## MIGRATION OF HEAVY ELEMENTS IN GROUND WATER

#### FOLLOWING URANIUM SOLUTION MINING OPERATIONS

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#### ABSTRACT

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> The attached report presents simulation models and example output for the analysis of heavy element migration in ground water from in-situ uranium solution mining sites under conditions of ground water flow. The models are one dimensional and include the effects of advection, dispersion, mass transfer, and equilibrium for selected heavy elements. Previous laboratory data for uranium, molybdenum, vanadium, selenium and arsenic were used to obtain necessary mechanistic relationships used in the models. Hydrologic characteristics and status of solution mining sites in Wyoming are presented.

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#### CHAPTER 1

#### INTRODUCTION

The work reported herein is a continuation of research into the study of migration of heavy elements from in-situ uranium solution mining sites (Humenick, et al., 1983). Initial work was performed in the laboratory to determine the mechanism of heavy element release and to provide data which could be used to develop simulation models for the transport and migration of heavy elements from commercial mining sites under the influence of natural ground water flow.

The objectives of this work were to develop simulation models based on mass transfer and equilibrium data from the previous work and to evaluate the importance of the parameters in the model in light of the extent of heavy element migration. The migration results are based on hydrologic conditions prevalent at commercial mining sites in Wyoming. Specific objectives were as follows:

1. To develop a simulation model to predict the migration of heavy elements (uranium, molybdenum, vanadium, selenium, and arsenic) under conditions of one-dimensional transport in confined ground water aquifers that have been subjected to uranium solution mining operations within and down dip of the mining area;

2. to produce a model that will account for the processes of advection, dispersion, and mass transfer within the ground water system;

3. to determine the significance of heavy element migration based on model predictions for typical Wyoming mining sites.

#### CHAPTER 2

## CHARACTERISTICS OF WYOMING IN-SITU URANIUM MINING SITES

To simulate actual mining sites in Wyoming, the permit files of the Department of Environmental Quality (DEQ) were used to accumulate as much hydrologic and geologic information as was available. Because of the dispersed nature of the information, its accumulation and summary was an important project task.

## Location and Status of Mining Sites

The majority of uranium mining activity in Wyoming occurs in the northeastern and south-central portion of the state. Johnson, Campbell, Converse, and Fremont Counties have the greatest amount of activity at the present time. The majority of solution mining efforts have taken place in these areas, also (Figure 1).

At the present time, only one commercial uranium in-situ development project is in operation in Wyoming. Sequoyah Fuels Corporation, a subsidiary of Kerr McGee Nuclear Corporation, is the operator. The project involves the Q Sand of the Fort Union formation in Converse County and is operated under a research and development permit issued by the DEQ. Table I summarizes the activity in Wyoming.

# WYOMING



FIGURE 1. In Situ Uranium Leaching Sites in Wyoming

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## Sites Shown in Figure 1

- 1. Arizona Public Services Co. Peterson Insitu Uranium Extraction Process
- 2. Uranium Resources Inc. North Platte Project
- 3. Cleveland Cliffs Iron Co. Collins Draw
- 4. Exxon Minerals Co. Highland Mine
- 5. Uranerz, USA, Inc. Ruth ISL Pilot Project
- Sequoyah Fuels Corporation
   Q Sand Project
- 7. Sequoyah Fuels Corporation O Sand Project
- 8. Wyoming Mineral Corporation Irigary Ranch
- 9. Ogle Petroleum Co. Bison Basin
- 10. Rocky Mountain Energy Nine Mile Lake
- 11. Western Nuclear Christensen Ranch
- 12. Teton Exploration Drilling Co. Leuenberger Site
- 13. Rocky Mountain Energy Reno Ranch

## TABLE I

## In-Situ Mining Operations in Wyoming

Operator	<u>Mine Name</u>	County	Formation
Commercial Scale			
Exxon Minerals Co.	Highland Mine	Converse	Fort Union
Wyoming Mineral Corp.	Irigary Ranch	Johnson	Wasatch
Rocky Mtn. Energy	Reno Ranch	Campbell	Wasatch
Ogle Petroleum Co.	Bison Basin	Fremont	Green River (Laney Member)
Teton Exploration	Leuenburger	Converse	Fort Union
Drilling Co.	-		
Research and Developm	ent		
Cleveland Cliffs	Collins Draw	Campbell	Wasatch
Iron Co.	oorrand braw	oumpberr	habaten
Kerr McGee Nuclear	Bill Smith Project	Converse	Fort Union
Kerr McGee Nuclear	Q Sand Project	Converse	Fort Union
Kerr McGee Nuclear	Bill Smith Mine 6001	Converse	Fort Union
Uranerz, USA, Inc.	Ruth ISL Pilot Project	Johnson	Wasatch
Uranium Resources, Inc.	North Platte Project	Converse	Fort Union
Arizona Public Services Co.	Peterson In-Situ Uranium Extraction Process	Converse	Fort Union
Tfn Files			
(DEQ still analyzi	ng data from these befor	e issuing perm	anent permit)
Rocky Mtn. Energy	Nine Mile Lake	Natrona	Mesaverda
Wyoming Mineral Co.	Irigary Ranch	Campbell	Wasatch
Rocky Mtn. Energy	Reno Ranch	Campbell	Wasatch
Western Nuclear	Christensen kanch	Campbell	Wasatch
Kerr-McGee	0 Sand Project	Converse	Fort Union
Licenses to Explore			
Rocky Mtn. Energy	Nine Mile Lake	Natrona	Mesaverda
Wyoming Mineral Co.	S-I-7 Pilot Test	Johnson	
Union Energy	Battle Springs	Sweetwater	
Mining Div.			
Nuclear Dynamics	Sundance Project	Crook	
Wold Nuclear Co.	Red Desert	Sweetwater	
Texasgulf, Inc.	Radon Springs	Fremont	

#### Ground Water Restoration

Reclamation or ground water restoration involves meeting certain contaminant criteria set by the DEQ and is based upon pre-existing conditions before mining commences. The restoration goal of any permitted operation is "background water quality." Background, as defined by DEQ, is "the constituents or parameters and the concentrations or measurements which describe water quality and water quality variability prior to subsurface discharge." If background quality cannot be achieved for certain elements, criteria are set for these constituents based on the present or potential economic use of the water. The state of Wyoming classifies its ground waters into four basic categories:

Class	I.	Suitable	for	domestic use.
Class	II.	Suitable	for	agricultural use.
Class	III.	Suitable	for	livestock.
Class	IV.	Suitable	for	industry.

Established criteria for each of the first three classes are listed in Table II. Additional criteria are outlined in DEQ's <u>Water Quality Rules and</u> Regulations, Chapter VIII.

Several methods exist by which ground water restoration can be obtained. They include:

- 1) Ground water sweep
- 2) Reverse osmosis
- 3) Electrodialysis
- 4) Anion/cation exchange.

Ground water sweep involves the direct removal of all contaminated waters with no subsequent reinjection. Several pore volumes of water must be removed from each pattern. In addition, pumps large enough to initiate effective ground water sweep are often expensive.

## TABLE II

## GROUND WATER QUALITY CLASSIFICATIONS

UNDERGROUND WATER			
CLASS	I	II	III
Use Suitability	Domestic	Agriculture	Livestock
Constituent			
or Parameter	Concentration*	Concentration*	Concentration*
Aluminum (Al)	···· ··· ··· ·	5.0	5.0
Ammonia	0.51		
Arsenic	0.05	0.1	0.2
Barium (Ba)	1.0		
Beryllium (Be)	6007 Page anti-	0.1	
Boron	0.75	0.75	5.0
Cadmium (Cd)	0.01	0.01	0.05
Chloride (Cl)	250.0	100.0	2000.0
Chromium (Cr)	0.05	0.1	0.05
Cobalt (Co)		0.05	1.0
Copper (Cu)	1.0	0.2	0.5
Cyanide (CN)	0.2		
Fluoride(F)	$1.4 - 2.4^2$		
Hydrogen Sulfide	0.05		
(H <sub>2</sub> S)			
Iron (Fe)	0.3	5.0	
Lead (Pb)	0.05	5.0	0.1
Lithium		2.5	
Manganese (Mn)	0.05	0.2	
Mercury (Hg)	0.002		0.00005
Nickel		0.2	
Nitrate (No <sub>2</sub> -N)	10.0		
Nitrite (NO <sub>2</sub> -N)	1.0		10.0
$(NO_2 + NO_2)$	-N		100.0
0il & Grease	Virtually Free	10.0	10.0
Phenol	0.001		
Selenium (Se)	0.01	0.02	0.05
Silver (Ag)	0.05		
Sulfate (SO,)	250.0	200.0	3000.0
Total Dissolved	500.0	2000.0	5000.0
Solids (TDS)			
Uranium (U)	5.0	5.0	5.0
Vanadium (V)		0.1	0.1
Zinc (Zn)	5.0	2.0	25.0
pH	6.5-9.0 s.u.	4.5-9.0 s.u.	6.5-8.5 s.u.
SAR		8	
RSC		1.25 mea/1	
Combined Total		1,	
Radium 226, and			
Radium 228 <sup>3</sup>	5pCi/1	5pCi/1	5pCi/l
	•	• ·	

## TABLE II (Cont'd.)

Total Strontium 90	8pCi/l	8pCi/1	8pCi/1
Gross alpha particle			
radioactivity (in-			
cluding Radium 226			
but excluding			
Radon and Uranium) <sup>5</sup>	15pCi/1	15pCi/1	15pCi/1
and the second			

\*mg/1, unless otherwise indicated

<sup>1</sup>Total ammonia-nitrogen.

