Slide 1

Presentation #5

- Given to the EPA on April 11, 2012, as the final presentation for the EPA Region 8's Regional Applied Research Effort funding

Slide 2

Using groundwater and solid-phase geochemistry for reactive transport modeling at the proposed Dewey Burdock uranium in-situ recovery site, Edgemont, South Dakota

By Raymond H. Johnson

Dewey Burdock site has been proposed for uranium ISR mining by Poweterch Uranium Corporation.
Overall USGS uranium research covers the full spectrum of uranium ore formational processes, evaluating potential undiscovered deposits to potential mining impacts.
Through a Region 8 interagency agreement (Regional Applied Research Effort), the USGS was asked to look at the groundwater flow and geochemistry of the Dewey Burdock site.

Slide 3

Goal

- Demonstrate how reactive transport modeling can be used as a tool to assess future influences of uranium in-situ recovery (ISR) mining on groundwater geochemistry

Reactive transport modeling couples groundwater flow and geochemistry. This research focuses more on the geochemistry since Petrotek, a consultant for Powertech, has been developing a large scale 3D groundwater flow model.

Slide 4

This Presentation

- Downgradient water quality after mining
  - Range of possibilities, through modeling
- Does not address water quality within the mining zone, post mining
  - Studied and modeled by others (Davis and Curtis, 2007, Nuclear Regulatory Commission document)
- Focus on what reactions might take place downgradient, with “assumed” post-mining water quality

Since this is predictive modeling, the post-mining water quality is not known and the quality is “assumed” for modeling purposes. Modeling uses a range of values.
During actual restoration, groundwater quality in the mining zone could be continually monitored. These values could be input into new downgradient water quality simulations until a downgradient target concentration is met.
Reference: Davis, J.A. and Curtis, G.P., 2007, Consideration of geochemical issues in groundwater restoration at uranium in-situ leach mining facilities: U.S. Nuclear Regulatory Commission, NUREG/CR-6870, 86 p.

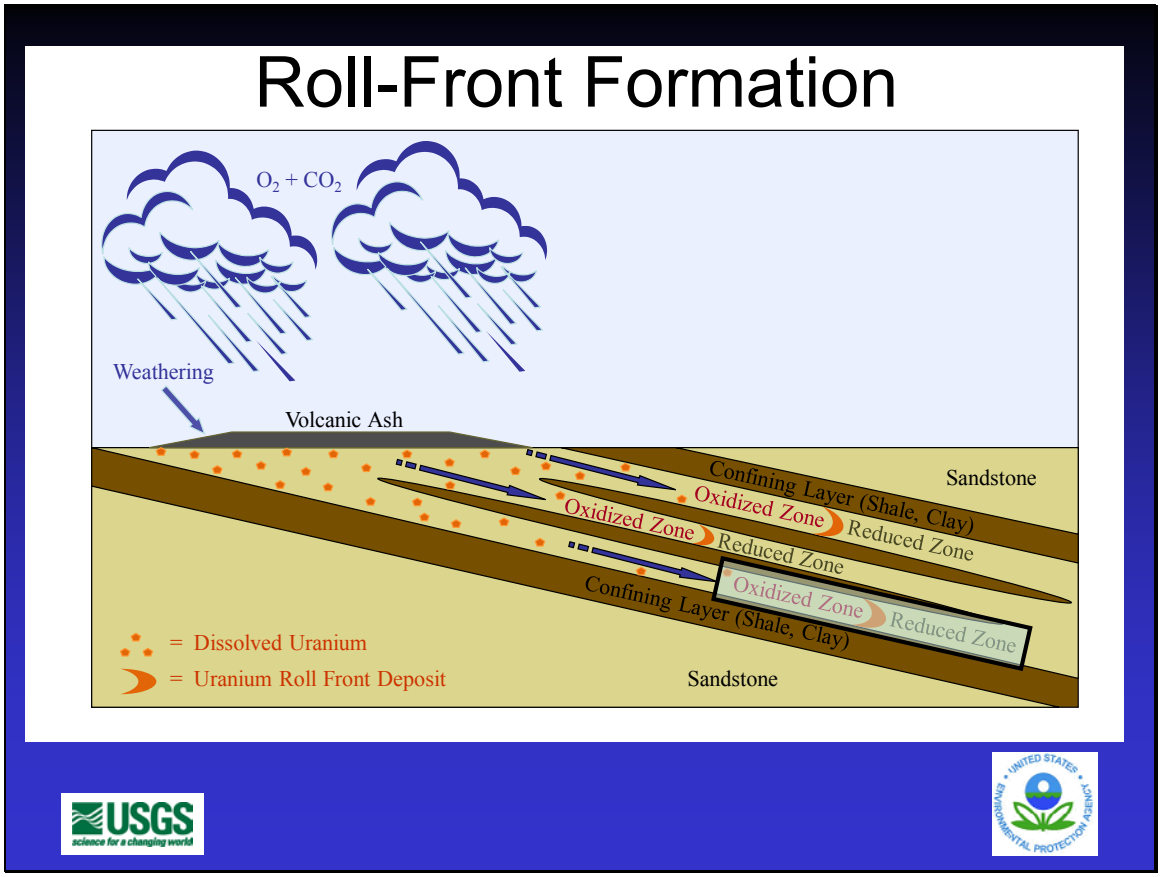
Slide 5

Outline

- Uranium in-situ recovery (ISR) mining/site overview
- Differences in Dewey and Burdock geochemistry
- 1D reactive transport modeling with PHREEQC
- 2D reactive transport modeling with PHAST
- Monitoring recommendations
- Conclusions

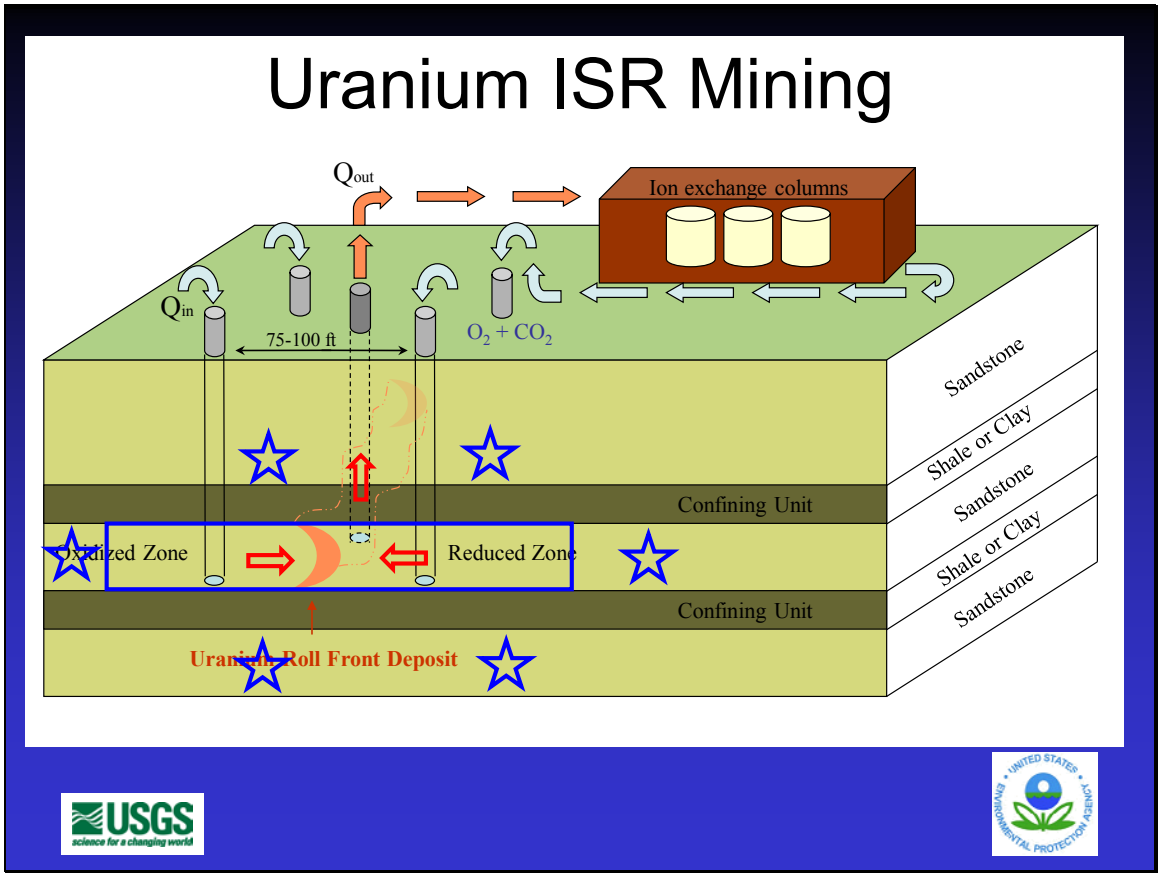
PHREEQC is a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations.
PHAST is a computer program for simulating groundwater flow, solute transport, and multicomponent geochemical reactions.

Slide 6



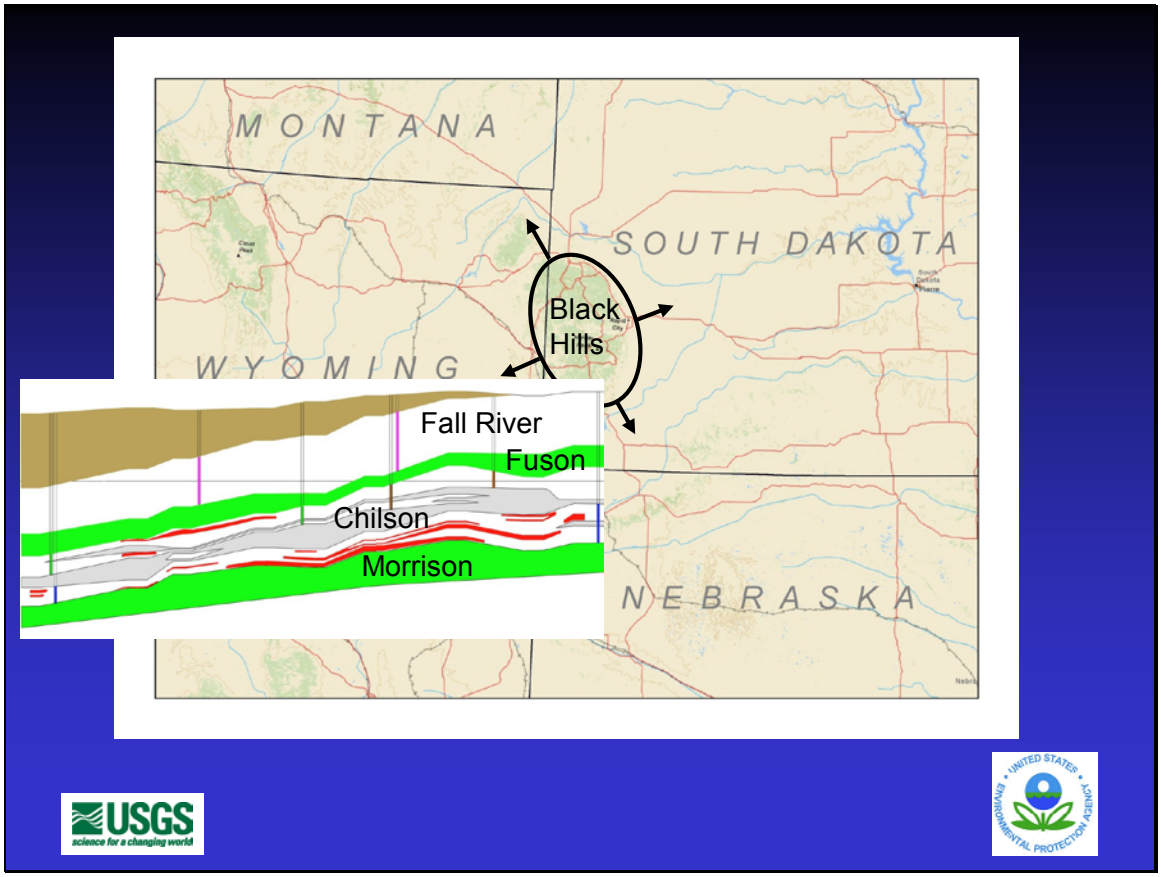
Uranium roll-front formation is often not in a single unit, but have stacked roll fronts, due to stratigraphy.
The black box conceptually indicates an area that is used for reactive transport modeling.
Uranium roll fronts occur at the oxidation/reduction interface because uranium becomes less soluble upon encountering reducing conditions.

Slide 7



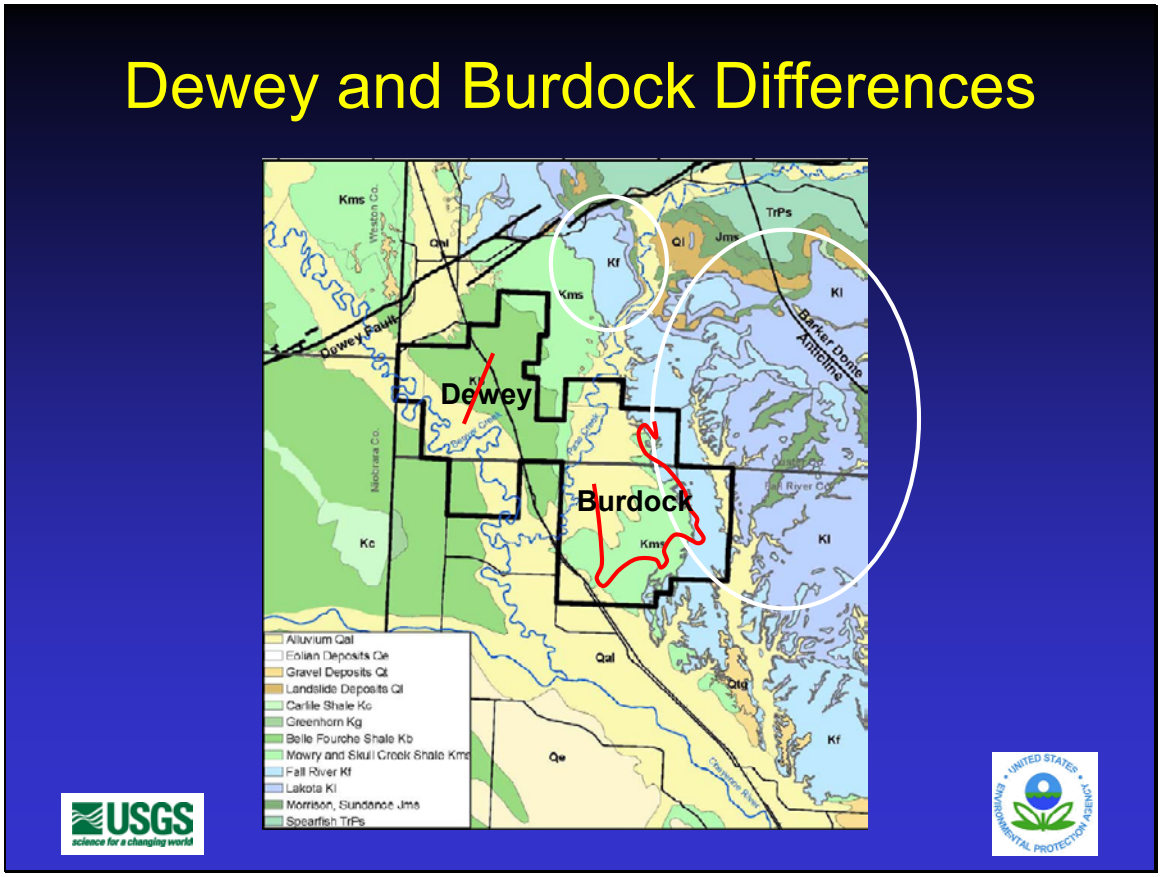
This slide shows a typical five-spot well pattern. In three dimensions, the wells follow the uranium deposit.
The blue box represents an aquifer exemption boundary. This boundary outlines a portion of the aquifer containing materials expected to be commercially producible.
The goal with the final restoration process after uranium recovery is to get this zone (blue box) back to pre-mining groundwater quality.
The stars represent a typical monitoring well pattern surrounding the recovery zone and located in the nearest aquifers above and below the recovery zone.
Ideally, these monitoring wells should never see any change in water quality.

