EPA REGION 8'S RESPONSE TO PETITION FOR REVIEW

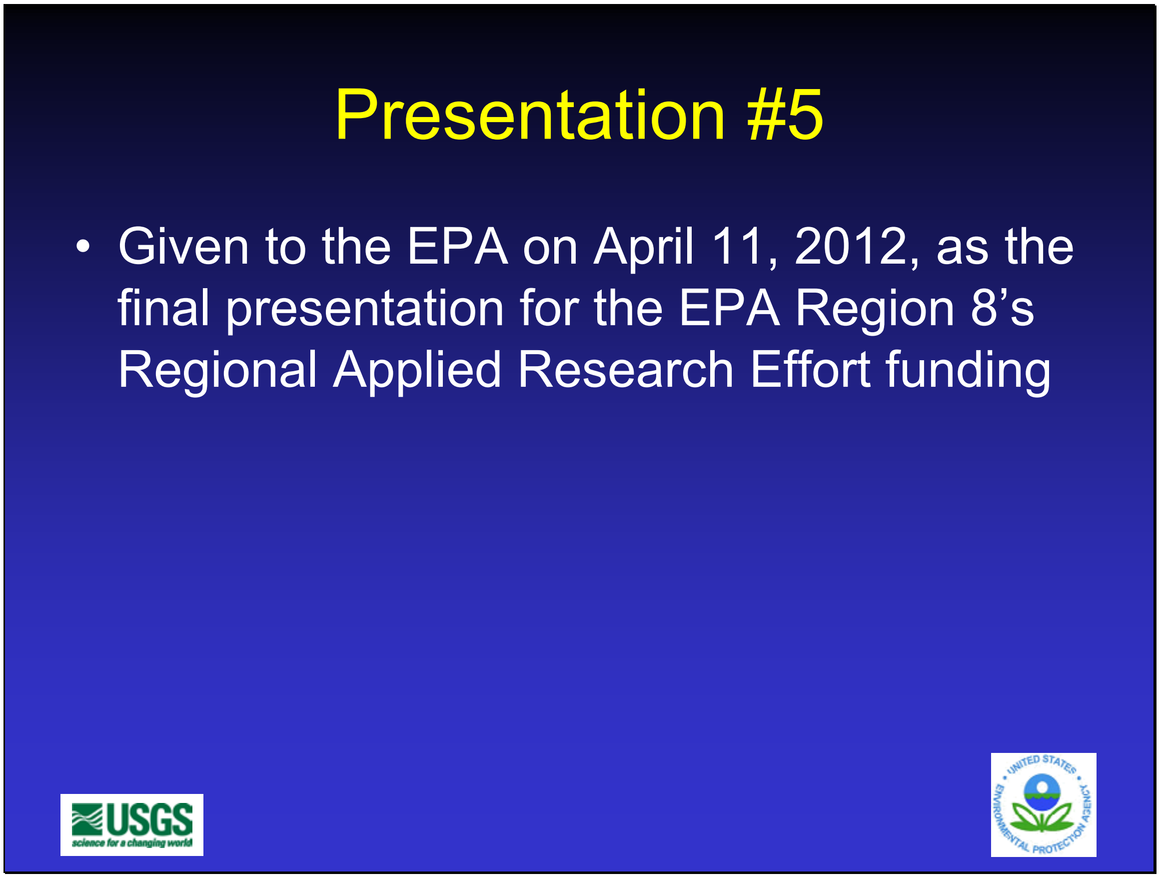
ATTACHMENT S

Johnson, 2012,
Using groundwater and solid-phase geochemistry for reactive transport modeling at the proposed Dewey Burdock uranium in situ recovery site, Edgemont, South Dakota, Final Regional Applied Research Effort Presentation to EPA;

Johnson, 2012,
Geochemical Data from Groundwater at the Proposed Dewey Burdock Uranium In-Situ Recovery Mine, Edgemont, South Dakota, USGS OF12-1070

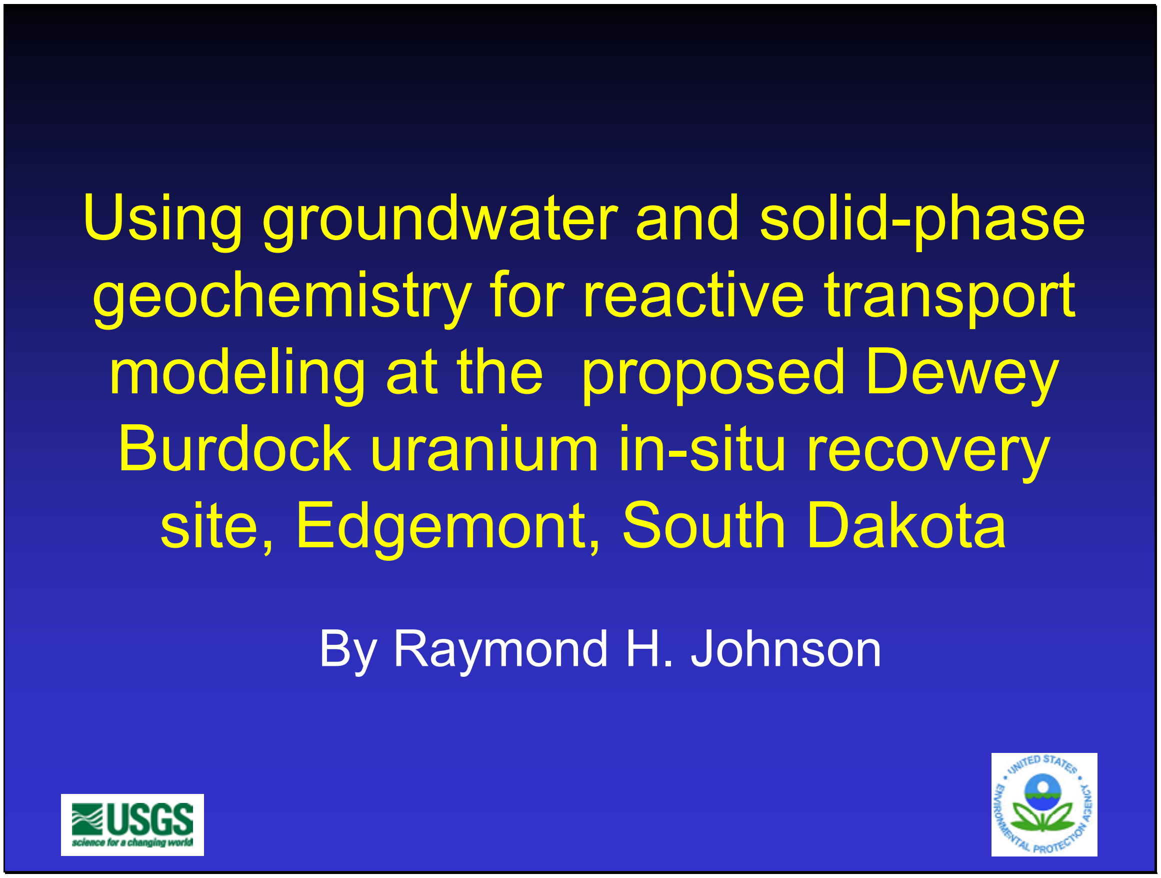
Administrative Record Document Nos. 148 and 149

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

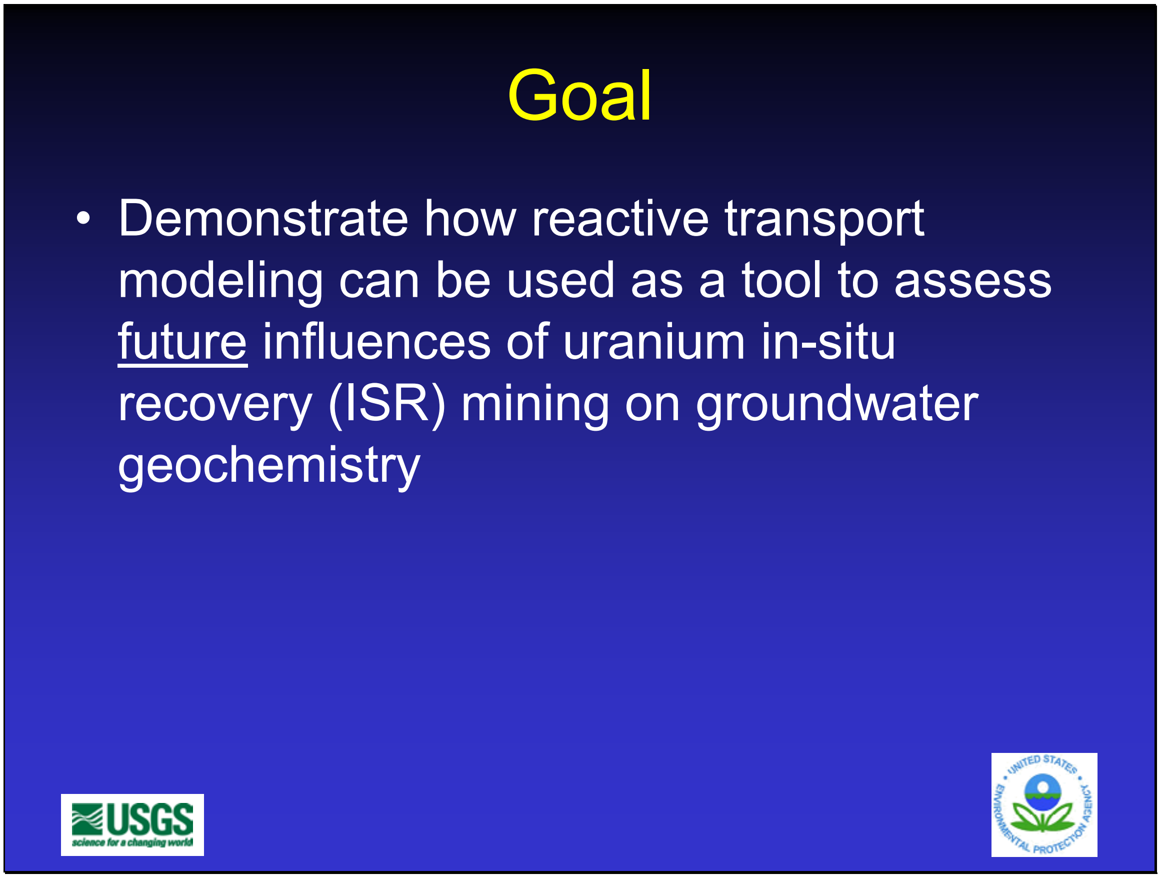


Using groundwater and solid-phase geochemistry for reactive transport modeling at the proposed Dewey Burdock uranium in-situ recovery site, Edgemont, South Dakota

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.

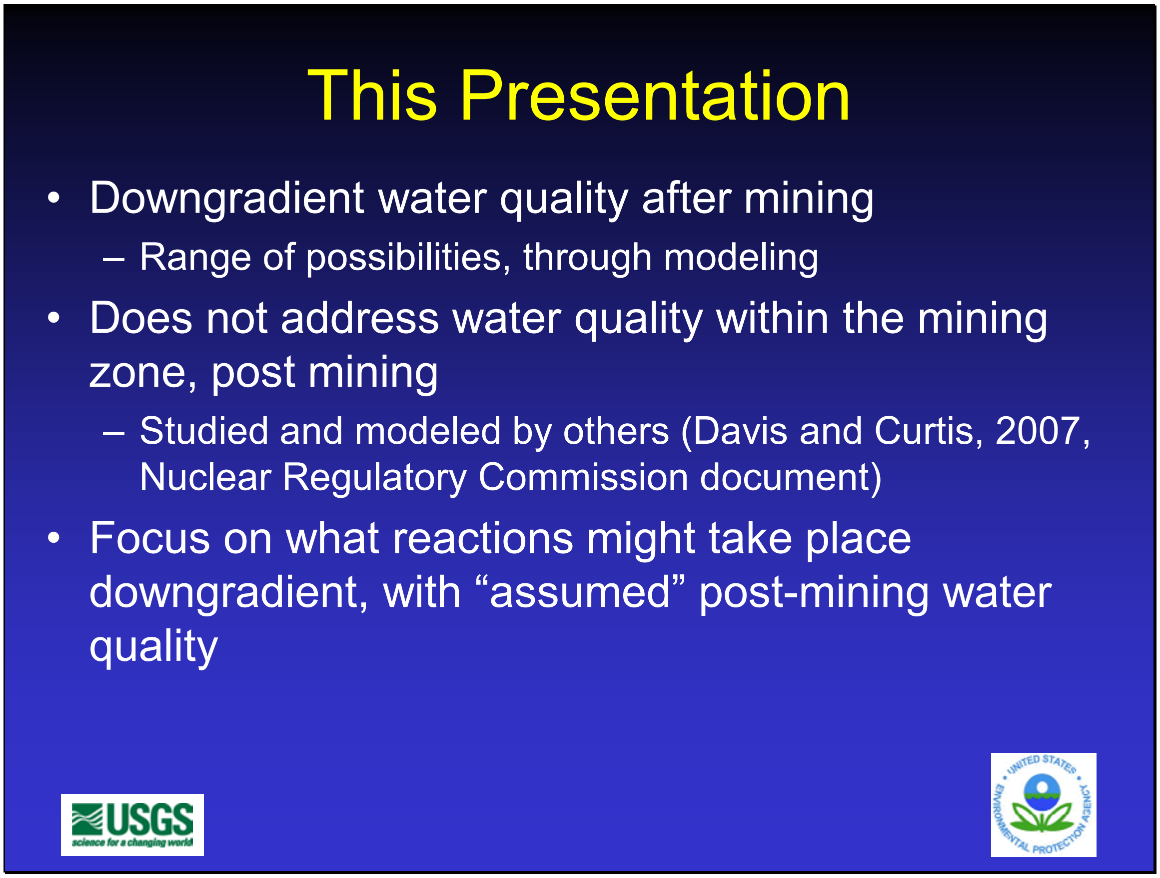
Slide 3



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

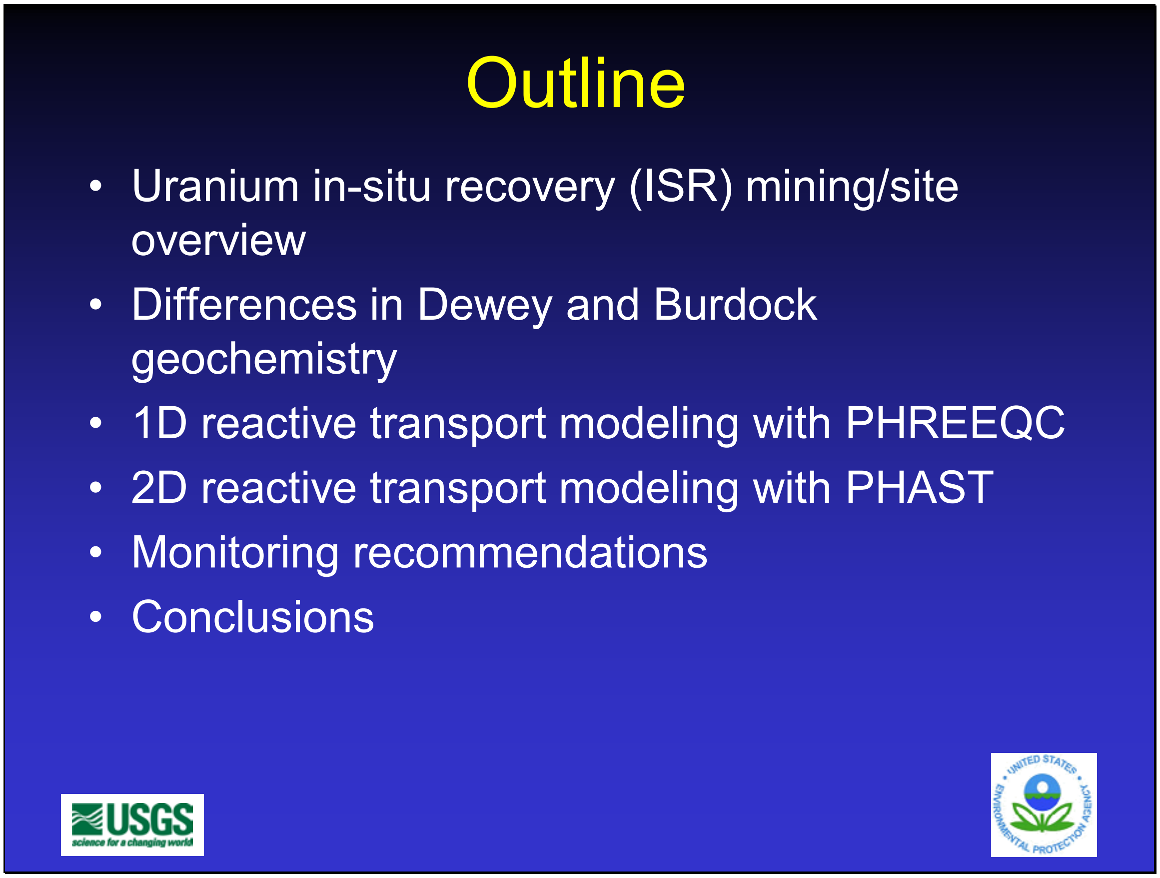
Reactive transport modeling couples groundwater flow and geochemistry. This research focuses more on the geochemistry since Petrotek, a consultant for Powertech, has been developing a large scale 3D groundwater flow model.



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.

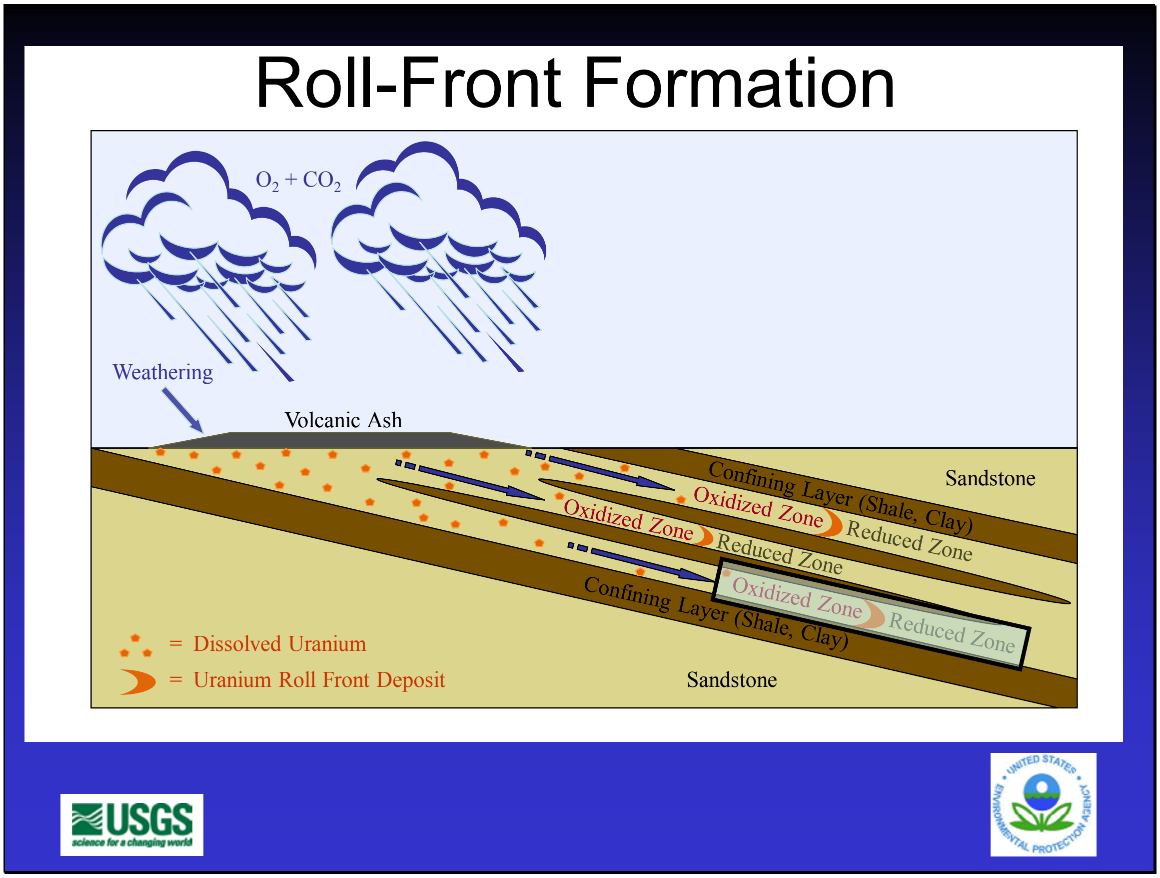


Outline

- 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

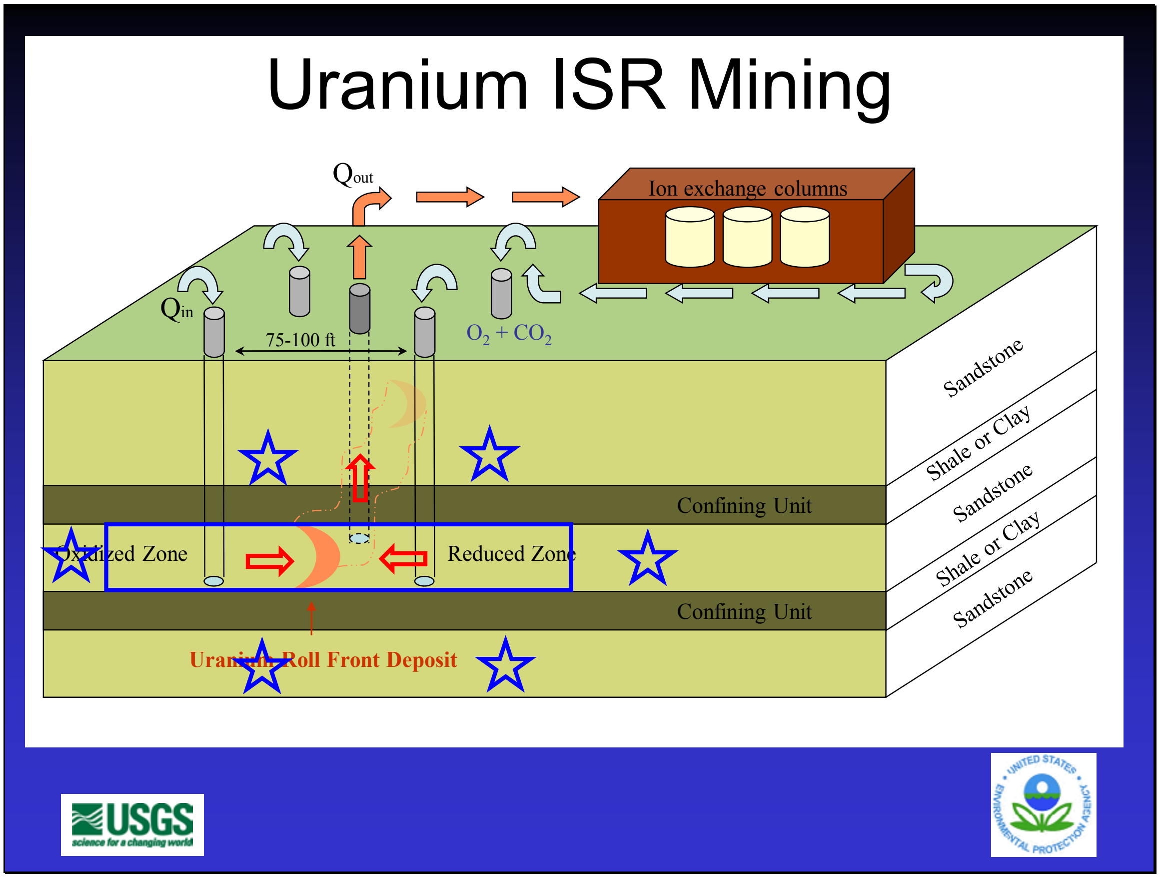
PHREEQC is a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations.
PHAST is a computer program for simulating groundwater flow, solute transport, and multicomponent geochemical reactions.

Slide 6



Roll-Front Formation

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.



Uranium ISR Mining

This slide shows a typical five-spot well pattern. In three dimensions, the wells follow the uranium deposit.

