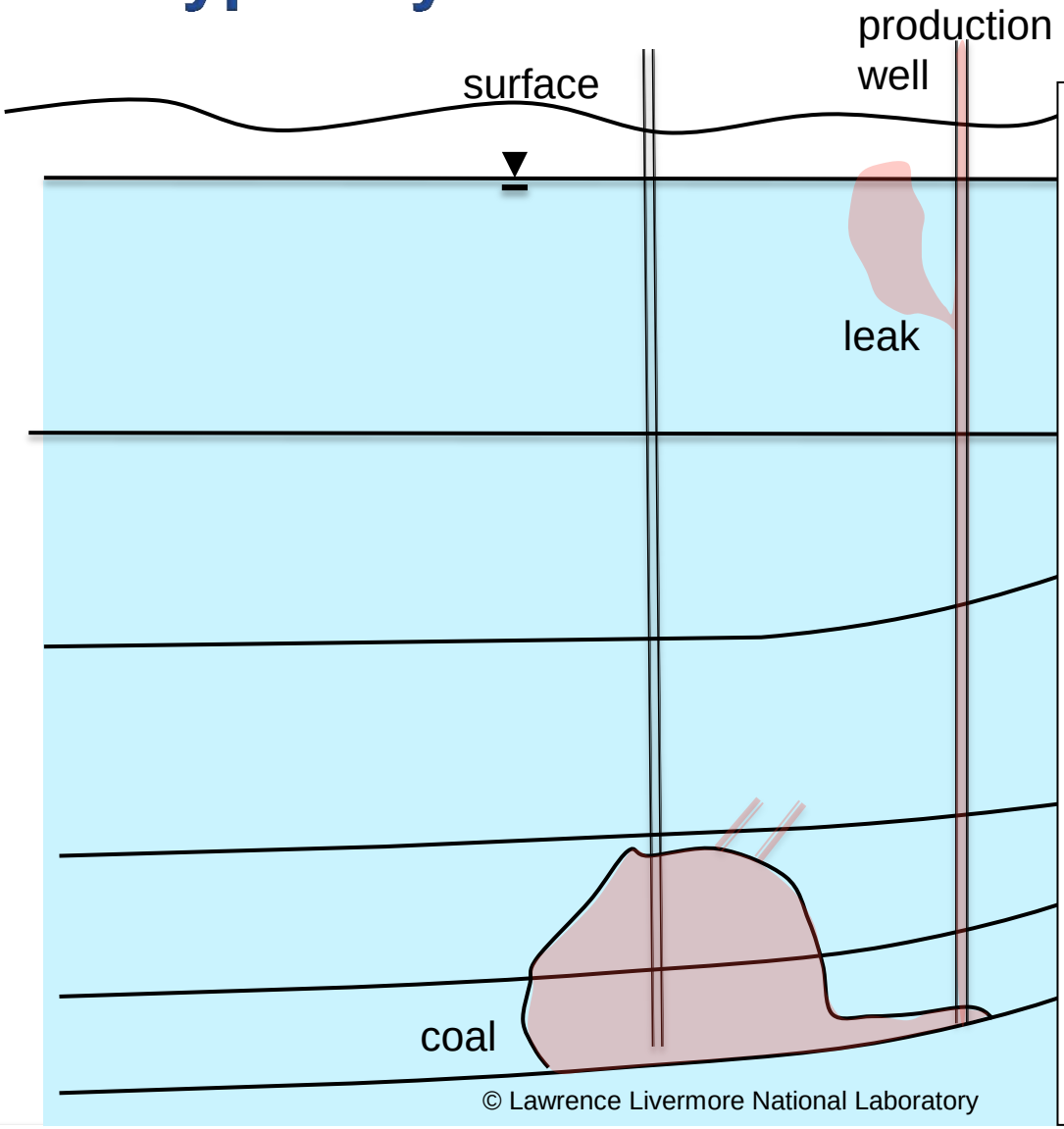
Causes of outward pressure gradients

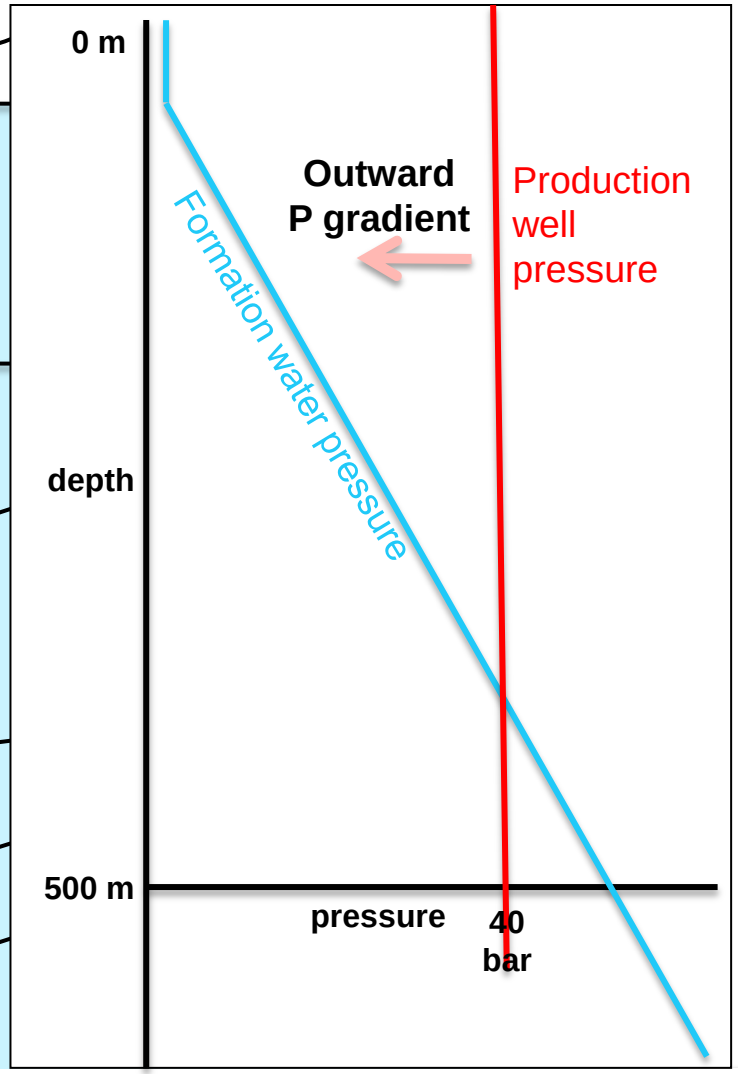
- Pressure in cavity is higher than intended
- Surrounding pressure is lower than thought