<sup>2</sup>Dependent on the annual average of the maximum daily air temperature: 1.4 mg/l corresponds with a temperature range of 26.3 to 32.5 degrees C, and 2.4 mg/l corresponds with a temperature of 12.0 degrees C (53.7 degrees F) and below.

<sup>3</sup>Requirements and procedures for the measurement and analysis of gross alpha particle activity, Radium 226 and Radium 228 shall be the same as requirements and procedures of the U.S. Environmental Protection Agency, National Interim Primary Drinking Water Regulations, EPA-570/9-76-003, effective June 24, 1977. Reverse osmosis is a process whereby pressure is applied to contaminated water withdrawn from a well pattern across a permeable membrane. Most of the water passes through the membrane, while most of the dissolved solids are rejected by the membrane and concentrated. The purified waster is then usually reinjected into the pattern. By reinjecting purified water into the well system, any contaminants left behind by leaching are diluted. The process continues until restoration is achieved.

Electrodialysis involves the use of semi-permeable membranes having anion and cation exchange properties. The membranes are alternately stacked, and a D.C. current is applied to them. In theory, the cation exchange membranes allow only the passage of cations, and the anion exchange membranes allow only the passage of anions. Therefore, with a number of alternating membranes set up, the eventual cleanup of produced waters takes place. In practice, removal of radiometrics is not always as complete as in reverse osmosis. Additionally, power requirements for the equipment is extensive, and initial capital outlay can be cost prohibitive and make the total project uneconomical. Advantages include low pressure operating conditions, reduced membrane fouling over reverse osmosis procedures, and lower chemical costs.

The anion/cation exchange units on the market incorporate resins which selectively remove particular anions and cations from a flow stream. Their drawbacks include the need to recharge or replace the resins after a certain period of time, expense of spent regenerant disposal, and difficulty in controlling the effluent quality of certain chemical species.

Full restoration of leached uranium sites is often dependent upon the lixiviant used to recover the uranium and upon the baseline classification of the water at the project outset. Problems have been most prevalent with

lixiviants containing ammonia. Ammonia has a high affinity for clay minerals in the formation and is difficult to flush out over a short period of time. The Cleveland Cliffs, Collins Draw, site is a case in point. The Wyoming DEQ has deemed Cleveland Cliffs's restoration efforts at this site unsuccessful due to ammonia contamination problems. No remedial action had been proposed at the time of this report.

Total dissolved solids (TDS) remaining in leached sites have also presented reclamation problems at several Wyoming leaching projects. It seems that restoration efforts can bring TDS levels down to baseline contaminant criteria; but after a period of time during which the site has been in a stability mode and only monitored, the TDS level will rise above baseline conditions at some sites. Such a rise may entail the need for further restoration efforts and a reevaluation of past restoration activity by the DEQ. The state currently requires a ground water stability mode of one year during which time leached site characteristics are monitored, and no restoration activity takes place.

#### Detailed Summaries of Wyoming Mining Sites

Information regarding the hydrologic and geologic character of the mining sites in Wyoming is necessary input for simulation of ground water contaminant migration from these sites. The following pages summarize important details about these sites. These data have been obtained from the permit application files of the DEQ.

One of the most important characteristics related to contaminant migration is the ground water velocity under normal flow conditions for that aquifer. The following pages show the range in velocity to be 1.23 ft/yr at the Leuenburger site to 52 ft/yr at the Q Sand Project. These velocities are

superficial or Darcy velocities. Actual velocities are obtained by dividing the Darcy velocity by the formation porosity. Ogle Petroleum Co. Bison Basin Mine

Location Fremont Co. 50 miles southeast of Lander T27N R97W Sec. 25

#### Geology

Formation	Green River		
Average sand thickness	15 feet - ore 6.3 feet		
Average porosity	27%		
Depth to formation	375 feet		

#### Hydrologic Characteristics

Average transmissivities ranged from 117 gpd/ft to 198 gpd/ft. The northern portion of the field had the greater transmissivity.

The average storage coefficient in the northern portion of the field was .000051. In the southern portion of the field storage coefficients ranged from .0000094 to .00017. A representative value of .000294 was calculated.

Hydraulic conductivity averaged 5.8  $gpd/ft^2$ .

A hydraulic gradient of .009 ft/ft yielded a reported groundwater velocity of 9 ft/yr in a southeast direction.

#### Activity

Currently, no mining is taking place at the site. No restoration has been performed. The mine is currently on standby status with periodic withdrawals to maintain a cone of depression in the area. Mine owners are seeking a buyer for the property.

Teton Exploration Drilling Co. Leuenburger Site

Location Converse Co. 8 miles northeast of Glenrock T34N R74W

## Geology

Formation	Fort Union			
Average sand thickness	50 feet			
Average porosity	20%			
Depth to formation	N sand 220 to 270 feet M sand 320 to 390 feet			

#### Hydrologic Characteristics

#### N sand

Average transmissivity = 700 gpd/ft.

Average storage coefficient = .000083.

Hydraulic conductivity = 14 gpd/ft2.

The groundwater velocity in the area is 2.5 ft/yr in a northeast direction.

#### M sand

Transmissivities ranged from 260 gpd/ft to 410 gpd/ft. Average transmissivity = 320 gpd/ft.

The calculated storage coefficient ranged from .00026 to .000065 and averaged .00095.

Average hydraulic conductivity =  $5.2 \text{ gpd/ft}^2$ .

The groundwater velocity in this sand is 1.23 ft/yr in a northeast direction.

#### Activity

Current operations are at a standstill. Teton

Exploration and Drilling has completed restoration but DEQ has not yet given its final approval. If market conditions rebound, and DEQ gives its approval, commercial development could begin sometime in the future. Rocky Mountain Energy Nine Mile Lake

Location Natrona Co. 12 miles north of Casper T35N R79W Secs. 27,34

## Geology

\*

Formation	Mesaverda - Teapot Sandstone
Sand thickness	30 to 80 feet
Average porosity	28%
Depth to formation	500 feet

#### Hydrologic Characteristics

Transmissivities ranged from 1300 gpd/ft to 3800 gpd/ft with a consistent increase from the southeast to the northwest. The average transmissivity was 2800 gpd/ft.

The average storativity was reported as .000084.

An average hydraulic conductivity was calculated to be 35 gpd/ft<sup>2</sup>. \*

A hydraulic gradient in the area of 0.0034 indicated a groundwater flow velocity of 18 ft/yr in an east-southeast direction.

#### Activity

Data has been submitted to the Wyoming Department of Environmental Quality on the restoration of three sites on the property. A fourth site will be restored upon final approval of restoration activities at the other three sites.

\* Calculated from available data.

Kerr McGee Nuclear (Sequoyia Fuels Corporation) Q Sand Project

Location Converse Co. 20 miles north of Glenrock T36N R74W Sec. 36

## <u>Geology</u>

-

Formation	Fort Union
Average sand thickness	25 feet
Average porosity	27%
Depth to formation	473 feet

## Hydrologic Characteristics

Average transmissivity	780 gpd/ft
Average storativity	.00018
Hydraulic conductivity	31 gpd/ft <sup>2</sup> .

Groundwater gradient is on the order of 50 ft/mile or .0095 ft/ft. This indicates a groundwater flow velocity on the order of 52 ft/yr \*. Flow is generally to the northeast.

## Activity

Currently being mined.

\* Calculated from available data.