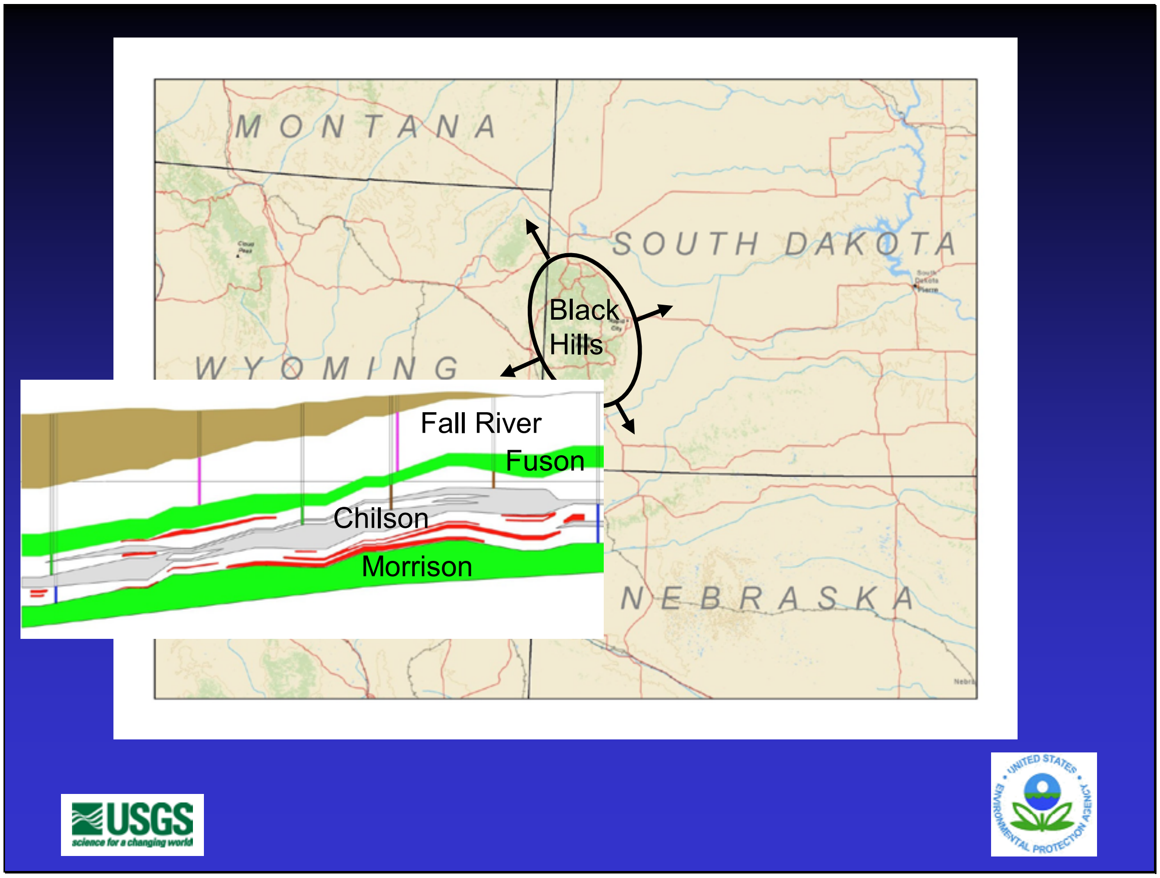
The blue box represents an aquifer exemption boundary. This boundary outlines a portion of the aquifer containing materials expected to be commercially producible.

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.

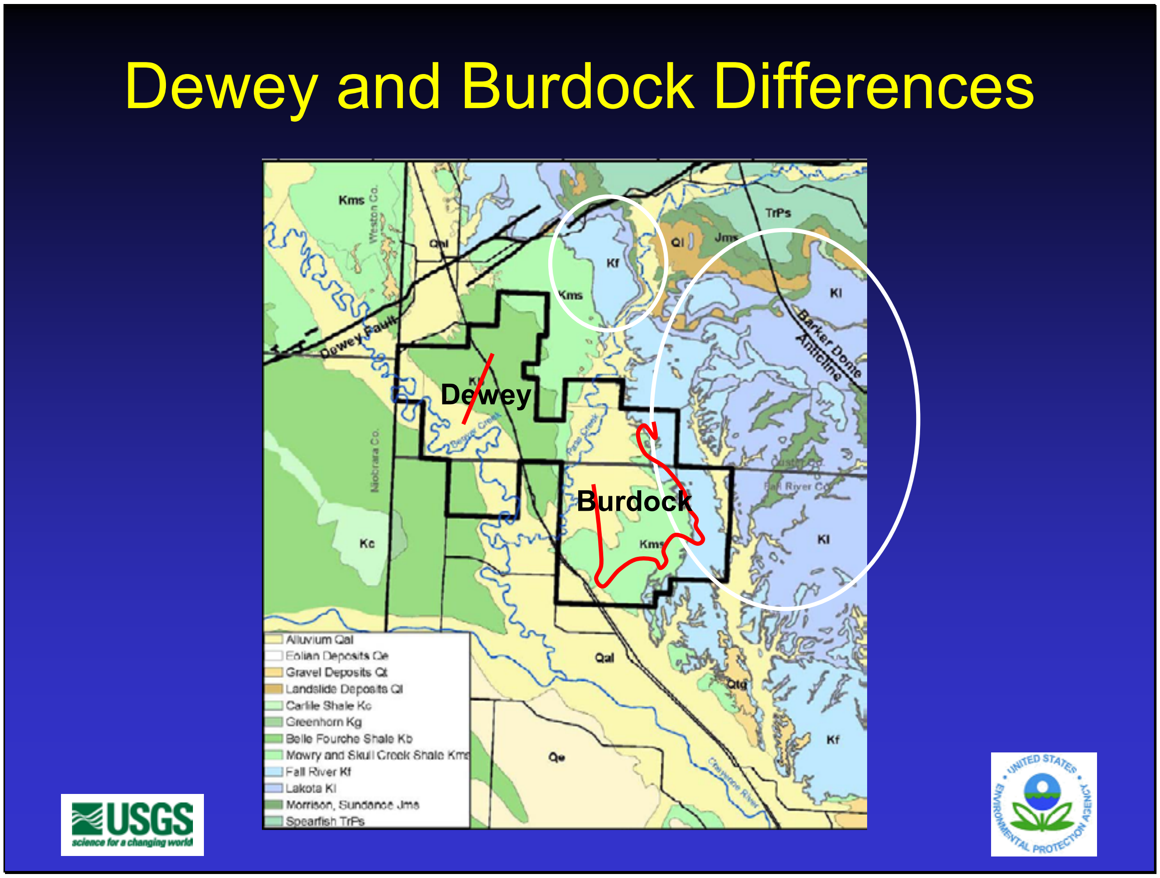
Ideally, these monitoring wells should never see any change in water quality.

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.

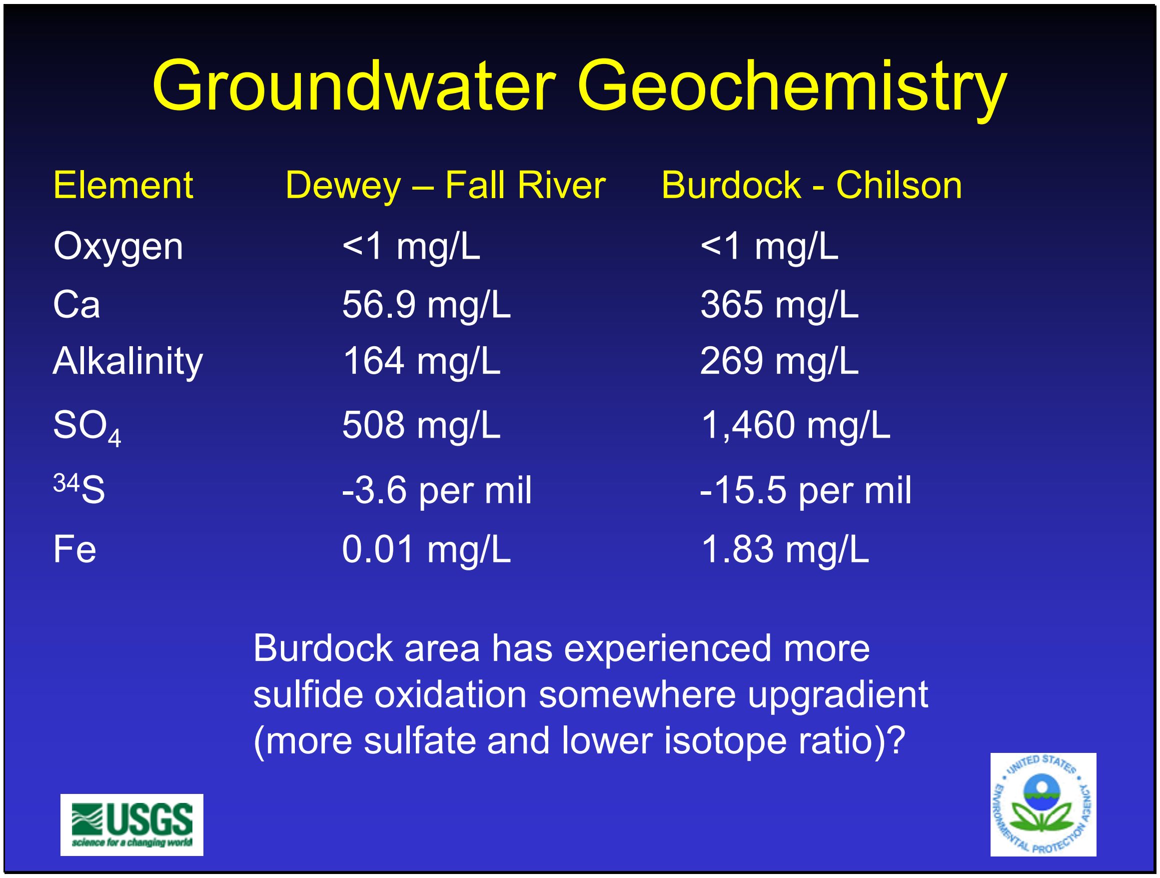
Slide 9



Dewey and Burdock Differences

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.

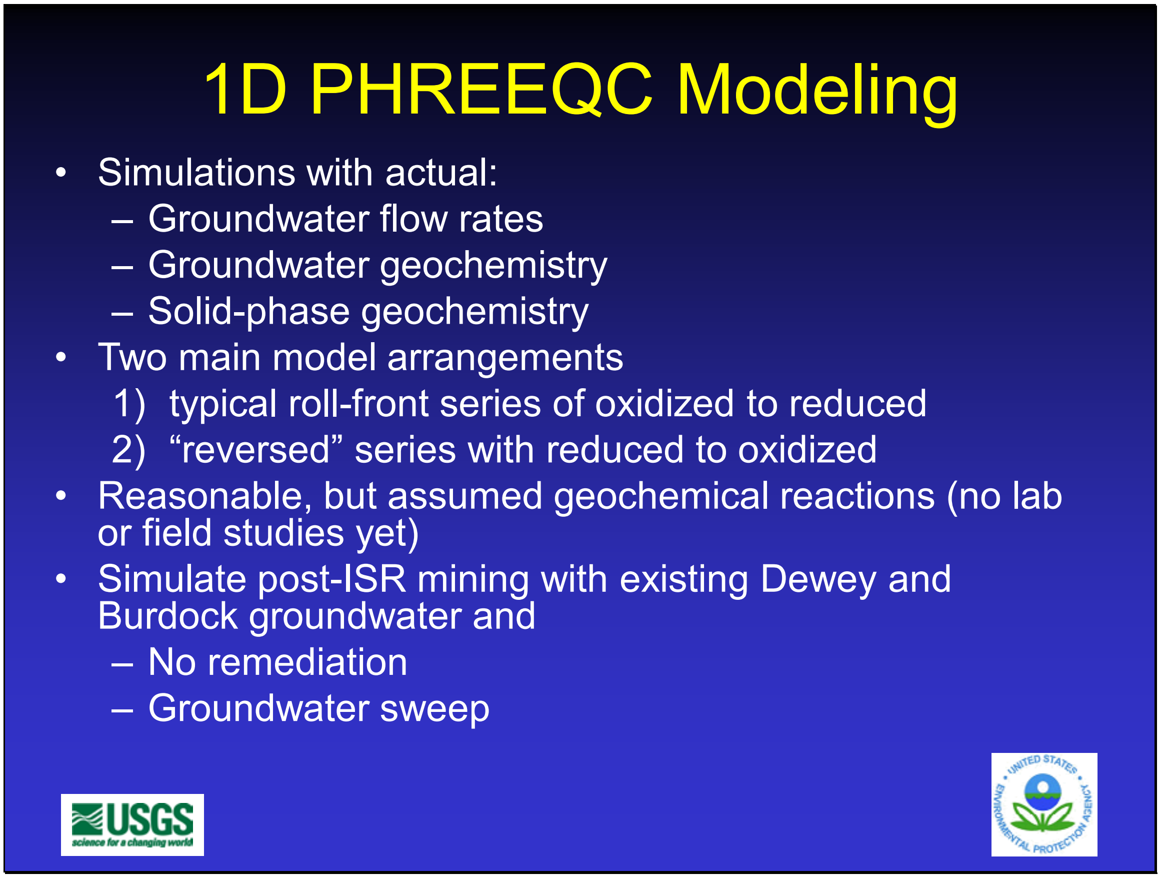
These are good average numbers for the Dewey and Burdock areas in the Fall River Formation and Lower Chilson Member of the Lakota Formation, respectively.

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

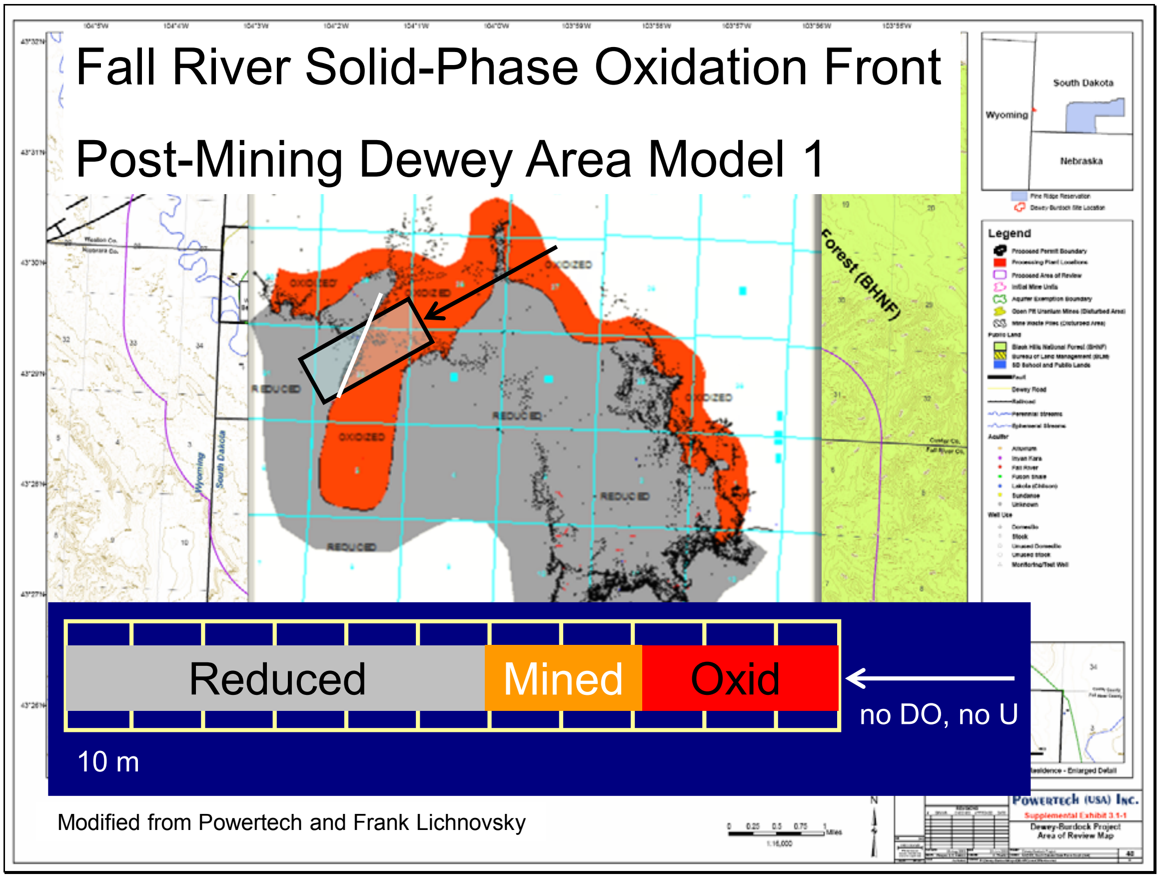


1D PHREEQC Modeling

- 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



Fall River Solid-Phase Oxidation Front

Post-Mining Dewey Area Model 1

Reduced

Mined

Oxid

no DO, no U

10 m

Modified from Powertech and Frank Lichnovsky

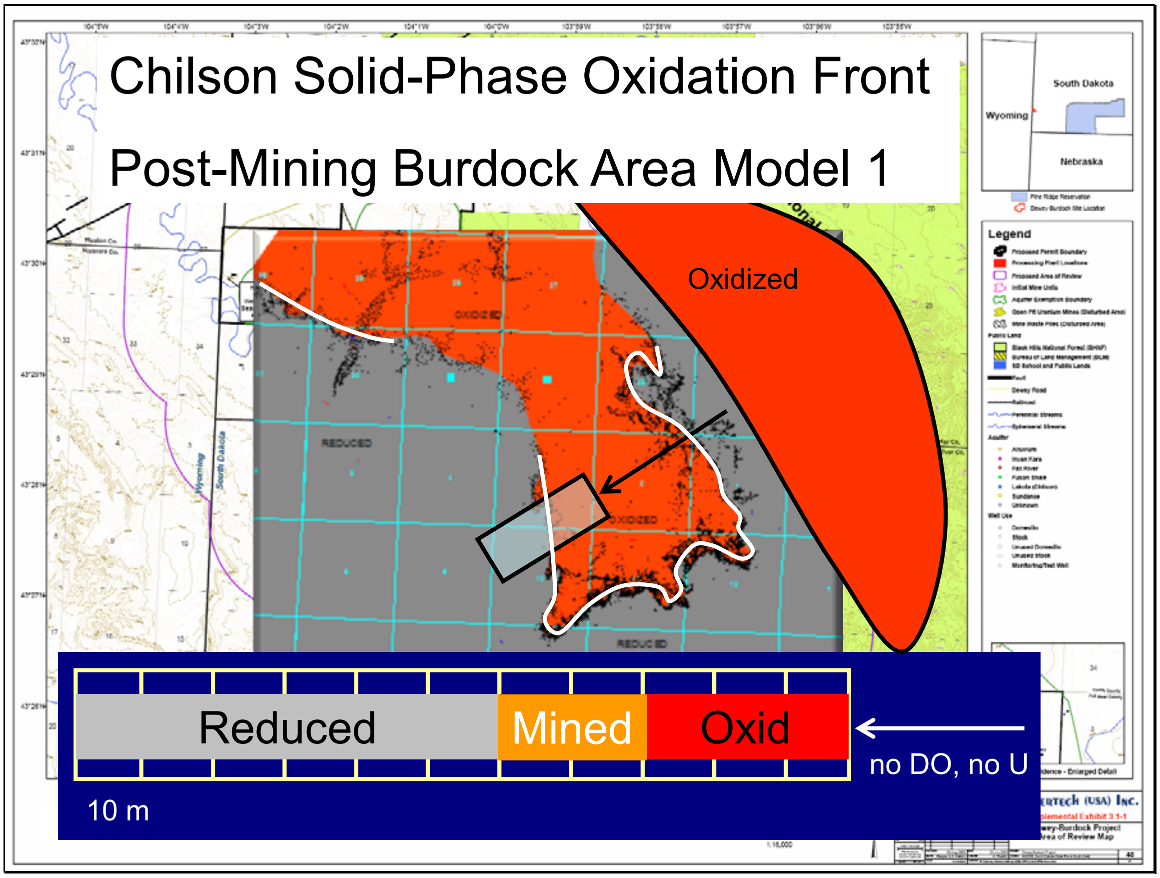
This slide and the next two slides show the interpreted oxidized and reduced zones by Frank Lichnovsky (Powertech) from review of cores (map view).

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.

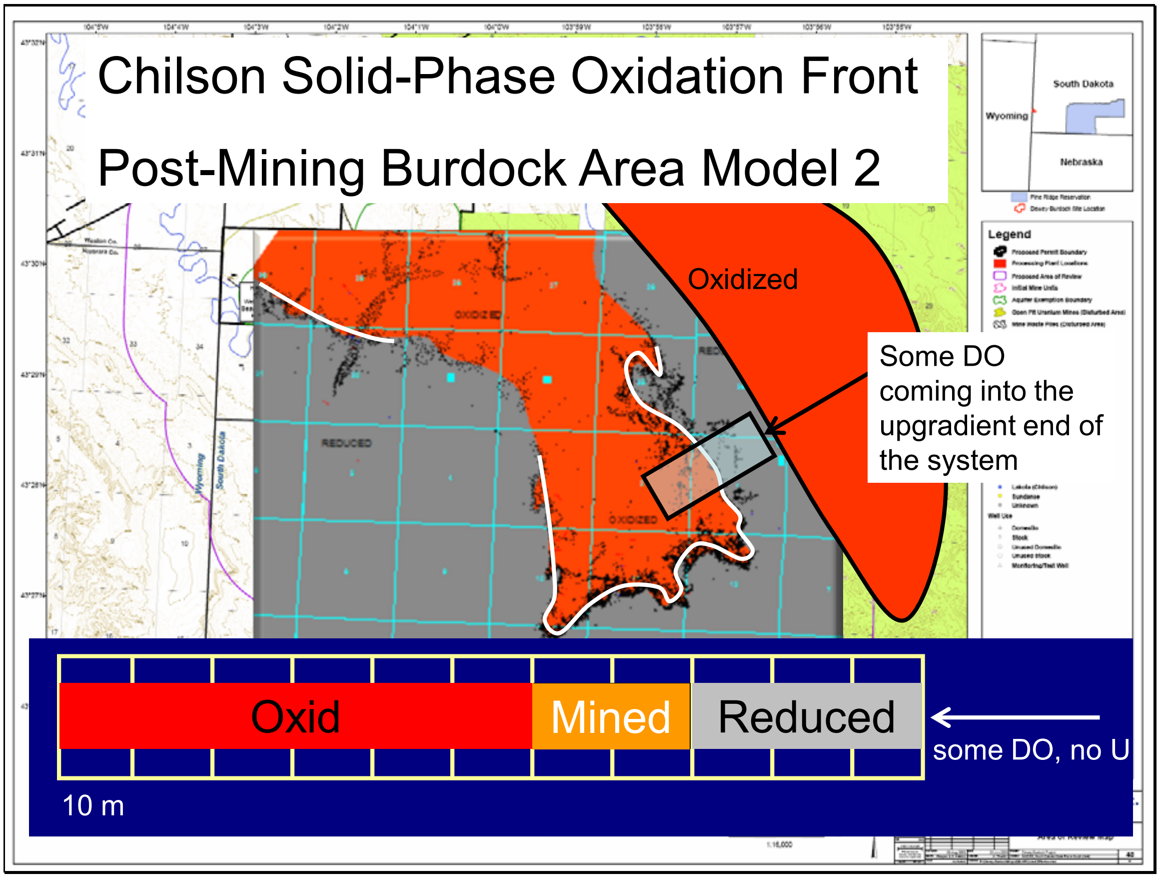
Slide 14



Chilson Solid-Phase Oxidation Front

Post-Mining Burdock Area Model 1

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.