- Cavity and its connected gas-filled fractures extend higher than thought
- Cavity intersects an open borehole or well and pressurizes the hole at shallower depths
- Pressure in product-gas pipe is always higher than surroundings at shallower depths

Risk factor: The pressure in the upper production well typically exceeds the surroundings pressure





Assuring inward pressure gradients

- Assure cavity pressure is what is intended
- Know the surrounding pressure field
- Know where the top of the cavity and its open fractures are
- Allow for uncertainties

Impermeable overburden may be necessary to limit buoyant gas fingering

- Buoyancy instability may cause gas to finger upward even though the water-saturated pressure gradient is downward
  - This conjecture needs analysis and research

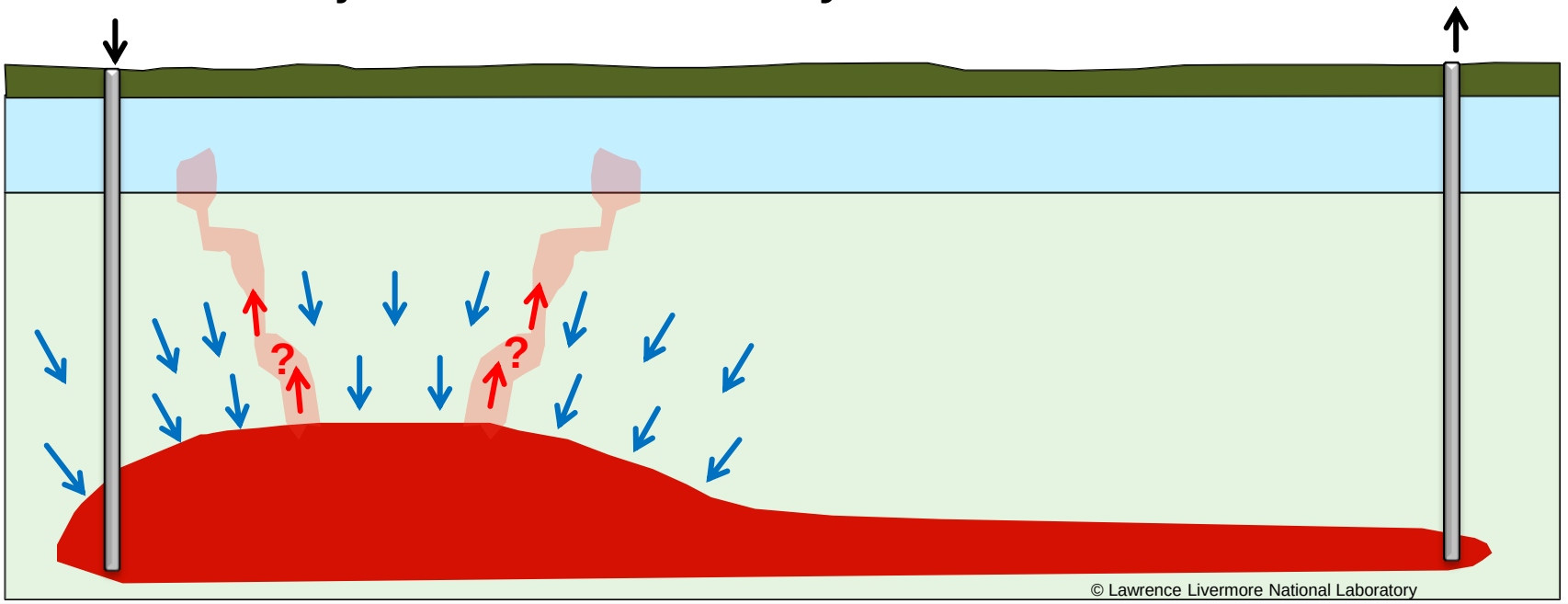
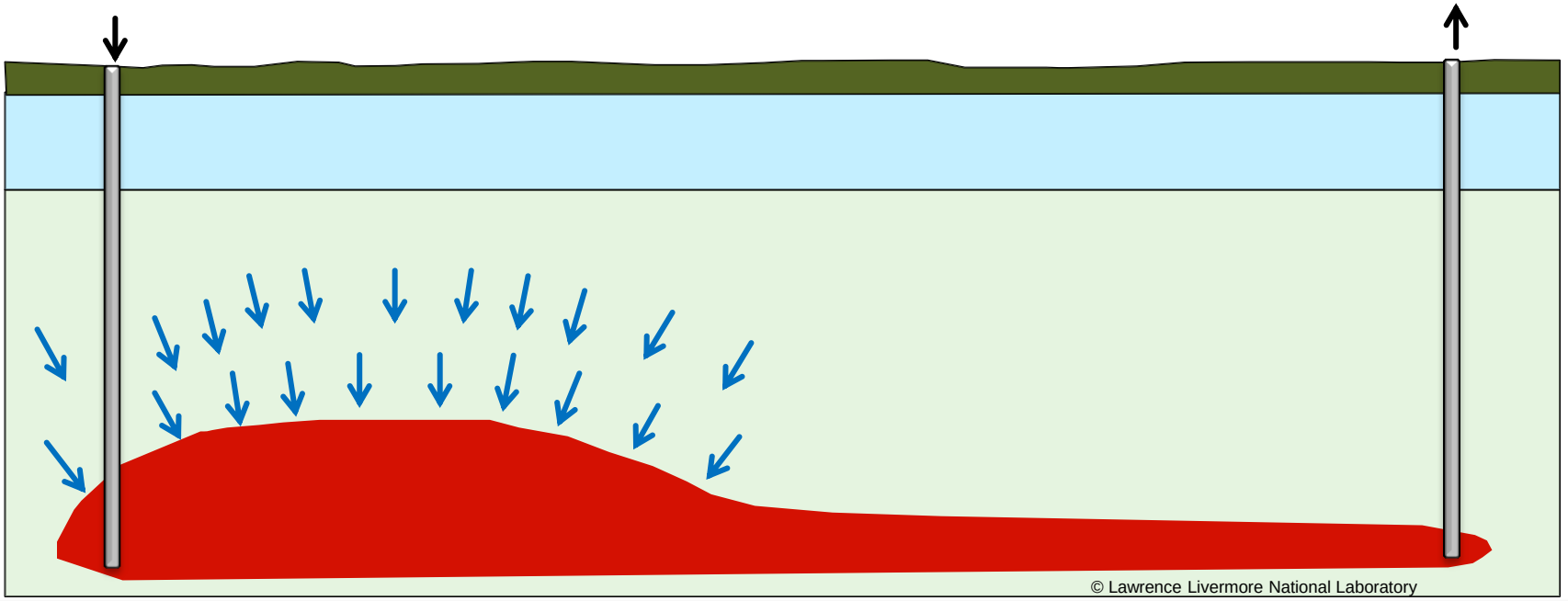