Kerr McGee Nuclear (Sequoyia Fuels Corporation) O Sand Project

Location Converse Co. 20 miles north of Glenrock T36N R74W Sec. 36

## Geology

Formation	Fort Union
Sand thickness	300 feet-ore 75 feet
Average porosity	27%
Depth to formation	500 feet

## Hydrologic Characteristics

Transmissivity = 7000 gpd/ft.

Storage coefficient = .00018.

Hydraulic conductivity =  $28.6 \text{ gpd/ft}^2$ .

Direction of groundwater flow is S35E. No flow velocity available.

## Activity

Wyoming DEQ has not yet issued a permit to mine. Operations will begin upon issuance of permit. Wyoming Mineral Corp. Irigary Ranch

Location Johnson Co. 50 miles southwest of Gillette T45N R77W Sec. 9

## Geology

\*\*

Formation	Upper Irigary Sandstone
Average sand thickness	100 feet
Average porosity	23.4%
Depth to formation	100-150 feet

#### Hydrologic Characteristics

Transmissivities ranged from 373 gpd/ft to 770 gpd/ft and averaged 501 gpd/ft.

Storage coefficients ranged from .00005 to .000026. Average storativity = .000023.

Hydraulic conductivity = 7.7 gpd/ft<sup>2</sup>. \*

A groundwater gradient of 0.009 ft/ft yielded a groundwater velocity of 13.7 ft/yr in a direction due west.

#### Activity

No mining activity has taken place for approximately two years. The mine is currently on standby status. Mining will continue sometime in the future.

\* Calculated from available data.

Uranerz, U.S.A., Inc. Ruth ISL Pilot Project

Location Johnson Co. 10 miles east of Linch T42N R76-77W Secs. 13,14

## Geology

-

Formation	Wasatch
Average sand thickness	90-100 feet
Average porosity	29%
Depth to formation	500-565 feet

## Hydrologic Characteristics

Transmissivities ranged from 68.2 gpd/ft to 231 gpd/ft. Average transmissivity = 141.9 gpd/ft.

Storage coefficients ranged between .00001 and .001. An average of .00063 was calculated from available data.

Hydraulic conductivity =  $2.5 \text{ gpd/ft}^2$ .

Natural groundwater flow in the area was reported as 2.5 ft/yr in a northwest direction.

#### Activity

Beginning restoration and reclamation activities are planned for the latter part of 1984. Additional plans have not been defined at present. Cleveland Cliffs Iron Co. Collins Draw Site

Location Campbell Co. 13 miles northeast of Linch T43N R76W Secs. 35,36

#### Geology

Formation	Wasatch
Average sand thickness	52 feet
Average porosity	28%
Depth to formation	431 feet

## Hydrologic Characteristics

Average transmissivity = 192 gpd/ft.

Average storage coefficient = .00017.

Average hydraulic conductivity = 3.7 gpd/ft<sup>2</sup>. \*

A groundwater gradient of .008 ft/ft yielded a groundwater velocity of 6.3 ft/yr in a direction N19W.

## Activity

Restoration activities continued through December 1982 at which time the mine was shut down into a groundwater stability mode. Wyoming DEQ has not given final approval of restoration. The company has no future plans for the mine.

\* Calculated from available data.

Uranium Resources Inc. North Platte Project

Location Converse Co. 12 miles east of Glenrock T34N R73W Sec. 15

#### Geology

Formation	Fort Union	
Average sand thickness	25 feet	
Average porosity	27% (estimated)	
Depth to formation	610 feet	

## Hydrologic Characteristics

Transmissivities varied between 400 gpd/ft and 490 gpd/ft. Average transmissivity = 440 gpd/ft.

Calculated storage coefficients varied between .0000018 and .00015. Average storage coefficient = .00005.

Average hydraulic conductivity =  $17.6 \text{ gpd/ft}^2$ .

No flow velocities or hydraulic gradients reported.

## Activity

Restoration considered complete February 1983.

Arizona Public Services Co. Peterson In Situ Uranium Extraction Processes

Location Converse Co. 12 miles east of Glenrock T34N R73W Secs. 26,35

#### Geology

Formation	Fort Union
Average sand thickness	40 feet
Average porosity	27%
Depth to formation	220-260 feet

## Hydrologic Characteristics

Transmissivities ranged from 242 gpd/ft to 372 gpd/ft. Mean transmissivity = 315 gpd/ft.

Storage coefficients ranged from .000018 to .00037 with an average value of .0001.

Hydraulic conductivity ranged from 5.4  $gpd/ft^2$  to 8.8  $gpd/ft^2$ . The average hydraulic conductivity was 7.7  $gpd/ft^2$ .

The hydraulic gradient in the area is .005 ft/ft and yielded a groundwater velocity of 5.94 ft/yr.

## Activity

Currently no mining is taking place.

Exxon Minerals Co.<sup>2</sup> Highland Mine

Location Converse Co. 16 miles NW of Douglas T36N R72W Secs. 21,24

#### Geology

Formation Fort Union Average sand thickness 23 feet Average porosity 29 % Depth to formation 300 feet

## Hydrologic Characteristics

Transmissivities ranged from 259 gpd/ft to 517 gpd/ft. Average transmissivity = 382 gpd/ft. Highest values of transmissivity were detected in the northeast portion of the site.

Storage coefficients ranged from .000018 to .000053. Average storage coefficient = .000037.

Hydraulic conductivity averaged 16.6 gpd/ft<sup>2</sup>. \*

Based on a hydraulic gradient of .0047 ft/ft, a groundwater flow of 18 ft/yr was calculated.

#### Activity

Mine officials indicate that restoration is complete. No further operations at the site are anticipated for the future.

\* Calculated from available data.

Western Nuclear Christensen Ranch

Location Campbell Co. 50 miles southwest of Gillette T44N R76W Secs. 17,20

#### Geology

Formation	Wasatch
Sand thickness	up to 300 feet
Average porosity	30%
Depth to formation	365 feet

#### Hydrologic Characteristics

Average transmissivity = 679 gpd/ft.

Average storage coefficient = .0007.

A hydraulic conductivity was calculated to be 2.3  $gpd/ft^2$ . \*

The groundwater velocity was indicated as being 5 ft/yr in a direction N57W.

## Activity

Currently a research and development permit is being sought for the property. If such a permit is approved by May, 1984 a pilot study will commence. Plans call for a second research and development site on the property sometime in 1985.

\* Calculated from available data.

#### CHAPTER 3

## MASS TRANSFER AND EQUILIBRIUM OF HEAVY ELEMENTS

Previous laboratory work performed at the University of Wyoming (1) produced the basic mass transfer and equilibrium data used to analyze the migration of heavy elements in ground water after solution mining had been performed. An analysis of the data in Reference 1 using a simple mass transport model produced a useful but somewhat unrealistic result which has subsequently been improved. The data have been reanalyzed according to the following surface partitioning model. The model is applied to the recirculating batch reactor data described in Reference 1.

## Surface Partitioning Model

The following is the nomenclature and dimensions for the parameters used in the model.

Notation		Dimensions
c	Solution phase concentration	mg/l
P	Solid phase concentration	mg/l
Г	Initial value of q	mg/l
ρ	Bulk density	kg/l bulk
n	Porosity	l voids/l bulk
К	Equilibrium distribution coef.	dimensionless
k	Mass transfer coef.	l day
Mo	Mass of ore	kg
¥v	Volume of voids (in column)	l

$$\Psi_{Ri}$$
Volume of reservoir & tubing after $\ell$  $i^{th}$  sample $i^{th}$  sample $\ell$  $\Psi_{Si}$ Volume of  $i^{th}$  sample $\ell$  $\Psi_{fi}$ Volume of fluid in apparatus after $\ell$  $i^{th}$  sample =  $\Psi_v + \Psi_{Ri}$  $i^{th}$  sample =  $\Psi_v + \Psi_{Ri}$  $c_i$ Concentration in  $i^{th}$  sample $mg/\ell$  $q^e, c^e$ Equilibrium valuesas above

The equilibrium or partitioning between the bulk solution and solid phases is given by

$$K = \frac{\rho q^{e}}{n c^{e}}$$
(1)

which has units of mg "sorbed"/mg "solution." In this equation, values for  $q^e/c^e$  were obtained from the equilibrium data from Reference 1 as shown in Figures 2 and 3.

Equation 2 establishes continuity of mass for each heavy element at any time t where the sum is taken over all samples taken from the batch reactors up to time t .

$$\Gamma M_{o} = q M_{o} + c \Psi_{v} + c \Psi_{Ri} + \sum_{i} c_{i} \Psi_{Si}$$
(2)

Equation 3 is simply the volume continuity for each experiment.

$$\Psi_{fo} = \Psi_{v} + \Psi_{Ro} = \Psi_{v} + \Psi_{Ri} + \Sigma \Psi_{Si}$$
(3)



FIG. 2. MASS INITIAL VS FINAL LIXIVIENT CONCENTRATION. URANIUM AND MOLYBDENUM



FIG. 3. MASS INITIAL VS FINAL LIXIVIENT CONCENTRATION. VANADIUM, SELENIUM, AND ARSENIC.