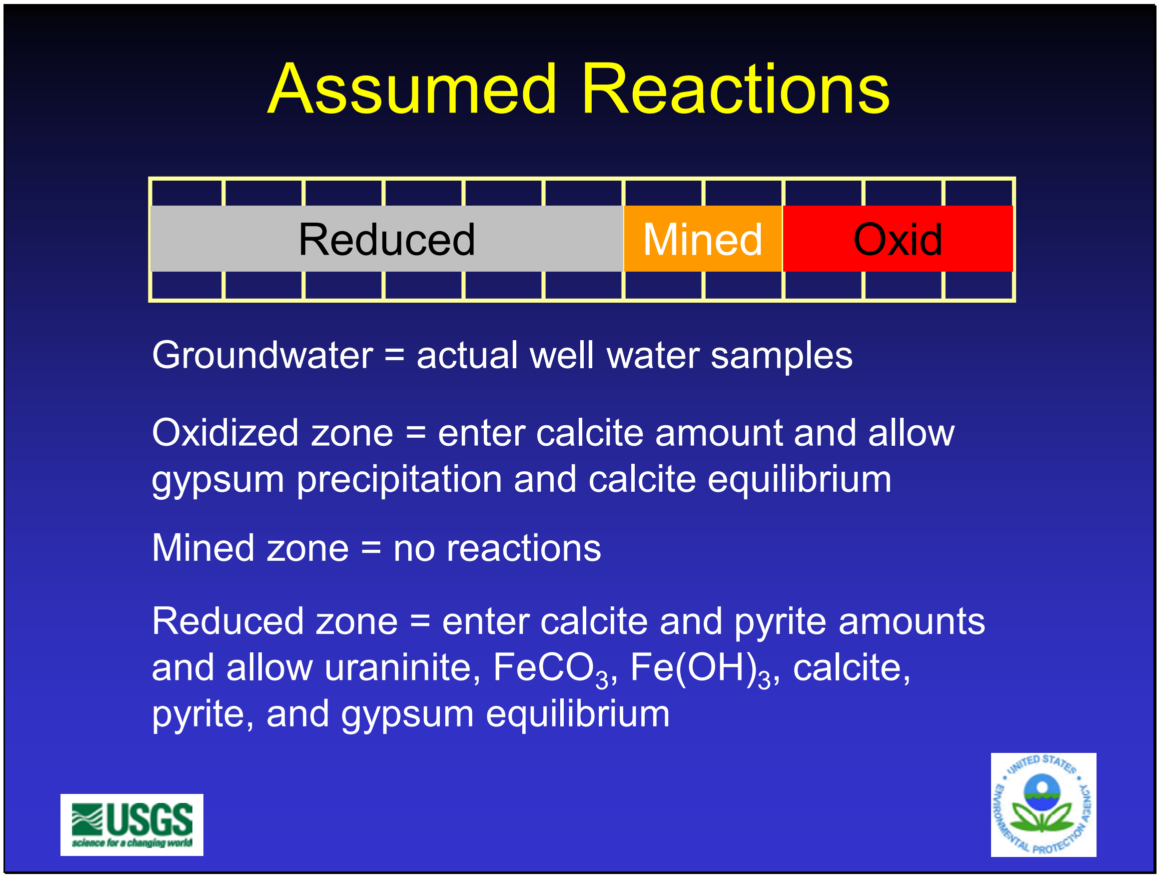


Chilson Solid-Phase Oxidation Front Post-Mining Burdock Area Model 2

Some DO coming into the upgradient end of the system

some DO, no U

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.



Assumed Reactions

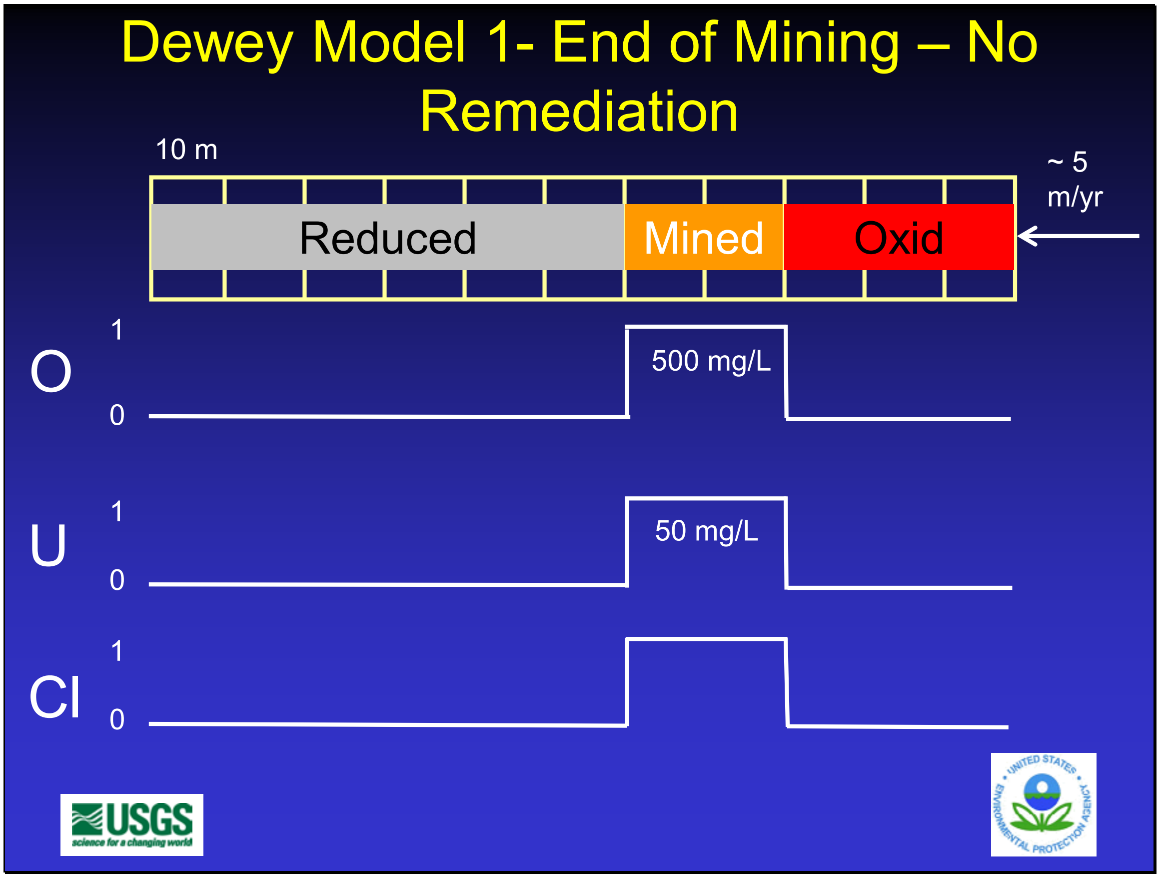
Groundwater = actual well water samples

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



Dewey Model 1- End of Mining – No Remediation

10 m

~ 5 m/yr

Reduced

Mined

Oxid

O

1

0

500 mg/L

U

1

0

50 mg/L

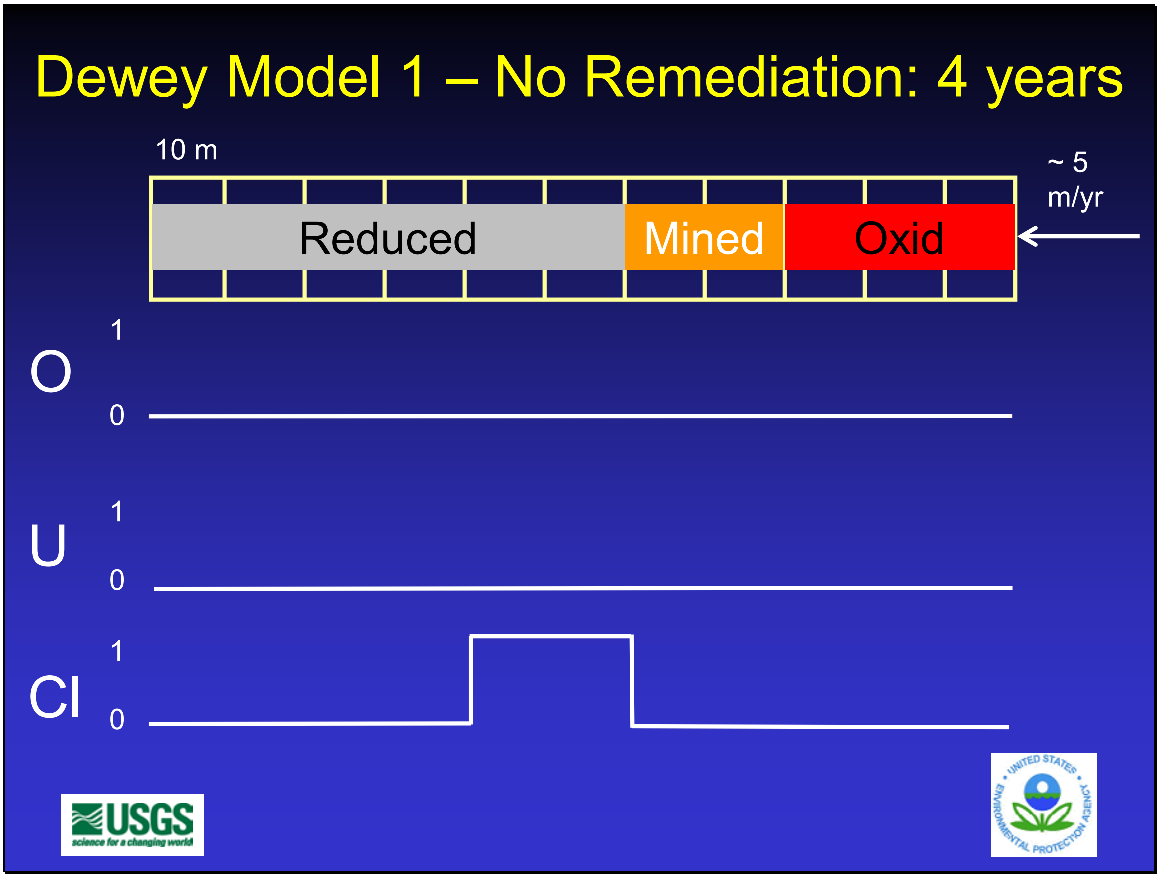
Cl

1

0

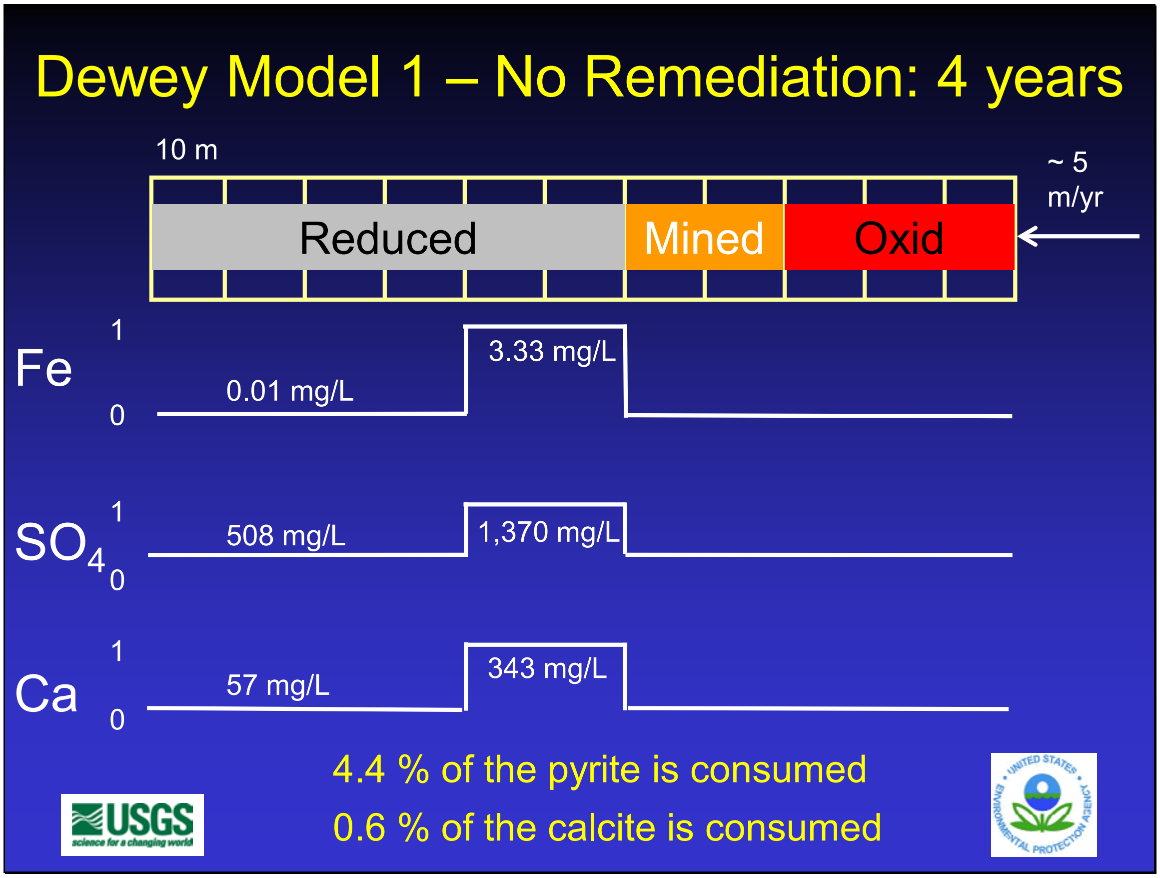
This slide shows assumed geochemistry for Dewey (model 1) at the end of mining. Next few slides will show transport without any remediation.
Exact chloride number is not used, since approximate value is unknown (depends on mining process).
Anticipated groundwater flow rate is at ~5 m/yr based on recent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

Slide 18



Dewey Model 1 – No Remediation: 4 years

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).



Dewey Model 1 – No Remediation: 4 years

10 m

~ 5 m/yr

Reduced

Mined

Oxid

Fe

1

0

0.01 mg/L

3.33 mg/L

SO_4

1

0

508 mg/L

1,370 mg/L

Ca

1

0

57 mg/L

343 mg/L

4.4 % of the pyrite is consumed

0.6 % of the calcite is consumed

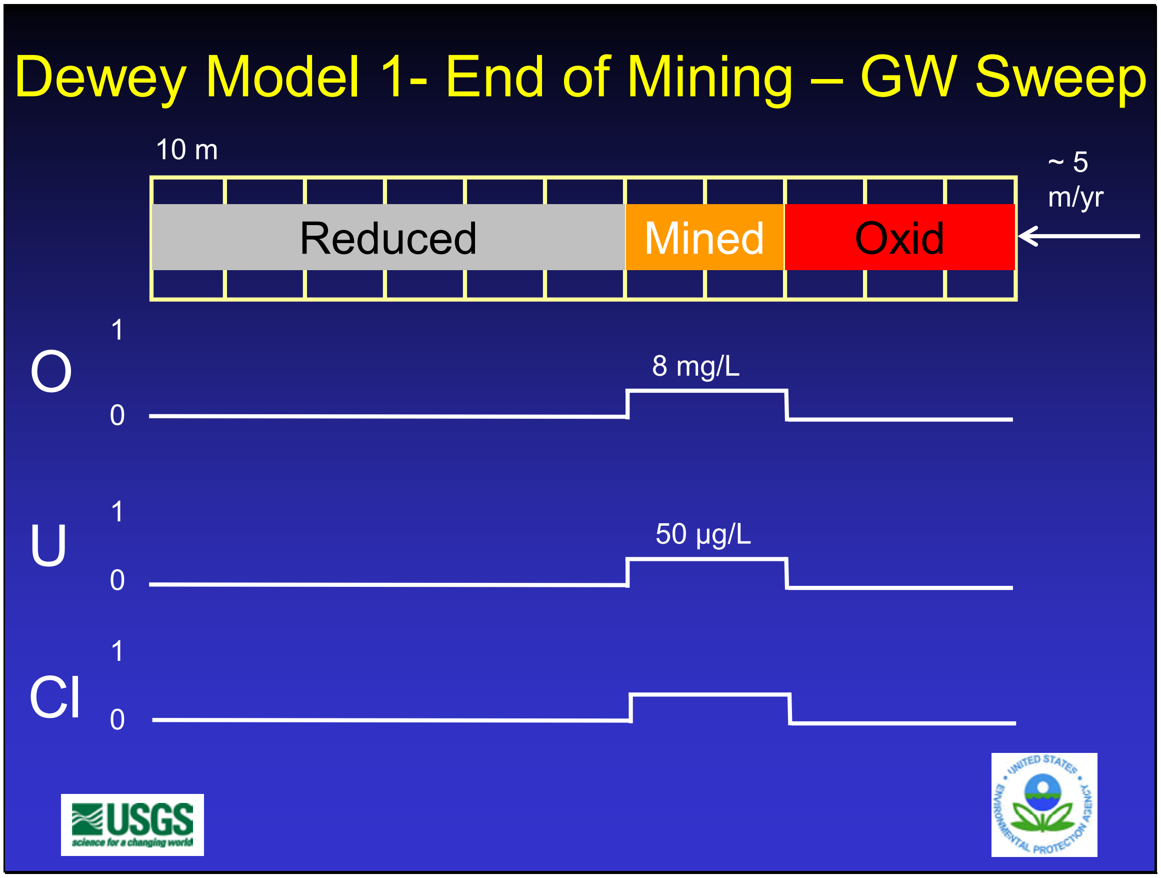
In this and all subsequent slides, three significant figures are indicated just for comparison purposes and are not meant to represent model predictions to this level of accuracy.

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.

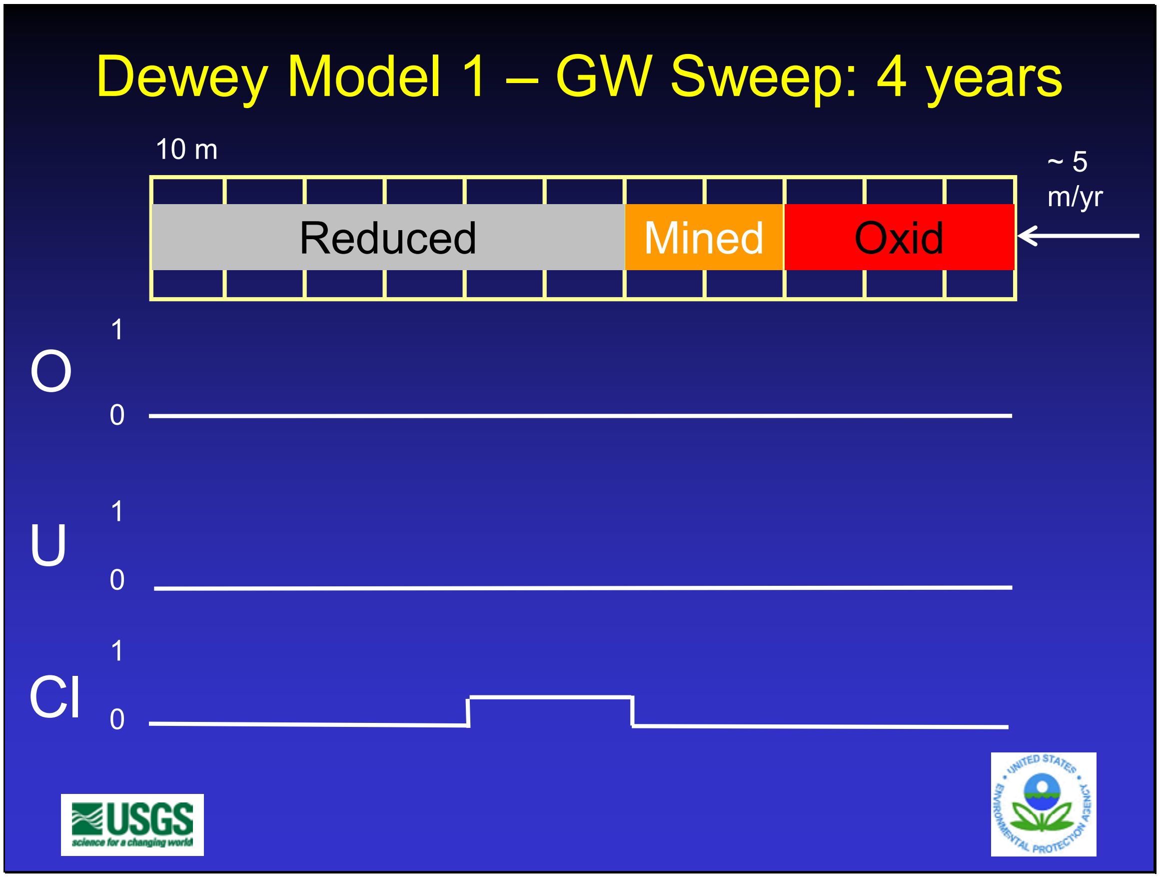
For reference, current maximum values in the Burdock area are 21 mg/L for iron and 1,800 mg/L sulfate and just less than 400 mg/L for calcium.

Slide 20

Dewey Model 1- End of Mining – GW Sweep



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.