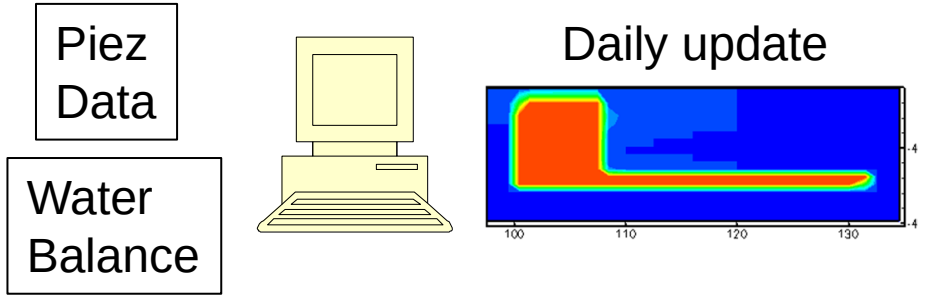
Figure with no gas-finger instability



Know the surrounding fluid pressure field

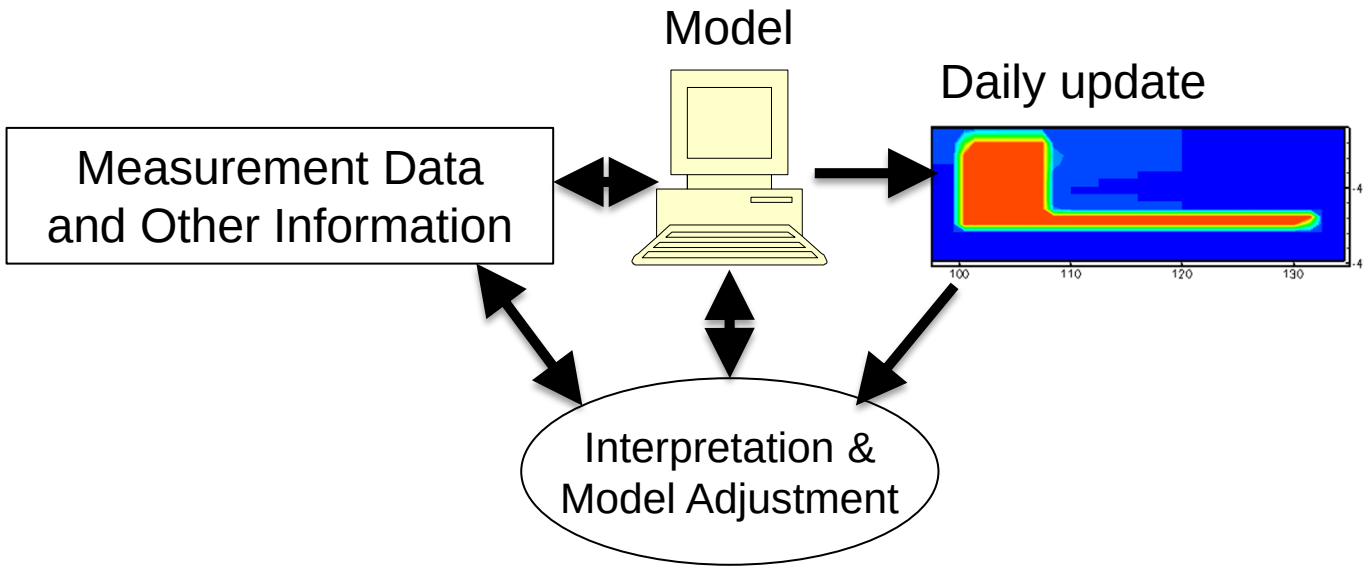
Monitor = Measure + Model

- Piezometer arrays
- Water balance

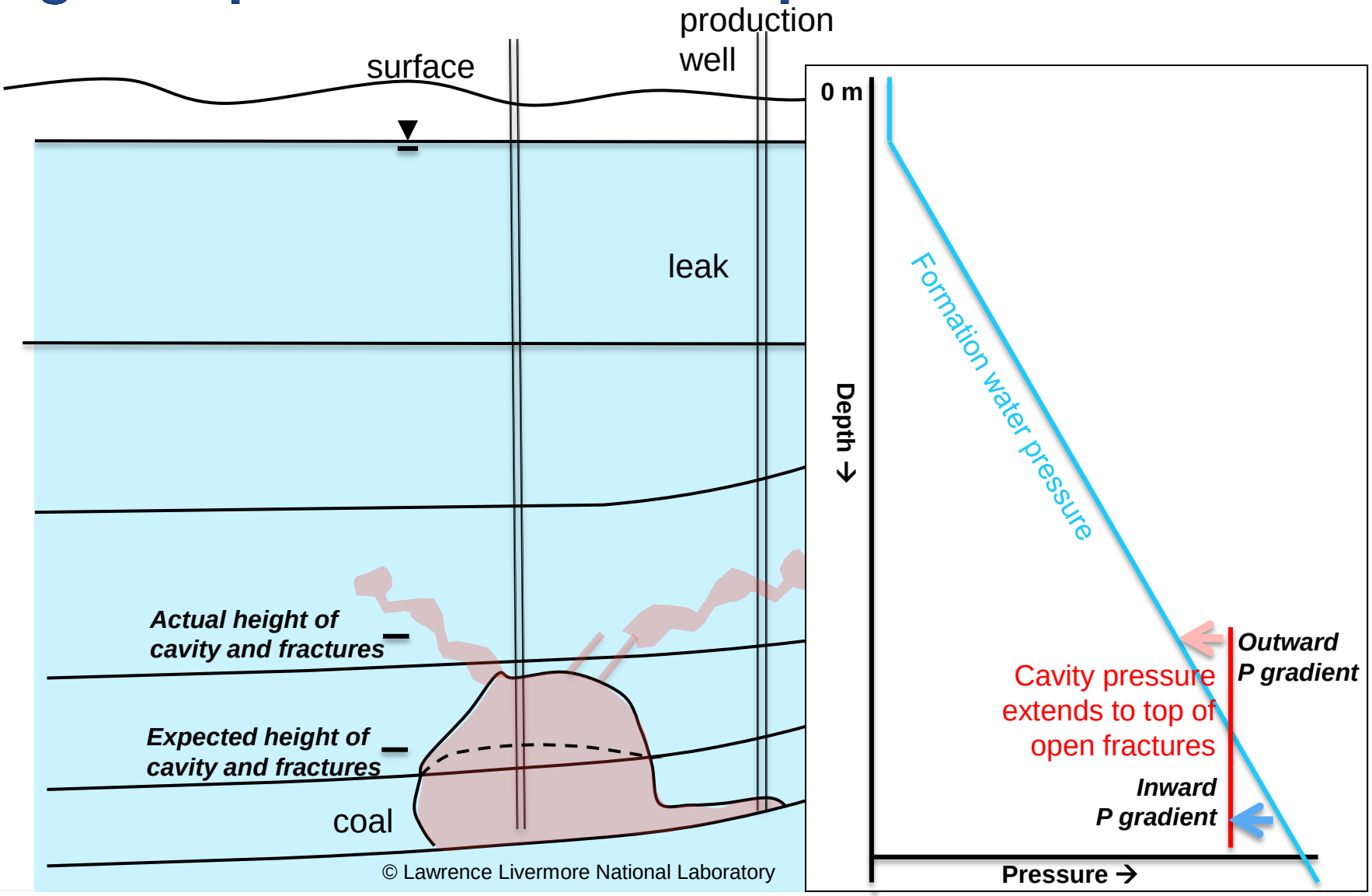


- Hydrology model continually updated with data
  - Unsaturated model
  - Look for changes in vertical connectivity
  - Look for changes in permeability
- Make best estimate of water pressures surrounding the top of the cavity and its fractures

A more detailed figure of the iteration between measurements, models, and interpretation



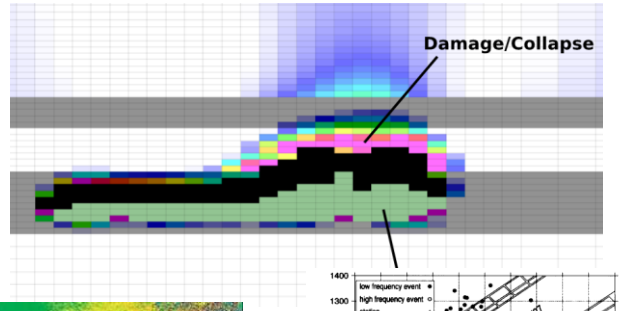
Risk factor: If cavity or open fractures grow upward more than expected