Slide 8



The black arrows indicate dip of geologic layers away from the Black Hills uplift and the inset is a cross section (courtesy of Powertech (USA) Inc.) in the Burdock area.
The Dewey Burdock site is at the southwestern edge of the Black Hills.
The blue arrow indicates regional groundwater flow down dip and then around the south end of the Black Hills.

Slide 9



The white circles indicate the recharge zone for the Fall River Formation (left) and the Lakota Formation (right).
The Fall River recharge area is quite small and close to Pass Creek; whereas, the Lakota recharge area is much larger and forms a separate drainage area.
Red lines indicate ore zones. Dewey area is in the Fall River Formation and Burdock area is in the Lower Chilson Member of the Lakota Formation.

Slide 10

Groundwater Geochemistry

Element	Dewey – Fall River	Burdock - Chilson
Oxygen	<1 mg/L	<1 mg/L
Ca	56.9 mg/L	365 mg/L
Alkalinity	164 mg/L	269 mg/L
SO_4	508 mg/L	1,460 mg/L
^{34}S	-3.6 per mil	-15.5 per mil
Fe	0.01 mg/L	1.83 mg/L

Burdock area has experienced more sulfide oxidation somewhere upgradient (more sulfate and lower isotope ratio)?

Numbers are from wells 685 (Dewey) and 684 (Burdock), which are used in the modeling.
At the Dewey Burdock site, the uranium roll fronts do not significantly influence the groundwater geochemistry (except for increases in radium and radon) due to the lack of oxygen.
These are good average numbers for the Dewey and Burdock areas in the Fall River Formation and Lower Chilson Member of the Lakota Formation, respectively.

Slide 11

Solid-Phase Geochemistry

Element	Dewey – Fall River	Burdock - Chilson	
Calcite	4-10 wt. %	< 0.15 wt. %	
Pyrite (reduced)	Near 0.5 wt. %	Near 0.5 wt. %	
Pyrite (oxidized)	0.0 wt. %	0.0 wt. %	
Gypsum	< 1 wt. %	0-2 wt. %	Occurs as secondary precipitate
Vanadium	High	Low	
Organic Carbon	Low	High	

Calcite, organic carbon, and vanadium contents are the big differences. Pyrite content in reduced zones is similar.

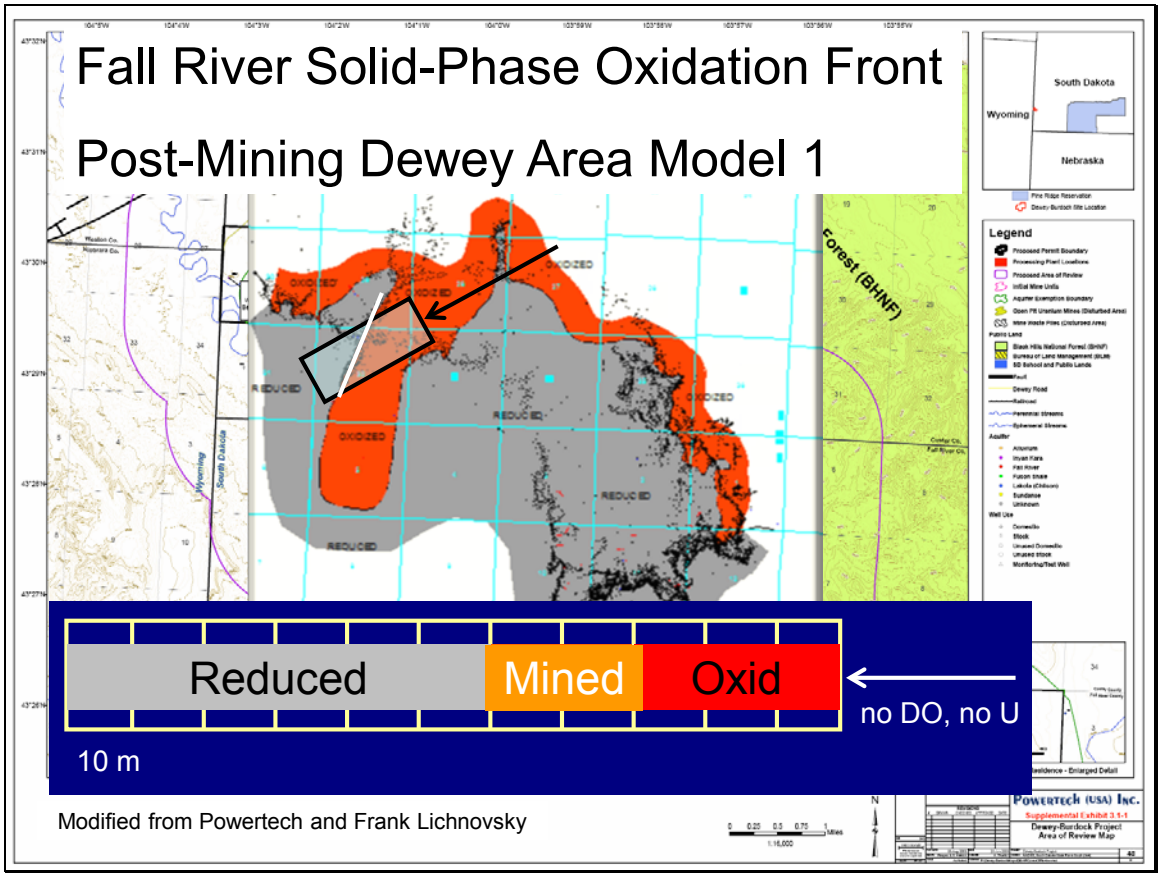
Slide 12

1D PHREEQC Modeling

- Simulations with actual:
  - Groundwater flow rates
  - Groundwater geochemistry
  - Solid-phase geochemistry
- Two main model arrangements
  1) typical roll-front series of oxidized to reduced
  2) "reversed" series with reduced to oxidized
- Reasonable, but assumed geochemical reactions (no lab or field studies yet)
- Simulate post-ISR mining with existing Dewey and Burdock groundwater and
  - No remediation
  - Groundwater sweep

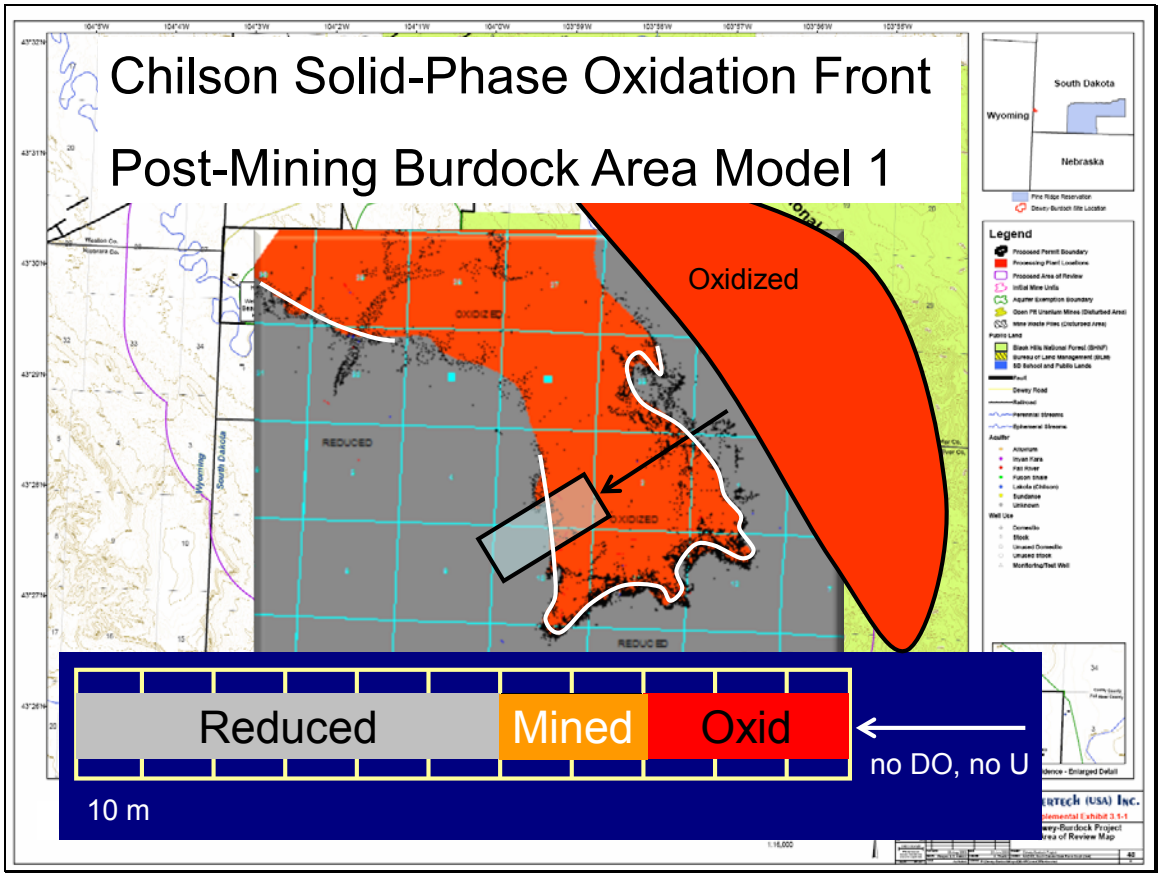
PHREEQC is a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations.

Slide 13



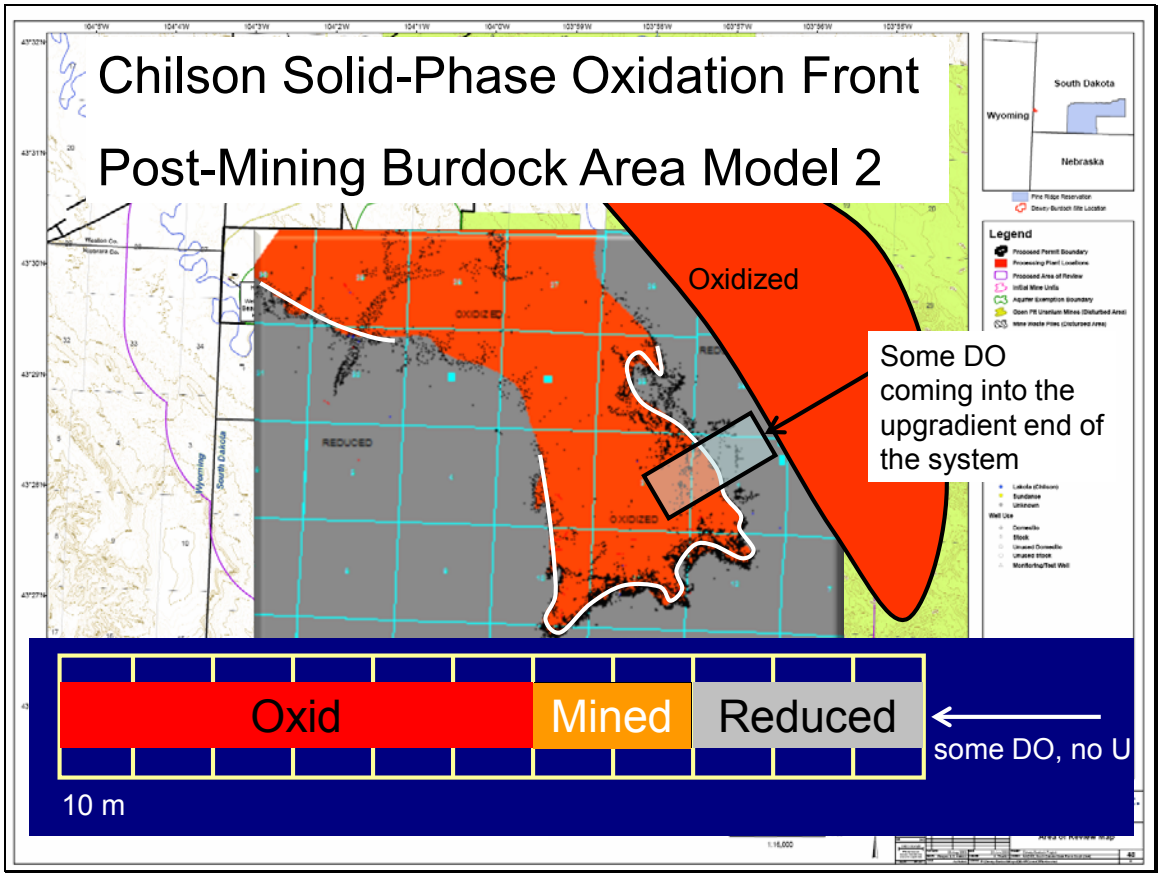
This slide and the next two slides show the interpreted oxidized and reduced zones by Frank Lichnovsky (Powertech) from review of cores (map view).
The box below the maps shows how each particular production zone is modeled in one dimension (1m cells).
Arrow indicates approximate current groundwater flow direction.
Oxidation “lobe” indicates a past combination of low reductant content (pyrite or organic carbon) versus oxygen input/groundwater flow.

Slide 14



Arrow indicates approximate current groundwater flow direction.
Large oxidized zone on the east side was added as a reasonable interpretation that the outcrop zone of the Chilson is oxidized (no core is available in this area).
White line indicates an approximate outline of the uranium ore zone.

Slide 15



Because of a change in groundwater flow direction, this area is now a “reduced to oxidized” solid-phase series through the ore zone (ore zone is the white line).
Arrow indicates approximate current groundwater flow direction.
Large oxidized zone on the east side was added as a reasonable interpretation that the outcrop zone of the Chilson is oxidized (no core is available in this area).
White line indicates an approximate outline of the uranium ore zone.