Dewey Model 1 – GW Sweep: 4 years

10 m

~ 5 m/yr

Reduced

Mined

Oxid

O

1

0

U

1

0

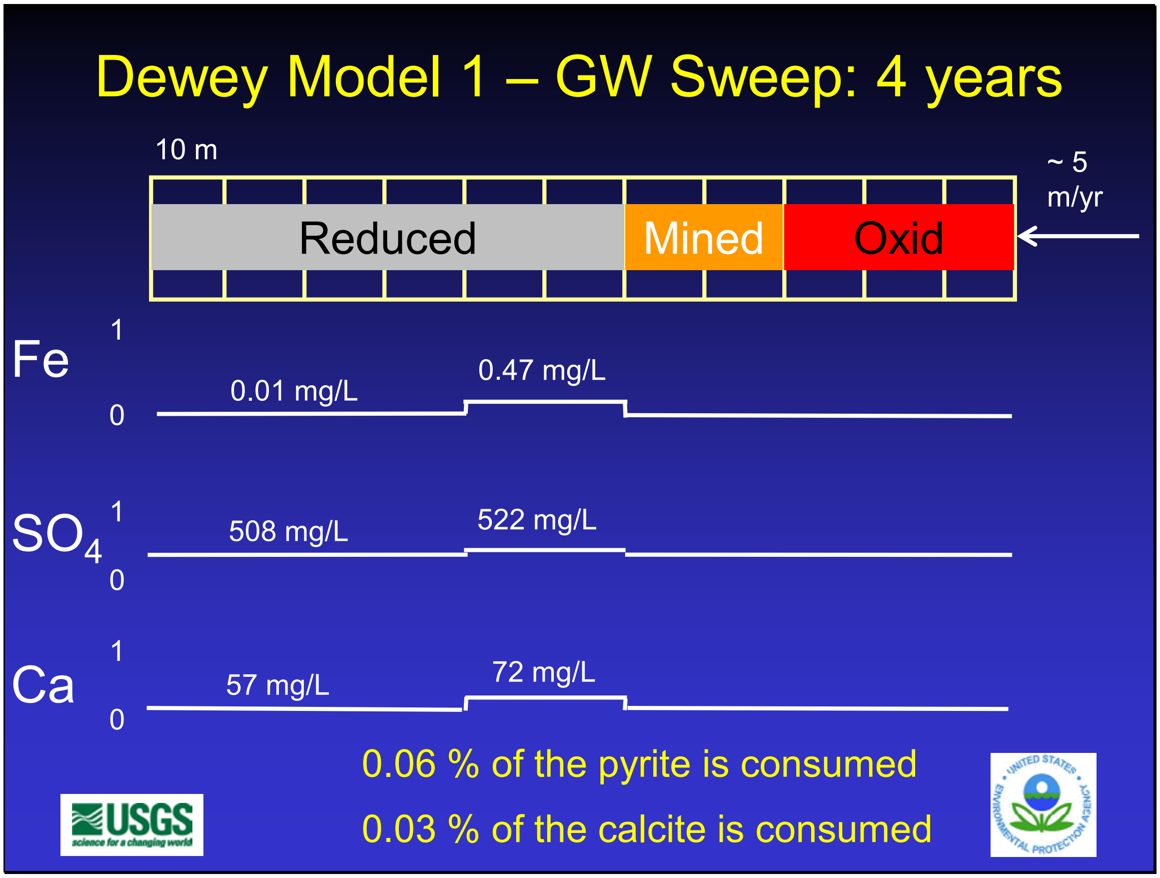
Cl

1

0

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



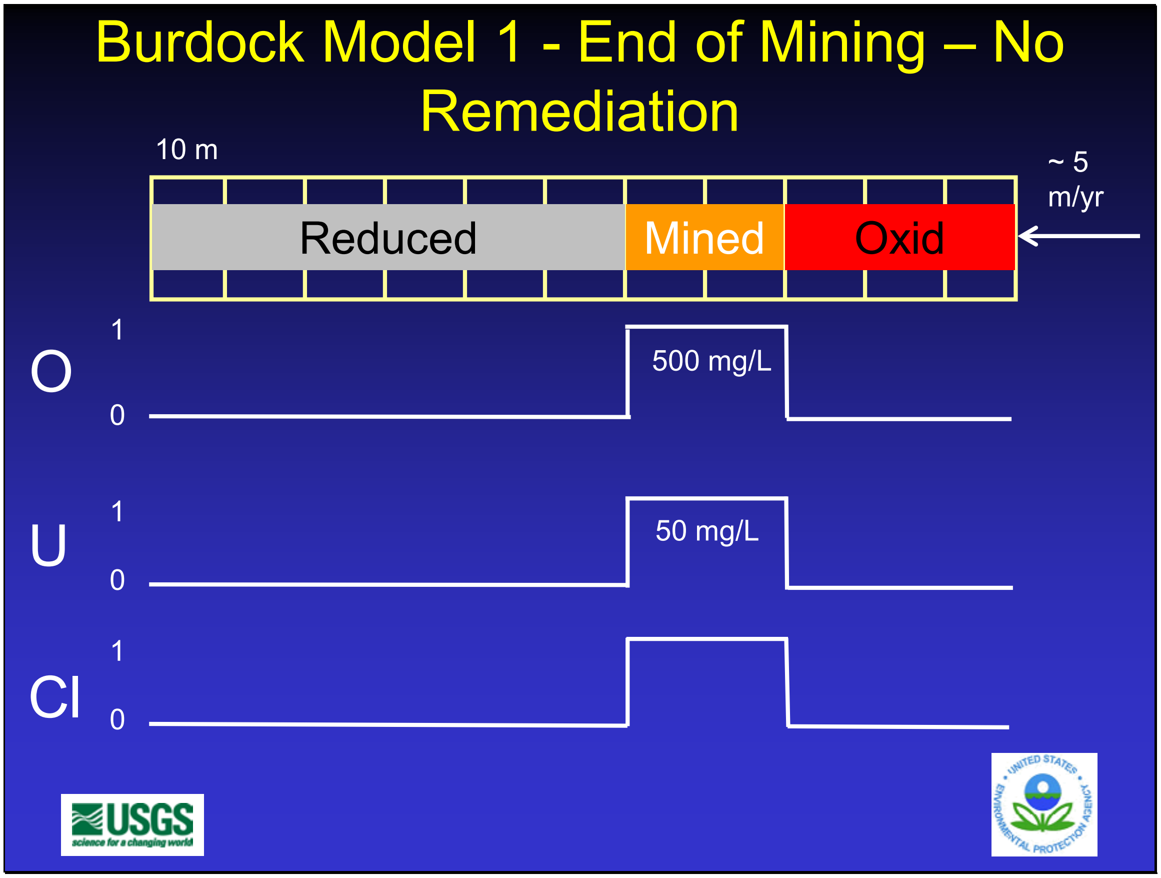
Dewey Model 1 – GW Sweep: 4 years

0.06 % of the pyrite is consumed

0.03 % of the calcite is consumed

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



Burdock Model 1 - End of Mining – No Remediation

10 m

~ 5 m/yr

Reduced

Mined

Oxid

O

1

0

500 mg/L

U

1

0

50 mg/L

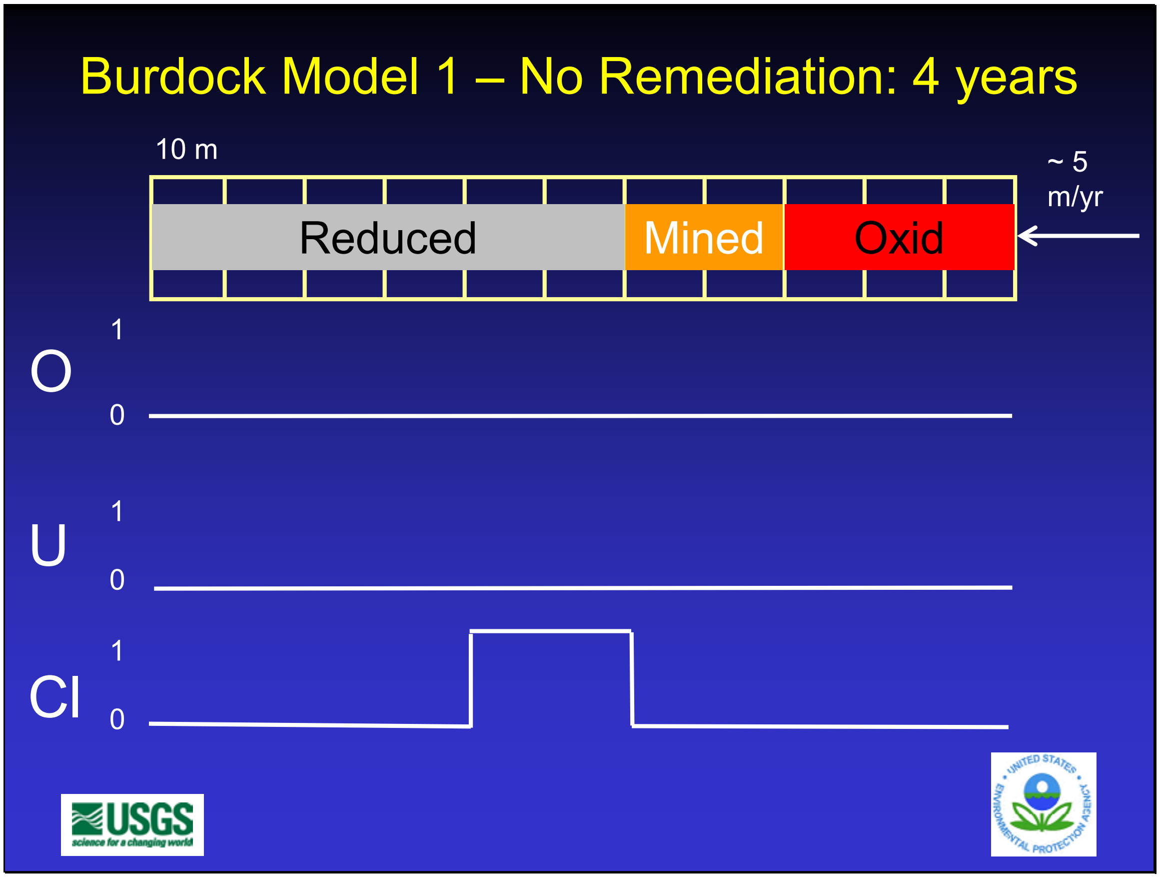
Cl

1

0

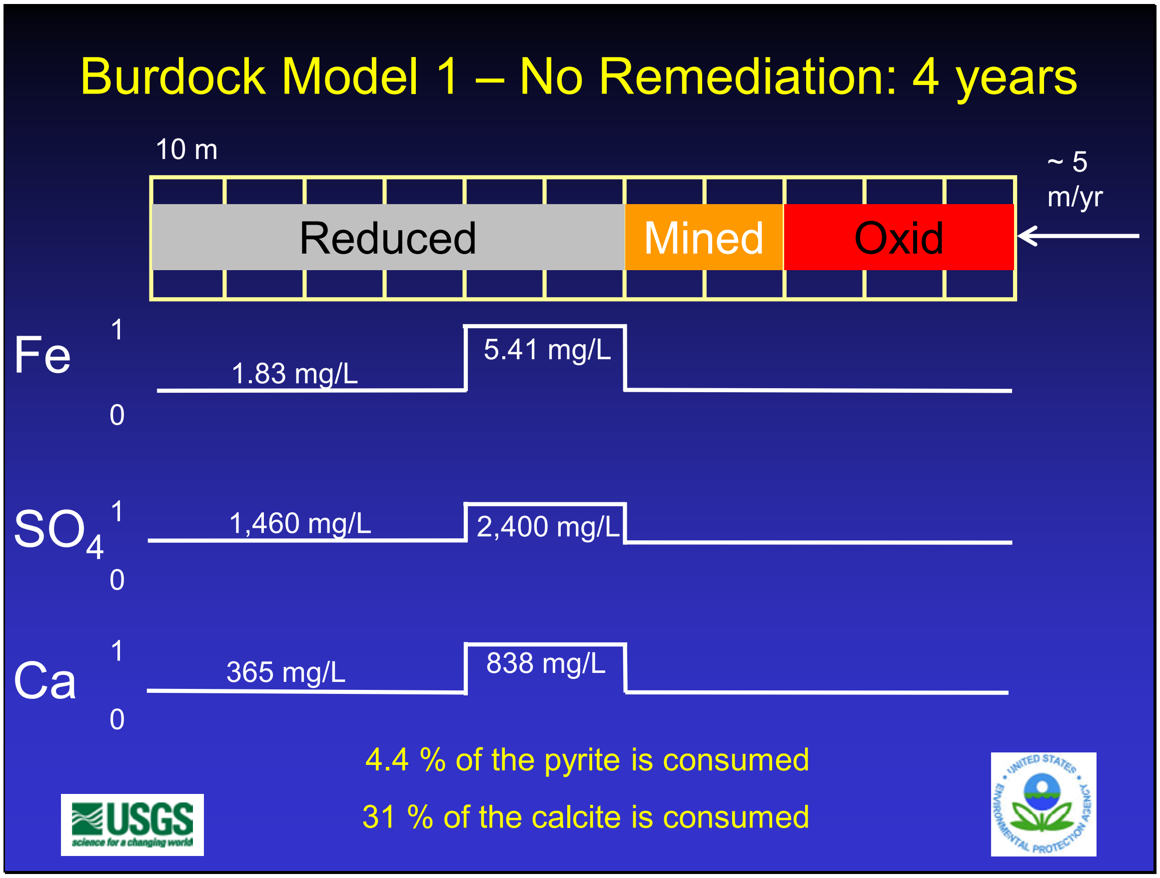
This slide shows assumed geochemistry for Burdock (model 1) at the end of mining.
Next few slides will show transport without any remediation.
Exact chloride number is not used, since approximate value is unknown (depends on mining process).
Anticipated groundwater flow rate is at ~5 m/yr based on recent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

Slide 24



Burdock Model 1 – No Remediation: 4 years

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).



Burdock Model 1 – No Remediation: 4 years

10 m

~ 5 m/yr

Reduced

Mined

Oxid

Fe

1

0

1.83 mg/L

5.41 mg/L

SO_4

1

0

1,460 mg/L

2,400 mg/L

Ca

1

0

365 mg/L

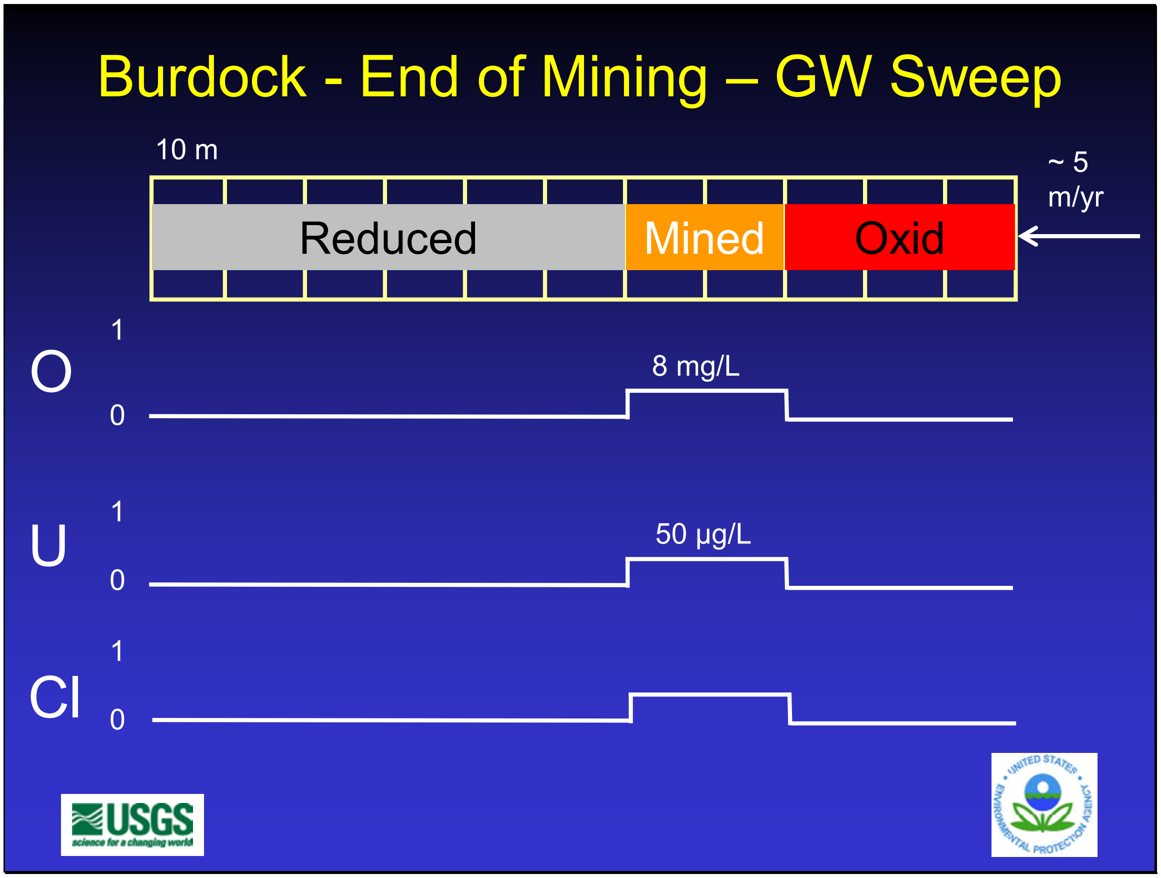
838 mg/L

4.4 % of the pyrite is consumed

31 % of the calcite is consumed

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.

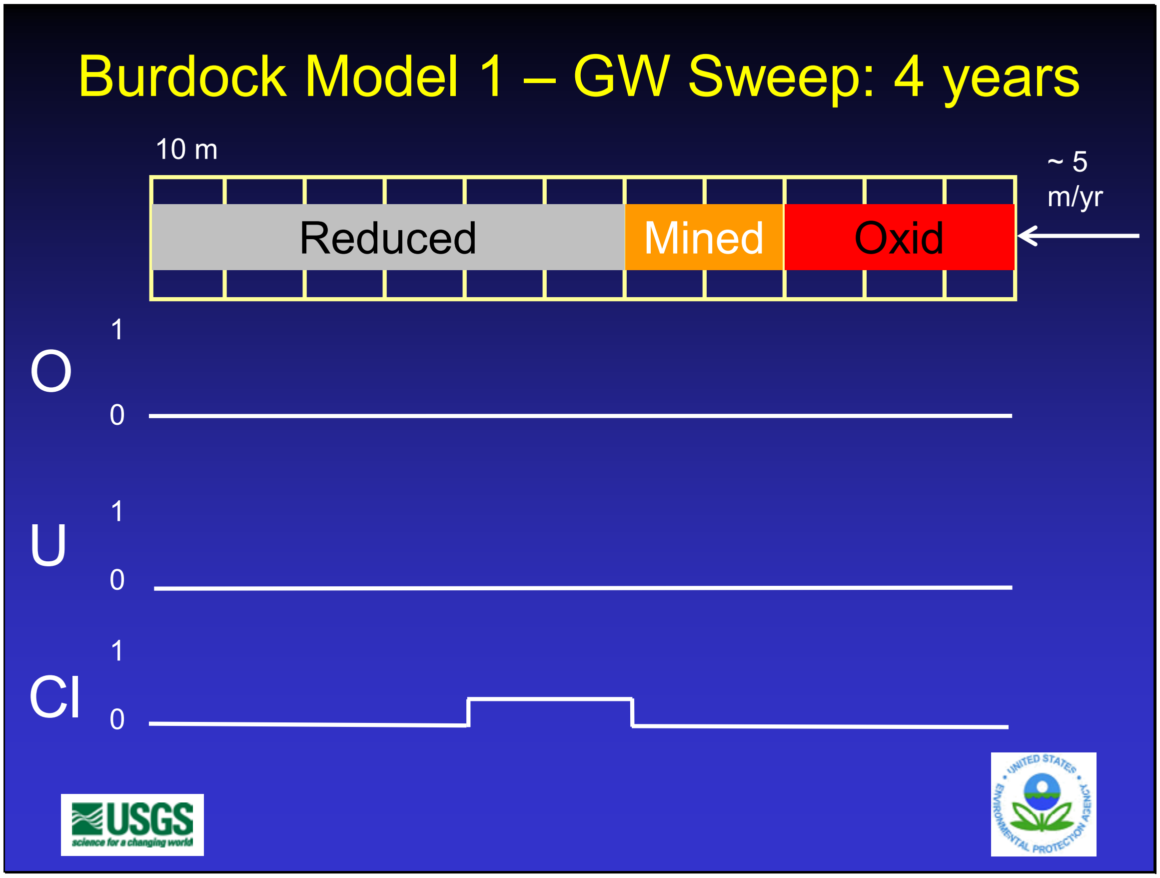
For reference, current maximum values in the Burdock area are 21 mg/L for iron and 1,800 mg/L for sulfate and just less than 400 mg/L for calcium.



Burdock - End of Mining – GW Sweep

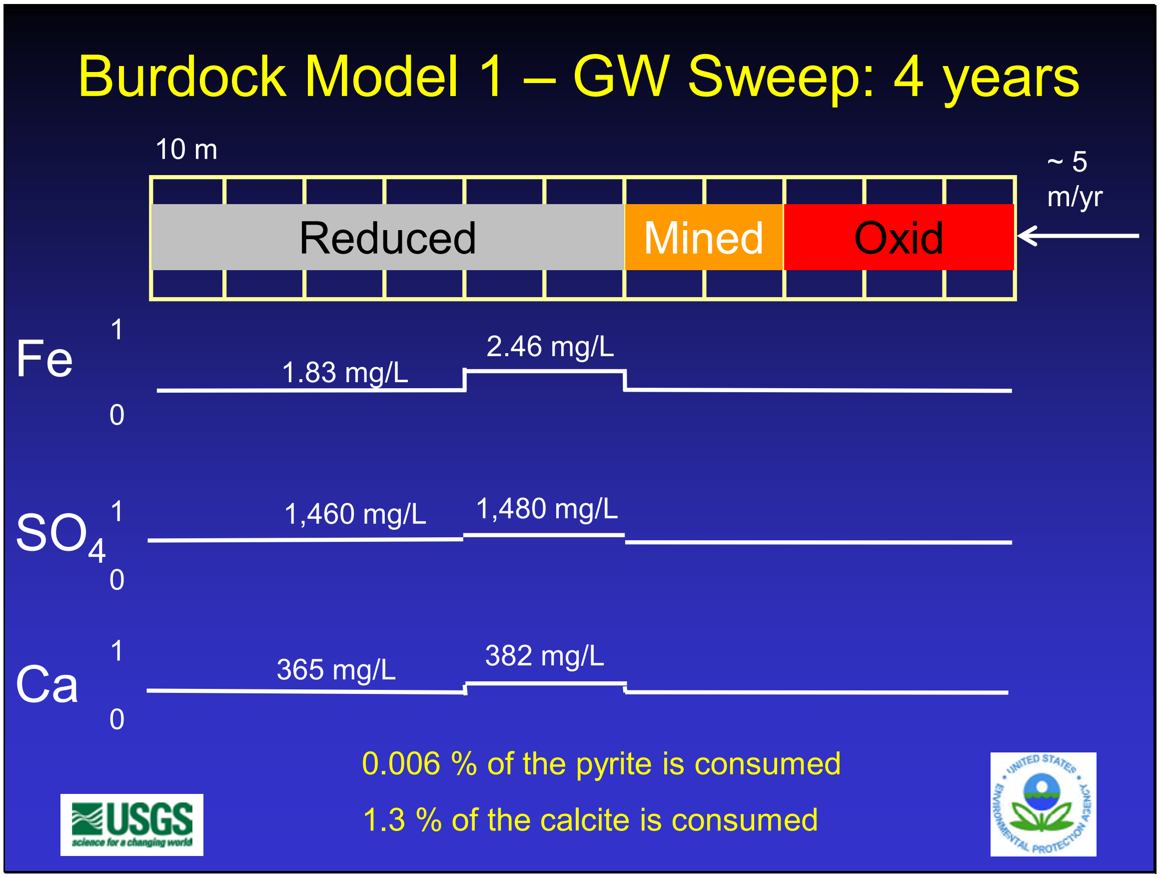
Same Burdock model 1 simulation, but with remediation by groundwater (GW) sweep.
Normalized to 1. One being no remediation.
Exact chloride number is not used, since approximate value is unknown (depends on mining process).
Anticipated groundwater flow rate is at ~5 m/yr based on recent hydraulic gradients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

Slide 27



Burdock Model 1 – GW Sweep: 4 years

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).



Burdock Model 1 – GW Sweep: 4 years

0.006 % of the pyrite is consumed

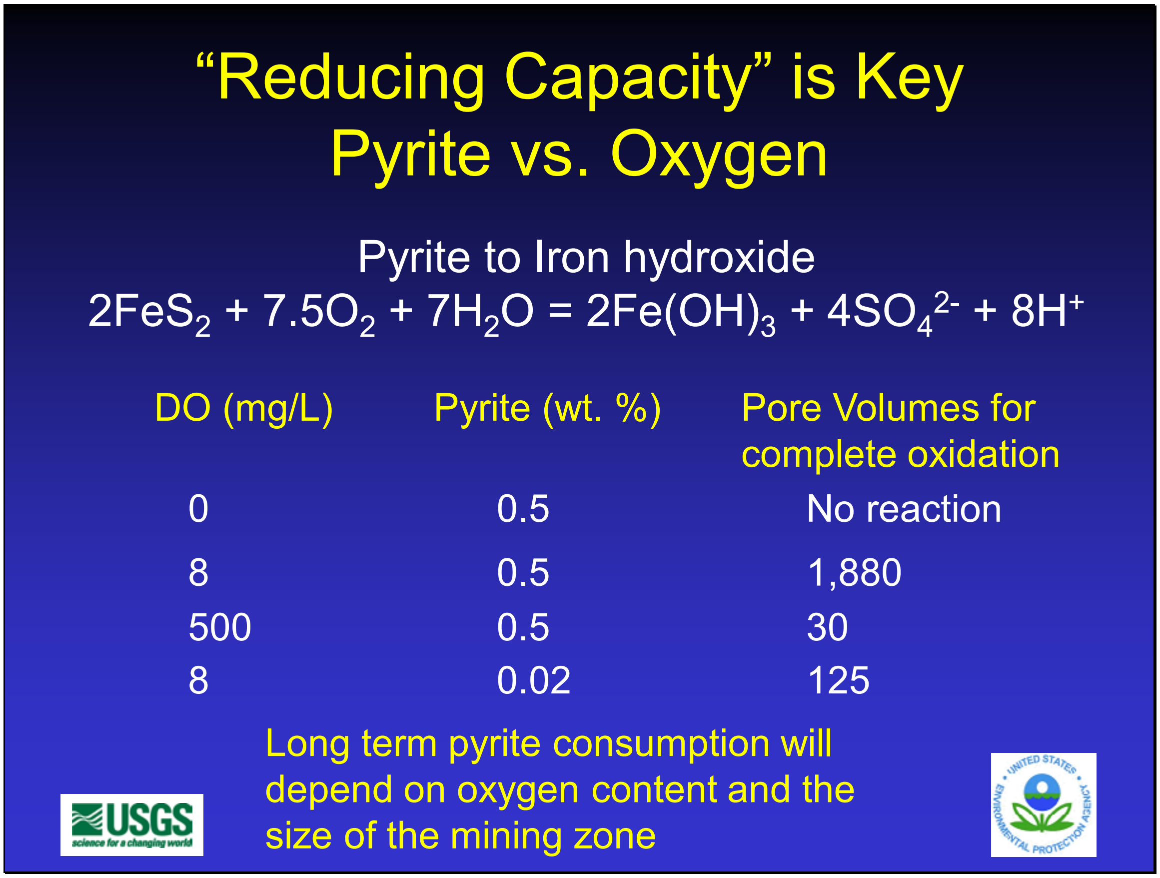
1.3 % of the calcite is consumed

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.