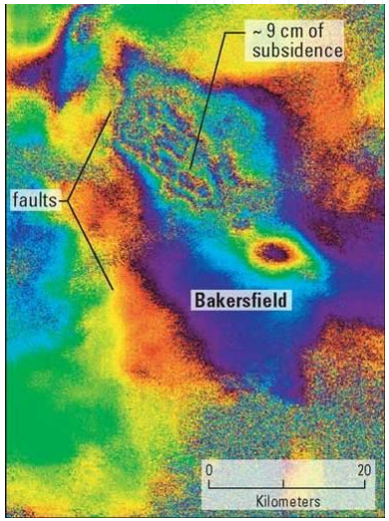


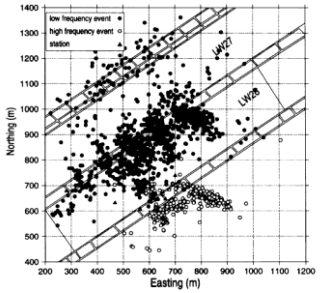
Know the height of cavity and fractures

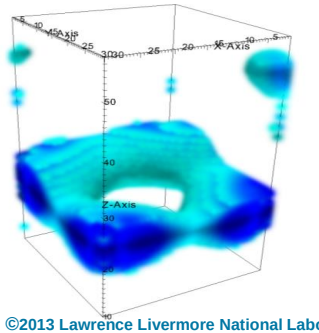
Monitor = Measure + Model

- Model expected and upper bound
- Measurements
  - T, P
  - Downhole tiltmeter
  - Strain or failure anchors
  - Seismic reflection
  - Acoustic/microseismic
  - Electrical resist. Tomog.
  - …
- Model interpretation









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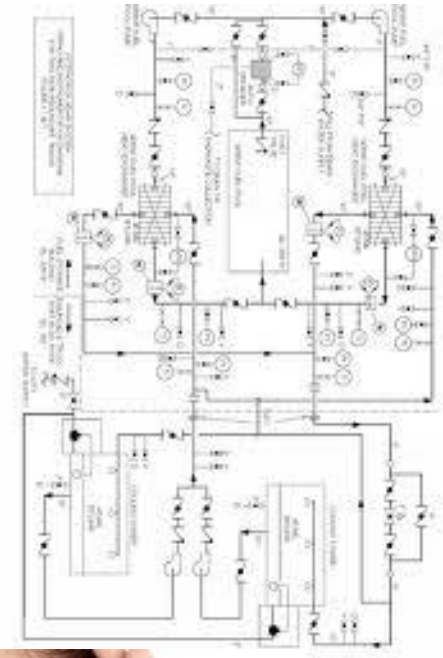
Assure control of pressures and flows

- Challenging environment
  - wide dynamic ranges
  - high and variable T, P
  - corrosive; dusty; tarry