Slide 16

Assumed Reactions

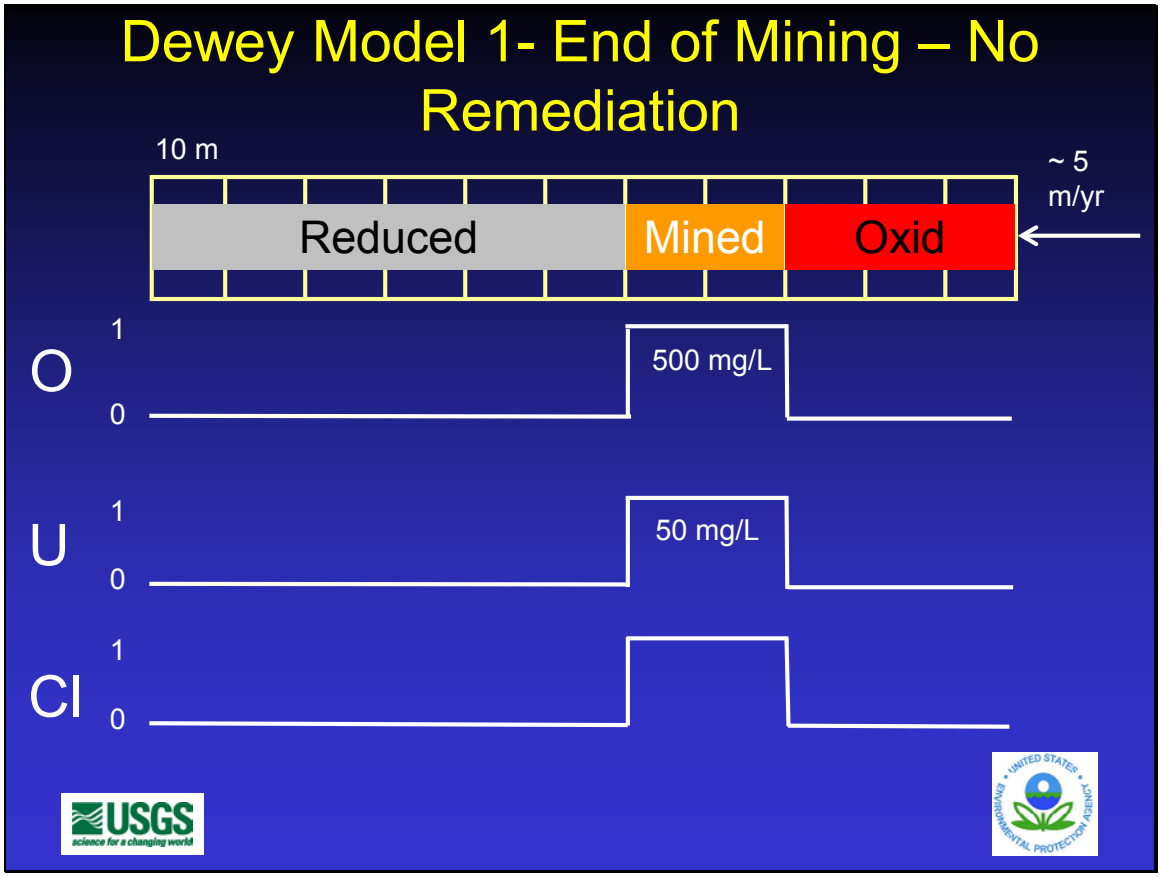
Groundwater = actual well water samples

Oxidized zone = enter calcite amount and allow gypsum precipitation and calcite equilibrium

Mined zone = no reactions

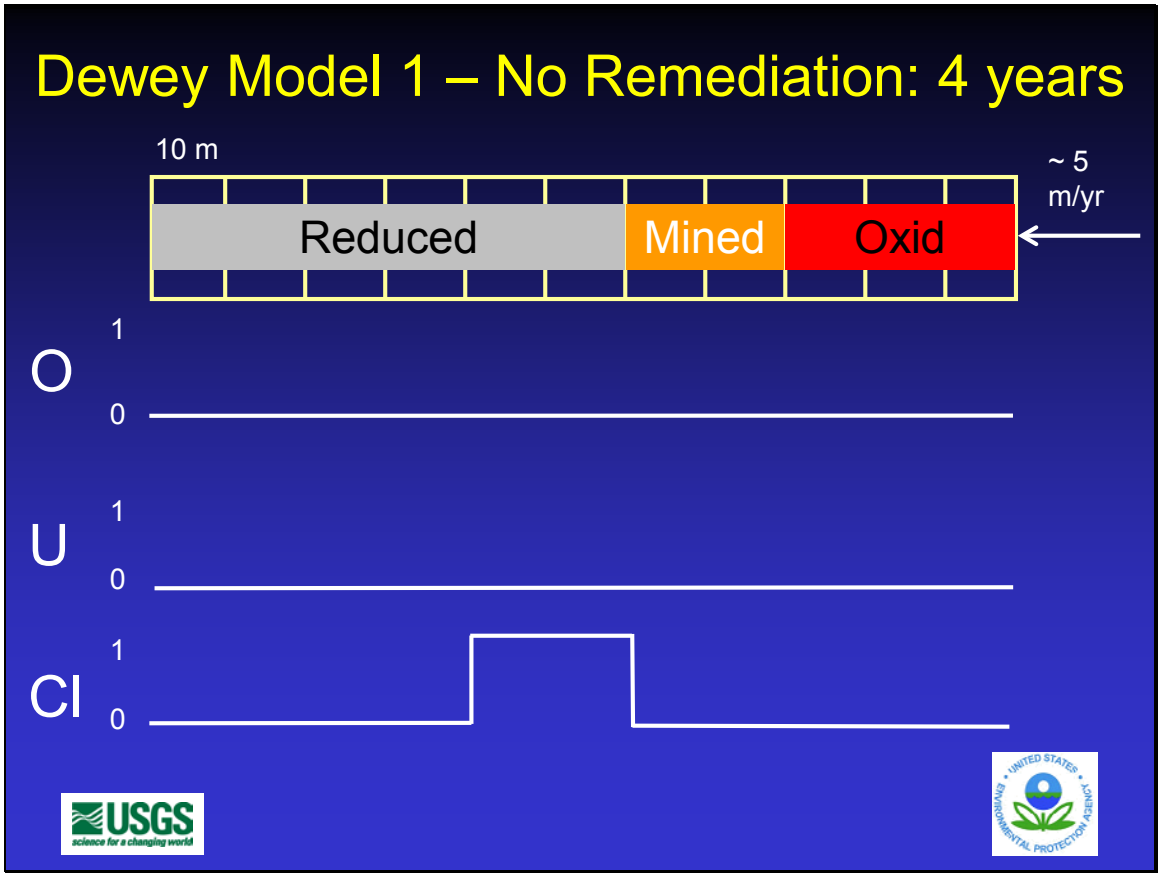
Reduced zone = enter calcite and pyrite amounts and allow uraninite, $FeCO_3$, $Fe(OH)_3$, calcite, pyrite, and gypsum equilibrium

Slide 17



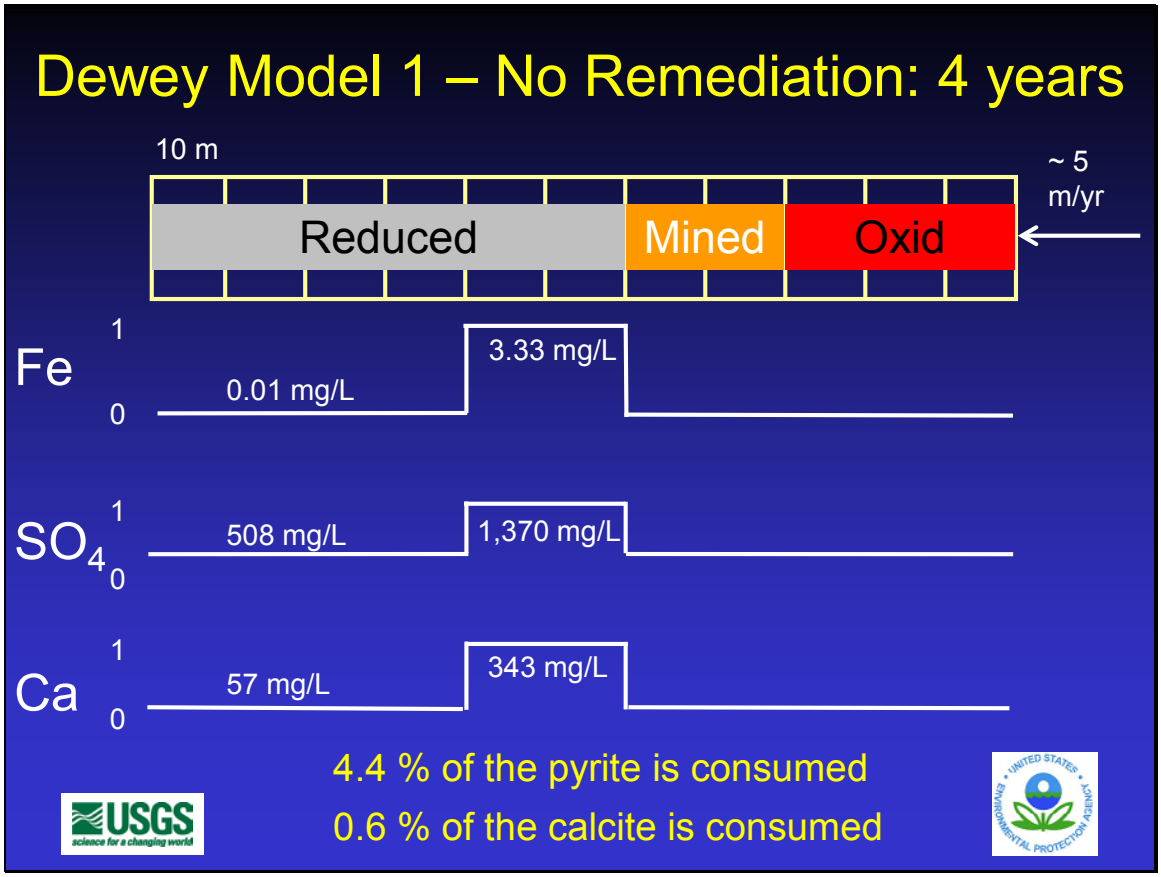
This slide shows assumed geochemistry for Dewey (model 1) at the end of mining. Next few slides will show transport without any remediation.
Exact chloride number is not used, since approximate value is unknown (depends on mining process).
Anticipated groundwater flow rate is at ~5 m/yr based on recent hydraulic gradients and hydraulic conductivities from aquifer tests.

Slide 18



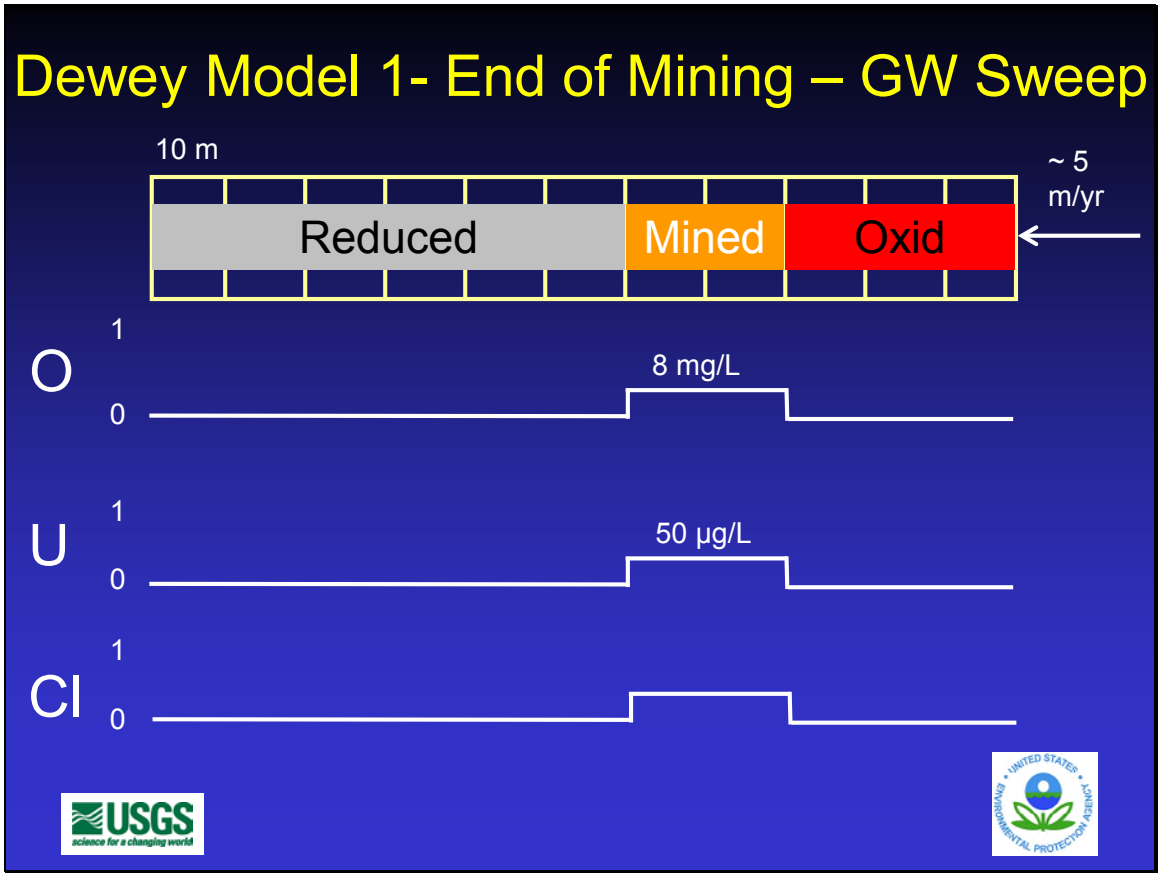
Chloride moves as a conservative tracer. Oxygen is consumed by pyrite oxidation and uranium is precipitated in the reduced zone, since all the pyrite in the first cell downgradient from the mined zone is not all consumed (remains reducing).

Slide 19



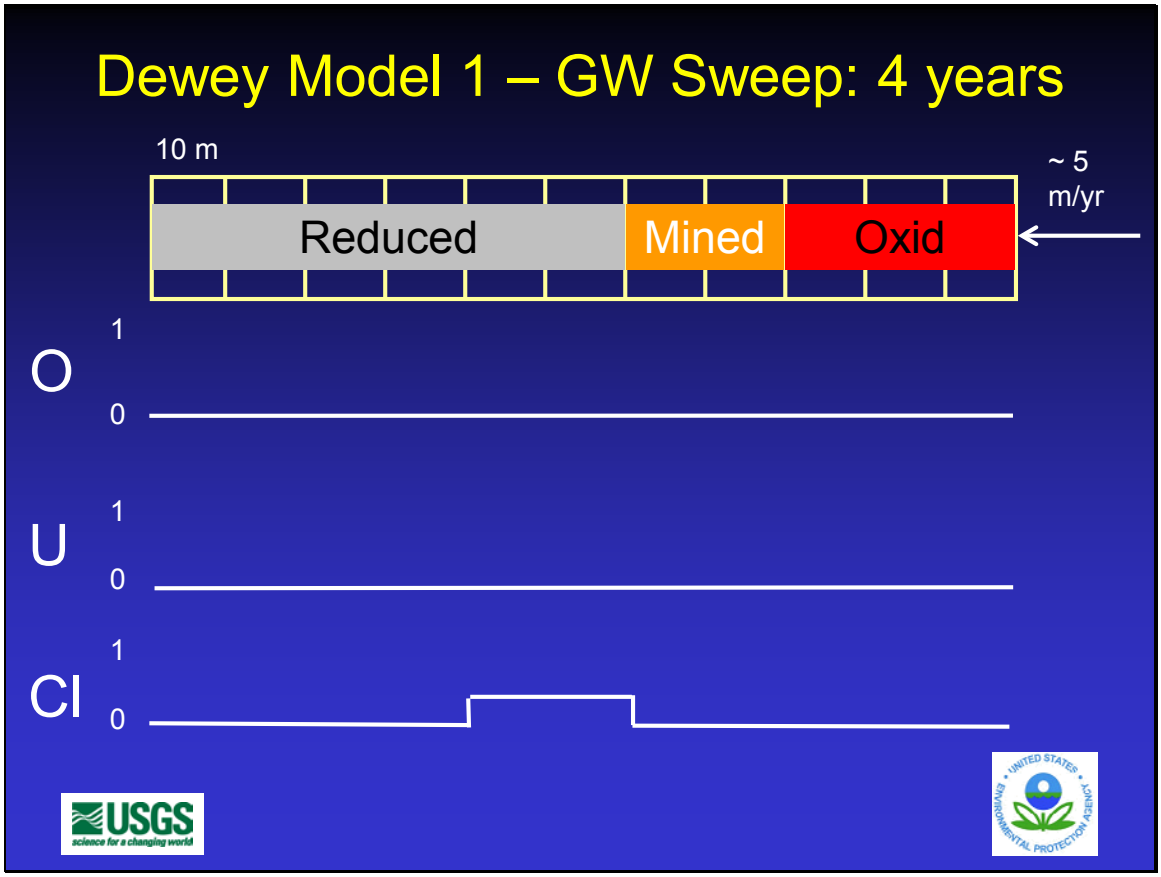
In this and all subsequent slides, three significant figures are indicated just for comparison purposes and are not meant to represent model predictions to this level of accuracy.
Geochemistry here is a result of sulfide oxidation that produces Fe and sulfate, and calcite is consumed (adds Ca and alkalinity to the groundwater) to buffer a lowering in pH from the sulfide oxidation.
For reference, current maximum values in the Burdock area are 21 mg/L for iron and 1,800 mg/L sulfate and just less than 400 mg/L for calcium.