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



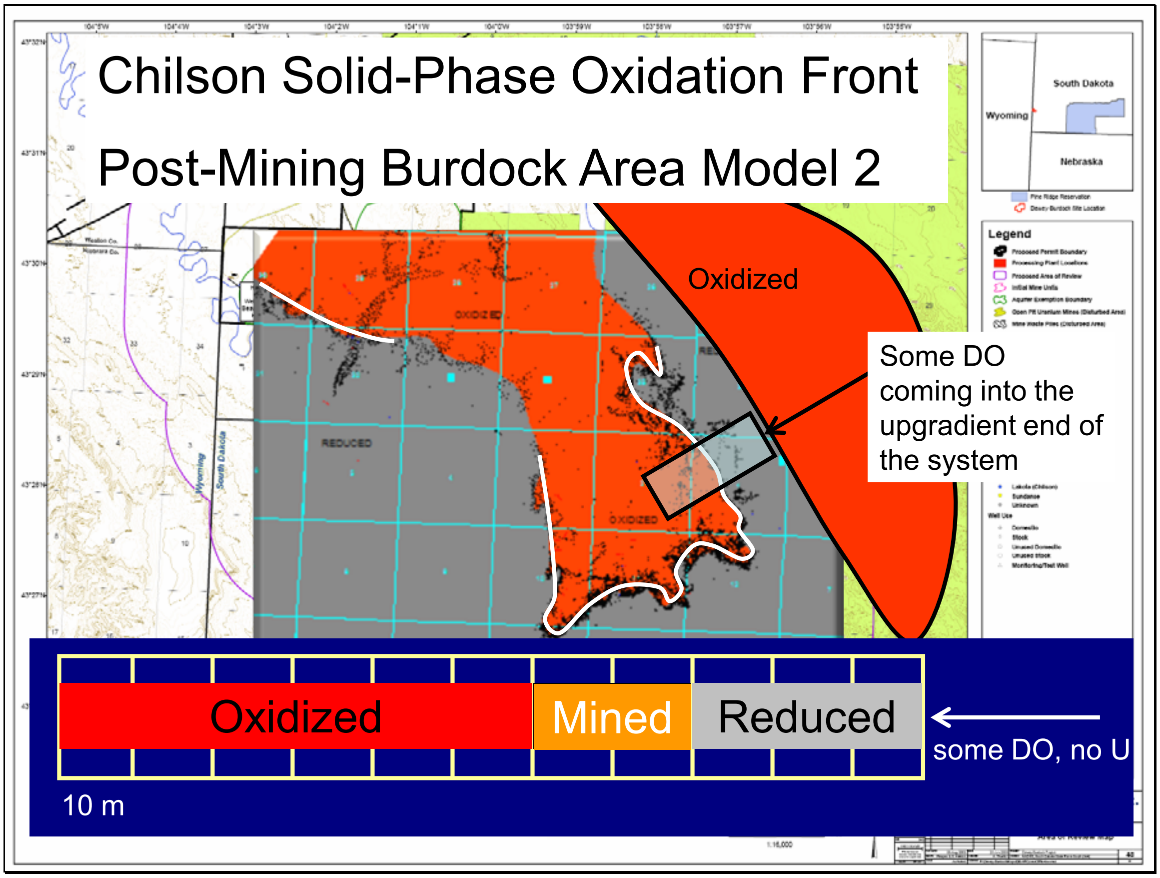
"Reducing Capacity" is Key
Pyrite vs. Oxygen

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



Chilson Solid-Phase Oxidation Front

Post-Mining Burdock Area Model 2

Oxidized

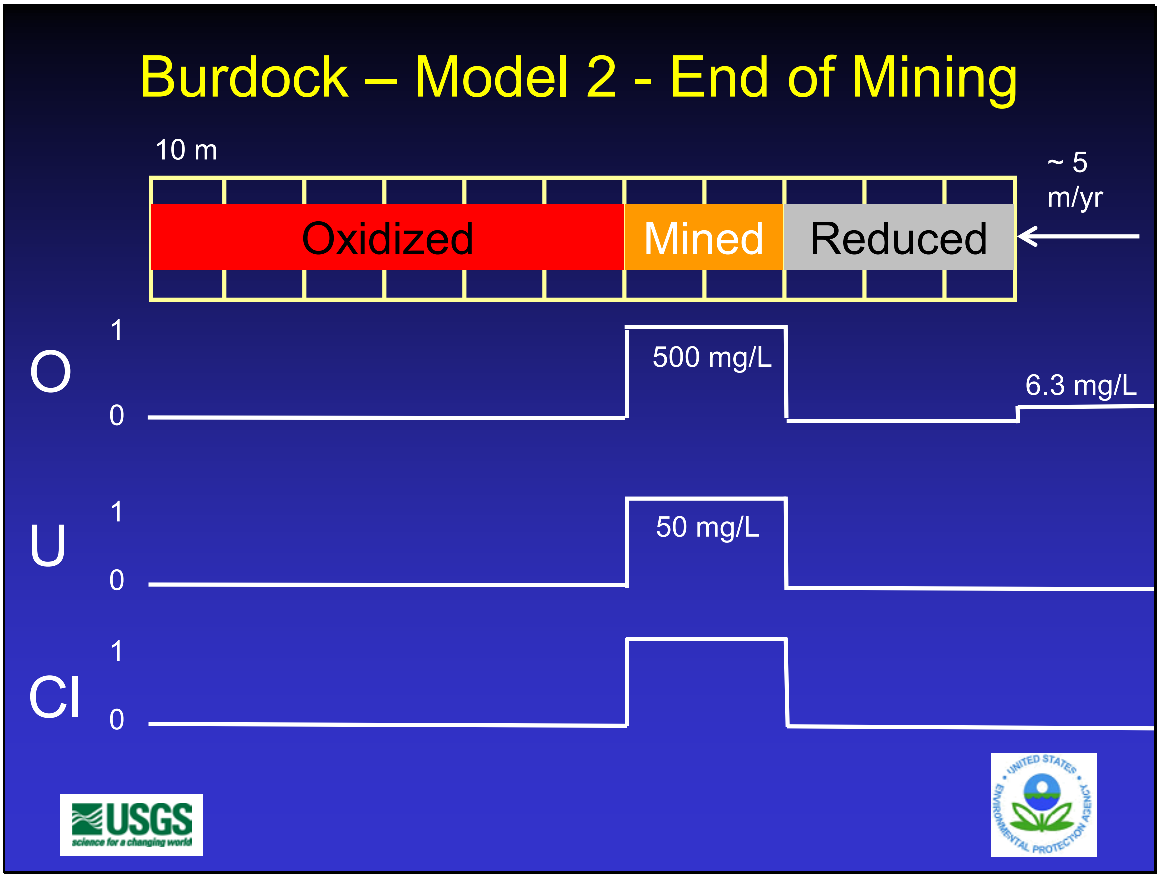
Some DO coming into the upgradient end of the system

Oxidized | Mined | Reduced

some DO, no U

10 m

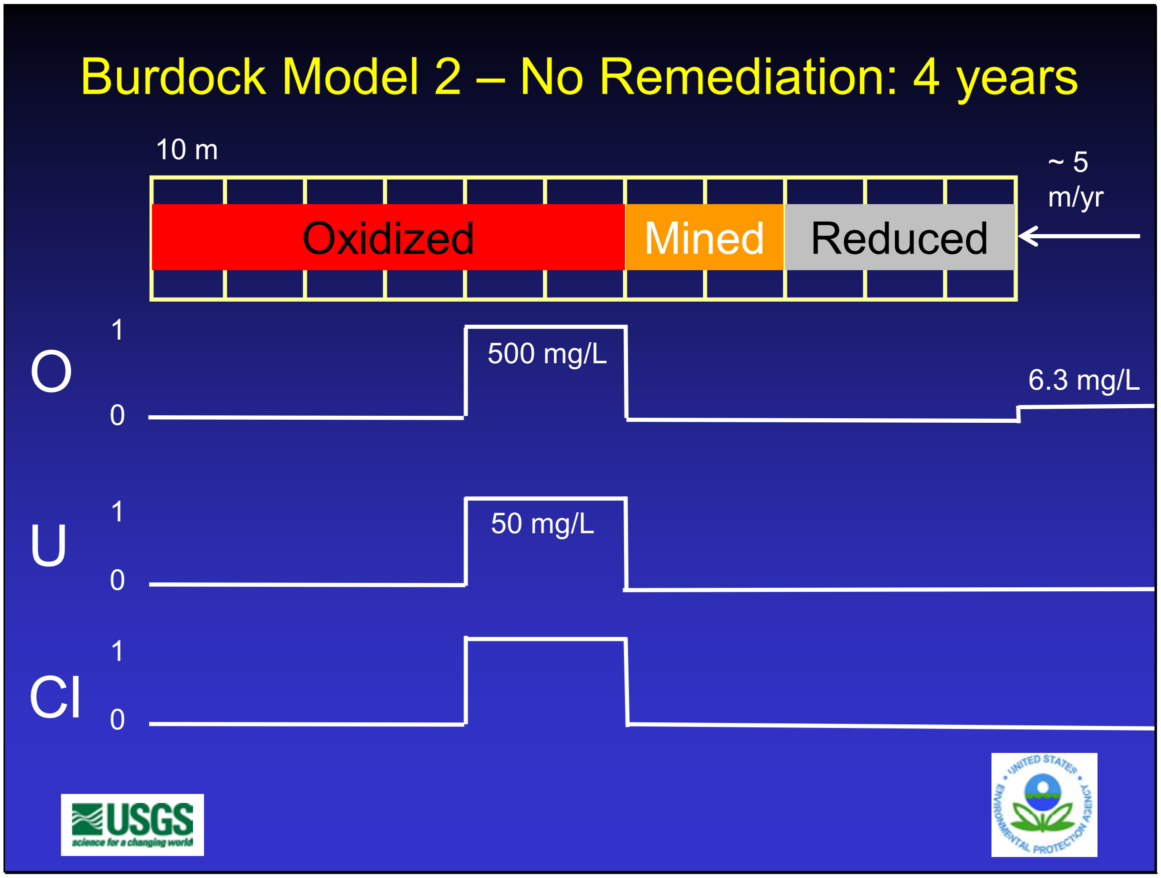
This is the second model type, where the oxidized zone is downgradient from the mined or recovery zone. Reduced zone is upgradient.
Arrow indicates approximate current groundwater flow direction.
Large oxidized zone on the east side was added as a reasonable interpretation that the outcrop zone of the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



Burdock – Model 2 - End of Mining

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

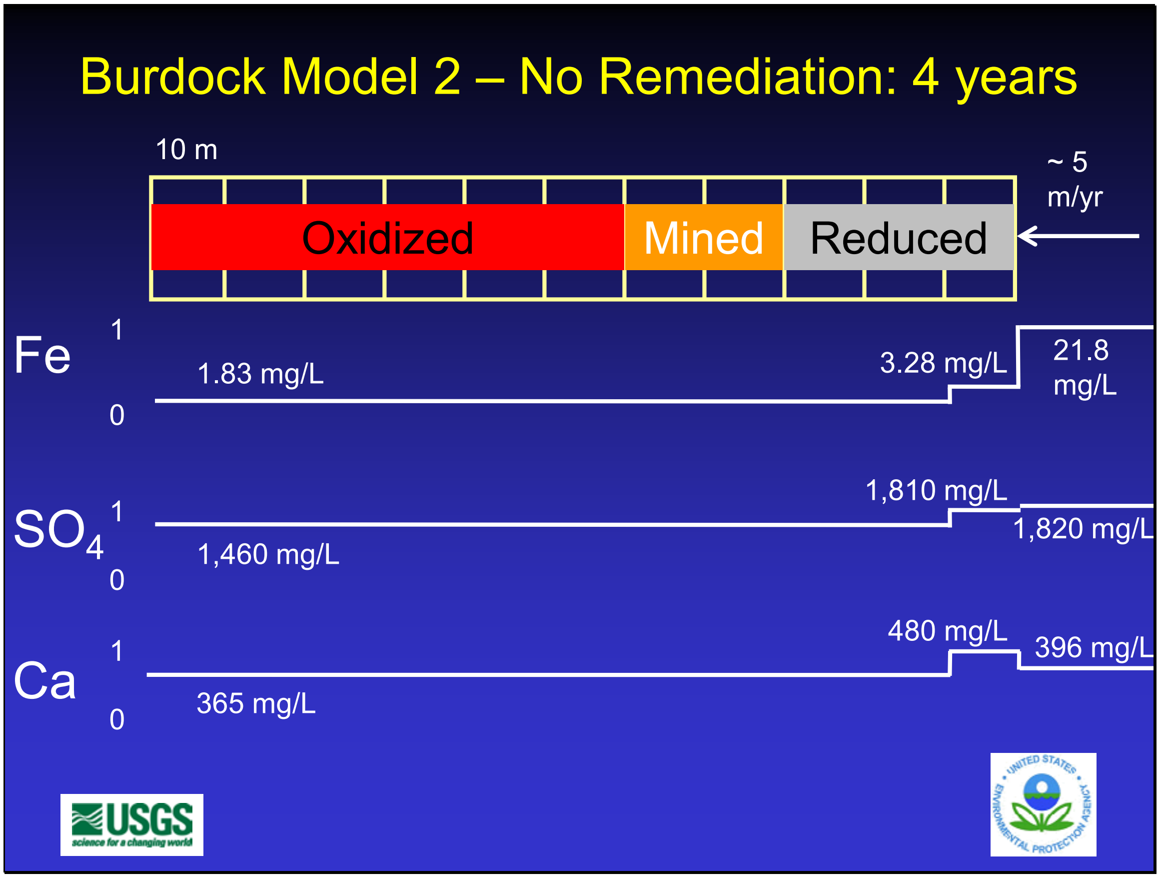


Burdock Model 2 – No Remediation: 4 years

Chloride, oxygen, and uranium move conservatively, as simulation does not have any reactions to remove any of these elements.

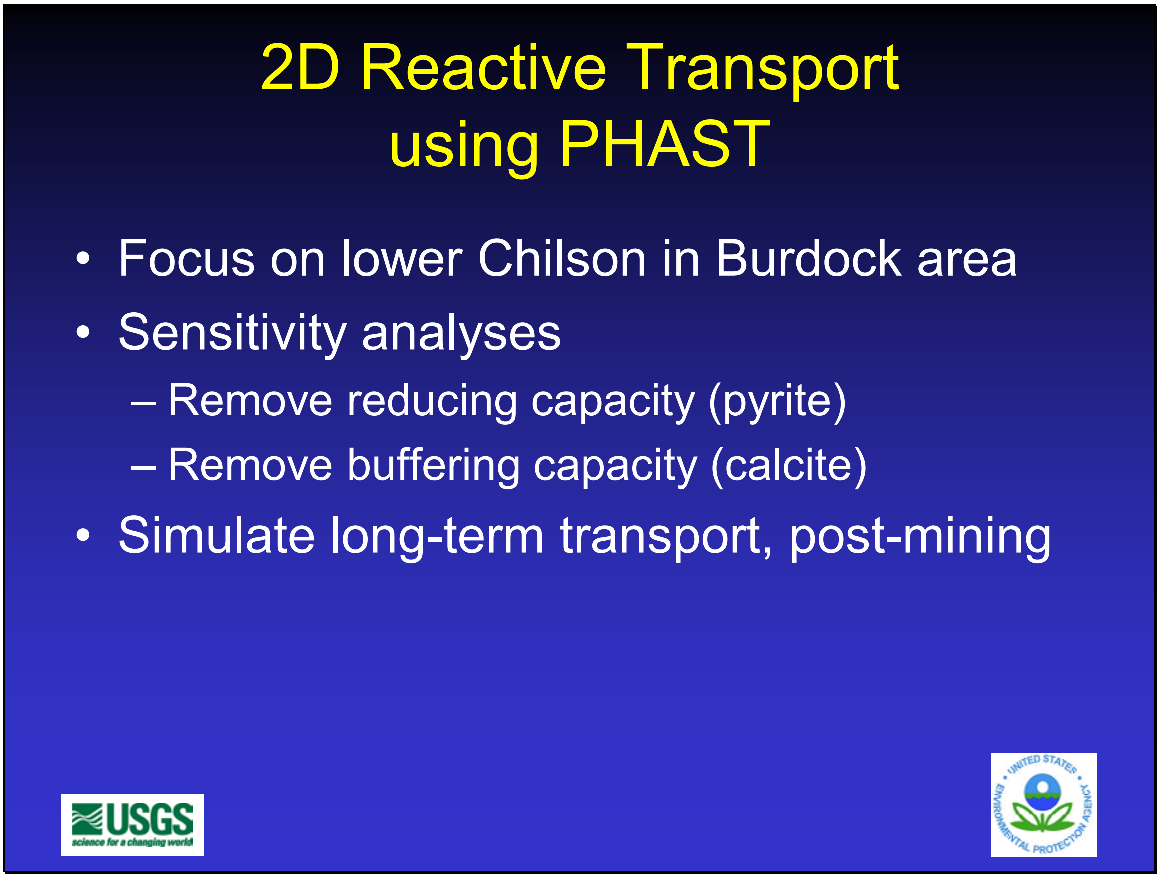
In reality, sorption of uranium to iron hydroxides is likely, but was not simulated.

Slide 33



Burdock Model 2 – No Remediation: 4 years

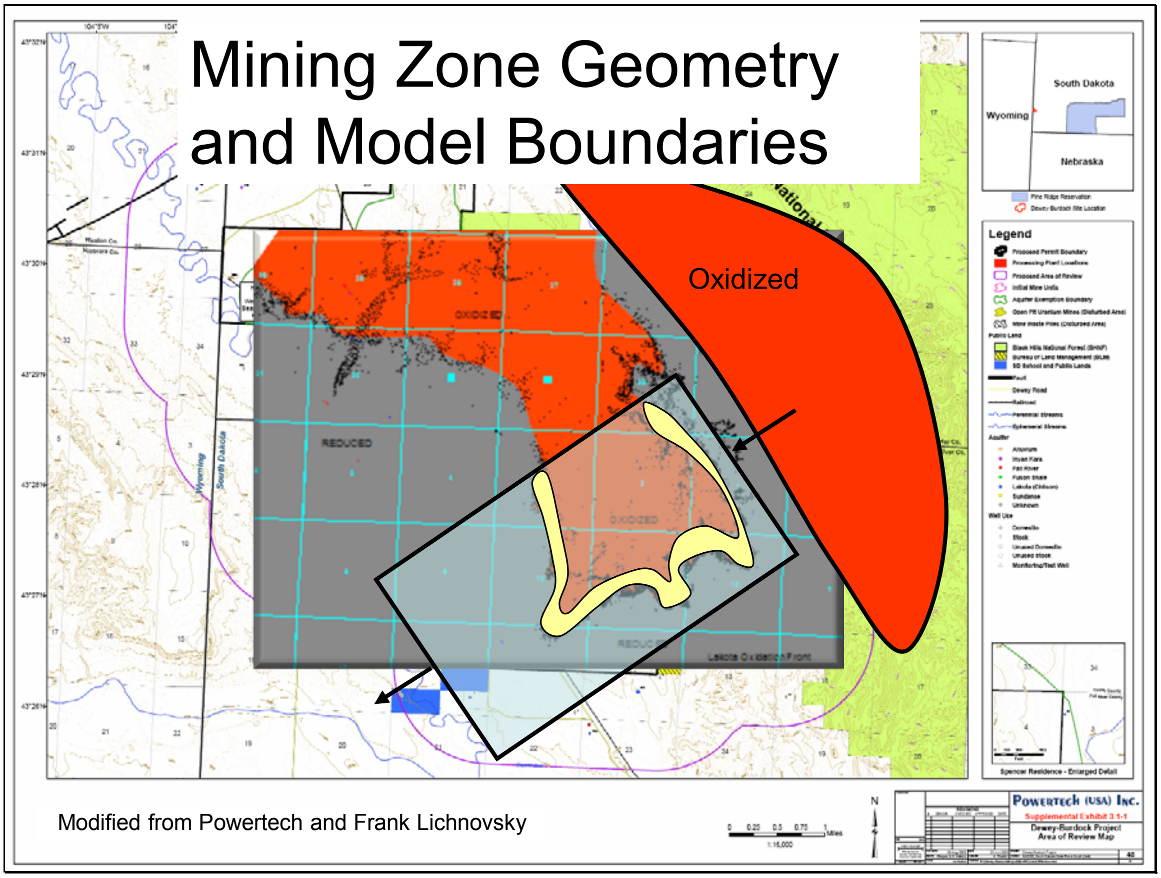
Incoming water here has the highest Fe, sulfate, and Ca in the area.
Oxidation of pyrite controls the reactions at the first cell due to incoming or "background" groundwater.
Downgradient from the mined zone, no reactions occur to change the Fe, sulfate, and Ca concentrations, due to lack of sulfide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



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.

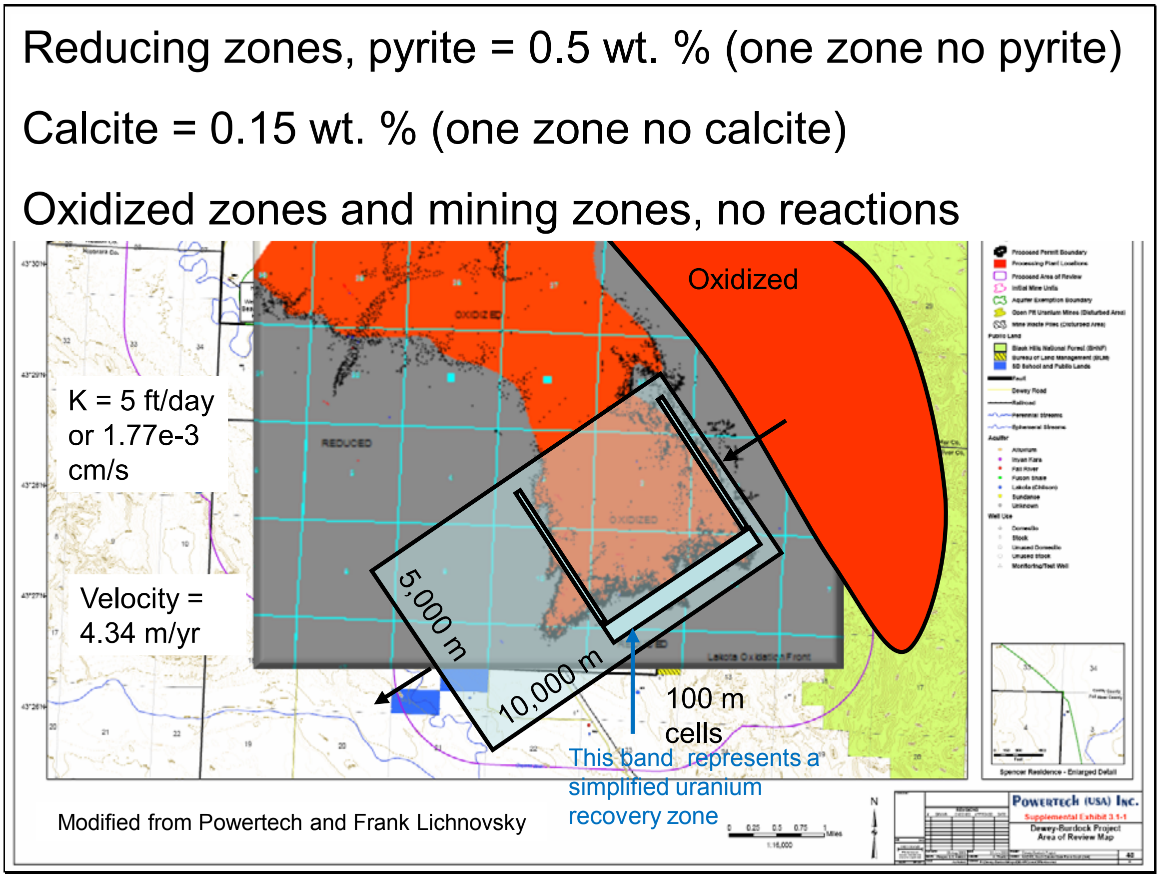


Mining Zone Geometry and Model Boundaries

Modified from Powertech and Frank Lichnovsky

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).

Slide 36



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

K = 5 ft/day or 1.77e-3 cm/s

Velocity = 4.34 m/yr

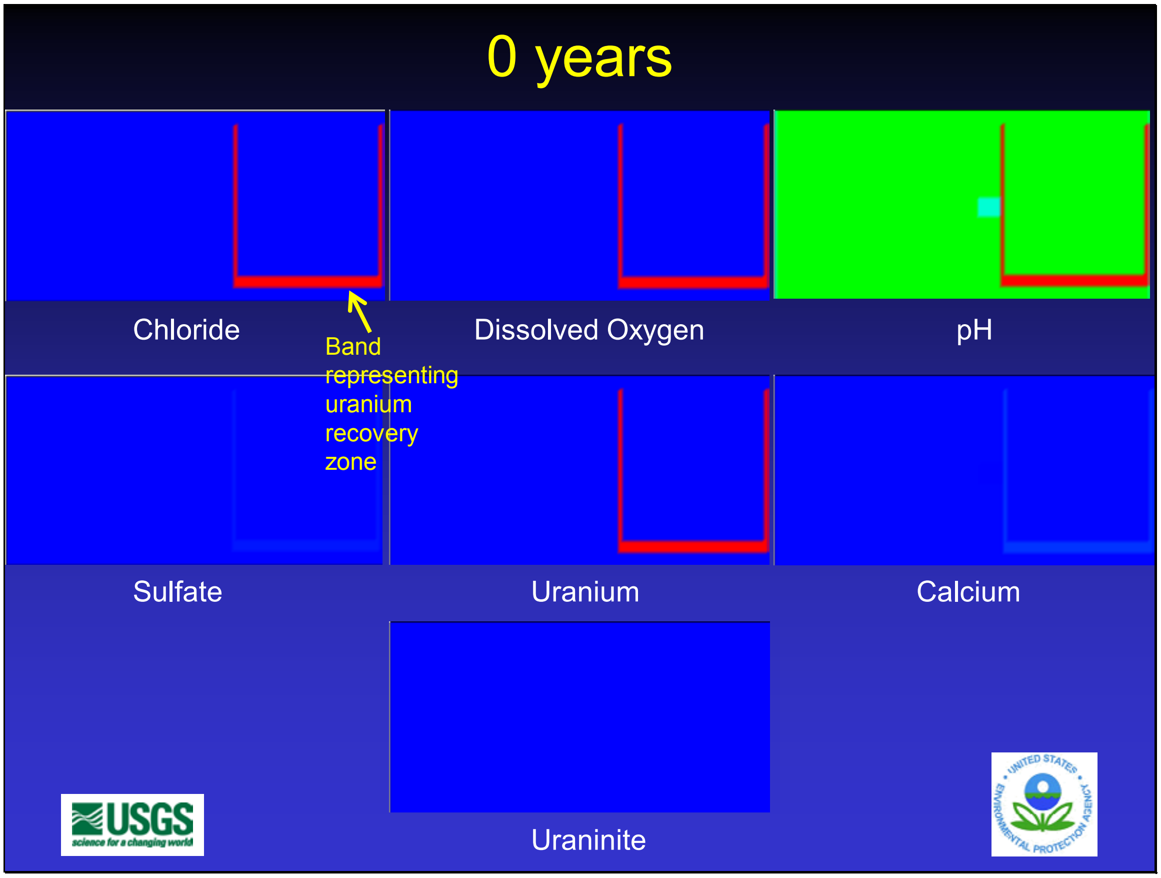
This band represents a simplified uranium recovery zone

Modified from Powertech and Frank Lichnovsky

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.