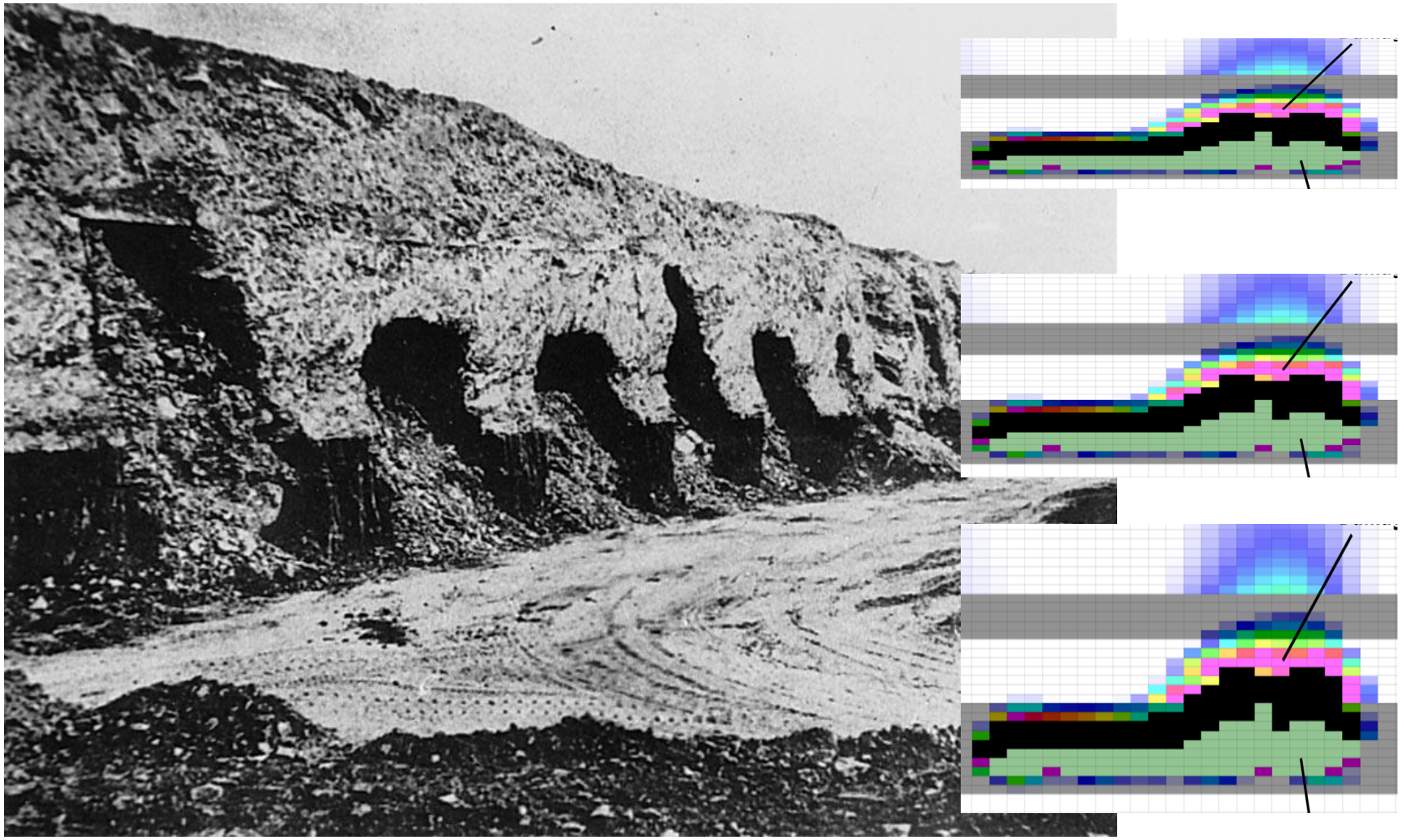


- Robust hardware
- Robust control systems
  - Variable operations
  - Wide dynamic ranges
  - Blockages

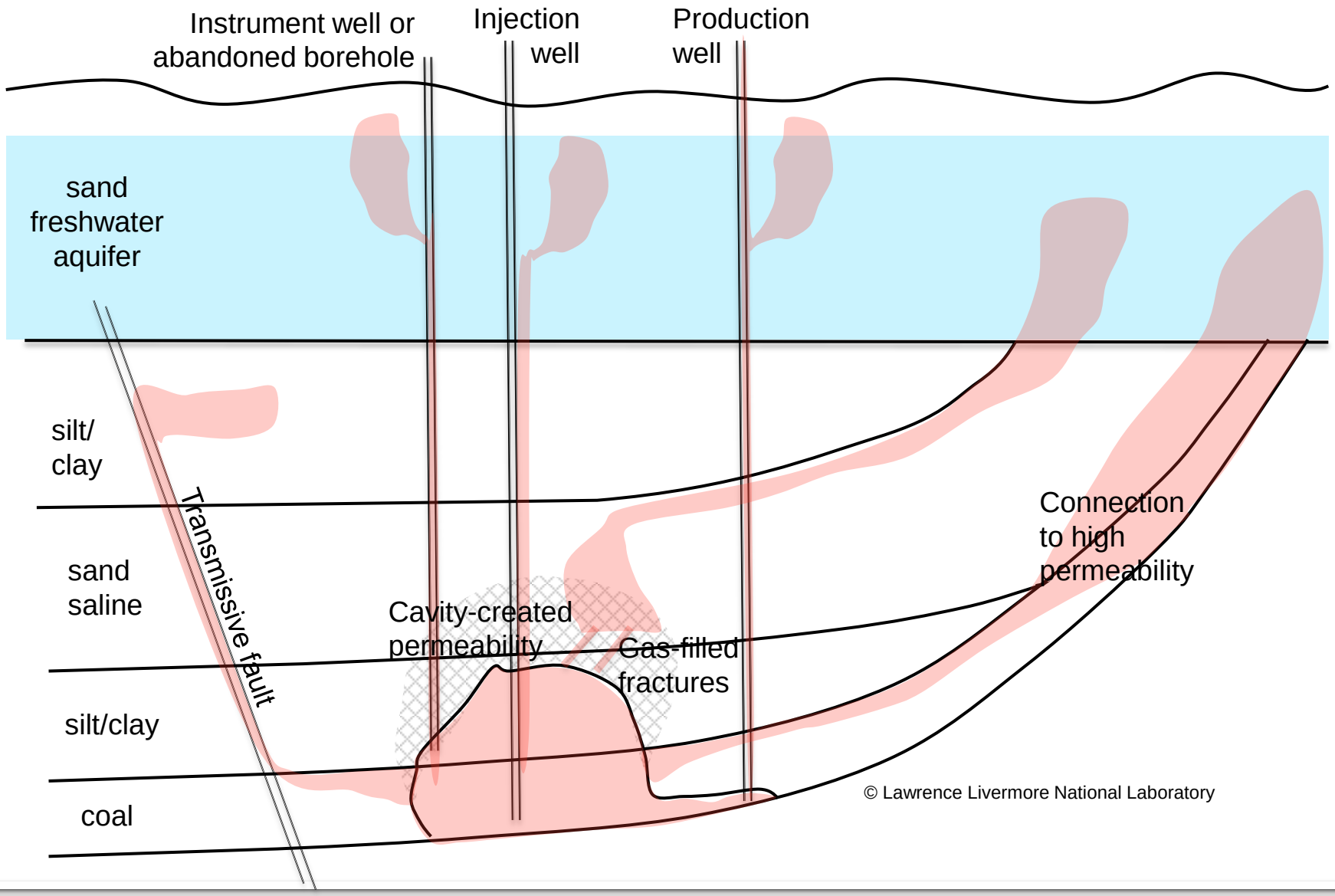
"Did you say 15 or 50?"