Slide 20



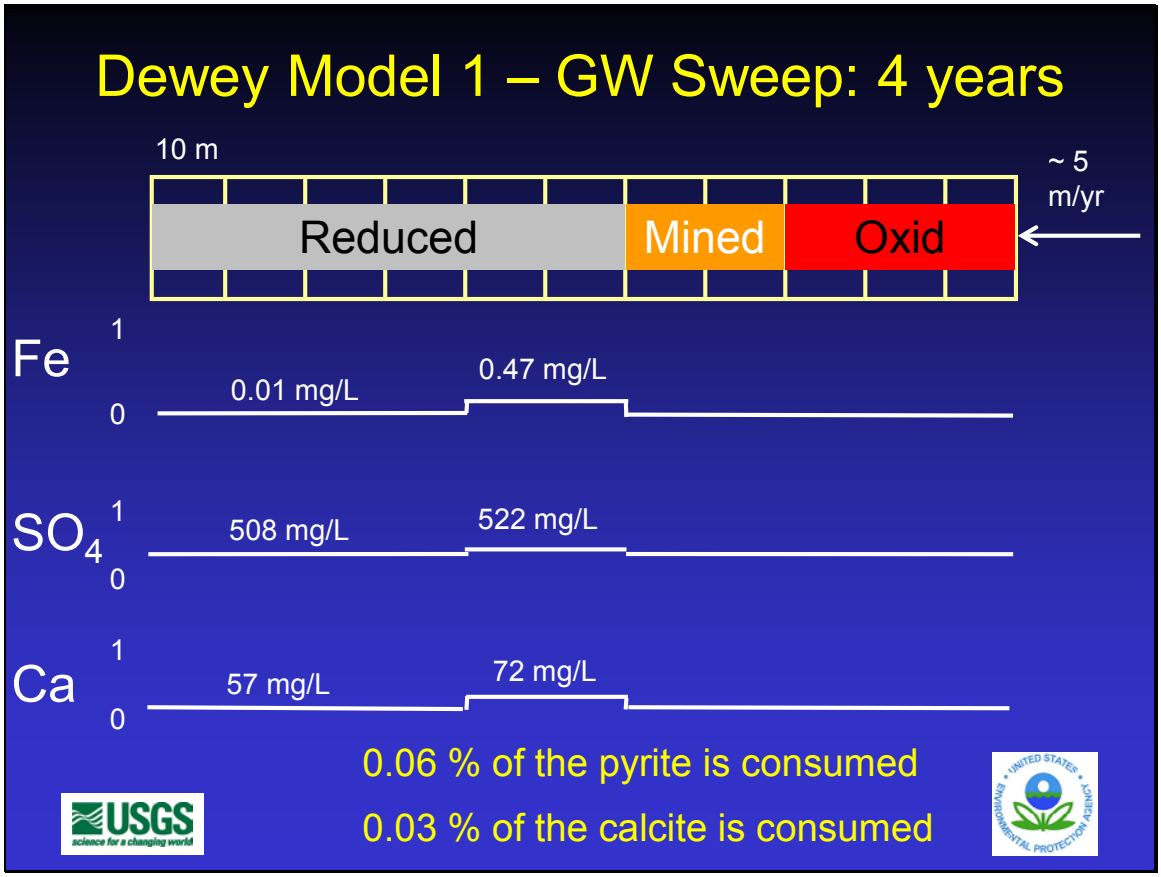
Same Dewey model 1 simulation, but with remediation by groundwater (GW) sweep.
Normalized to 1. One being no remediation.
Exact chloride number is not used, since approximate value is unknown (depends on mining process).
Anticipated groundwater flow rate is at ~5 m/yr based on recent hydraulic gradients and hydraulic conductivities from aquifer tests.

Slide 21



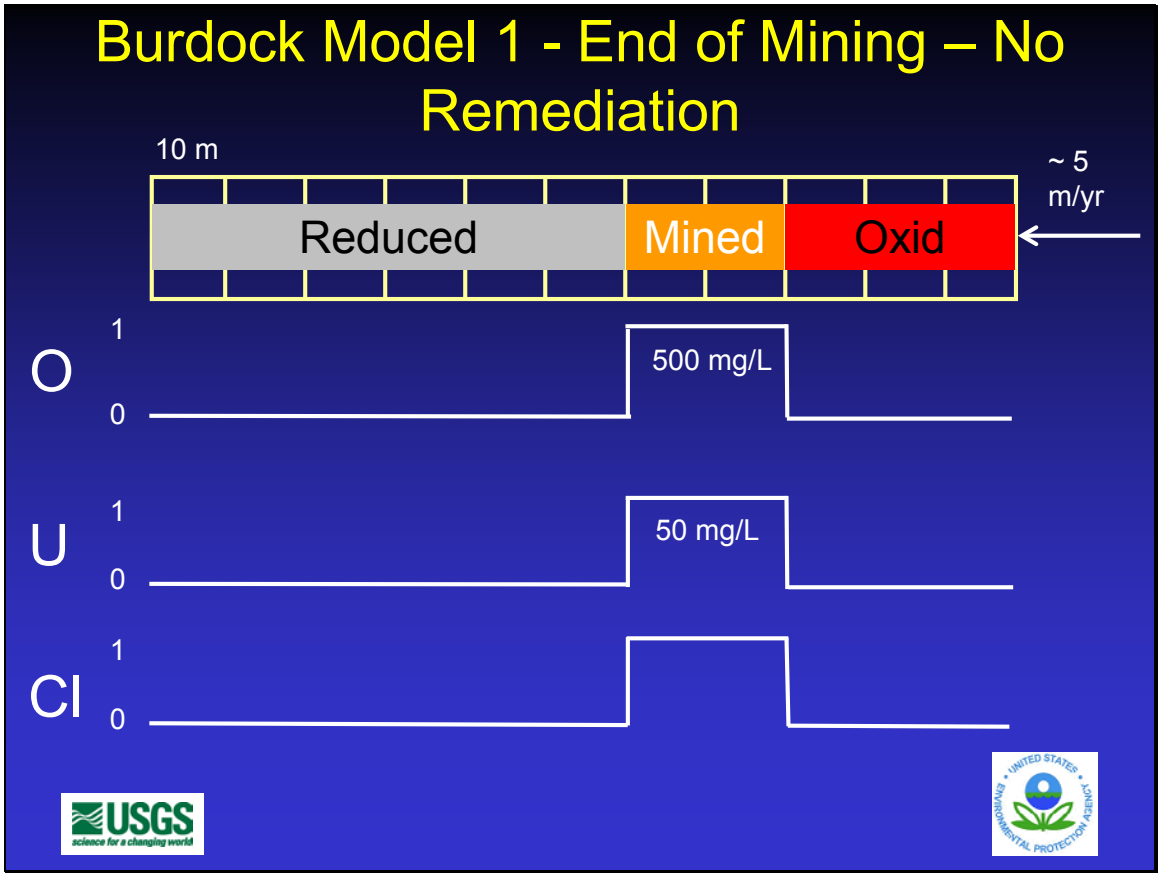
Chloride moves as a conservative tracer. Oxygen is consumed by pyrite oxidation and uranium is precipitated in the reduced zone, since all the pyrite in the first cell downgradient from the mined zone is not all consumed (remains reducing).

Slide 22



EPA secondary drinking water standard for iron in groundwater is 0.3 mg/L.
Geochemistry here is a result of sulfide oxidation that produces Fe and sulfate, and calcite is consumed (adds Ca and alkalinity to the groundwater) to buffer a lowering in pH from the sulfide oxidation.
Main difference between GW sweep and no remediation is the difference in oxygen left in solution, which then drives the sulfide oxidation reaction (GW sweep, less oxygen in solution, so less sulfide oxidation and resulting products in solution).

Slide 23



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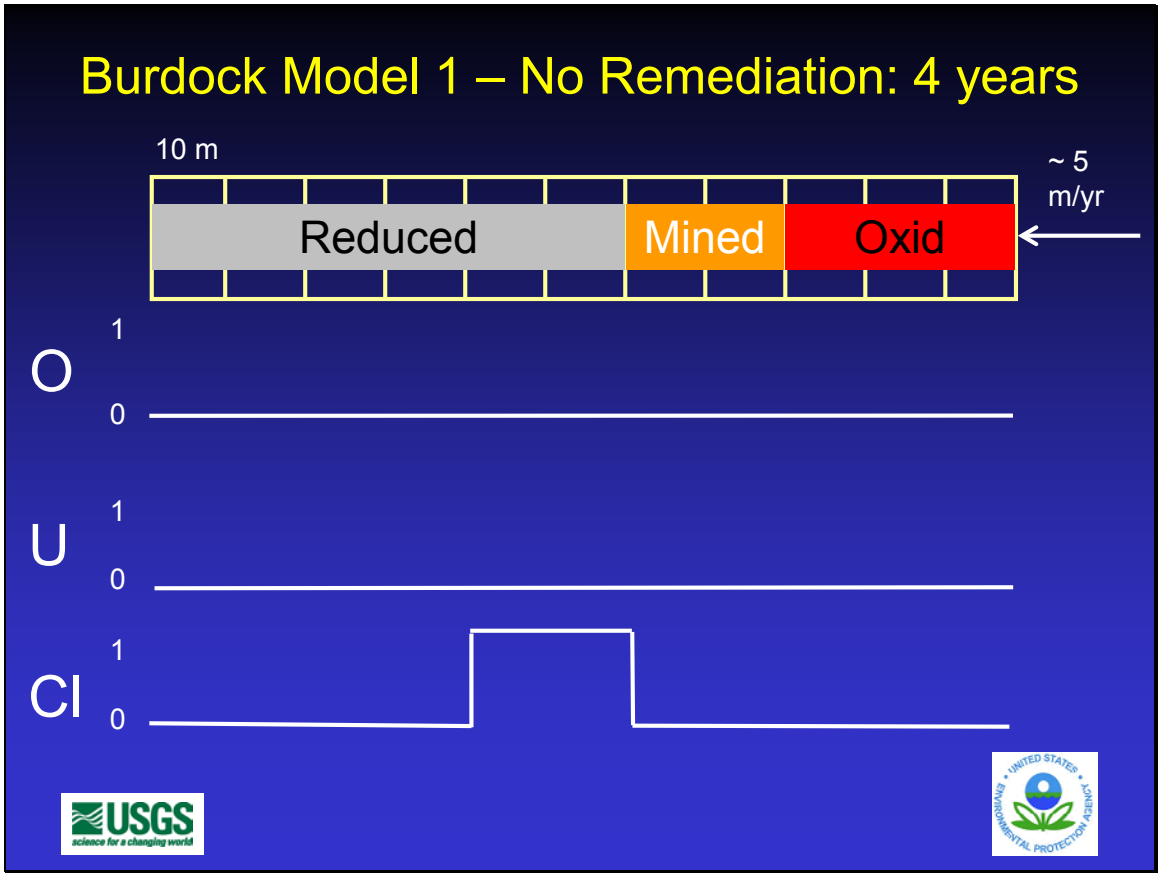
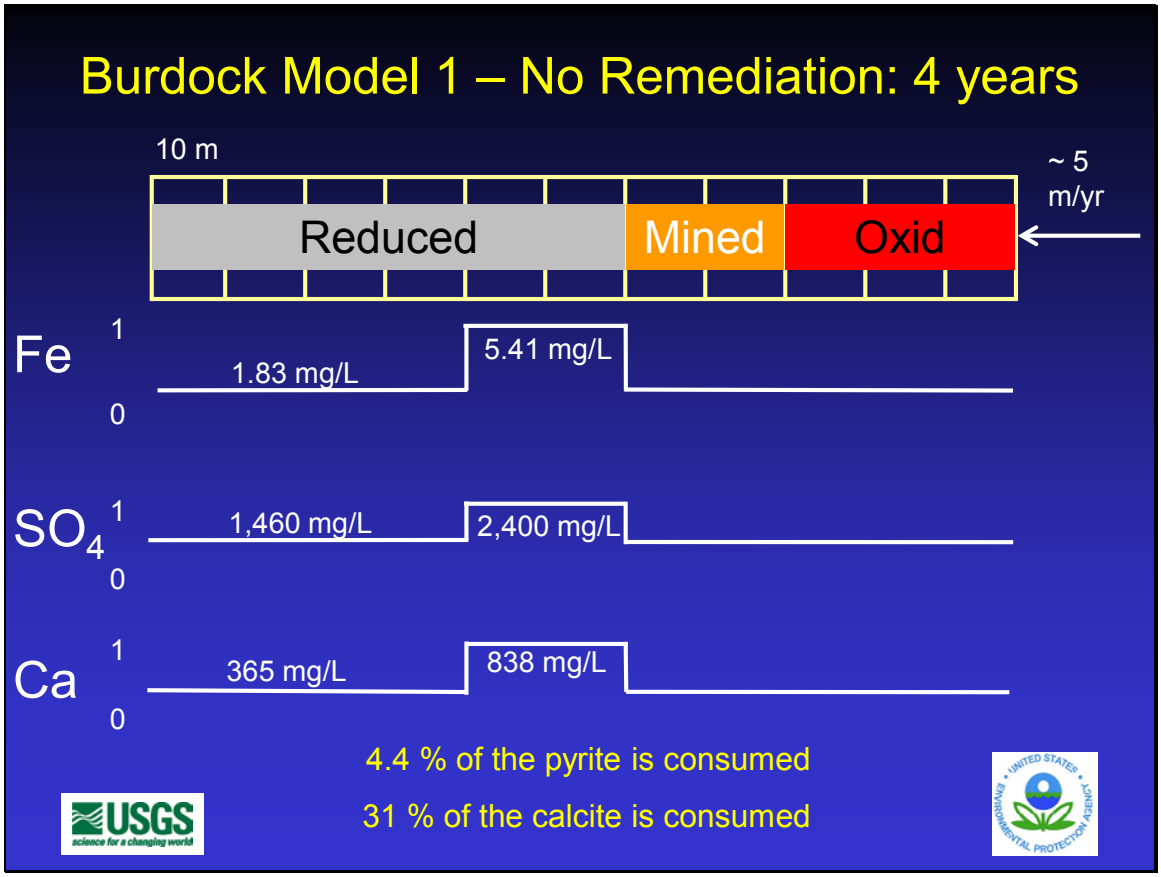
Anticipated groundwater flow rate is at ~5 m/yr based on recent hydraulic gradients and hydraulic conductivities from aquifer tests.

Slide 24



Chloride moves as a conservative tracer. Oxygen is consumed by pyrite oxidation and uranium is precipitated in the reduced zone, since all the pyrite in the first cell downgradient from the mined zone is not all consumed (remains reducing).