Here  $\Psi_{fo}$  and  $\Psi_{Ro}$  are the initial values for the volume of fluid in the apparatus and reservoir.

Writing Eq. 2 for equilibrium conditions, results in

$$\Gamma M_{o} = q^{e} M_{o} + c^{e} \Psi_{fi} + \sum_{i} c_{i} \Psi_{Si}$$
(4)

and combining Eq. 4 with Eq. 1 gives

$$\mathbf{c}^{\mathbf{e}} = \frac{\Gamma - \frac{1}{M_{o}} \sum_{i} \mathbf{c}_{i} \mathbf{\forall}_{Si}}{\frac{\mathbf{n}K}{\rho} + \frac{\mathbf{\forall}_{fi}}{M_{o}}}$$
(5)

This result will be useful later when the data from the batch reactors are analyzed. In general, for any time period between samples, Eq. 2 gives

$$q = \Gamma - c \frac{\Psi_{fi}}{M_o} - \frac{1}{M_o} \sum_{i} c_i \Psi_{Si}$$
 (6)

## Analysis of Recirculating Batch Reactor Data

The recirculating batch reactors were small columns (12.54 cm inside diameter containing about 100 gms of ore) through which various fluids were recirculated from a reservoir (see Reference 1 for details of experimental apparatus). Samples of the fluids were withdrawn occasionally for heavy element analysis until an equilibrium concentration was established in the recirculating fluid. The purpose of these experiments was to determine the rate of heavy element release to the recirculating fluid. The recirculating fluid initially had the composition of a typical ground water at uranium

solution mining sites. Thus, the experiments simulated release of heavy elements to ground water when normal ground water flow was reestablished at these sites.

Because the rate of heavy element release to the recirculating fluid was observed to be slow compared to the flow through velocity, it was assumed that mixing (dispersion) within the column was insignificant. Thus, basic equations for conservation of mass for the heavy elements were written as follows.

Solution phase:

$$\frac{dc}{dt} + \frac{\rho b}{n} \frac{dq}{dt} + u \frac{dc}{dx} = 0$$
(7)

Solid phase:

$$\frac{\rho}{n} \frac{dq}{dt} = k(c - \frac{\rho q}{nK})$$
(8)

The third term in Eq. 7 represents the advective transport due to flow-through (seepage) velocity u. Again, because the kinetics of mass transfer was observed to be very slow, it was assumed that at any time t , the bulk solution concentration in and out of the column was very nearly the same. Thus,  $dc/dx \approx 0$  and the term was neglected.

Equation 8 is the mass conservation equation for the solid phase, and  $c - \rho q/nK$  is the generalized driving force for mass release. (Note: at equilibrium, this driving force vanishes.) Now, neglecting the advective term in Eq. 7 and combining Eqs. 7 and 8, one finds

$$\frac{\mathrm{d}c}{\mathrm{d}t} + k\left[c - \frac{\rho q}{nK}\right] = 0 \tag{9}$$

In the general case, this equation cannot be solved because both c and q are functions of time. However, the experimental data can be used via Eq. 6 which relates c and q, so Eq. 9 may be written

$$\frac{dc}{dt} + k(1 + \frac{\rho \Psi_{fi}}{nKM})_{o} \quad c = \frac{k\rho}{nK} \left(\Gamma - \frac{1}{M}\sum_{o i} c_{i} \Psi_{Si}\right)$$
(10)

Now the forcing function (right-hand side) in Eq. 10 is a piecewise constant, and the equation may be solved for time intervals between samples.

For simplicity, write Eq. 10 as

$$\frac{dc}{dt} + a_n c = b_n \tag{11}$$

where

$$a_{n} = k(1 + \frac{\rho \Psi_{fi}}{n KM_{o}})$$
(12)

$$b_{n} = \frac{k\rho}{nK} \left( \Gamma - \frac{1}{M_{o}} \sum_{i} c_{i} V_{Si} \right)$$
(13)

Using initial conditions of  $c(t=0) = c_{n-1}$ , and defining  $g_n$  as

$$g_{n} = \frac{b_{n}}{a_{n}} = \frac{\begin{pmatrix} \Gamma & M_{o} & - & \Sigma & c_{i} \forall Si \end{pmatrix}}{(\frac{nM_{o}K}{\rho} + \forall f_{n-1})}$$
(14)
The concentration,  $c_n$ , at time  $t = \Delta t_n$  which is the time between samples having concentrations of  $c_n$  and  $c_{n-1}$  is

$$c_n = g_n - (g_n - c_{n-1})e^{-a_n\Delta t}n$$
 (15)

For purposes of obtaining values of the mass transfer coefficient, k, from the experimental data, Eq. 15 is solved for  $a_n$  and values of k determined for various time intervals during each run.

$$k = \frac{a_{n}}{\frac{\Psi_{f}}{1 + \frac{\Psi_{f}}{(q^{e}/c^{e})M_{o}}}}$$
(16)

The values for k were then averaged for each run.

Because of the simple way  $g_n$  enters Eq. 15, it was interesting to evaluate its physical significance. Returning to the definition of  $g_n$  (Eq. 14), the total mass of heavy element remaining in the system between time  $t_n$ and  $t_{n-1}$  is

$$\Gamma \stackrel{n-1}{=} C_{i} \stackrel{r}{=} C_{i} \stackrel{r}{=} S_{i}$$

and  $\Psi_{f_{n-1}}$  is the corresponding fluid volume. The term  $\frac{nKM}{\rho}$  can be shown to be equal to  $(q^e/c^e)M_o$  which has units of (volume of voids) (mass sorbed/mass solution). Therefore,  $nKM_o/\rho$  is the hypothetical volume which would be occupied by the mass of heavy element at equilibrium if it was in the solution phase rather than the sorbed phase. Thus,

 $g_n = \frac{mass remaining}{actual fluid volume + hypothetical volume}$ 

and this represents a concentration which is a driving force for mass transfer.

#### Determination of Mass Transfer Coefficients

The previous section shows the development of the equations used to determine values for the mass transfer coefficients. The basic idea was to obtain the rate of heavy element release between sampling periods and average the values obtained during each run. The results of these calculations follow. All k values were for a temperature of approximately 21°C.

<u>Uranium</u>. Figure 4 shows the results of calculations for the mass transfer coefficient for uranium. It was found that the ground water velocity had some effect on the value for k. In Chapter 2, natural ground water flow velocities were seen to be very low in typical uranium solution mining ore bodies. These values were well below that which could be practically used in the laboratory experiments. Thus, some adjustment of linear extrapolation to the lowest values for k might be warranted.

The difficulty of extrapolation of data to actual ground water velocities is shown in Figure 4. When simulations are carried out as described in Chapter 4, a range such as that shown in the figure may be used to find the most conservative prediction by the appropriate computer code.

<u>Molybdenum</u>. Figure 5 shows a similar velocity response for molybdenum as that for uranium. In this instance, the mass transfer coefficient is proportional to the 0.29 power of the velocity.



FIGURE 4. MASS TRANSFER COEFFICIENT FOR URANIUM VS SUPERFICIAL (DARCY) VELOCITY



FIGURE 5. MASS TRANSFER COEFFICIENTS FOR SELENIUM, MOLYBDENUM, AND ARSENIC.

<u>Vanadium</u>. Only one run was able to yield data for vanadium. Most runs had such low concentrations of vanadium in the recirculating ground water that the analytical results were questionable. The only value obtained was 0.034day<sup>-1</sup> at a superficial (Darcy) velocity of 28.4 m/day. To obtain values at lower Darcy velocities, extrapolation similar to uranium or molybdenum are recommended.

<u>Selenium</u>. The velocity response for selenium was found to be nonlinear. However, Figure 5 shows the relationship obtained, and extrapolation may be achieved on a slope similar to uranium and molybdenum.

<u>Arsenic</u>. Figure 5 also shows arsenic to follow a similar pattern as uranium and molybdenum in the range of experimental results. Again, determination of values for low velocities will require extrapolation.

# **CHAPTER 4**

#### SIMULATION MODEL

In this chapter, two simulation models are developed to predict the migration of heavy elements from a uranium solution mining zone under conditions of ground water flow. The model thus simulates the transport of residual heavy elements left behind in the mining zone after mining operations have ceased and normal conditions have returned to the aquifer. Both models are one-dimensional transport models that account for advection, dispersion, heavy element mass transfer, and sorption.