- Human error
  - Robust QA program, training, methodical operations

Allow for uncertainties +/- ?



Possible natural and man-made pathways



Possible permeable paths for gas escape and contaminant transport

- Natural permeability field and vertical connectivity
  - Faults
  - Up-dipping permeable strata (Rawlins)
  - Paleo channel cuts through impermeable strata
- Cavity growth through a barrier layer into a permeable zone (HoeCreek-3)
- Increased permeability from stress changes and fracturing (HoeCreek-3)
- Flow paths within or outside of boreholes or wells
  - Open hole or well (RockyMountain-1)
  - Poorly shut-in
  - Poor external grouting (Rawlins)
- Failure of production well (Cougar)

Site selection is very important. The permeability field strongly affects the amount of gas escape and contaminant transport to protected groundwater

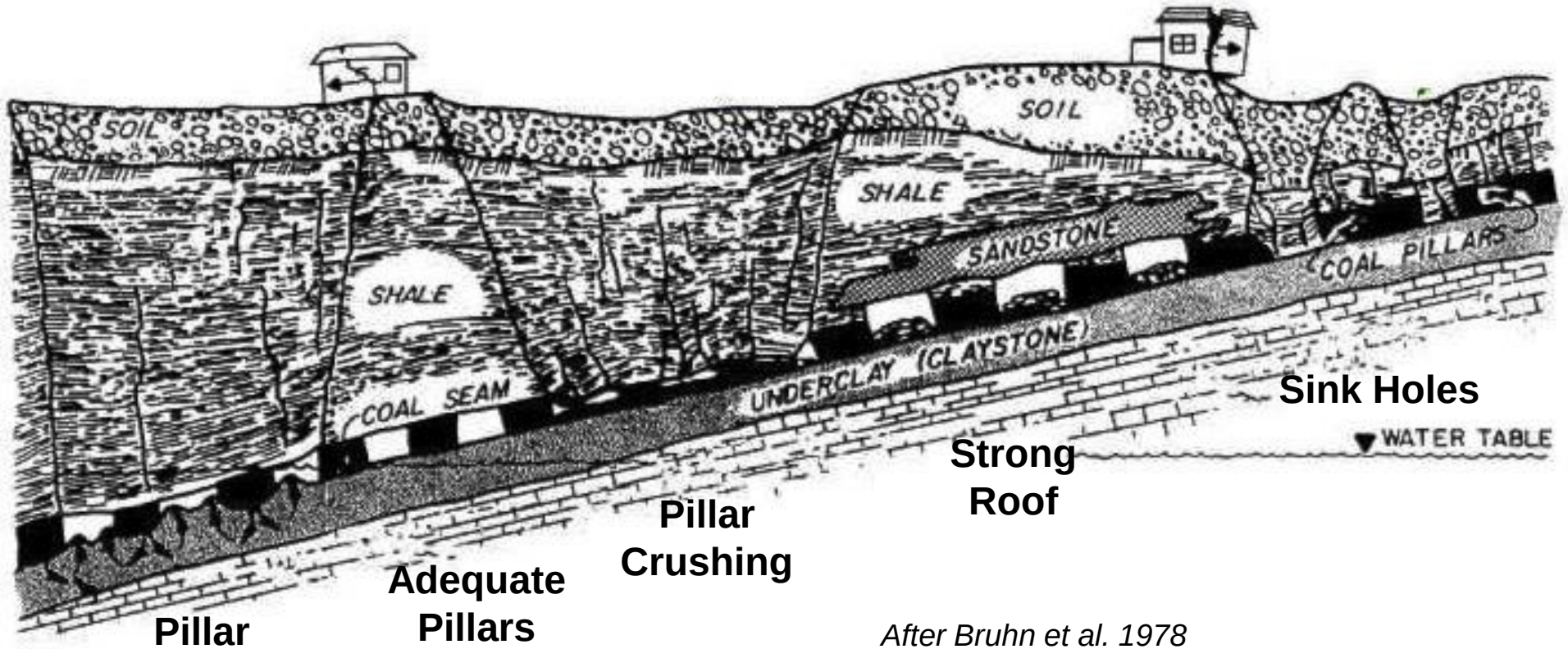
Favorable

- Valuable/protected groundwater is nonexistent or shallow
- Thick low-permeability strata above cavity
- Low dip, anticline
- No/few/small fractures, joints, or transmissive faults
- Mapped and properly closed boreholes
- Strong rock supports economically-wide cavity with minimal vertical collapse

Unfavorable

- Valuable/protected groundwater close to UCG
- No robust low-permeability strata in between
- Dip, syncline
- Fractures, joints, transmissive faults
- Unmapped or improperly closed boreholes
- Weak rock – excessive vertical collapse for economical cavity width

Stress changes from UCG cavity excavation can increase permeability and fractures



After Bruhn et al. 1978

Figure: Subsidence modes [after Bruhn et al. 1978].