Slide 25



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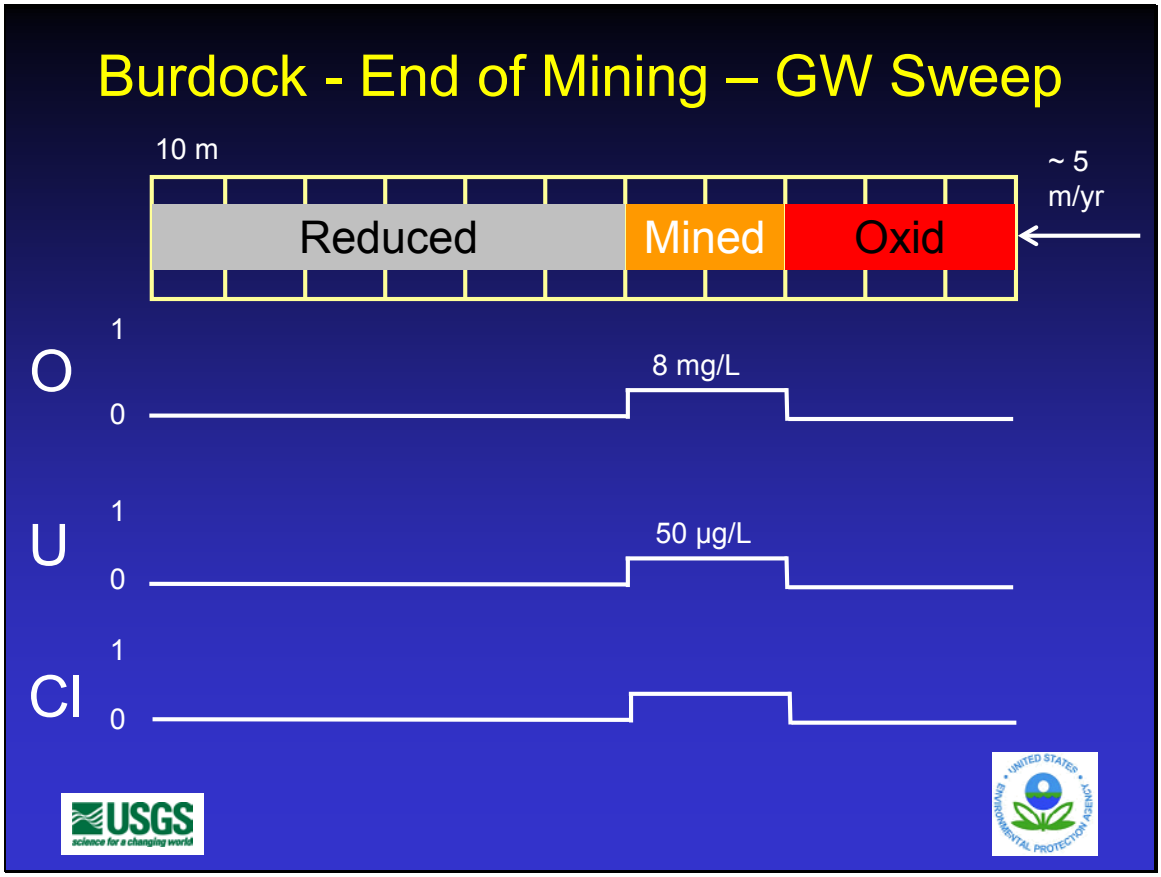
For reference, current maximum values in the Burdock area are 21 mg/L for iron and 1,800 mg/L for sulfate and just less than 400 mg/L for calcium.

Slide 26



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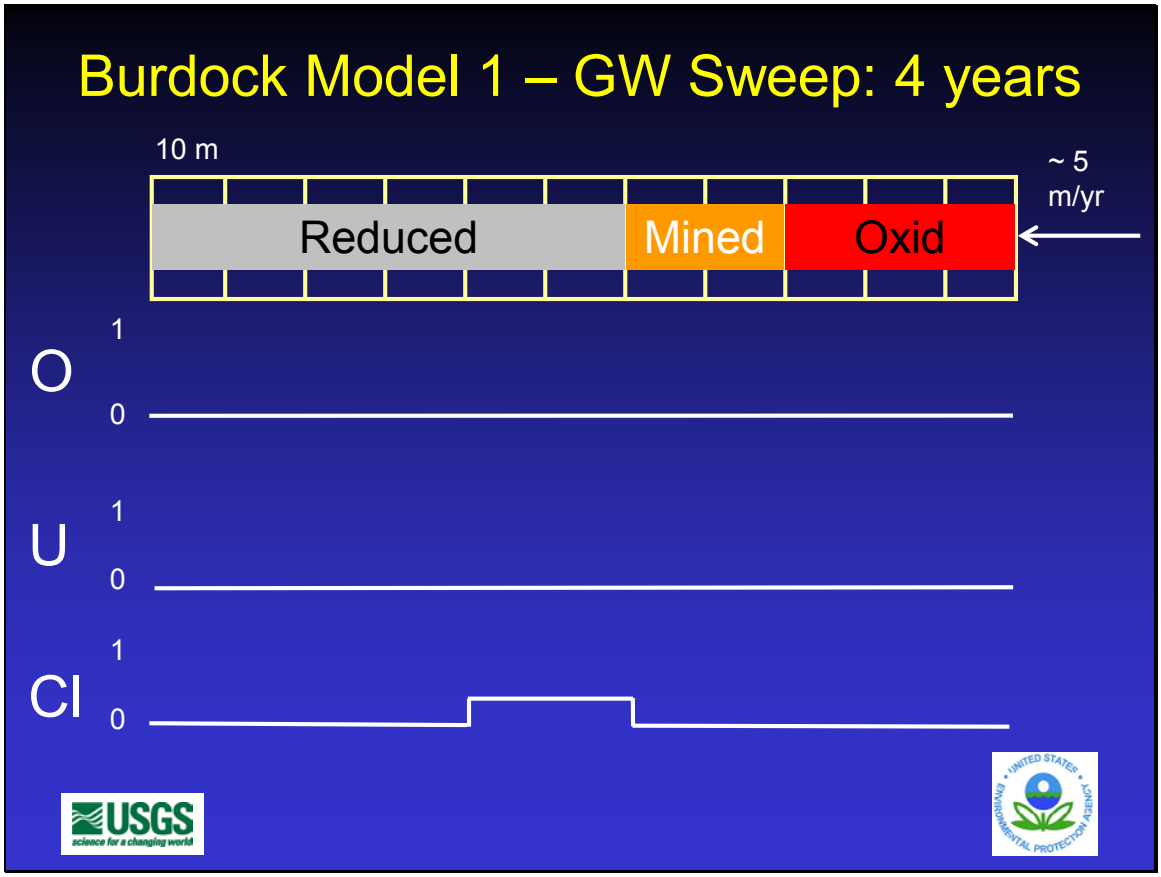
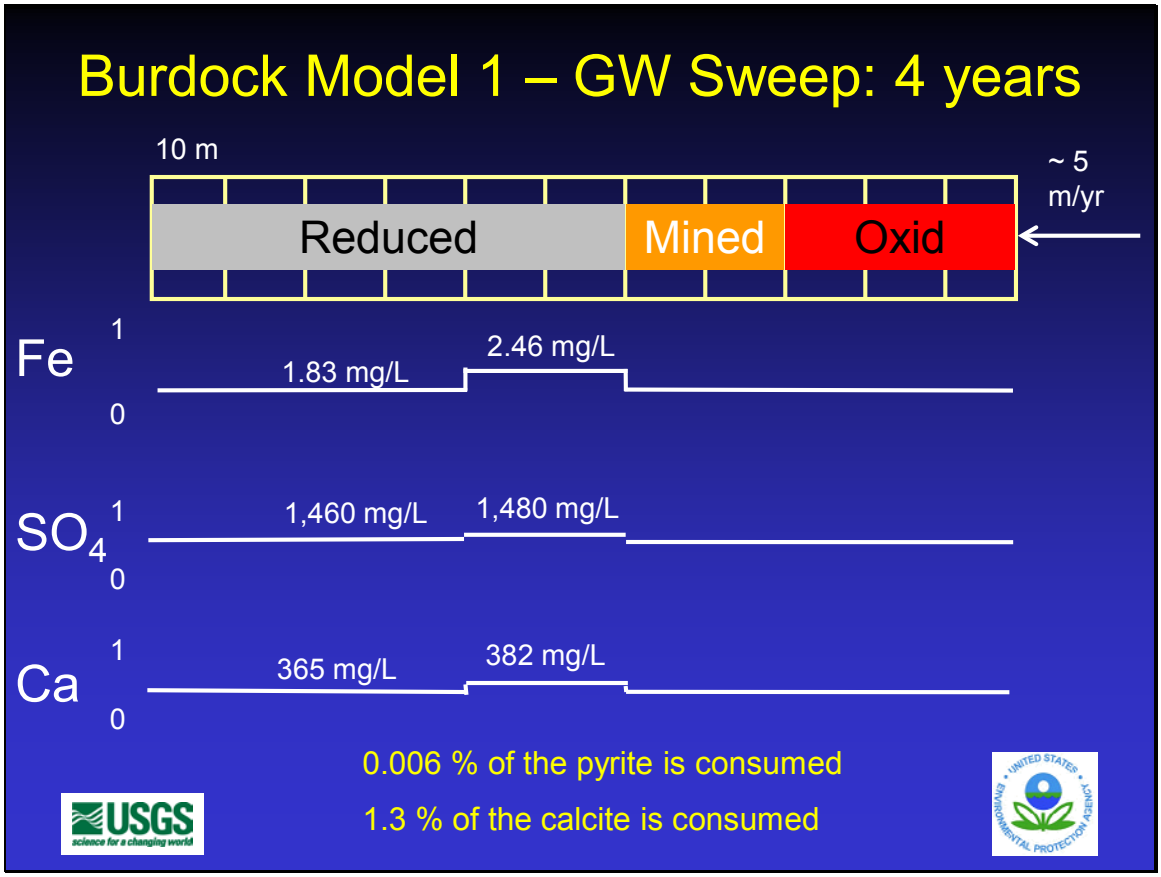
Anticipated groundwater flow rate is at ~5 m/yr based on recent hydraulic gradients and hydraulic conductivities from aquifer tests.

Slide 27



Chloride moves as a conservative tracer. Oxygen is consumed by pyrite oxidation and uranium is precipitated in the reduced zone, since all the pyrite in the first cell downgradient from the mined zone is not all consumed (remains reducing).

Slide 28



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For reference, current maximum values in the Burdock area are 21 mg/L for iron and 1,800 mg/L sulfate and just less than 400 mg/L for calcium.
Main difference between GW sweep and no remediation is the difference in oxygen left in solution, which then drives the sulfide oxidation reaction (GW sweep, less oxygen in solution, so less sulfide oxidation and resulting products in solution).

Slide 29

"Reducing Capacity" is Key
Pyrite vs. Oxygen

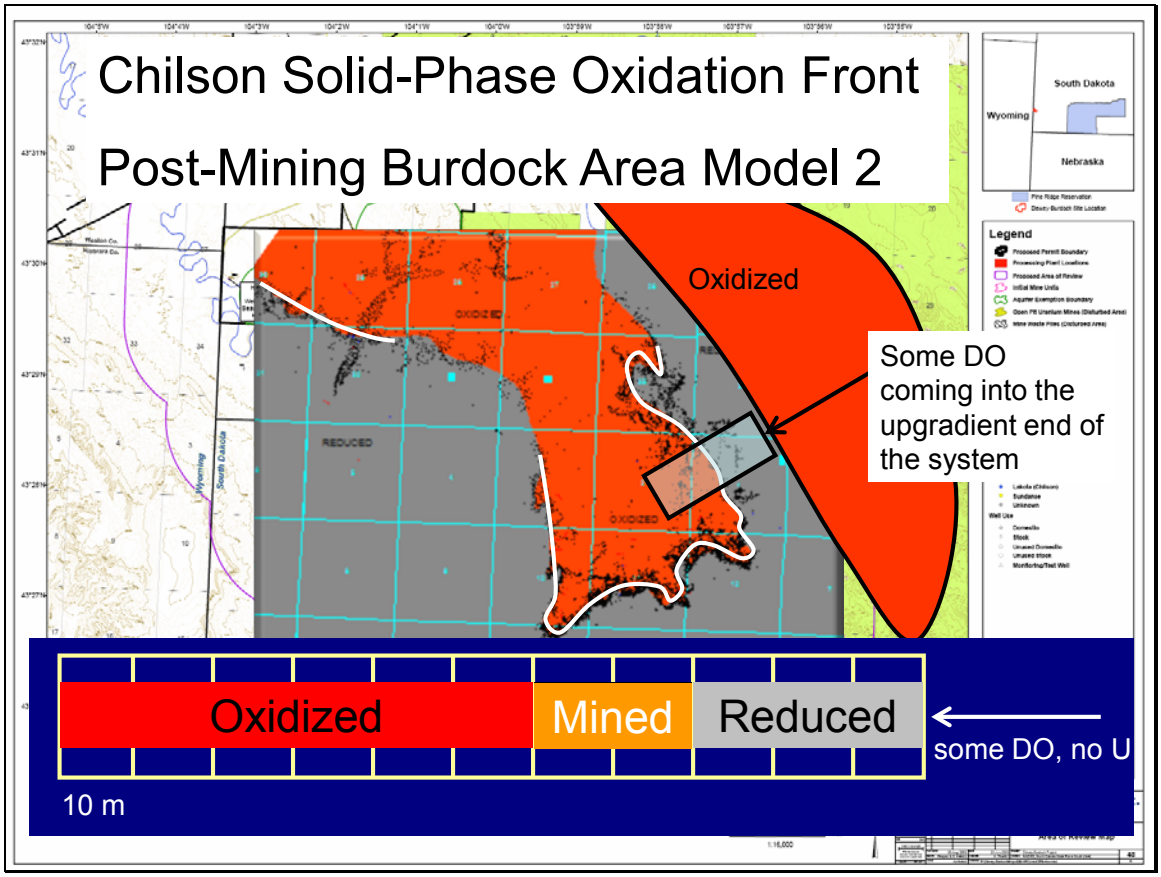
Pyrite to Iron hydroxide

$$2FeS_2 + 7.5O_2 + 7H_2O = 2Fe(OH)_3 + 4SO_4^{2-} + 8H^+$$

DO (mg/L)	Pyrite (wt. %)	Pore Volumes for complete oxidation
0	0.5	No reaction
8	0.5	1,880
500	0.5	30
8	0.02	125