The two models differ as follows:

- Model A: Mass transfer is two-directional (both to and from the solid phase) throughout the simulated domain.
- Model B: Mass transfer occurs only within the mining zone and only from the immobile phase to the mobile phase. Outside the mining zone, heavy element migration is controlled only by advection and dispersion.

#### Simulation Development

For both models, the fundamental continuity equations for the solution and solid phase are, respectively:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} - D \frac{\partial^2 c}{\partial x^2} + k(c - \frac{\rho}{n} \frac{q}{K}) = 0$$
(1)

$$\frac{\rho}{n}\frac{\partial q}{\partial t} - k(c - \frac{\rho}{n}\frac{q}{K}) = 0$$
 (2)

Here the nomenclature is the same as that in Chapter 3. Additional parameters are x, the distance in the direction of one-dimensional ground water flow;

D, the coefficient of hydrodynamic dispersion; and u, the seepage velocity in the x direction.

For simplification, the following dimensionless variables are introduced:

$$\overline{\mathbf{x}} = \frac{\mathbf{X}}{\mathbf{L}}$$
;  $\overline{\mathbf{t}} = \frac{\mathbf{V}\mathbf{t}}{\mathbf{L}}$ ;  $\overline{\mathbf{D}} = \frac{\mathbf{D}}{\mathbf{u}\mathbf{L}}$ ;  $\overline{\mathbf{c}} = \frac{\mathbf{p}\mathbf{q}}{\mathbf{n}}$ ;  $\overline{\mathbf{k}} = \frac{\mathbf{k}\mathbf{L}}{\mathbf{u}}$ 

In terms of these new variables, Equations (1) and (2) become

$$\frac{\partial c}{\partial t} + \frac{\partial c}{\partial x} - \overline{D} \frac{\partial^2 c}{\partial \overline{x}^2} + \overline{k} (c - \frac{\overline{c}}{K}) = 0$$
(3)  
$$\frac{\partial \overline{c}}{\partial t} = \overline{k} (c - \frac{\overline{c}}{K})$$
(4)

Equations (3) and (4) are not solved directly. Instead, new variables are defined as

$$A = c - \frac{\bar{c}}{K}$$
;  $B = c + \bar{c}$ ;  $\bar{k} = \bar{k}(\frac{1+K}{K})$ 

In terms of these new variables, equations (3) and (4) become

$$\frac{\partial A}{\partial \overline{t}} + \frac{\partial c}{\partial \overline{x}} - \overline{D} \frac{\partial^2 c}{\partial \overline{x}^2} + \overline{k} A = 0$$
(5)

$$\frac{\partial B}{\partial t} + \frac{\partial c}{\partial x} - \overline{D} \frac{\partial^2 c}{\partial x^2} = 0$$
(6)

Equations (5) and (6) are analyzed as follows: For computational simplicity, an explicit finite difference solution algorithm was used. Upwind differencing was used to avoid numerical dispersion. With an explicit solution, there are a number of stability requirements. Stability associated with the decay term is guaranteed as follows:

Decay Term

In equation (5),  $\Delta A$  is separated into two terms,  $\Delta A$  and decay  $\Delta A$  transport.

Considering just the decay terms,

$$\frac{dA}{d\bar{t}} = -\bar{\bar{k}}A \rightarrow A^{\bar{t}+\Delta\bar{t}} = A^{\bar{t}} \exp(-\bar{\bar{k}}\Delta\bar{t})$$

and thus

$$\Delta A_{\text{decay}} = A^{\overline{t}} \left[ \exp(-\overline{k}\Delta\overline{t}) - 1 \right]$$
(7)

# Transport Term

For both Equations (5) and (6), the change associated with transport is (using upwind differencing)

$$\Delta A_{\text{trans.}} = \Delta B_{\text{trans.}} = \frac{\overline{D}\Delta \overline{t}}{\Delta \overline{x}^2} (c_{i+1}^n - 2c_i^n + c_{i-1}^n) - \frac{\Delta \overline{t}}{\Delta \overline{t}} (c_i^n - c_{i-1}^n)$$
$$= \frac{\overline{D}\Delta \overline{t}}{\Delta \overline{x}^2} c_{i+1}^n - (\frac{2\overline{D}\Delta t}{\Delta \overline{x}^2} + \frac{\Delta \overline{t}}{\Delta \overline{x}}) c_i^n + (\frac{\overline{D}\Delta \overline{t}}{\Delta \overline{x}^2} + \frac{\Delta \overline{t}}{\Delta \overline{x}}) c_{i-1}^n$$
(8)

where the notation  $c_i^n$  is the concentration at the i<sup>th</sup> node point at time step n. Using Equations (7) and (8), the changes  $\Delta A$  and  $\Delta B$  during the time step are found for each node point. These changes are related to the original concentration variables by

$$c_{i}^{n+1} = \frac{KA_{i}^{n+1} + B_{i}^{n+1}}{1 + K}$$
(9)

$$= {n+1 \atop i} = {K(B_i^{n+1} - A_i^{n+1}) \over 1 + K}$$
 (10)

# Final Equations

Combining equations (7) through (10), we obtain

$$c_{i}^{n+1} = \frac{\overline{D}\Delta\overline{t}}{\Delta\overline{x}^{2}} c_{i+1}^{n} - \left(\frac{2\overline{D}\Delta\overline{t}}{\Delta\overline{x}^{2}} + \frac{\Delta\overline{t}}{\Delta\overline{x}} - \frac{Ke^{-\overline{k}}\Delta\overline{t} + 1}{1 + K}\right) c_{i}^{n}$$
$$+ \left(\frac{\overline{D}\Delta\overline{t}}{\Delta\overline{x}^{2}} + \frac{\Delta\overline{t}}{\Delta\overline{x}}\right) c_{i-1}^{n} - \left(\frac{e^{-\overline{k}}\Delta\overline{t} - 1}{1 + K}\right) \overline{c}_{i}^{n}$$
(11)

$$\bar{c}_{i}^{n+1} = \frac{K(1 - e^{-\bar{k}\Delta t})}{1 + K} C_{i}^{n} + \left[\frac{K + e^{-\bar{k}\Delta t}}{1 + K}\right] \bar{c}_{i}^{n}$$
(12)

Equations (11) and (12) are used in the computer algorithms given in Appendix A.

Boundary Conditions 1. c(x = 0,t) = 0Set i=1 in (11) and let  $c_0^n = 0$ 

2. 
$$\frac{\partial c(x=L,t)}{\partial x} = 0$$
 (N nodes)  
Set i = N in (11) and let  $c_{N+1}^{n} = c_{N}^{n}$ 

# Stability Criteria1. $\Delta x > u\Delta t$ (Courant condition)2. $D = \alpha u > \frac{u\Delta x - u^2\Delta t}{t}$ (Upwind Differencing)

3. 
$$k \leq \frac{K}{(1+K)\Delta t}$$
 In  $\left\{\frac{K}{(1+K)(\frac{u\Delta t}{\Delta x^2})(2\alpha+u\Delta t)-1}\right\}$ 

 $\alpha$  = dispersivity

u = seepage velocity

The third stability condition is empirical and is based upon keeping the coefficient multiplying  $c_i^n$  in Eq. 11 negative. All three criteria are checked before a simulation.

#### Discussion of Parameters Used During Simulation

- 1. The distance simulated was 5000 ft using 100 cells (N = 100) and; thus, the cells size  $\Delta x = 50$  ft. The number of cells in the mine zone, NSTAR, varied from 1 to 10. Note that the mining zone is within the distance simulated, L, and that in the plotted concentration profiles the mining zone starts at x = 0.
- DELT (∆t) was adjusted for each run so that stability was maintained and printing and plotting occurred at desired time intervals. NSTEP, NPRNT, and NPLOT were adjusted accordingly.
- 3. The initial concentration in the mine zone, CINT, was chosen to be 20 mg/l. Since the equations are linear, any other choice would have simply rescaled the concentrations. By plotting relative concentrations c/CINT and  $\overline{c}/K*CINT$ , the plots would look the same regardless of the value of CINT chosen. Note that  $\overline{c}/K*CINT$  is the fraction of initial heavy element remaining on the ore in the mining zone.
- 4. Reported superficial velocities, V, varied from 1 to 50 ft/yr. A typical value of 10 ft/yr was chosen for these simulations. A value of V = 10 ft/yr corresponds to a seepage velocity of  $u = V/n \approx 30$  ft/yr. With a

distance L = 5000 ft, this gives a flow thru time for the domain of L/u = 166.7 yrs.