Stress changes from UCG cavity excavation can increase permeability and fractures

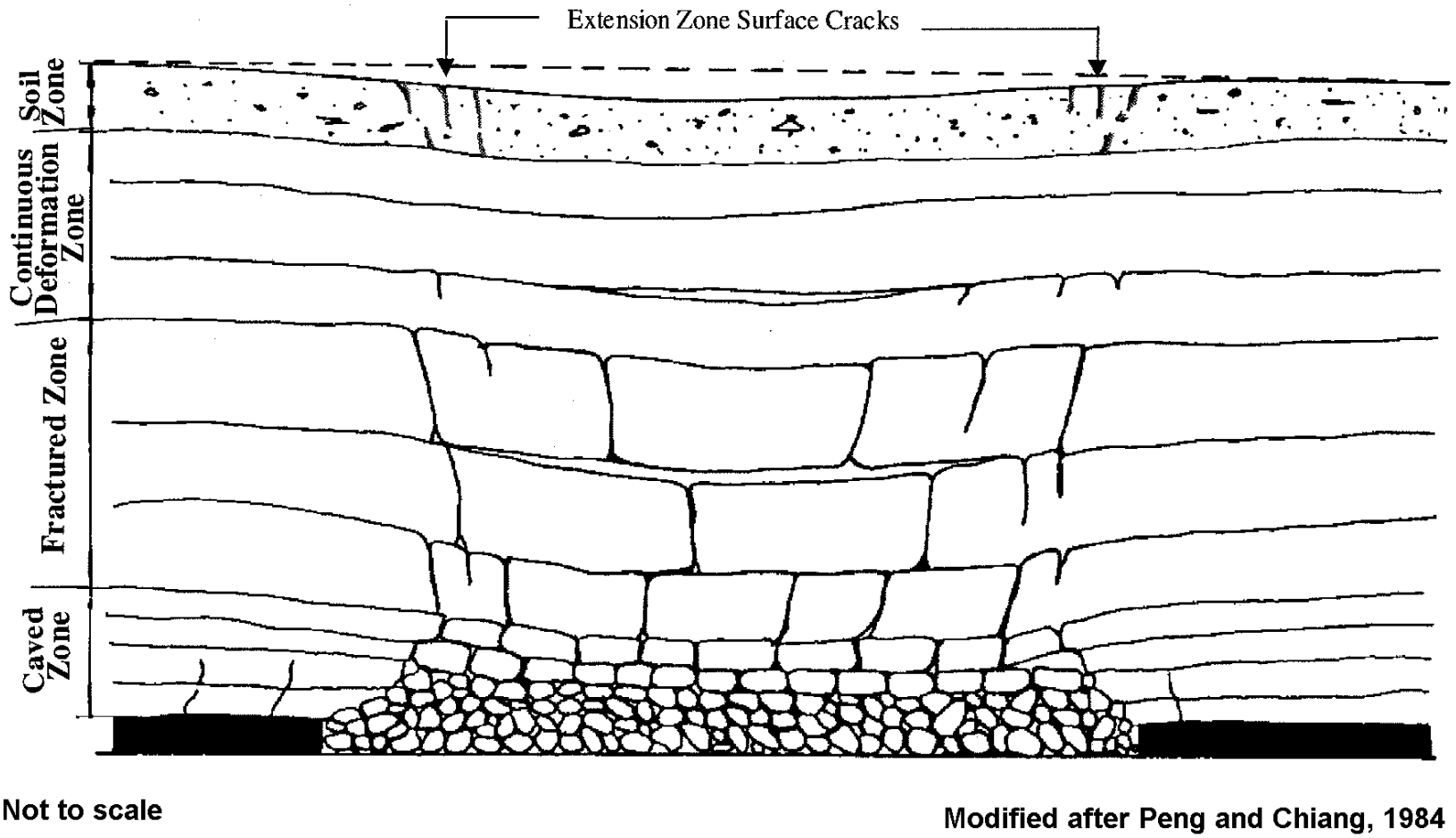


Figure: Overburden changes due to large-width cavity extraction.

UCG cavities can affect the surrounding permeability field

Figure: A large chimney collapse occurred after shut-in of the Hoe Creek III pilot test. The coal seams gasified were between 129 and 182 feet (39.3 – 55.5 m) below surface.

Production well containment must be robust

- Product gas pressure will greatly exceed that of shallow surroundings
- Shallow leaks have more impact
- Different than oil/gas wells
  - High and variable temperature
  - Corrosive tarry particulate gas
- UCG industry on learning curve
  - Proprietary designs limit peer review
- QC construction
- Realistic testing and operational testing
- Leak detection

Prevent leaks from the production well

- Different than oil/gas production wells
  - High and variable temperature
  - High pressure at shallow depths
- UCG industry on learning curve
- Proprietary designs limit peer review
- Robust design and materials
  - Redundancy? – double containment?
  - Thermal expansion
  - Corrosion
- QC'd installation
- Rigorous realistic testing
  - With cycled high temperatures
  - Develop procedure to test mid-operation
- Operational monitoring (annular leak detection)

Other wells and boreholes can become pathways

- Applies to in-use wells, closed characterization boreholes, and old exploration holes
- Cavity intersects an open borehole or well
  - Cavity collapse, rock shear, thermal stresses
- Hole or casing will fill with gas at the cavity pressure
- Not engineered to contain hot pressurized gas
  - Large ΔP where shallow is likely place to leak out
- Similar issues to a lesser extent with pathways of fractures or voids through grout
  - Poor filling or cracks from thermal or mechanical stresses

Combinations to worry about

Causes of outward pressure gradients

- Pressure in cavity becomes higher than intended
- Surrounding fluid pressure becomes lower than thought
- Buoyant instability gas fingers
- Cavity and its connected gas-filled fractures extend higher than thought
- Cavity intersects an open borehole or well
- Pressure in product-gas pipe is always higher than surroundings at shallower depths

Permeable escape paths

- Natural permeability field and vertical connectivity, including dipping strata, transmissive faults
- Increase in permeability of surroundings from stress changes and fracturing
- Cavity and its fractures grow up through a barrier layer into a permeable stratum
- Cavity grows out more than expected and intersects a fault or well
- Vertical connectivity within or outside of open, poorly shut-in, or poorly grouted boreholes/wells
- Failure of product-gas pipe and/or production well casing/grouting

Four "A-List" scenarios

- Leak from product gas line into shallow permeable surroundings
- Higher-than-expected upward growth of cavity and open fractures
- All the other scenarios – any one could bite you
- The ones we haven't thought of !