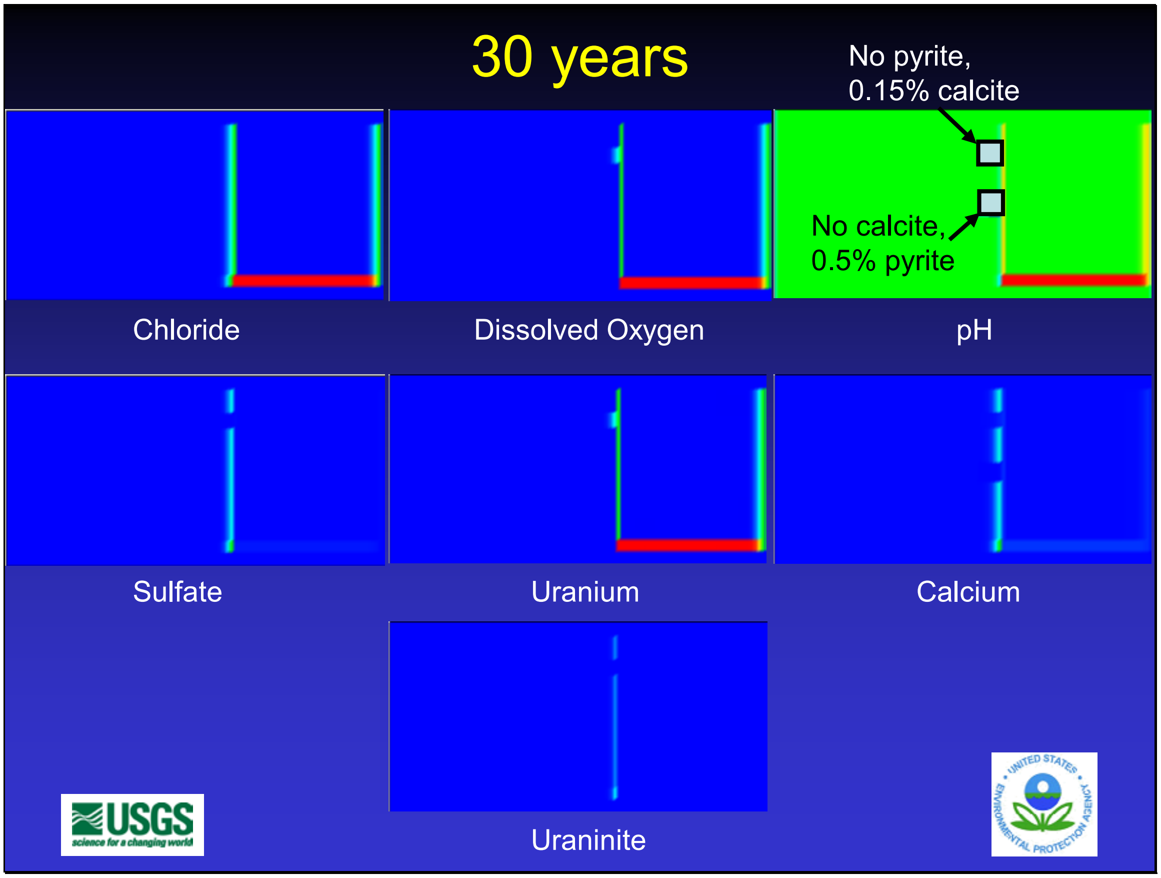


0 years

Band representing uranium recovery zone

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



30 years

No pyrite,
0.15% calcite

No calcite,
0.5% pyrite

Chloride

Dissolved Oxygen

pH

Sulfate

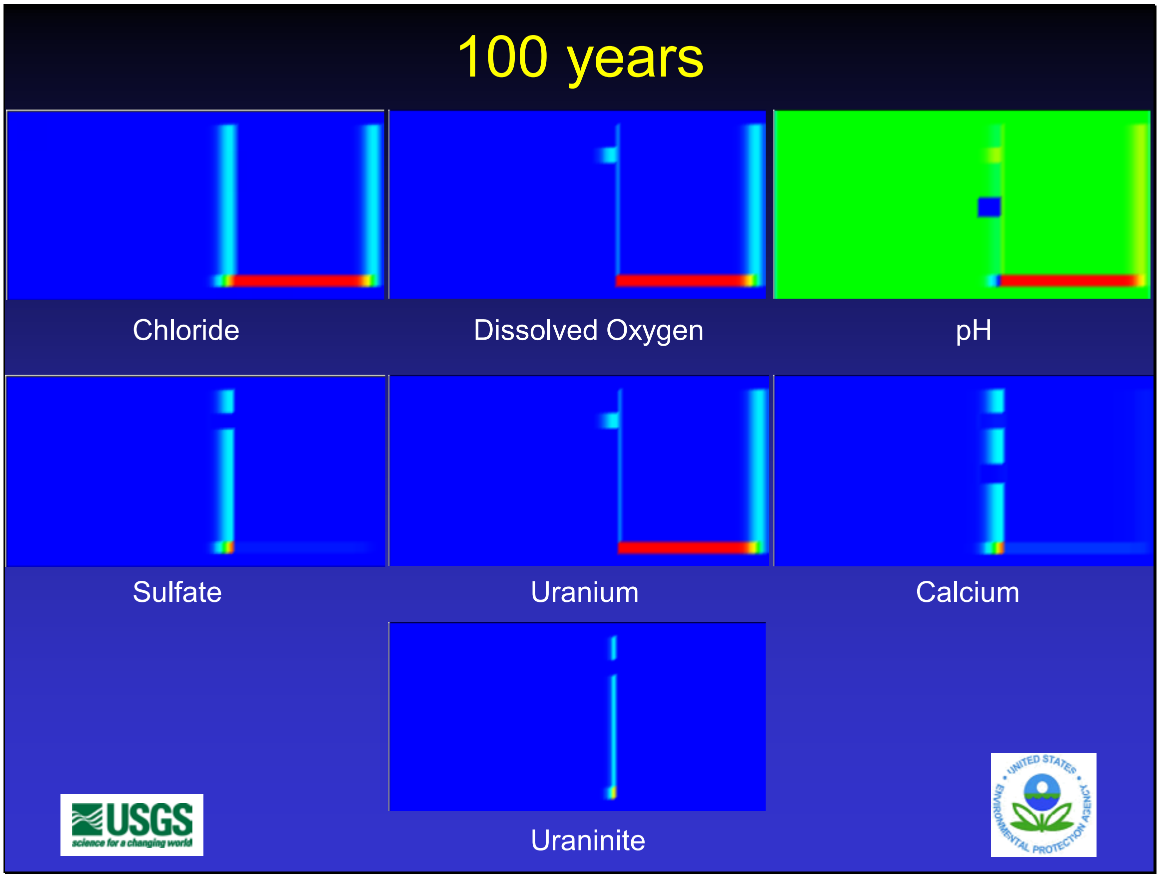
Uranium

Calcium

Uraninite

Note artificially added zone to highlight reactions.

Slide 39



100 years

Chloride

Dissolved Oxygen

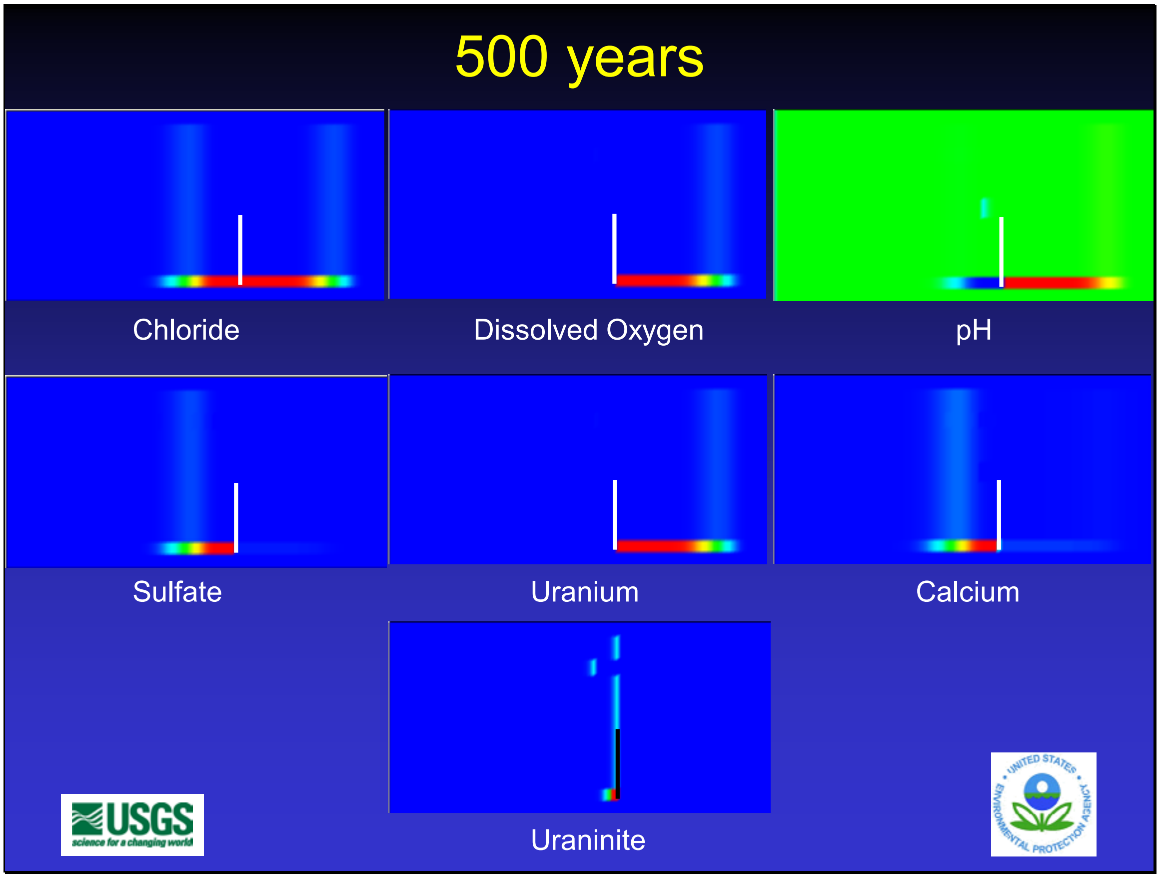
pH

Sulfate

Uranium

Calcium

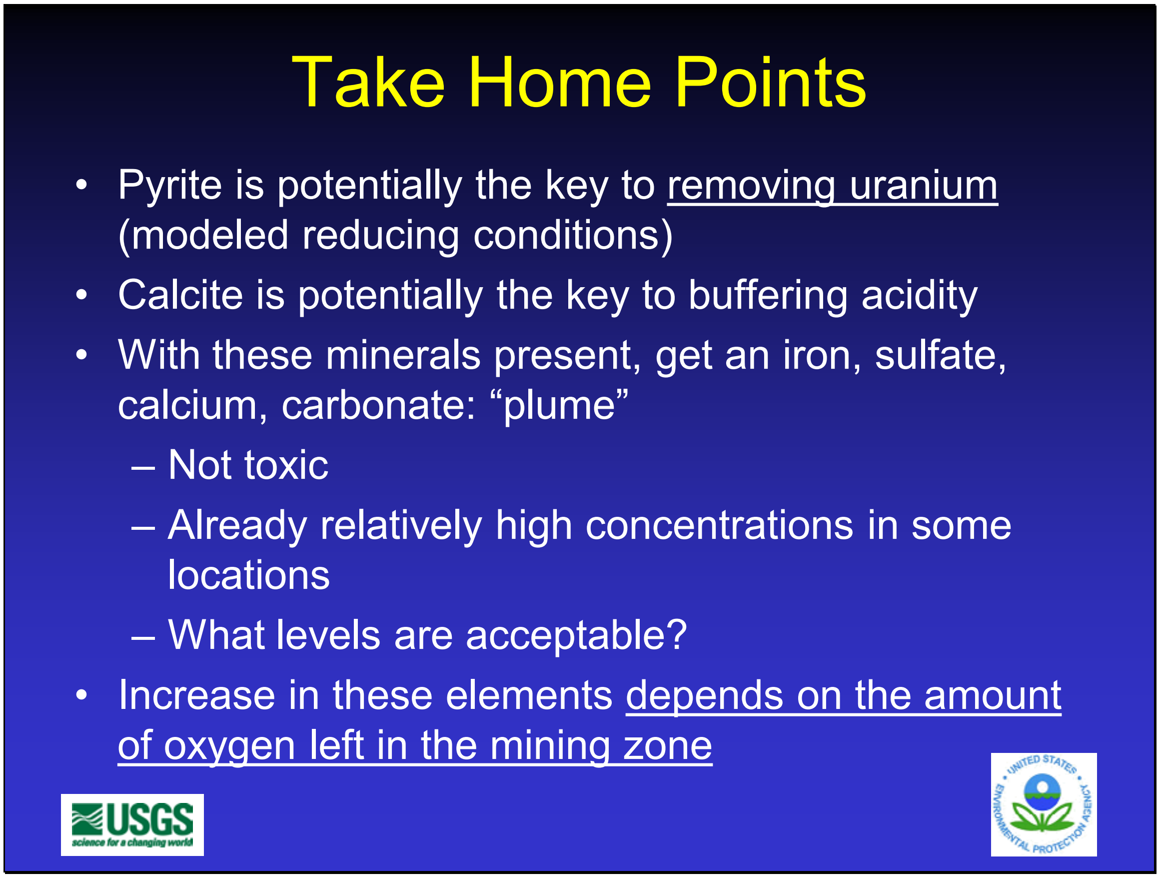
Uraninite



500 years

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.

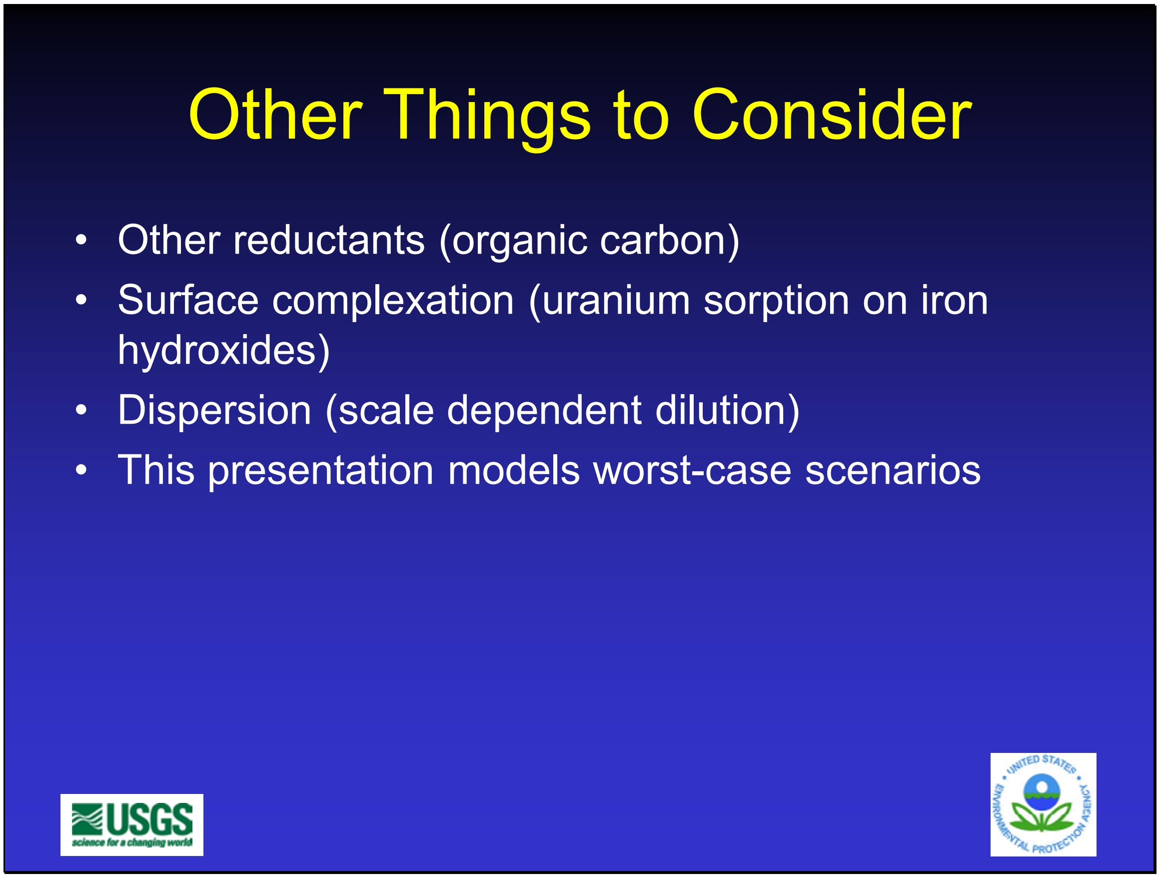
Slide 41



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.

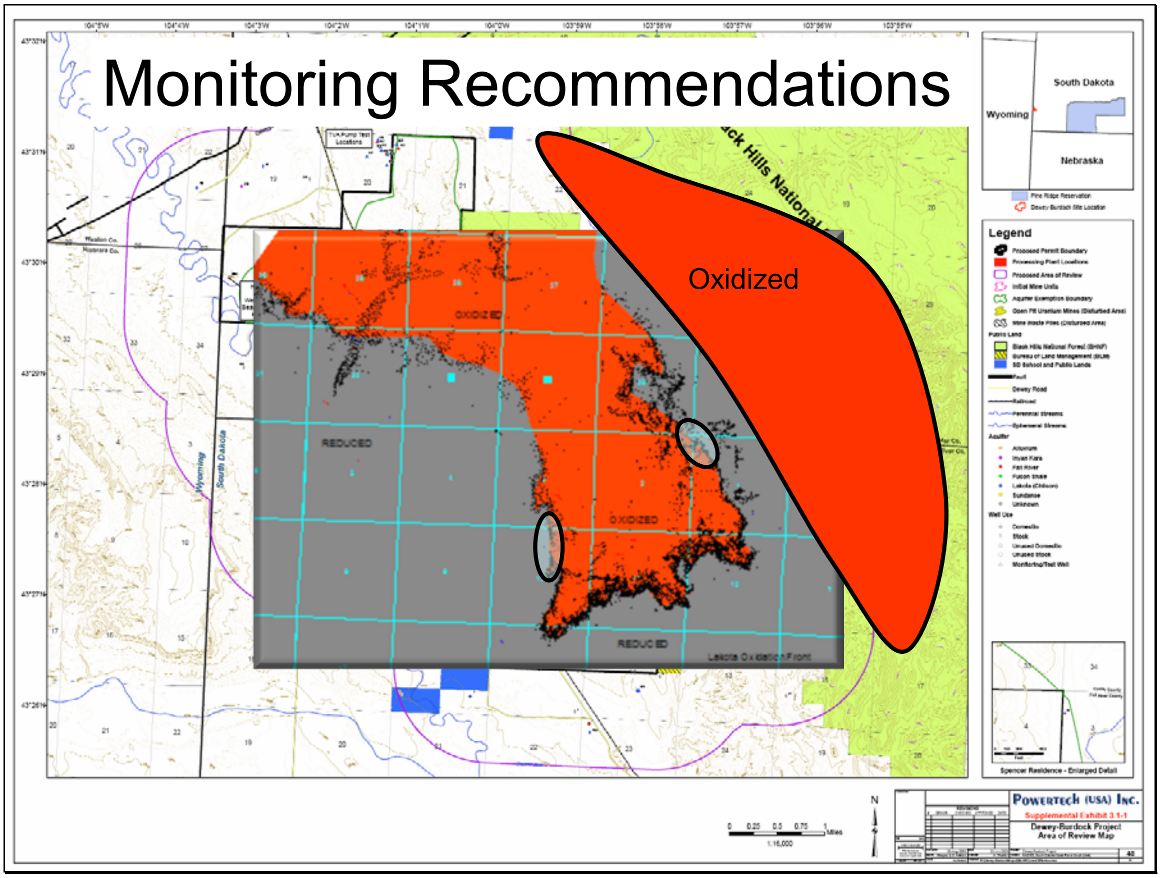


Other Things to Consider

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

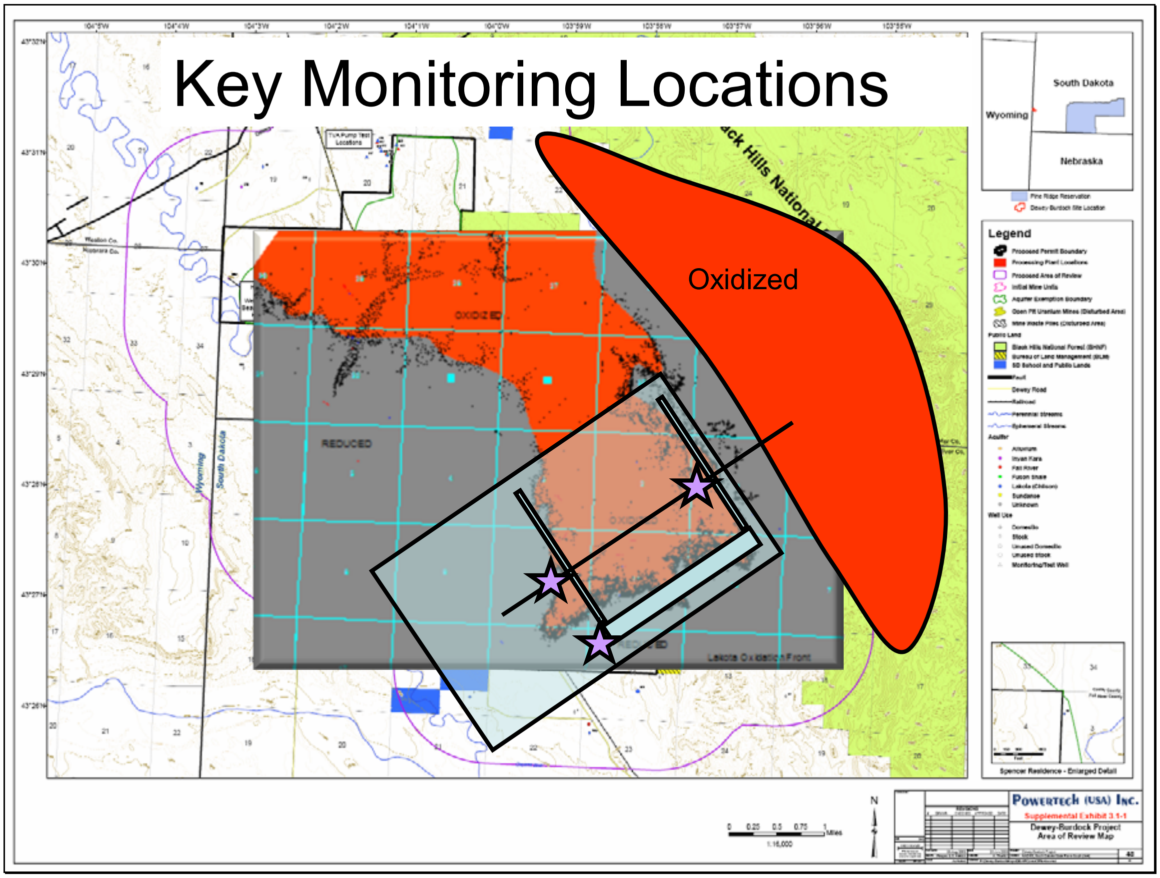
Note that no dispersion was added to any of the simulations in this presentation and all dispersion seen was purely numerical.