- 5. A porosity of 0.3 was used for all runs (n = 0.3).
- 6. The choice of an appropriate dispersivity  $\alpha$  = DIS is uncertain. The following model is usually used for the coefficient of hydrodynamic dispersion.

The term  $\alpha$  u represents the mixing associated with the complex structure of the porous matrix. Typical values of d<sub>d</sub> generally vary from 0.005 to 0.25 ft<sup>2</sup>/yr. When values of  $\alpha$  are measured in the laboratory for uniform soils,  $\alpha$  generally ranges from 0.1 to 10 mm. However, in the field, the soils are not homogeneous, and much larger values are reported; for example, 100 m and larger. Regardless, it is apparent that  $\alpha u \gg D_d$  in the field, and the model used in the simulation code is  $D = \alpha u$ . Values of  $\alpha$  of 10, 25, and 100 ft are used, which is expected to be in the relevant range.

- 7. The values of K(=EQ) are obtained from Figures 2 and 3. Simulations shown are for uranium which has  $q^e/c^e = 3.1 \text{ mg/kg ore/mg/l}$ . Using a bulk density,  $\rho$ , of 1.9 gm/cm<sup>3</sup> and a porosity of 0.3, K has a dimensionless value of about 20. (EQ = 20).
- 8. The mass transfer coefficient, k(=KIN), may be obtained from Figures 4 and 5. Because of the uncertainty in extrapolation of data to low seepage velocities, a range of values were used in the simulations for

uranium to determine the sensitivity of this parameter to the concentration profiles. Values for k used in the attached simulations were varied between  $0.023 \text{ yr}^{-1}$  to  $7.0 \text{ yr}^{-1}$ .

# Summary of Simulation Runs

A number of preliminary computer runs were carried out to verify the mathematical model, to show that it was working properly, to test the stability criteria, and to examine model sensitivity to input parameter values. These runs are not presented here.

The following runs provide the basis for discussion of results. For each run, both models were simulated with the indicated values for listed parameters. Plots of the computer outputs are shown in Figures 6 through 17.

Run 1

$$u = 30 \text{ ft/yr}$$
 $K = 20.0$  $k = 0.023 \text{ yr}^{-1}$  $\Delta t = 1 \text{ yr}$  $L = 5000 \text{ ft}$  $\alpha = 10 \text{ ft}$  $\Delta x = 50 \text{ ft}$  $NSTAR = 4$ 

Run 2

$$u = 30 ft/yr$$
 $K = 20$ 
 $k = 0.023 yr^{-1}$ 
 $\Delta t = 0.25 yr$ 
 $L = 5000 ft$ 
 $\alpha = 100 ft$ 
 $\Delta x = 50 ft$ 
 NSTAR = 4

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FIGURE 6. OUTPUT FOR RUN 1. MODEL A



FIGURE 7. OUTPUT FOR RUN 2. MODEL A.



FIGURE 8. OUTPUT FOR RUN 3. MODEL A.

# CONCENTRATION PROFILES



FIGURE 9. OUTPUT FOR RUN 4. MODEL A.



FIGURE 10. OUTPUT FOR RUN 5. MODEL A.



FIGURE 11. OUTPUT FOR RUN 6, MODEL A







FIGURE 13. OUTPUT FOR RUN 2. MODEL B.



FIGURE 14, OUTPUT FOR RUN 3. MODEL B.



FIGURE 15. OUTPUT FOR RUN 4. MODEL B.



FIGURE 16. OUTPUT FOR RUN 5. MODEL B.

# CONCENTRATION PROFILES



FIGURE 17. OUTPUT FOR RUN 6. MODEL B.

Run 3

u =	30 ft/yr	K = 20
k =	$0.23 \text{ yr}^{-1}$	$\Delta t = 1 yr$
L =	5000 ft	$\alpha = 10$ ft
$\Delta x =$	50 ft	NSTAR = 4
Run 4		
u =	30 ft/yr	K = 20
k =	7.0 $yr^{-1}$	$\Delta t = 0.2 \text{ yr}$
L =	5000 ft	$\alpha = 25 ft$
$\Delta x =$	50 ft	NSTAR = 4
Run 5		
u =	30  ft/yr	K = 20
k =	0.023 yr 1	$\Delta t = 1.0 \text{ yr}$
L =	5000 ft	$\alpha = 25 \text{ ft}$
$\Delta x =$	50 ft	NSTAR = 10
Run 6		

Same as Run 5, except NSTAR = 1.

# Discussion of Simulation Runs

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It is important to note from the dimensionless form of the equations that the simulation results depend on two variables,  $\bar{x} = X/L$  and  $\bar{t} = Vt/L$ , and on three parameters:

$$\overline{D} = \frac{D}{uL} = \frac{\alpha}{L}$$
;  $\overline{k} = \frac{kL}{u}$ ; K

In addition, we assume that K is fixed from the experimental data at K = 20. Again, with L and u fixed, we may vary the parameters  $\overline{D}$  and  $\overline{k}$  by varying  $\alpha$  and k, respectively.

Comparison of runs 1 and 2 shows the influence of mixing  $(\overline{D})$  for fixed kinetics  $(\overline{k})$ . The decrease in maximum concentration is more evident for model B than for model A; however, in both cases, the differences are significant. It is noted that these results are conservative in that transverse dispersion is neglected in a one-dimensional model.

Comparison of runs 1, 3 and 4 shows the influence of the mass transfer coefficient  $(\bar{k})$ . The most dramatic effect noted with model A was the tremendous decrease in the rate of migration of the species between runs 1 and 3. It appears that for  $k > 0.23 \text{ yr}^{-1}$ , the rate of migration approaches that of the equilibrium theory:

$$u_{\text{chemical}} = \frac{u_{\text{water}}}{1 + K}$$

and the effective rate of migration of the metals is  $u = 30/21 \approx 1.5$  ft/yr. Comparison of runs 3 and 4 shows that a further increase in k does not significantly affect the rate of migration, but the maximum concentrations do increase. (This is shown even though  $\alpha$  is greater in 4 than in 3.) Run 4, Model A, shows that the conditions of equilibrium are satisfied for k = 7 yr<sup>-1</sup>. Note that the scaled solution and solid phase concentrations are the same as they would be for equilibrium. The same runs for model B show that the only influence of increasing k is to increase the maximum concentrations.

Finally, comparison of runs 1, 5 and 6 show the influence of the mining zone size, all for a low  $k = 0.023 \text{ yr}^{-1}$ . Especially for model B, but also for Model A, an increase in size corresponds to an increase in maximum concentration downstream from the mine. There is no influence on the rate of migration, but since the water is in contact with the mine zone longer, more mass is released, leading to higher concentrations.

It is apparent from the wiggles in the concentration plots that the solutions are near instability. However, the wiggles are dampened, and the solutions remain accurate (for runs 5 and 6).

#### Conclusions

While these few simulation runs have hardly been exhaustive, they do lead to a number of important conclusions.

- 1. The simpler model B shows an increase in maximum concentrations downstream of the mining zone with increasing k and size of the mine zone, and with decreasing dispersivity  $\alpha$ . This model is probably not very realistic in that there is no mechanism for restabilization of the metal released from the mine zone. Considering the 100-200 yr. time period for water to travel 1 mile, this seems unlikely, although conservative answers are obtained. Hereafter, just Model A is considered.
- 2. The dispersivity is an important parameter inversely related to the maximum downstream concentrations. In reality, the effective value of α probably increases with distance of migration from the mine, as a greater range of hydraulic heterogeneities are encountered. α could likely be less than 1 ft. in the immediate vicinity of the mine. However, the range 10-100 ft. is probably representative for the region and type of aquifers considered.
- 3. The value of k plays a dual role. As k increases from 0.023 to 0.23  $yr^{-1}$ , the rate of migration is greatly influenced. Already at k = 0.23  $yr^{-1}$  the rate of migration approaches that of an equilibrium model with retardation factor  $R_d = 1 + K = 21$ . Further increases in k do not greatly affect the rate of migration, but they do result in an increase in maximum observed concentration. For k = 7  $yr^{-1}$ , equilibrium between the mobile and immobile phases is rapidly approached (in hydrogeologic time), and one might suggest a mathematical model as follows:



$$c(x,t) = \frac{c_0}{2} \left\{ erf(\frac{R_d a - (R_d x - ut)}{\sqrt{4R_d Dt}}) + erf(\frac{R_d a + (R_d x - ut)}{\sqrt{4R_d Dt}}) \right\}$$

$$R_d = 1 + K$$
  
erf = error function  
 $C_o = initial temperature$   
 $D = \alpha u$ 

If the metal is reduced and stabilized according to a first order rate law, with rate coefficient  $\lambda$ , then the equation above would be multiplied by  $e^{-\lambda t}$ . The model above implies chemical equilibrium between a mobile and immobile phase, with decay (stabilization).