Scenario notes

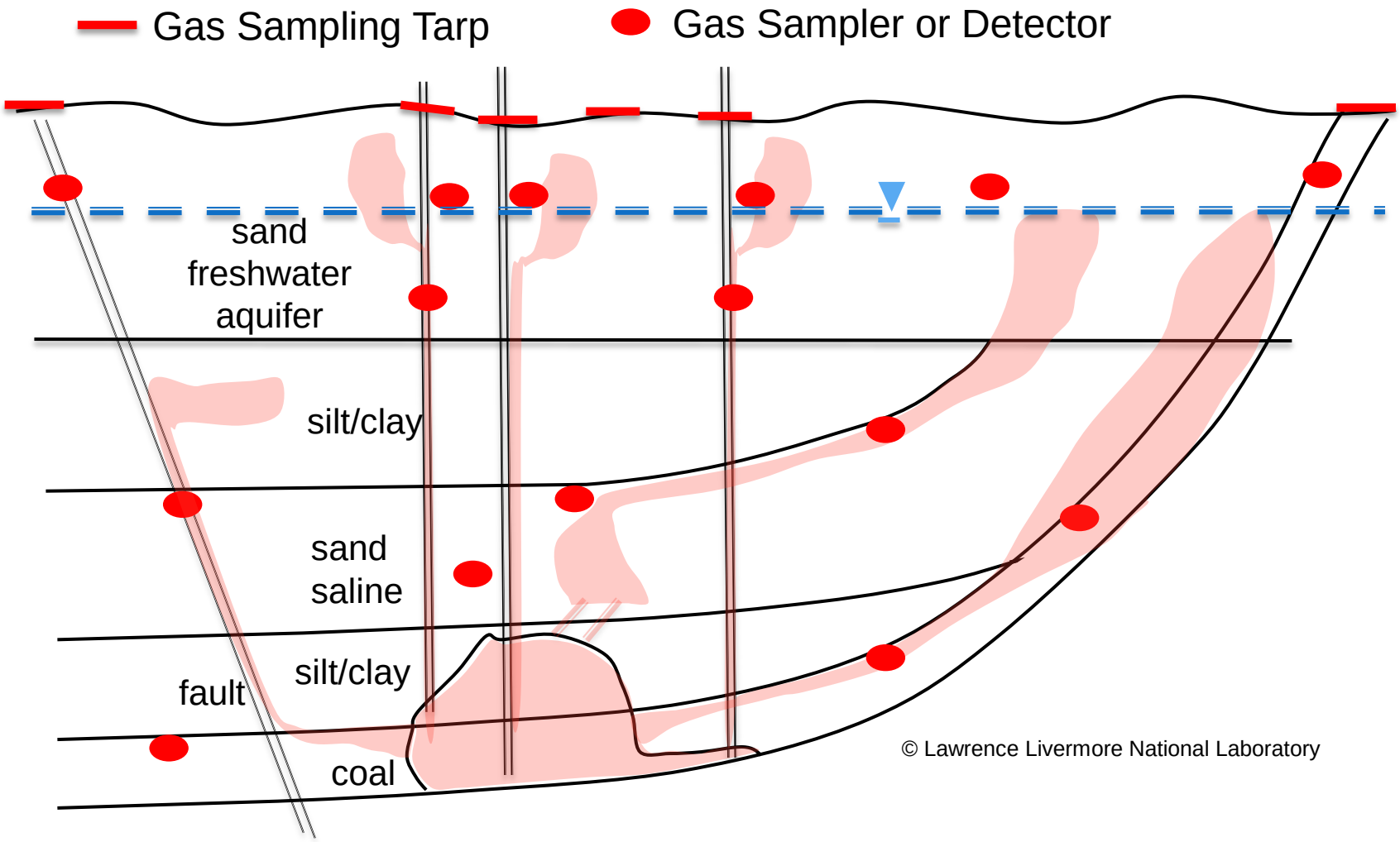
- Leak from product gas line into shallow permeable surroundings
  - Large pressure difference
  - Changing thermal stresses challenge fittings, connections, grouting
  - Shallow likely to be close to valuable/protected groundwater
- Higher-than-expected upward growth of cavity and open fractures
  - Relative overpressure likely
  - Penetration through barrier strata to a high-permeable stratum
  - High permeability created by reduced stress and/or fractures

Early detection by discovering gas leaks

Gas leaks may be the easiest, quickest way to detect problems before contaminants are transported far

- Mass balance from balances and/or tracers
- Subsurface and surface detection
  - Look along likely paths
  - In saturated zone, monitor for physical changes
  - In unsaturated zone, sample + real-time cheap detector
- Good choices for analytes
  - H_2, CO, H_2S
  - Major components with low background
  - Conserved
  - Fast and cheap detection
- Must do background first!

Gas detection and sampling for early far-field detection of escaping gas



Gas detection & sampling for early far-field detection of gas leaks

- Detection of gas where water-saturation is expected
  - Roof of seam or permeable zone up-dip from gasification
- Good places to sample
  - Unsaturated zone above likely paths
    - unsaturated zone of a fault
    - above the border of a low-permeability lens
  - Exterior of wells
    - Annulus or outside of product or instrument wells
  - Ground surface above likely paths
    - Tenting around wellheads
  - Water sampling well headspace
- Good choices for analytes
  - CO, H_2, H_2S, NH_3, TOC, benzene,BTEX, acetone, napthalene, phenolics, pyridine
  - Major components
  - Unnatural or low background
  - Conserved
  - Fast and cheap detection

Groundwater sampling helps people feel good but is too little detection too late

- **Must do background**
- **By the time you get a hit from a far-field groundwater sampling station you already have a problem**
- **Hit or miss** – Negative does not prove anything; finger may have missed station
- Inner zone positives provide important early information but must be socialized with regulators
- Middle ring detection shows contaminants have escaped the near-cavity containment zone
- Outer ring detection shows a very large volume of subsurface has been contaminated

Prevention is better than remediation

Large quantities of contaminants left far outside the containment zone are infeasible or very expensive to remediate

- Model transport, sorption, decomposition
- Hydraulic containment
- Long term monitoring
- Acceptability depends on site and details

Preventing groundwater contamination requires care at many steps

- Select site
- Analyze failure modes
- Design, construct, test
- Assure operations and control
- Monitor and model
- Detect early