Slide 43



Monitoring Recommendations

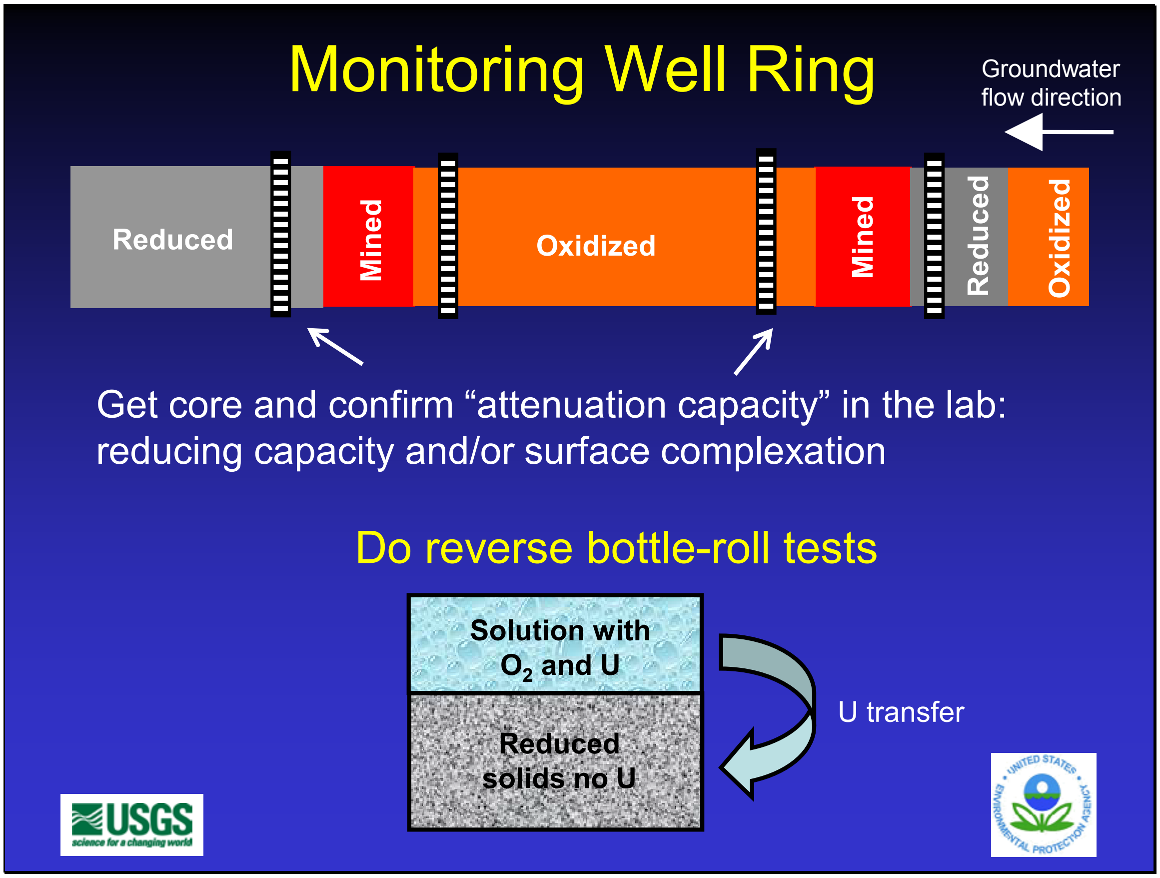
Circles indicate possible monitoring well rings.



Key Monitoring Locations

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



Monitoring Well Ring

Get core and confirm “attenuation capacity” in the lab: reducing capacity and/or surface complexation

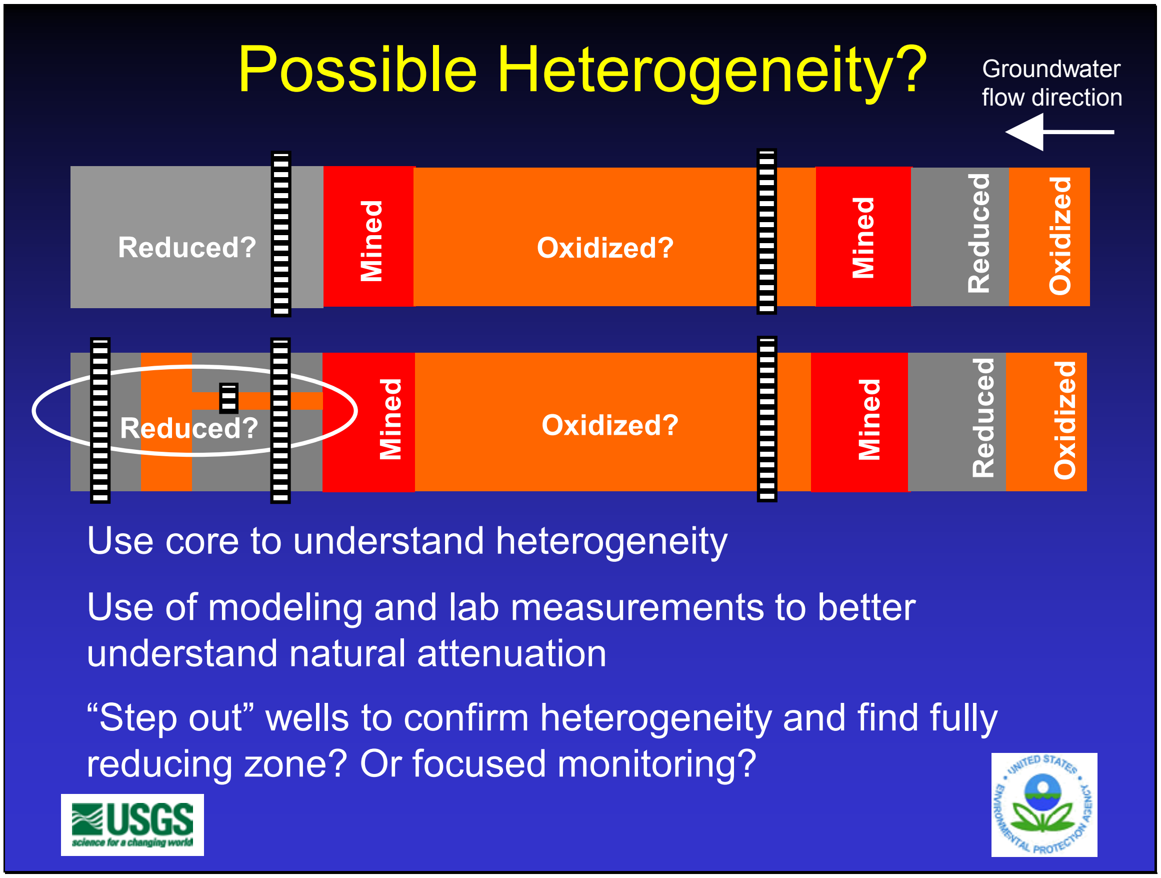
Do reverse bottle-roll tests

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



Possible Heterogeneity?

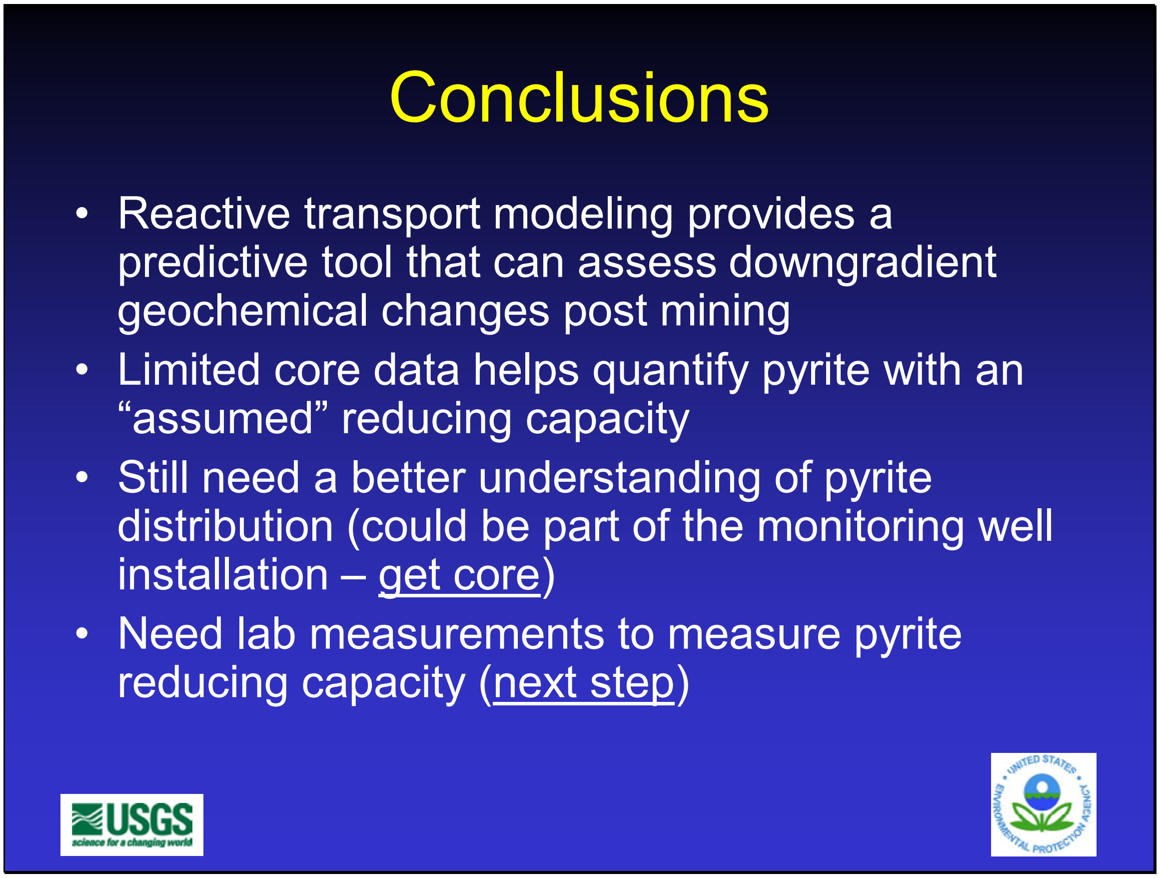
Use core to understand heterogeneity

Use of modeling and lab measurements to better understand natural attenuation

“Step out” wells to confirm heterogeneity and find fully reducing zone? Or focused monitoring?

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.

Questions?

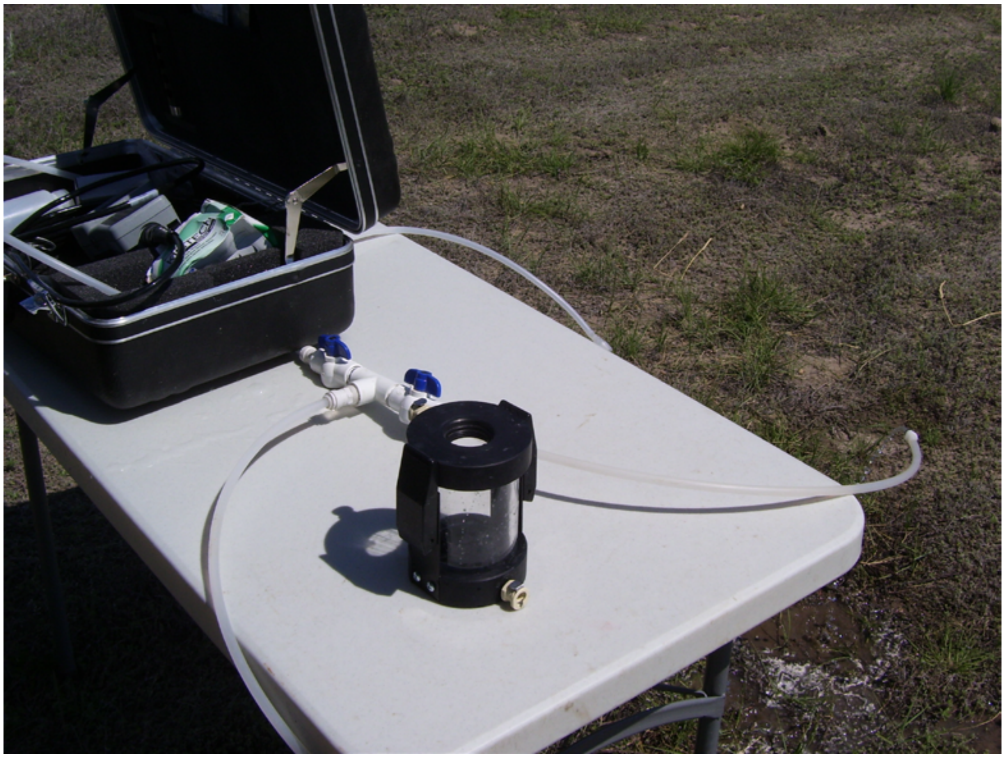
Get Core!

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).

In cooperation with the U.S. Environmental Protection Agency

Geochemical Data from Groundwater at the Proposed Dewey Burdock Uranium In-Situ Recovery Mine, Edgemont, South Dakota

By Raymond H. Johnson



Open-File Report 2012–1070

U.S. Department of the Interior
U.S. Geological Survey

U.S. Department of the Interior
KEN SALAZAR, Secretary

U.S. Geological Survey
Marcia K. McNutt, Director

U.S. Geological Survey, Reston, Virginia: 2012

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Geochemical Data from Groundwater at the Proposed Dewey Burdock Uranium In-Situ Recovery Mine, Edgemont, South Dakota

By Raymond H. Johnson

Abstract

This report releases groundwater geochemistry data from samples that were collected in June 2011 at the Dewey Burdock proposed uranium in-situ recovery site near Edgemont, South Dakota. The sampling and analytical methods are summarized, and all of the data, including quality assurance/quality control information are provided in data tables.

Introduction

Powertech Uranium Corporation (Powertech) has proposed to mine uranium at the Dewey Burdock site using in-situ recovery methods. The Dewey Burdock site is located in the southwestern region of the Black Hills of South Dakota (fig. 1). The uranium recovery license application by Powertech to the United States Nuclear Regulatory Commission (NRC) is publicly available and contains background information about the site along with technical details and baseline sampling data. The NRC application Web site is: *http://www.nrc.gov/materials/uranium-recovery/license-apps/dewey-burdock.html* (with detailed application documents under the "application documents" link). A brief summary of the site history is provided by Powertech at *http://www.powertechuranium.com/s/DeweyBurdock.asp*.

At the Dewey Burdock site, uranium occurs as roll-front ore bodies in several sandstone units of the Inyan Kara Group of Early Cretaceous Age. The Late Jurassic Morrison Formation underlies the Inyan Kara Group. In the vicinity of the mine site, the Inyan Kara Group is comprised of the Fall River Formation (upper unit) and the Lakota Formation (lower unit). The Lakota Formation is comprised of the Chilson and the Fuson Members, with the Fuson Member occurring between the Fall River and Lakota Formations. Uranium roll-front deposits occur in the Fall River Formation and the Chilson Member of the Lakota Formation. Other geologic units of interest for the study area are the surface alluvial aquifers and the Unkpapa aquifer underlying the Morrison Formation. The well location symbols on the maps in figures 2 through 4 are color coded to indicate the aquifer screened interval for each well.

The U.S. Geological Survey (USGS) collected 28 groundwater samples from monitoring wells (figs. 2 through 4) in and around the Dewey Burdock site during the last two weeks of June 2011. This sampling was completed with funding from the U.S. Environmental Protection Agency (USEPA) Region 8's Regional Applied Research Effort (RARE) Program. USEPA is responsible for evaluating the site through its underground injection control program (*http://www.epa.gov/region8/water/uic*) and Powertech has submitted a separate permit application to USEPA (see documentation in a link within the above USEPA Web site). While these new samples provide data on major ion and metal concentrations that overlap with Powertech's baseline sampling, the main intent of this sampling is to get isotopic measurements that will be used to better understand the hydrogeologic system.

Sampling Methods

Groundwater samples were collected using either a peristaltic pump (used in shallow wells), a bailer (used when access problems were encountered), installed pump, or using a low-flow, submersible, stainless steel pump. Many of the wells are under artesian pressure and are flowing, with a valve assembly attached at the surface to control the flow (fig. 5). This same valve assembly was present in all wells with installed pumps. For wells with installed pumps or that were flowing, approximately three well bore volumes were purged prior to sampling.

A peristaltic pump was used in shallow 2-inch diameter wells where the water table was less than 27 feet below the top of the well casing. The sample tubing was placed approximately 1 foot above the bottom of the well and groundwater was purged until field parameters stabilized, which usually occurred within a few minutes. New polyethylene sample tubing was used for each well.

The submersible pump was a Geotech SS Geosub model by Geotech Environmental. The stainless pump was placed at approximately 50 feet below the water table and a drop tube assembling was lowered ahead of the pump to the bottom of the well (*http://www.geotechenv.com/pdf/ground_water_sampling_equipment/ss_geosub_wcontroller.pdf*). The tubing and pump were then pulled back so the intake was one foot from the bottom of the well. This allowed for direct sampling within the well screen and within the active groundwater flow zone using micropurge sampling. Groundwater was purged until field parameters stabilized, which usually occurred within a few minutes and was generally a function of meter stabilization (partially because of added pumping pressure) and not a change in groundwater conditions. New polyethylene sample tubing was used for each well.

A bailer was used in well 680 when the installed pump in the well failed after having purged three casing volumes. The well head was opened and the bailer was used to get water within the casing. A bailer was also used for well NBA, a newly installed well with a 2-inch diameter casing where the water table was below the limit of the peristaltic pump. A bailer was used to purge the well of three casing volumes before sampling. Sampling was completed using the peristaltic pump with new sample tubing to get water out of the bailer and through an inline filter.

For all samples, groundwater sampling was completed through a "T-valve" apparatus that split the flow into a flow through cell for field parameter measurement and a separate line for filling sample bottles (fig. 6). The sample line included an inline 0.45 micron filter that was used for all bottles except for tritium (sample NBA was filtered for tritium also, as the sediment load was high). Field parameter measurements of pH, specific conductance, temperature, dissolved oxygen, and oxidation/reduction potential were all done using a YSI 556 multiparameter meter that screwed directly into the flow through cell (see cover photograph), thereby eliminating any contact with the atmosphere.

Nine aliquots of water provided samples for (1) cations/metals, (2) $^{234}U/^{238}U$ activity ratios, (3) anions, (4) dissolved organic carbon, (5) iron pairs (Fe^{3+}/Fe^{2+}), (6) tritium, (7) stable isotopes (^{18}O and deuterium), (8) sulfur isotopes (^{34}S), and (9) carbon isotopes (^{14}C). Details on bottle type, bottle size, rinsing, filtration, and preservative methods are listed in table 1. Any acids used for preservatives were ultra pure and made specifically for sample preservation. For bottles that were rinsed, rinsing was completed three times prior to filling the bottle.

Table 1. Bottle type and size, rinsing, filtration, and preservation for analytes.

[HDPE, high density polyethylene; mL, milliliter; L, liter; µm, micrometer; HNO_3, nitric acid; HPO_4, phosphoric acid; HCl, hydrochloric acid]

Analytes	Bottle Type	Bottle Size	Rinsing	Filtration	Preservative
Cations and dissolved metals	HDPE	30 mL	New bottle, rinse with sample water	0.45-µm	5 drops HNO_3 or to pH less than 2
$^{234}U/^{238}U$	HDPE	30 mL	New bottles, rinse with sample water	0.45-µm	5 drops HNO_3 or to pH less than 2
Anions	HDPE	30 mL	New bottle, rinse with sample water	0.45-µm	Keep cool
Dissolved organic carbon	Amber glass	125 mL	New bottles, cleaned and burned, do not rinse with sample water	0.45-µm	5 drops HPO_4 or to pH less than 2, keep cool
Dissolved iron species	Amber polyethylene	60 mL	New bottle, rinse with sample water	0.45-µm	5 drops HCl or to pH less than 2, keep cool
Tritium	HDPE	500 mL	New bottles, rinse with sample water	None	None
Water Isotopes: ^{18}O and Deuterium	Borosilicate glass	60 mL	New bottles, rinse with sample water	0.45-µm	None
^{34}S	HDPE	125 mL	New bottles, rinse with sample water	0.45-µm	2 drops of HNO_3 to reduce biotic activity
^{14}C	Amber glass	1 L	New bottles, cleaned and burned, do not rinse with sample water	0.45-µm	Keep cool

Analytical Methods

This section describes the analytical procedures completed on each of the nine water sample aliquots. The cations/metals sample was analyzed at the USEPA (Ada, Oklahoma) and at the USGS laboratories (Denver, Colorado). USEPA analyses were made using inductively coupled plasma – optical emission spectrometry (ICP-OES, Perkin-Elmer Optima 3300DV) using EPA Method 200.7 and inductively coupled plasma – mass spectrometry (ICP-MS, PQExcell, Thermo Elemental) using USEPA Method 6020. USGS analyses were made using ICP-MS at the USGS Mineral Resources Laboratory (Denver, Colorado) following the method described in Lamothe and others (2002).

The $^{234}U/^{238}U$ activity ratios were analyzed by Michael Ketterer at the Northern Arizona University in Flagstaff, Arizona using a sector field Thermo X Series II quadrupole ICP-MS unit. Details on the analytical method can be found in file Appendix F.

Dissolved anions were analyzed by the USEPA laboratories (Ada, Oklahoma) using capillary electrophoresis with ultraviolent (UV) detection (USEPA Method 6500). Capillary ion electrophoresis is a free-zone electrophoretic technique optimized for the analysis of anions with molecular weights of less than 200 grams/mole. The anions migrate and are separated according to their mobility in the electrolyte when an electrical field is applied through the open tubular fused silica capillary.

Concentrations of dissolved inorganic carbon were measured by the USEPA laboratories (Ada, Oklahoma) with a Dohrmann DC-80 Carbon Analyzer (USEPA Method 9060A). Iron pairs (Fe^{3+}/Fe^{2+}) were completed by David Fey at the USGS Mineral Resources Laboratory (Denver, Colorado) using the ferrozine method for iron species discussed in Bangthanh To and others (1999). Tritium analyses were completed by Robert Michel at the USGS Isotope Laboratory in Menlo Park, California using liquid scintillation counting with a detection limit of approximately 0.6 tritium units (TU) (similar to USEPA method 906.0). Oxygen- and hydrogen-isotopic ratios of water were analyzed using a high temperature conversion elemental analyzer linked to a continuous flow isotope ratio mass spectrometer (Finnigan Delta plus XP). These analyses followed the methods presented by Lu (2009). Sulfur isotopes (^{34}S) were analyzed by Christopher Eastoe at the University of Arizona following the method of Coleman and Moore (1978). Additional analytical procedures for that laboratory can be found at *http://www.geo.arizona.edu/research/iso_analytical.html.*

Data

All of the resulting data are provided in table 2. Sample identification numbers in table 2 match the well identification numbers used in Powertech permit application documents. Original labeling included “B” and “D” in the sample name for ease of sample identification (found in appendix files) by area, “B” for Burdock and “D” for Dewey, but were not included in the final data table (table 2).

The samples in table 2 have been organized by categories to reflect geologic units that the wells are screened in along with general area locations. These are purely initial categories used by the author for later use in interpretations.

Quality Assurance/Quality Control

For all USEPA solution measurements, quality assurance tests involved duplicate samples, blanks, sample matrix spikes, calibration check standards, and second-source quality control samples. Data for the laboratory quality assurance/quality control (QA/QC) checks are included in the original data that can be found in the appendixes. Uranium isotope data also included internal laboratory checks that can be found in Appendix F. All other laboratories used typical internal reference standards for the appropriate analyses and QA/QC information is available upon request. No internal laboratory QA/QC issues were found.

In addition to the internal laboratory checks, three duplicate samples and five blanks were submitted as part of the QA/QC process. Data from these duplicates and blanks are reported in table 3. No QA/QC issues were found in any of the duplicate samples. Blanks for all of the different sampling conditions are represented (Geosub pump, peristaltic pump, and bailer sampling). For metals, cations, and anions, a few blanks did show values above the detection limits, but generally these values were well below any sample results. Only one blank had an iron concentration that was high enough compared to the groundwater samples to be of concern. Iron in the bailer blank (B-VS4) was 3.72 µg/L, which is likely because of incomplete cleaning of the bailer. Cleaning the bailer was difficult because of limited access inside the bailer in addition to sample NBA (well sampled prior to blank) having a high silt content. As a result, any measured iron values below 4 µg/L, may not be accurate, especially for samples using a bailer. Sample data were not blank corrected.