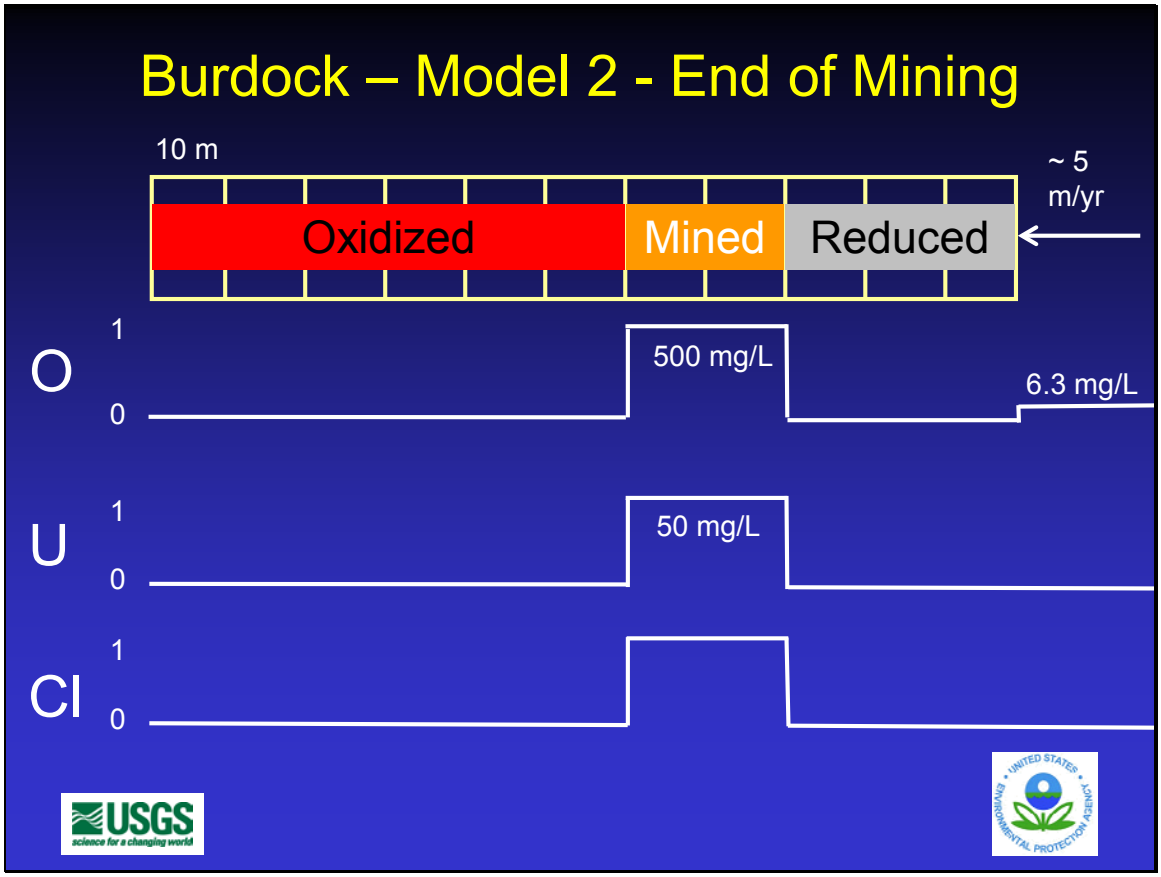
Long term pyrite consumption will depend on oxygen content and the size of the mining zone

Slide 30



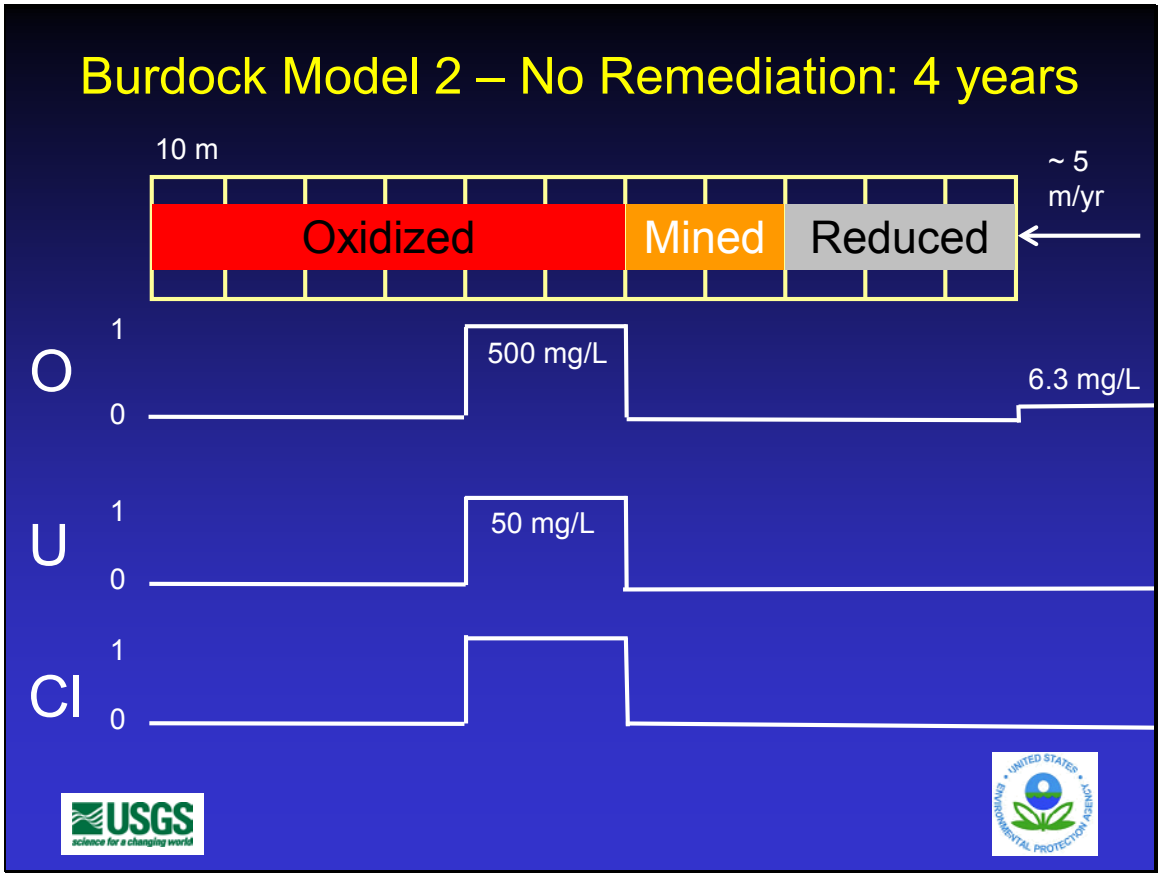
This is the second model type, where the oxidized zone is downgradient from the mined or recovery zone. Reduced zone is upgradient.
Arrow indicates approximate current groundwater flow direction.
Large oxidized zone on the east side was added as a reasonable interpretation that the outcrop zone of the Chilson is oxidized (no core is available in this area).

Slide 31



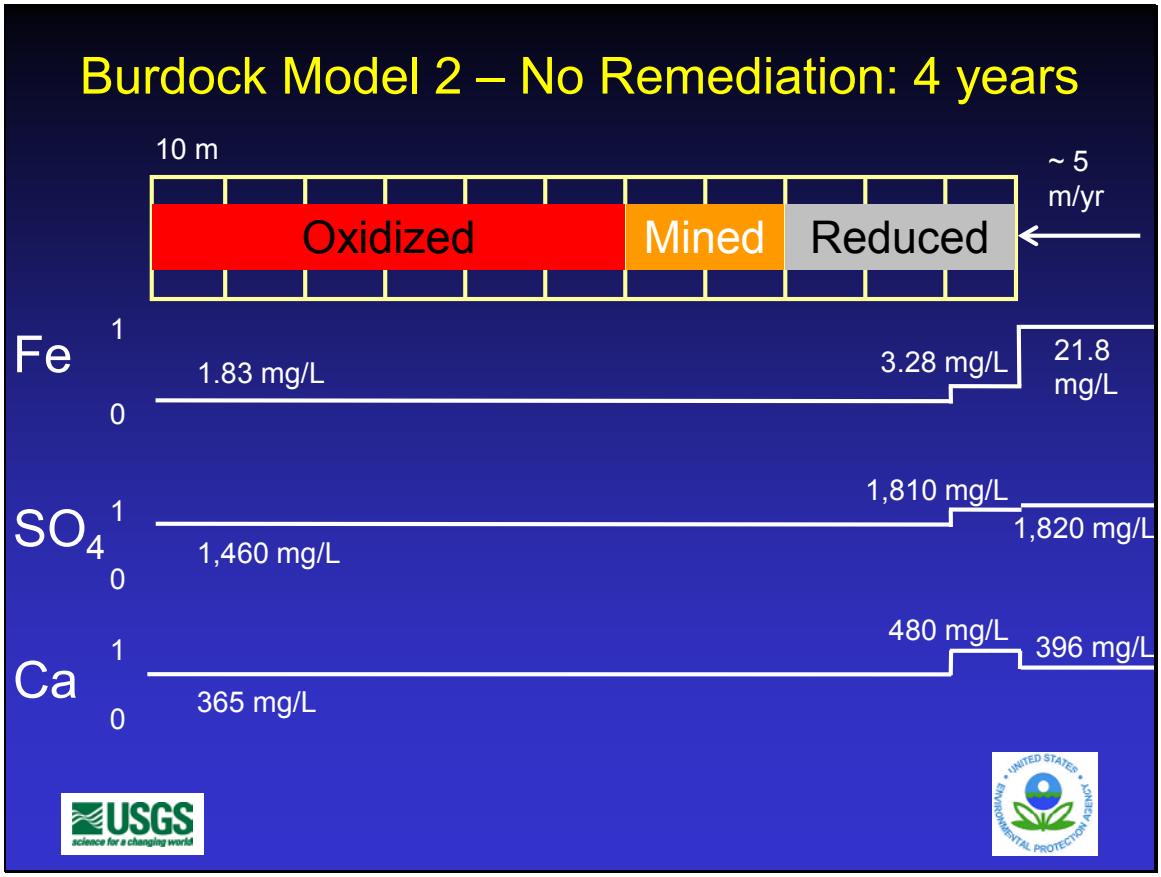
This slide shows assumed geochemistry for Burdock (model 2) at the end of mining. Next few slides will show transport without any remediation.
Note addition of incoming water with oxygen (but no U or Cl) at the first cell. This is "background" groundwater represented by well 3026.

Slide 32



Chloride, oxygen, and uranium move conservatively, as simulation does not have any reactions to remove any of these elements.
<u>In reality, sorption of uranium to iron hydroxides is likely, but was not simulated.</u>

Slide 33



Incoming water here has the highest Fe, sulfate, and Ca in the area.
Oxidation of pyrite controls the reactions at the first cell due to incoming or “background” groundwater.
Downgradient from the mined zone, no reactions occur to change the Fe, sulfate, and Ca concentrations, due to lack of sulfide oxidation.
<u>Again, in reality, sorption of uranium to iron hydroxides is likely, but was not simulated.</u>

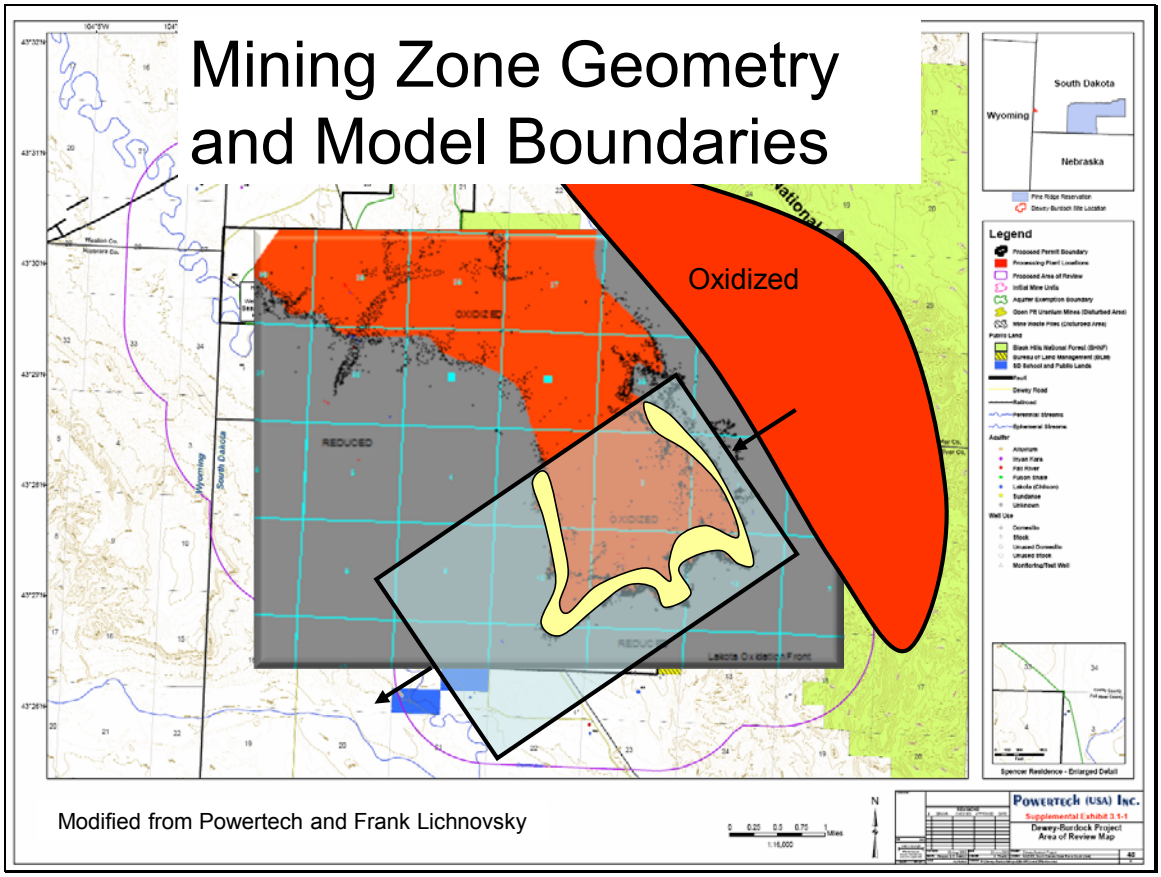
Slide 34

2D Reactive Transport using PHAST

- Focus on lower Chilson in Burdock area
- Sensitivity analyses
  - Remove reducing capacity (pyrite)
  - Remove buffering capacity (calcite)
- Simulate long-term transport, post-mining

PHAST is a computer program for simulating groundwater flow, solute transport, and multicomponent geochemical reactions.
PHAST couples groundwater flow and geochemistry.

Slide 35



Reminder of map with oxidation and reduction zones.
Red = oxidized zones
Gray = reducing zones.
Box = simulation zone
Yellow = proposed mining/recovery zone (in the Chilson Member).