# REFERENCES

 Humenick, M. J., W. L. Dam, and J. I. Drever, "Heavy Element Release to Ground Water at In-Situ Uranium Mining Sites: Phase I," Wyoming Water Research Center Report A-037-WYO, prepared for the U.S. Department of the Interior, University of Wyoming, Laramie, WY, August 31, 1983. APPENDIX A

COMPUTER ALGORITHMS FOR MODELS A AND B

PROGRAM TWOPOR (INPUT, OUTPUT, TAPE5=INPUT, TAPE6=OUTPUT, PLOT) С С С PROGRAM THOPOR: ONE-DIMENSIONAL TRANSPORT OF A SOLUTE IN A С DUAL POROSITY (FLOWING AND STAGNANT PHASES) С GROUNDWATER AQUIFER USING AN EXPLICIT FINITE С DIFFERENCE SOLUTION WITH UPSTREAM DIFFERENCING C AND TIME AVERAGING FOR MASS TRANSFER С С С C С С С DEFINITION OF VARIABLES С С CONCENTRATION IN JTH CELL FOR 1) SOLUTE AT C(I,J)= BEGINNING OF TIME STEP (I=1), 2) SOLID PHASE AT С BEGINNING OF TIME STEP (I=2), 3) SOLUTE AT END С С OF TIME STEP (I=3), AND 4) SOLID PHASE AT END С OF TIME STEP (I=4) С С CINT INITIAL SOLUTE CONCENTRATION = С DELX Ξ CELL SIZE С DELT = SIZE OF TIME STEP С DIS = DISPERSIVITY С EQ = PARTITION COEFFICIENT С MASS TRANSFER COEFFICIENT KIN = С = NUMBER OF CELLS N С NUMBER OF TIME STEPS BETWEEN PLOTTING OUTPUT NPLOT Ξ С NUMBER OF TIME STEPS BETWEEN PRINTING OUTPUT NPRNT = С NSTAR = NUMBER OF CELLS IN INITIAL CONTAMING С NSTEP = NUMBER OF TIME STEPS ACTIVE POROSITY С POR = С v = SEEPAGE VELOCITY IN AQUIFER С С С NOTE: PASSIVE PHASE CONCENTRATION MEASURED IN SAME UNITS AS SOLUTION PHASE CONCENTRATION; TO GET UNITS OF MASS С С PER MASS, MULTIPLY BY THE POROSITY AND DIVIDE BY С THE BULK DENSITY С С REAL KIN DIMENSION C(4,100),XARRAY(102),BARRAY(102),CARRAY(102),CMAX(100), 1 THAX(100) С С READ AND PRINT INPUT DATA C READ (5,5) N,NSTAR,NSTEP,NPRNT,NPLOT WRITE (6,5) N,NSTAR,NSTEP,NPRNT,NPLOT 5 FORMAT (5110) READ (5,10) DELX, DELT, CINT, DIS, V, KIN, EQ, POR WRITE (6,10) DELX, DELT, CINT, DIS, V, KIN, EQ, POR 10 FORMAT (8F10.4) C C С COMPUTE DIMENSIONLESS VARIABLES C DT=DELT+V/(FLOAT(N)+DELX) KIN=KIN+FLOAT(N)+DELX+(1.0+EQ)/(V+EQ)

MODEL A

```
DX=1.0/FLOAT(N)
      D=(DIS/(FLOAT(N)+DELX))-0.5+(DX-DT)
С
      WRITE (6.20) DX,DT,D,KIN
   20 FORMAT (4F10.6)
С
С
      INITIALIZE CONCENTRATIONS
С
С
      DO 30 J=1.N
      C(1,J)=0.0
      C(2+J)=0.0
      C(3, J) = 0.0
      C(4+J)=0.0
      XARRAY(J)=0.0
      CARRAY(J)=0.0
      BARRAY(J)=0.0
      CMAX(J)=0=0
      TMAX(J)=0.0
   30 CONTINUE
С
С
      INITIALIZE MASS BALANCE
С
      TMASSI=CINT+(1+FR)+DELX+POR+FLOAT(NSTAR)
      FMOUT=0.0
С
      DO 40 J=1.NSTAR
      C(1,J)=CINT
      C(2,J)=CINT+EQ
      CMAX(J)=CINT
   40 CONTINUE
С
C
С
      SET-UP PLOTS
С
      CALL PLOTS(0,0,4LPLOT)
      CALL PLOT(1.75,1.,-3)
      CALL AXIS(0.,0.,13HDISTANCE X/L,-13,5.,0.,0.,0.2)
      CALL AXIS(0.,0.,14HCBAR/(CINT+EQ),14,4.,90.,0.,0.25)
      CALL PLOT(0.,4.,3)
      CALL PLOT(5.,4.,2)
      CALL PLOT(5.,0.,2)
      CALL PLOT(0-,5-,-3)
      CALL AXIS(0.,0.,13HDISTANCE X/L,-13,5.,0.,0.,0.2)
      CALL AXIS(0.,0.,6HC/CINT,6,4.,90.,0.+0.25)
      CALL PLOT(0.,4.,3)
      CALL PLOT(5.,4.,2)
      CALL PLOT(5.,0.,2)
      CALL SYMBOL(1.,4.25,.14,22HCONCENTRATION PROFILES,0.,22)
С
С
С
С
      COMPUTE FINITE DIFFERENCE COEFFICIENTS
С
      A1=D+DT/(DX+DX)
      A2=(2.0+D+DT/(DX+DX))+(DT/DX)-((1.0+EQ+EXP(-KIN+DT))/(1.0+EQ))
      A3=(D+DT/(DX+DX))+(DT/DX)
       A4=(EXP(-KIN+DT)-1.0)/(1.0+EQ)
      B1=(EQ*(1.0-EXP(-KIN*DT)))/(1.0+EQ)
      B_{2}=(E_{0}+E_{0}+E_{0}+E_{0})/(1-0+E_{0})
C
      WRITE (6,45) A1,A2,A3,A4,B1,B2
```

ŝ

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```

```
45 FORMAT (6F10.5)
С
C
С
      START COMPUTATIONS
С
      TIME=0.0
      M=N-1
      DO 100 I=1,NSTEP
      TIME=TIME+DELT
      TMASS=0.0
С
С
      COMPUTATION FOR FIRST CELL
С
      C(3,1)=A1+C(1,2)-A2+C(1,1)-A4+C(2,1)
      C(4,1)=B1*C(1,1)+B2*C(2,1)
С
С
      COMPUTATION FOR WIDDLE CELLS
С
      DO 50 J=2.M
С
       C(3,J)=A1+C(1,J+1)-A2+C(1,J)+A3+C(1,J-1)-A4+C(2,J)
       C(4,J) = B1 + C(1,J) + B2 + C(2,J)
   50 CONTINUE
С
С
       COMPUTATION FOR LAST CELL
С
       C(3+N)=(A1-A2)+C(1+N)+A3+C(1+M)-A4+C(2+N)
       C(4,N) = B1 + C(1,N) + B2 + C(2,N)
С
С
       COMPUTATION FOR MASS FLUX OUT
C
       FHOUT=FHOUT+V+POR+DELT+(C(1,N)+D+FLOAT(N)+C(1,1))
С
С
      PRINT RESULTS FOR TIME STEP
С
       IE (MOD(I,NPRNT).NE.0.) GO TO 80
С
С
       MASS BALANCE COMPUTATIONS
С
       00 55 J=1.N
       THASS=THASS+DELX+POR+(C(3,J)+C(4,J))
   55 CONTINUE
C
       RESID=TMASSI-TMASS-FMOUT
С
С
       WRITE AND PLOT OUTPUT
С
       WRITE (6,60) TIME, THASS, RESID
: C
   60 FORMAT (//,6HTIME =,F10.2,10X,12HTOTAL MASS =,E10.3,10X,
      123HMASS BALANCE RESIDUAL =,E10.3)
       WRITE (6,70) (C(3,J),J=1,N)
       WRITE (6,70) (C(4,J),J=1,N)
    70 FORMAT (10X.10F10.2/(12X.10F10.2))
    80 CONTINUE
С
  WEIGHT (MOD(I,NPLOT).NE.O..AND.I.NE.NPRNT) GO TO 86
       DO 82 J=1.N
       XARRAY(J)=FLOAT(J)+DX
       BARRAY(J)=C(4,J)/(CINT+EQ)
       CARRAY(J)=C(3,J)/CINT
    82 CONTINUE
```

```
XARRAY(N+1)=0.0
      BARRAY(N+1)=0.0
      CARRAY(N+1)=0.0
      XARRAY(N+2)=0.2
      BARRAY(N+2)=0.25
      CARRAY(N+2)=0.25
С
С
      CALL PLOT(0.,-5.,-3)
      CALL LINE(XARRAY, BARRAY, N, 1,0,2)
      CALL PLOT(0.,5.,-3)
      CALL LINE (XARRAY, CARRAY, N, 1, 0, 2)
C
С
С
   86 CONTINUE
C
С
С
С
      UPDATE CONCENTRATIONS FOR NEXT TIME STEP
С
      DO 90 J=1.N
      C(1,J)=C(3,J)
      C(2,J)=C(4,J)
       IF (C(3, J).LE.CMAX(J)) GO TO 90
       CMAX(J) = C(3, J)
       THAX(J)=TIME
   90 CONTINUE
  100 CONTINUE
С
С
       WRITE AND PLOT MAXIMUM HOBILE PHASE CONCENTRATION
C
       WRITE (6,105)
  105 FORMAT (10X,29HMAXIMUM SOLUTE CONCENTRATIONS,//)
       WRITE (6,70) (CMAX(J),J=1,N)
       WRITE (6,70) (TMAX(J),J=1,N)
С
       DO 110 J=1,N
       CARRAY(J)=CMAX(J)/CINT
  110 CONTINUE
C
       CALL LINE(XARRAY, CARRAY, N, 1, -1, 14)
С
       CALL PLOT(0.,0.,999)
.
C
      STOP
      END
```