Acknowledgments

Funding from the US EPA made this data collection possible. Special thanks go to Richard Wilkin (USEPA, Ada, Oklahoma) for managing the USEPA contract and organizing the sample submittals to the appropriate USEPA laboratories. We are grateful for well access provided by individual land owners and through arrangements made by Powertech. Powertech employees, Wyatt Van Eaton and Mike Beshore provided invaluable assistance in accessing the wells and assisting with equipment logistics. Facilities for equipment storage and a convenient staging area were provided by Mark Hollenbeck. In addition, the groundwater sampling included assistance from Brian Zimmerman, Andrew Mahan, Valois Shea, Tanya Gallegos, and John Horton.

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Lamothe, P.J., Meier, A.L., and Wilson, S.A., 2002, The determination of forty-four elements in aqueous samples by inductively coupled plasma–mass spectrometry, *in* Taggart, J.E., ed., chap. H, Analytical methods for chemical analysis of geologic and other materials, U.S. Geological Survey: U.S. Geological Survey Open-File Report 02-223-H, 11 p., available at *http://pubs.usgs.gov/of/2002/ofr-02-0223/H21&23OFR99-151_M.pdf.*

Lu, F.H., 2009, Online high-precision δ^2H and δ^{18}O analysis in water by pyrolysis: Rapid Communications in Mass Spectrometry, v. 23, p. 3144-3150.

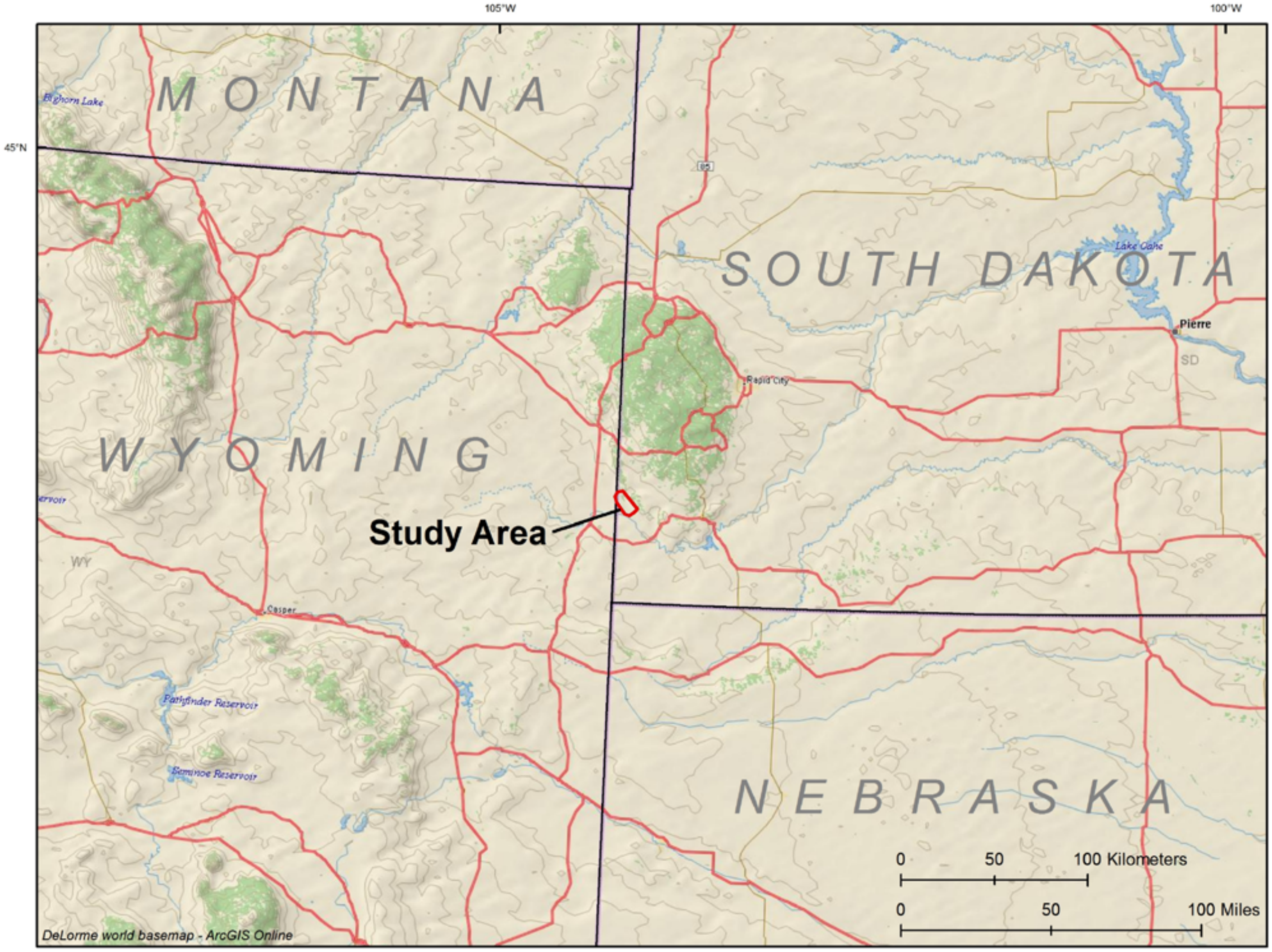


Figure 1. Location of study area.

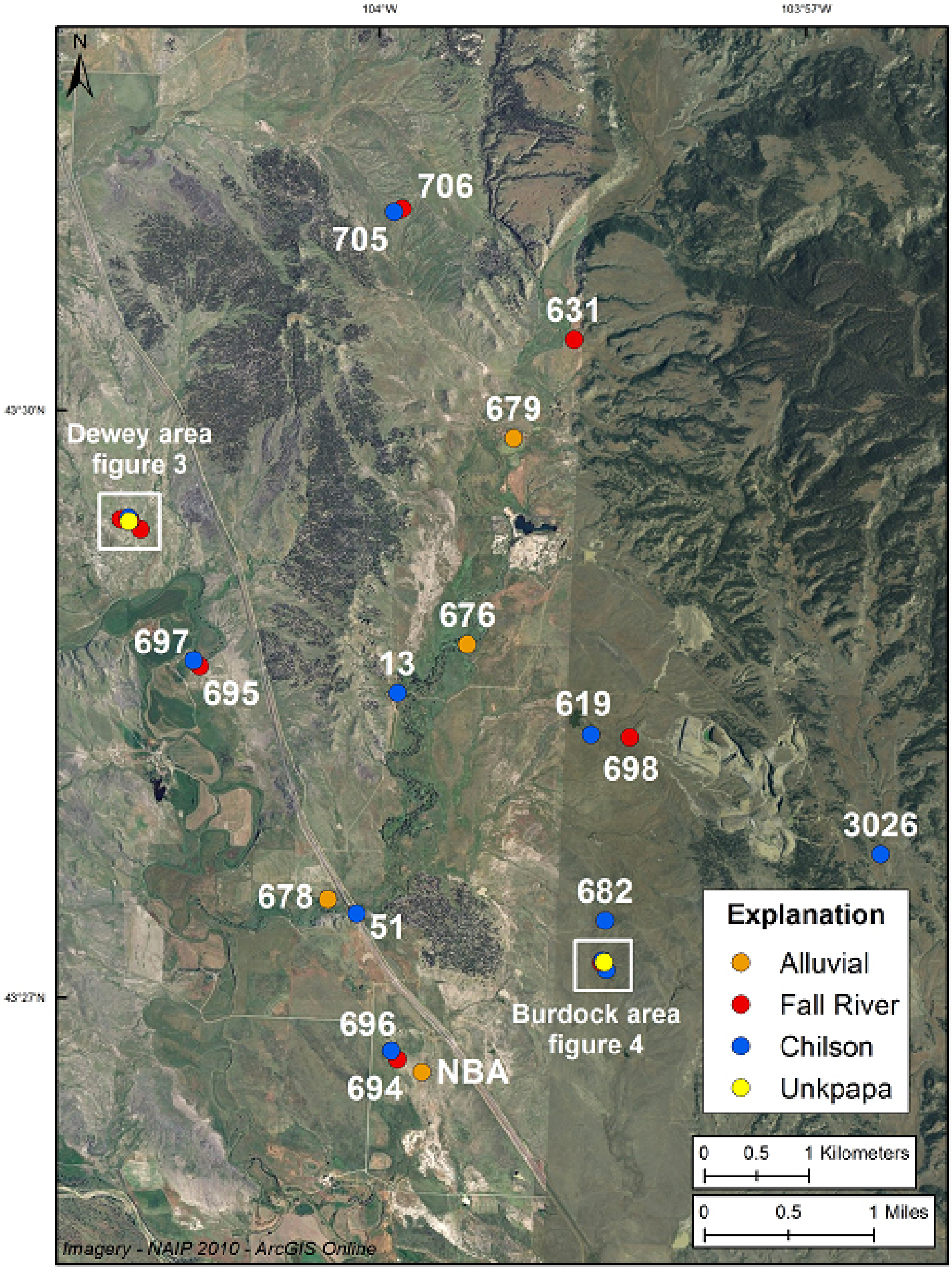
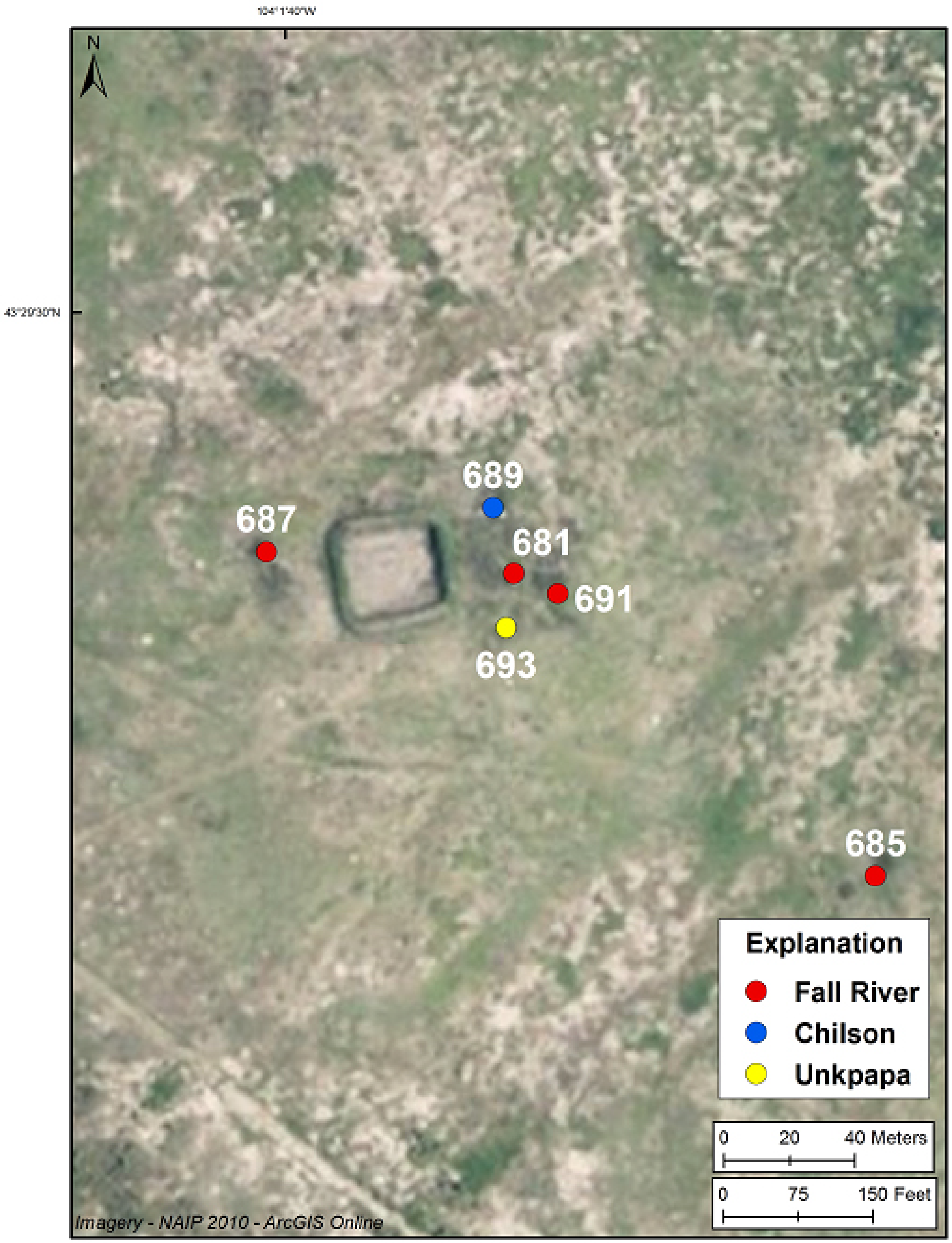


Figure 2. Satellite imagery overlain with monitoring well locations. Labels indicate well identification number. White boxes indicate location of expanded views for figures 3 and 4.



Imagery - NAIP 2010 - ArcGIS Online

Figure 3. Expanded view of Dewey area. Labels indicate well identification number.

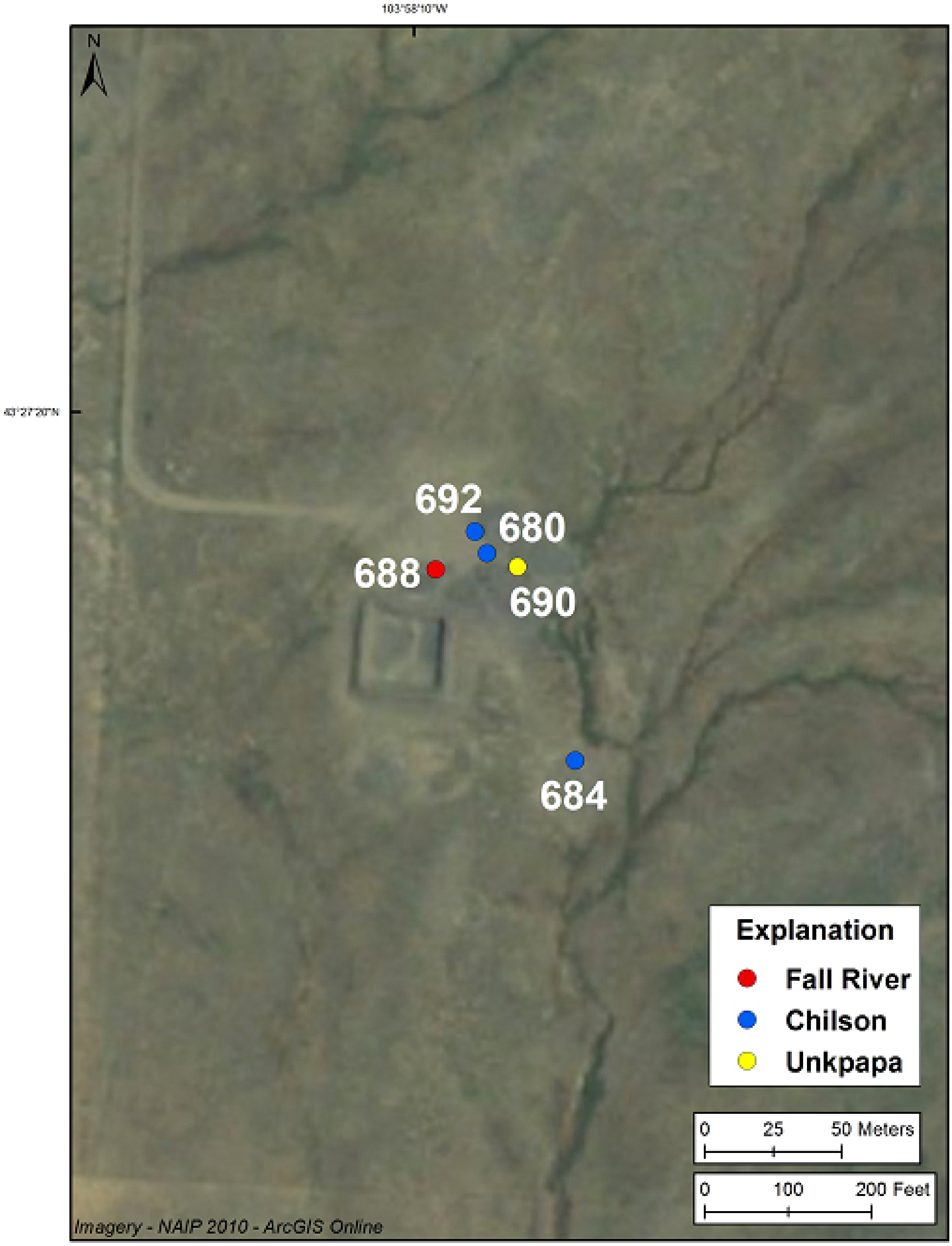


Figure 4. Expanded view of Burdock area. Labels indicate well identification number.

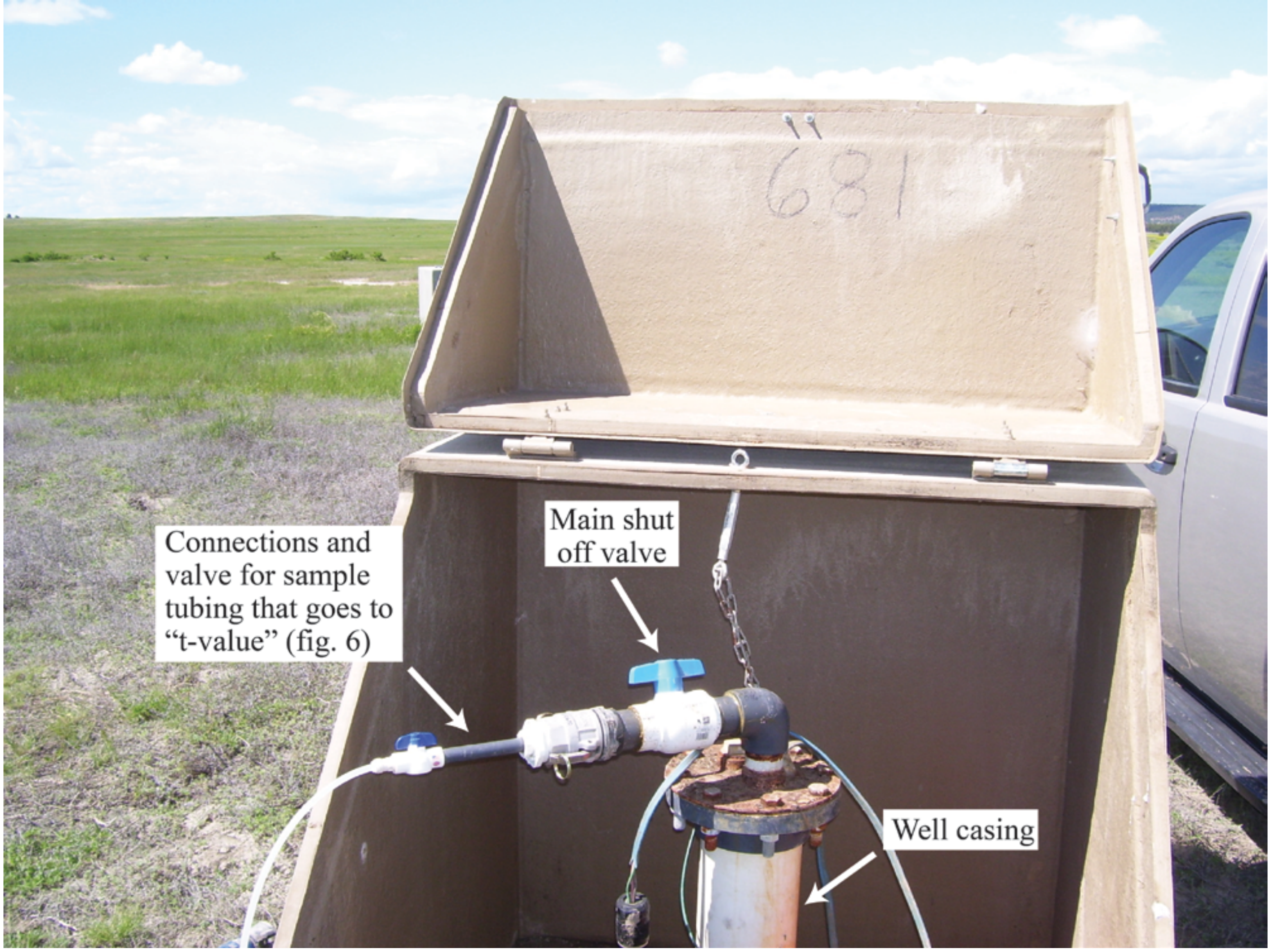


Figure 5. Typical wellhead control valves.

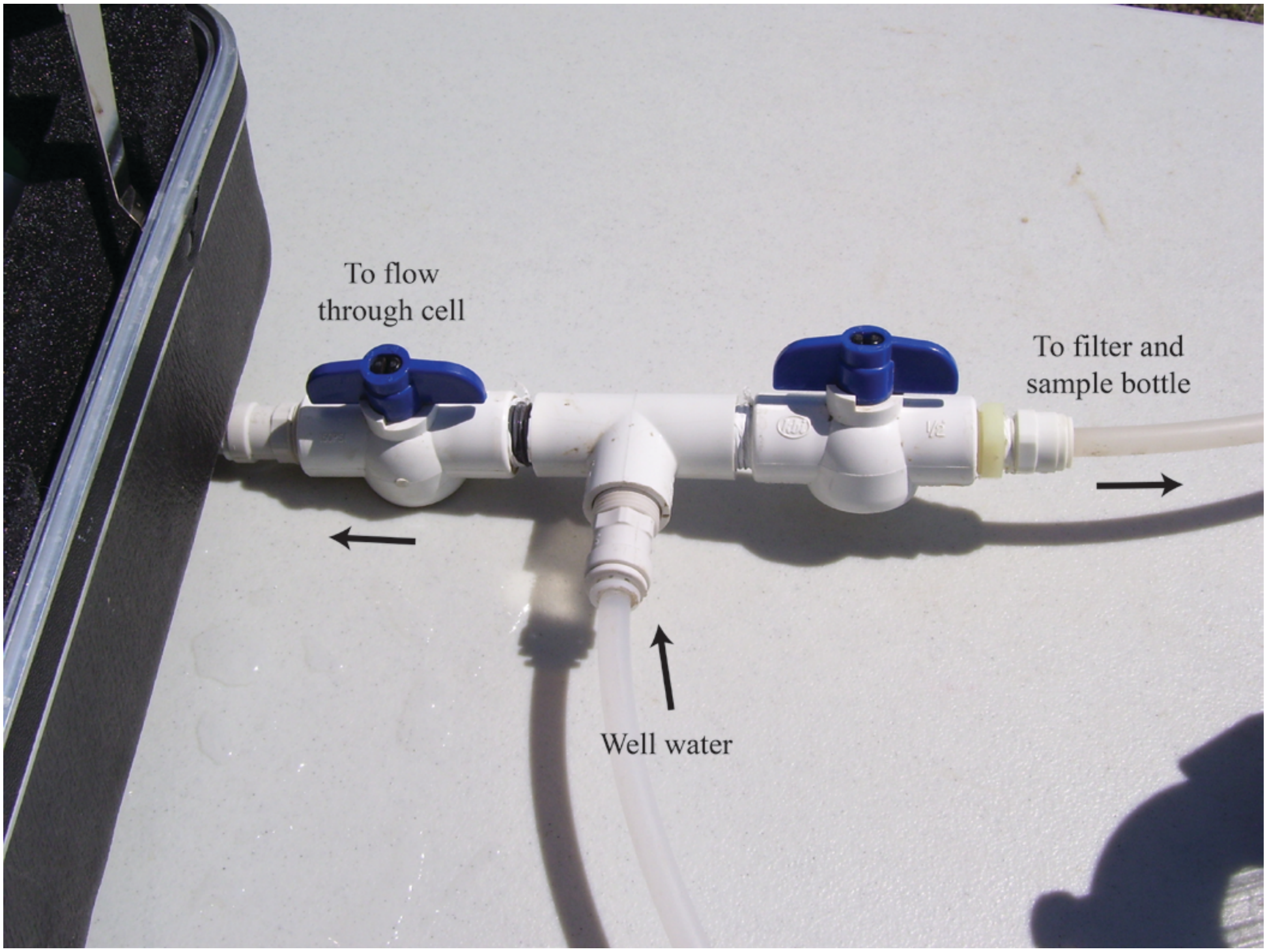


Figure 6. “T-valve” used for sampling.