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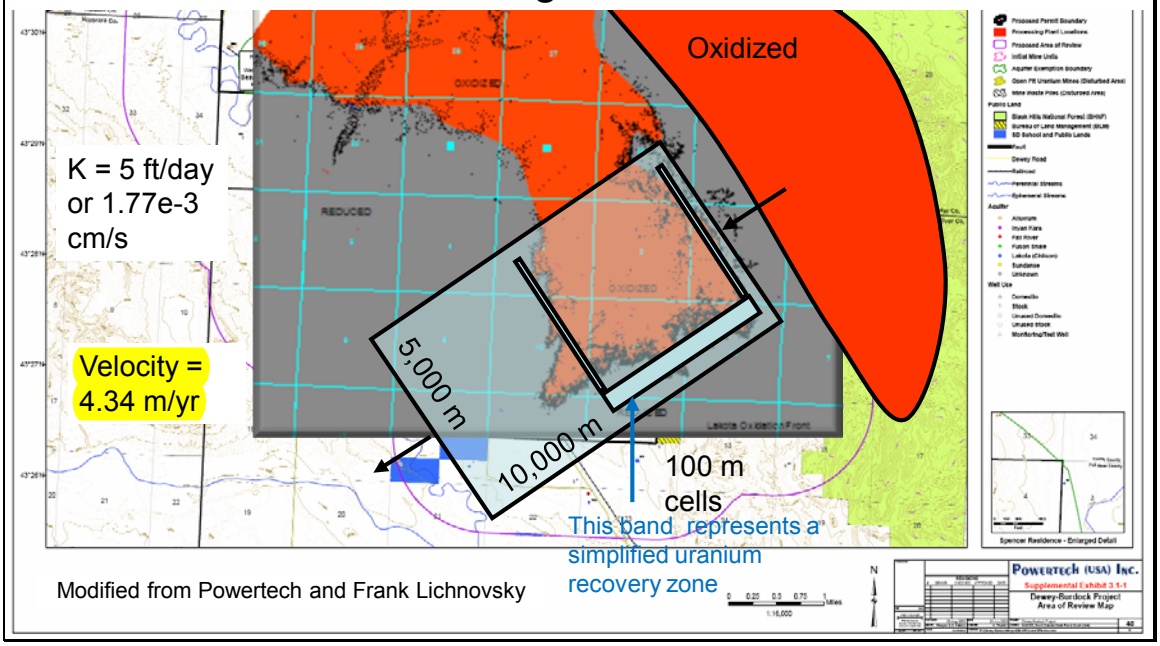
Reducing zones, pyrite = 0.5 wt. % (one zone no pyrite)

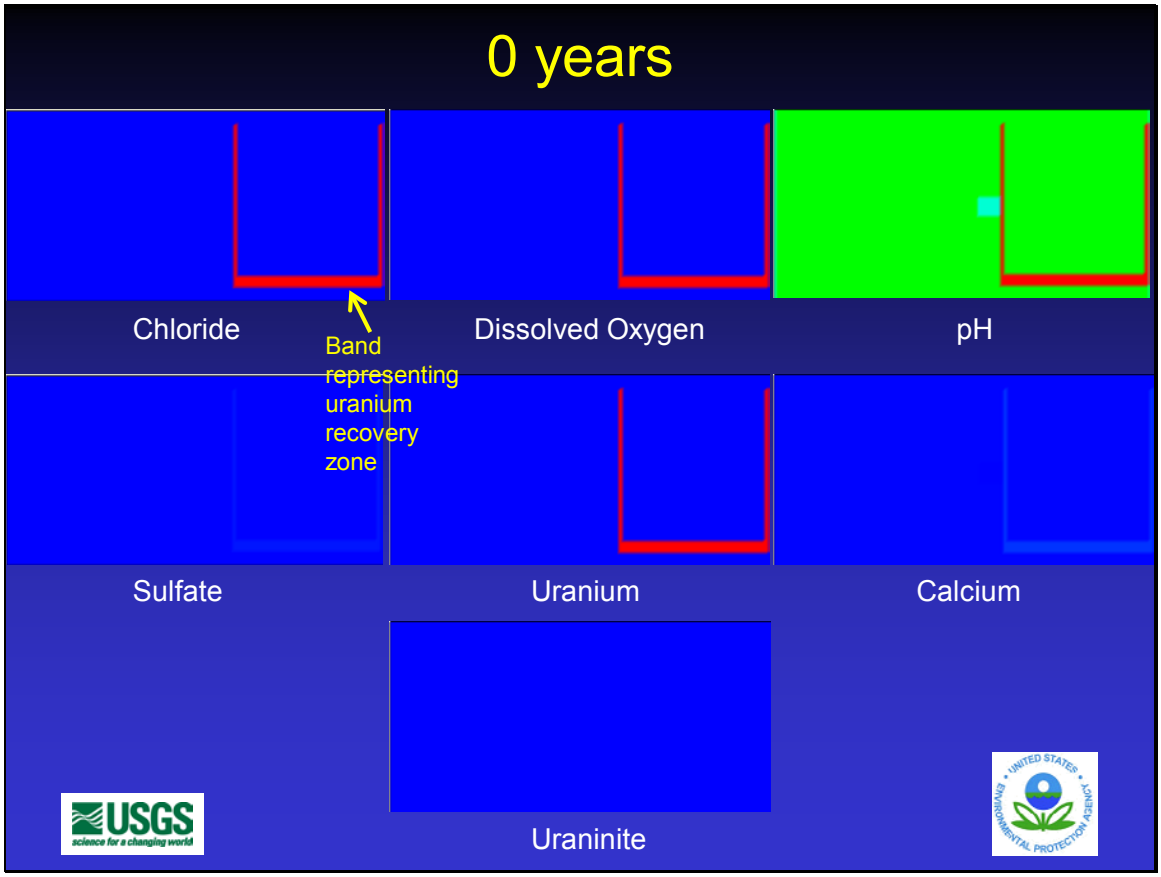
Calcite = 0.15 wt. % (one zone no calcite)

Oxidized zones and mining zones, no reactions



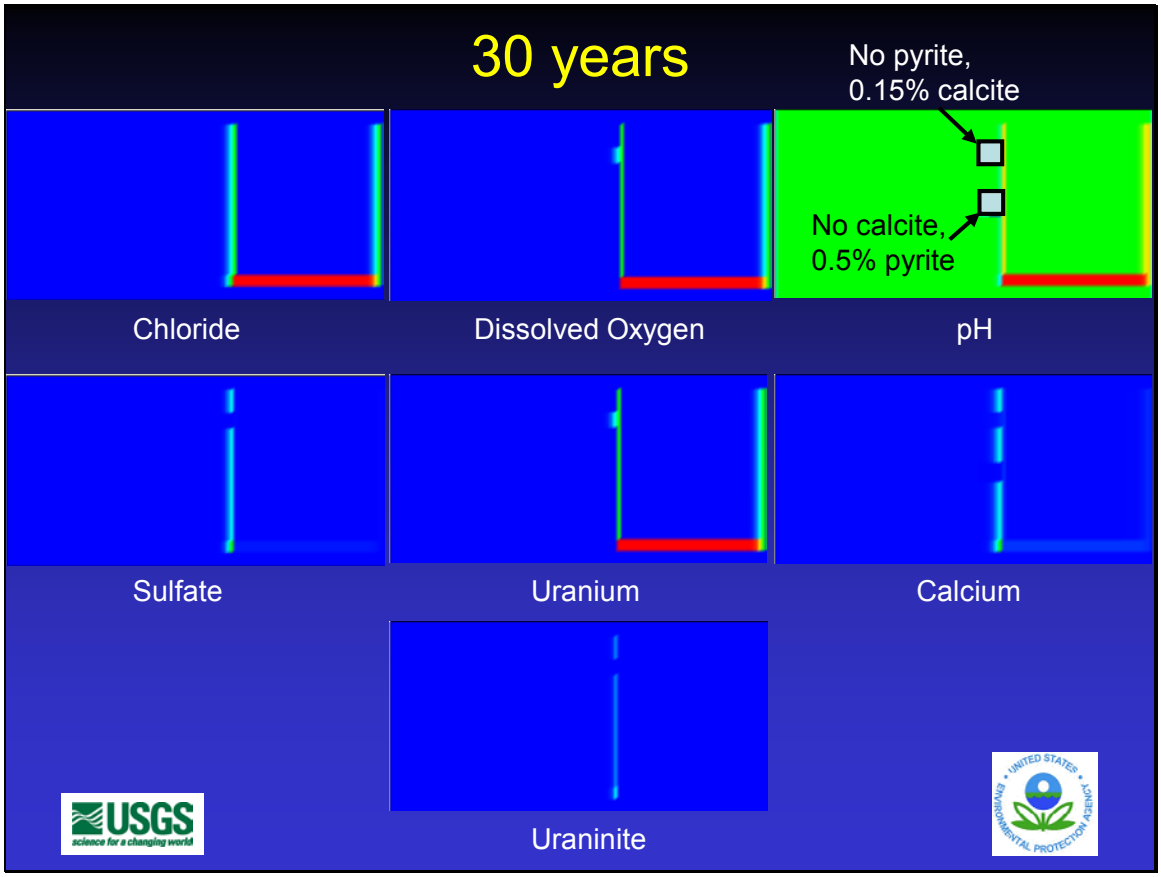
In general, the reducing zone (gray) contains approximately 0.5 wt. % pyrite and calcite at 0.15 wt. % (based on a few cores). The simulated oxidized zones contain no pyrite and the same amount of calcite (0.15 wt. %).
In addition, the modeling looks at downgradient effects in artificially added zones (sensitivity analyses) where (1) calcite is present but no pyrite is present and (2) pyrite is present but no calcite is present.
U shape in the simulation zone is a simplified uranium recovery zone, which highlights shape effects in subsequent slides.

Slide 37



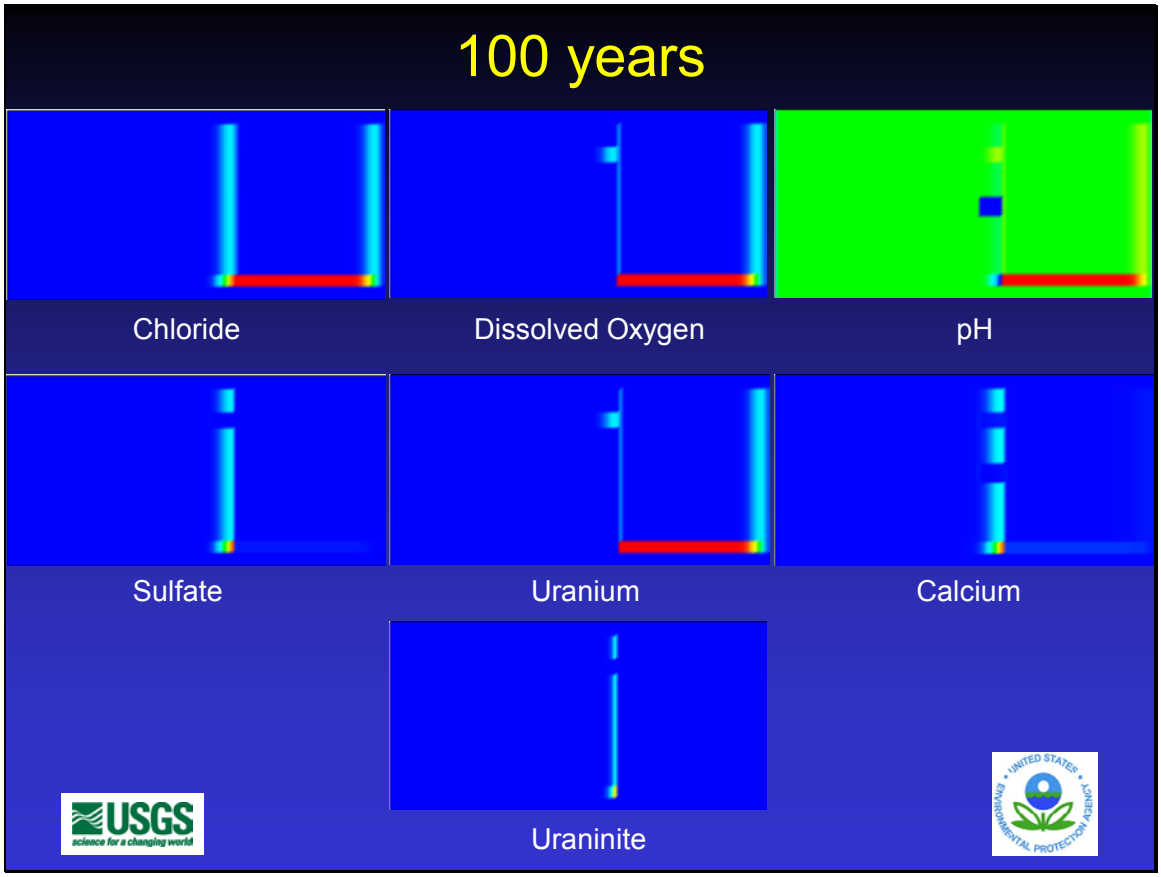
These are worst-case scenario simulations, where no restoration has occurred (still have Cl, DO, and U in solution).
Red U-shape indicates mining/recovery zone. Red = higher concentration. Blue = lower concentration.
pH difference is very minimal and color is a result of contouring.

Slide 38

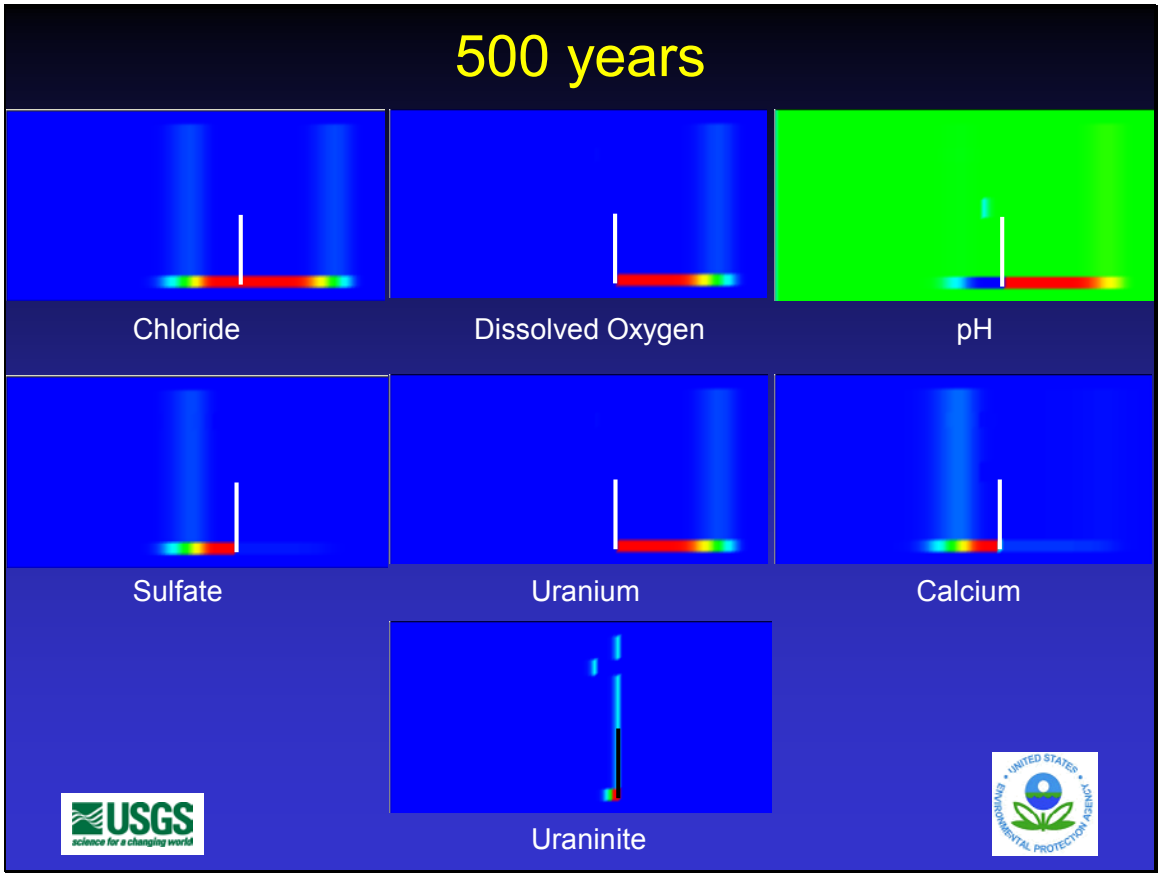


Note artificially added zone to highlight reactions.

Slide 39


100 years
Chloride
Dissolved Oxygen
pH
Sulfate
Uranium
Calcium
Uraninite
USGS
science for a changing world
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Slide 40



Lines are added to indicate the end of the U-shaped mining zone, for reference. Chloride moves conservatively, but does undergo numerical dispersion.
Reactions are the same as seen in the 1D simulations. Leftover oxygen drives sulfide oxidation, which adds Fe (not shown) and sulfate to the groundwater. Sulfide oxidation lowers the pH, which is buffered by calcite dissolution (puts Ca and alkalinity into solution). Pyrite oxidation consumes oxygen, but generally enough pyrite is present in the reducing zones to allow for uranium precipitation. Note that the artificial zone with no pyrite shows that uraninite is formed only where pyrite is present. In addition, the bottom of the U-shape creates an area where dissolved oxygen continues to produce sulfide oxidation compared to the upper limbs, where the oxygen in the recovery zone is fully consumed.

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Take Home Points

- Pyrite is potentially the key to removing uranium (modeled reducing conditions)
- Calcite is potentially the key to buffering acidity
- With these minerals present, get an iron, sulfate, calcium, carbonate: “plume”
  - Not toxic
  - Already relatively high concentrations in some locations
  - What levels are acceptable?
- Increase in these elements depends on the amount of oxygen left in the mining zone

Last point is the focus for restoration efforts where reductants are added in order to re-establish reducing capacities and consume any leftover oxygen.

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Other Things to Consider

- Other reductants (organic carbon)
- Surface complexation (uranium sorption on iron hydroxides)
- Dispersion (scale dependent dilution)
- This presentation models worst-case scenarios

Note that no dispersion was added to any of the simulations in this presentation and all dispersion seen was purely numerical.

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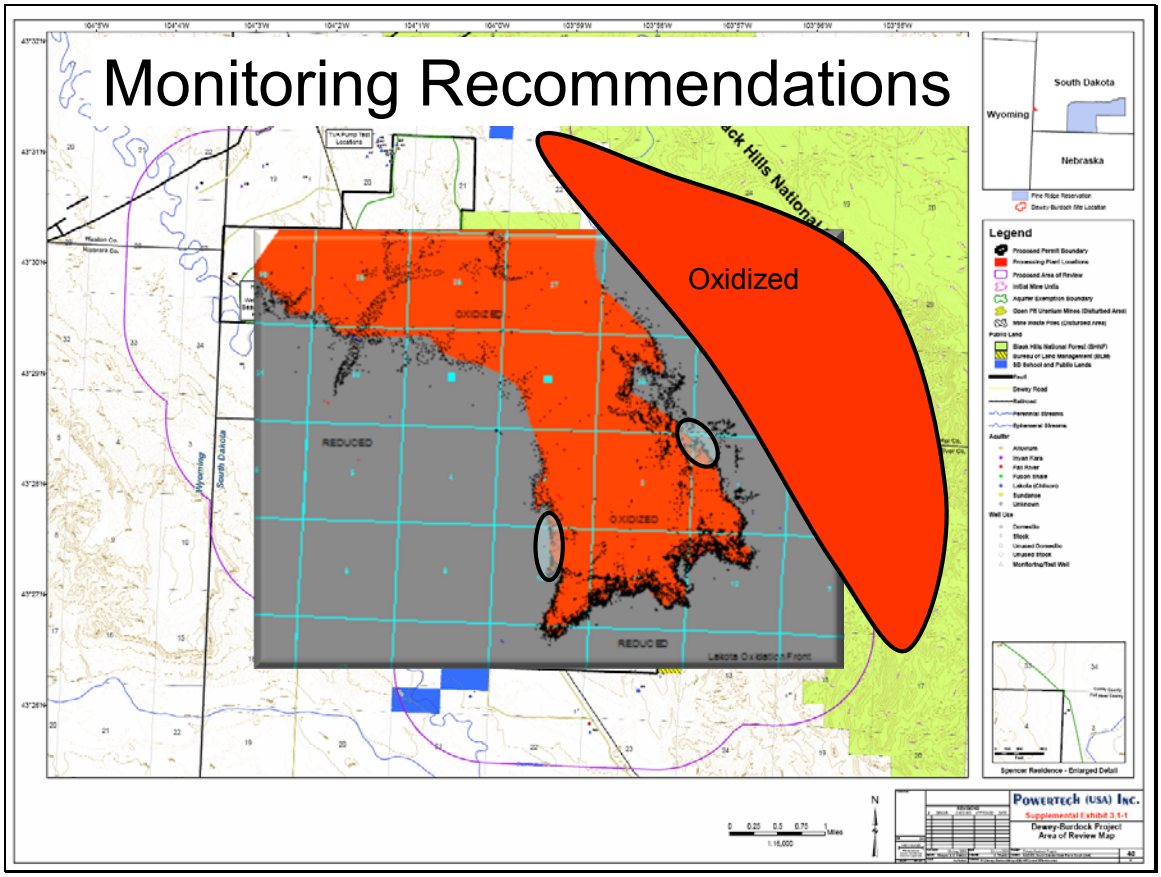
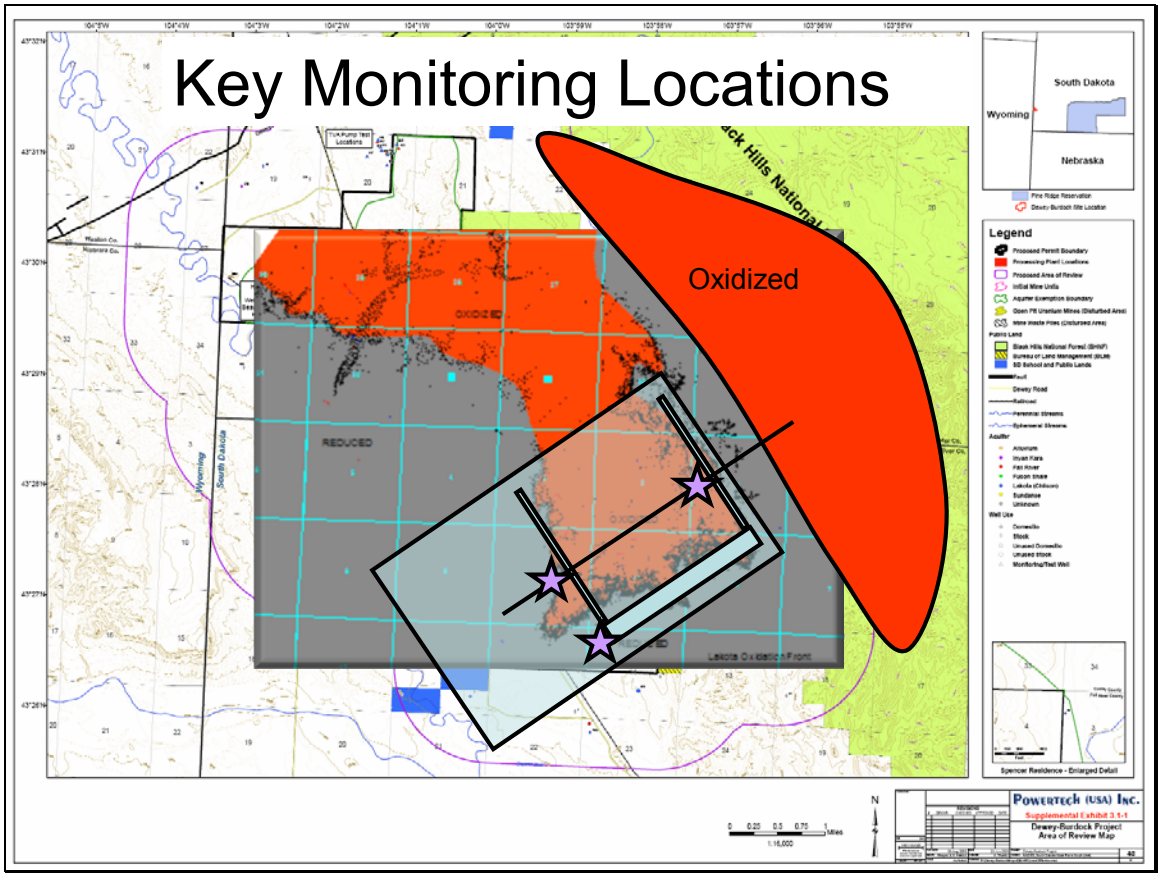


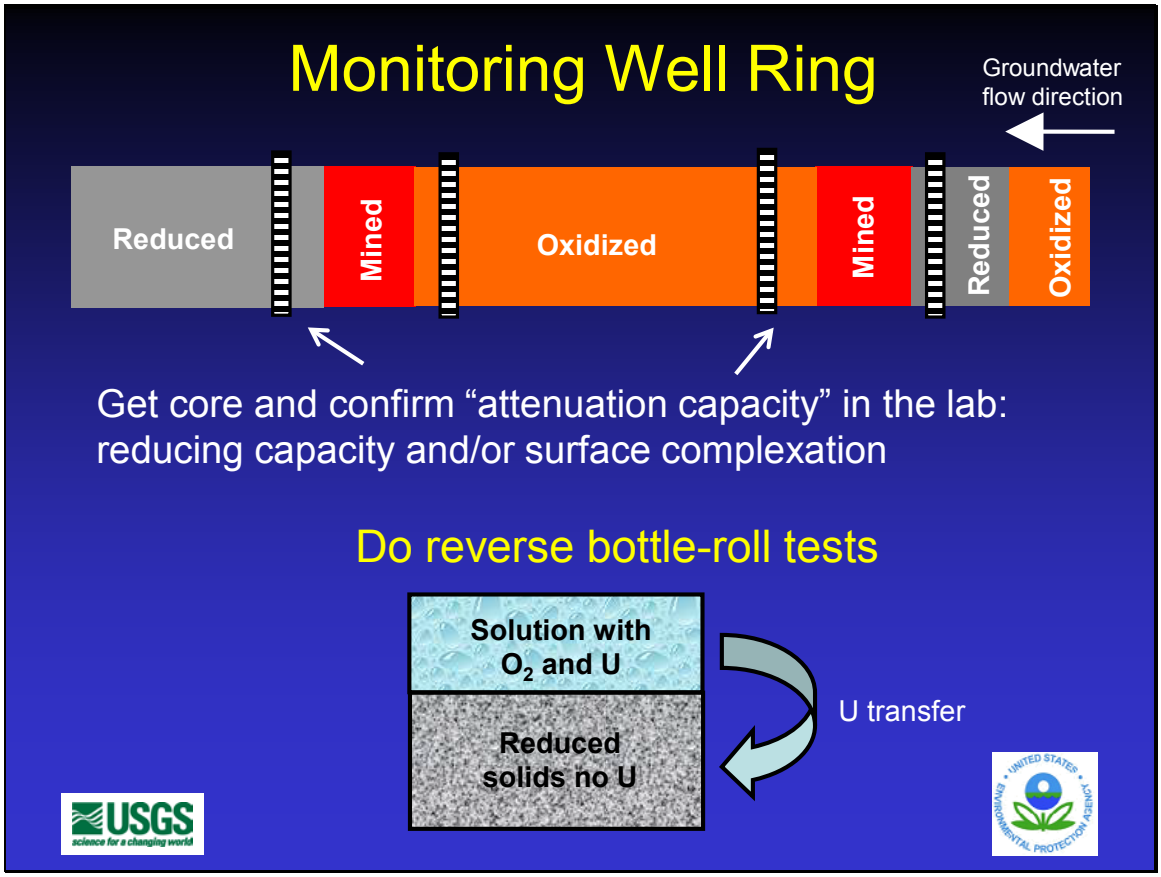
Circles indicate possible monitoring well rings.

Slide 44



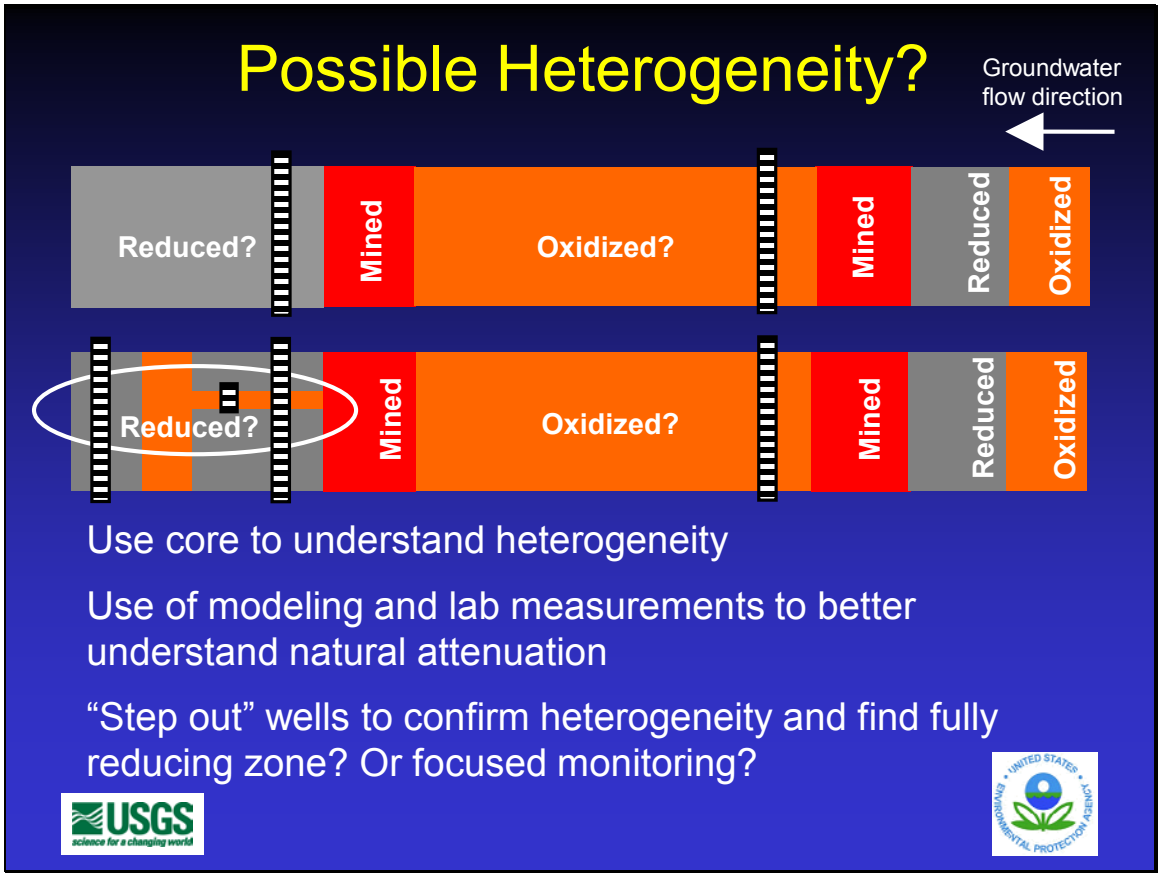
Stars indicate important monitoring locations.
Most important being the “bottom of the U-shape” where the combination of groundwater flow aligned with the recovery zone creates one location where all the sulfide oxidation reaction occurs.

Slide 45



For mining zones, companies often do a batch test with ore and lixiviant in a bottle that is constantly rotated to determine uranium recovery (bottle-roll tests).
A reverse bottle-roll test would take reduced material with no uranium ore and add uranium-rich water to see how much uranium would be left in solution after mixing for a certain period of time.
This type of a test would help quantify the natural attenuation capacity of the aquifer material (reduction/precipitation reaction for reduced material and sorption reactions for oxidized material).

Slide 46



If natural attenuation capacity in oxidized material is much less than the reduced zone material, understanding heterogeneity and possible "stringers" of oxidized material becomes important to monitor appropriately.

Slide 47

Conclusions

- Reactive transport modeling provides a predictive tool that can assess downgradient geochemical changes post mining
- Limited core data helps quantify pyrite with an "assumed" reducing capacity
- Still need a better understanding of pyrite distribution (could be part of the monitoring well installation – get core)
- Need lab measurements to measure pyrite reducing capacity (next step)

Measurements of uranium sorption capacity of oxidized solid-phase material are also important.

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Core in photo shows the abrupt contrast between reducing material on the left (black and contains pyrite) compared to the oxidizing material on the right (pink, no pyrite).