	MODEL	В	
C	PROGRAM	THOPGICI	NPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT,PLOT)
с с с с с с с с с с с с с с	PROGRAM	TWGP01:	ONE-DIMENSIONAL TRANSPORT OF A SOLUTE IN A DUAL POROSITY (FLOWING AND STAGNANT PHASES) GROUNDWATER AQUIFER USING AN EXPLICIT FINITE DIFFERENCE SOLUTION WITH UPSTREAM DIFFERENCING AND TIME AVERAGING FOR MASS TRANSFER. TRANSFER IS ONE DIRECTIONAL.
C C			
с с с	DEETNIT		DTADIES
C	DELTMIT	IUN UF WA	NIADECS
C C C C C C	C(I,J)	= CON BEG BEG OF OF	CENTRATION IN JTH CELL FOR 1) SOLUTE AT INNING OF TIME STEP (I=1), 2) SOLID PHASE AT INNING OF TIME STEP (I=2), 3) SOLUTE AT END TIME STEP (I=3), AND 4) SOLID PHASE AT END TIME STEP (I=4)
C	CINT	= INI	TIAL SOLUTE CONCENTRATION
C		= CEL	L SIZE E DE TIME STER
C	DIS	= DIS	PERSIVITY
C	EQ	= PAR	TITION COEFFICIENT
C	N	= NUM	BER OF CELLS
C	NPLOT		BER OF TIME STEPS BETWEEN PLOTTING OUTPUT
C	NSTAR	= NUH	BER OF CELLS IN INITIAL CONTAMINE ATED ZONE
C	NSTEP	= NUM	BER OF TIME STEPS
C	PUR V	= ACT = SEE	PAGE VELOCITY IN AQUIFER
C			
	NOTE:	PASSIVE P Solution Per Mass, The Bulk	HASE CONCENTRATION MEASURED IN SAME UNITS AS PHASE CONCENTRATION; TO GET UNITS OF MASS MULTIPLY BY THE POROSITY AND DIVIDE BY DENSITY
C	•		
	REAL KI	N	AN WARRANT RADAW/1001 CARRAV(1001 CHAV/1001-
	DIMENSI 1 TMAX(1	ON C(4+10 .00)	U) • XARRAT(102) • BARRAT(102) • CARRAT(102) • CHAR(100) •
C			
C	READ AN	D PRINT I	INPUT DATA
5	READ (5 Write ( Format	,5) N,NST 6,5) N,NS (5110)	AR,NSTEP,NPRNT,NPLOT STAR,NSTEP,NPRNT,NPLOT
10	READ (5 WRITE ( Format	;,10) DELX (6,10) DEL (8F10.4)	L,DELT,CINT,DIS,V,KIN,EG,POR LX,DELT,CINT,DIS,V,KIN,EQ,POR
C			가 있다. 방법 특별 방법은 방법은 동안에 있는 것이 있는 것이 있는 것이 있는 것이 있는 것이 있는 것이 있다. 가지 않는 것이 있는 것이 있는 것이 있는 것이 있는 것이 있는 것이 있는 것이 있는 같은 것이 같은 동안에 있는 것이 같은 것이 있는 것이 있는 것이 없는 것이 없는 것이 없는 것이 있는
C C C	COMPUTE	DIMENSIO	DNLESS VARIABLES
	DT=DELT	+V/(FLOAT	r(N)+DELX)

```
KIN=KIN*FLOAT(N)*DELX*(1+0+EQ)/(V*EQ)
      DX=1.0/FLOAT(N)
      D=(DIS/(FLOAT(N)*DELX))-0.5*(DX-DT)
С
      WRITE (6,20) DX,DT,D,KIN
   20 FORMAT (4F10-6)
С
С
С
      INITIALIZE CONCENTRATIONS
С
      DO 30 J=1.N
      C(1,J)=0.0
      C(2,J)=0.0
      C(3,J)=0.0
      C(4,J)=0.0
      XARRAY(J)=0.0
      CARRAY(J)=0.0
      BARRAY(J)=0.0
      CMAX(J)=0.0
      14AX(J)=0.0
   30 CONTINUE
С
С
      INITIALIZE MASS BALANCE
С
      THASSI=CINT+(1.+EQ)+DELX+POR+FLOAT(NSTAR)
      FHOUT=0.0
С
      DO 40 J=1,NSTAR
      C(1,J)=CINT
      C(2,J)=CINT*EQ
      CMAX(J)=CINT
   40 CONTINUE
С
С
С
      SET-UP PLOTS
С
      CALL PLOTS(0,0,4LPLOT)
      CALL PLOT(1.75,1.,-3)
      CALL AXIS(0.,0.,13HDISTANCE X/L,-13,5.,0.,0.,0.2)
      CALL AXIS(0.,0.,14HCBAR/(CINT+EQ),14,4.,90.,0.,0.25)
      CALL PLOT(0-,4-,3)
      CALL PLOT(5.,4.,2)
      CALL PLOT(5.,0.,2)
      CALL PLOT(0-,5-,-3)
      CALL AXIS(0.,0.,13HDISTANCE X/L,-13,5.,0.,0.,0.2)
      CALL AXIS(0.,0.,6HC/CINT,6,4.,90.,0.,0.25)
      CALL PLOT(0.,4.,3)
      CALL PLOT(5-,4-,2)
      CALL PLOT(5.,0.,2)
      CALL SYMBOL(1.,4.25,.14,22HCONCENTRATION PROFILES,0.,22)
С
C
C
C.
      COMPUTE FINITE DIFFERENCE COEFFICIENTS
С
      A1=D+DT/(DX+DX)
      A2=(2.0+0+0T/(DX+0X))+(0T/DX)-((1.0+EQ+EXP(-KIN+DT))/(1.0+EQ))
      A3=(D+DT/(DX+DX))+(DT/DX)
      A4=(EXP(-KIN+DT)-1.0)/(1.0+E0)
      A5=(2.0*D*DT/(DX*DX))+(DT/DX)-1.0
      B1=(EQ+(1.0-EXP(-KIN+DT)))/(1.0+E9)
      B2=(EQ+EXP(-KIN+DT))/(1.0+EQ)
```
```
С
        WRITE (6.45) A1.A2.A3.A4.B1.B2
     45 FORMAT (6F10-5)
  С
  С
        START COMPUTATIONS
  С
  С
        TIME=0.0
        M=N-1
        DO 100 I=1,NSTEP
         TIME=TIME+DELT
         TMASS=0.0
  С
  C
        COMPUTATION FOR FIRST CELL
  С
         C(3,1)=A1*C(1,2)-A2*C(1,1)-A4*C(2,1)
        C(4,1)=B1+C(1,1)+B2+C(2,1)
  С
    .
         DO 50 J=2+M
  С
  C
         COMPUTATION FOR MIDDLE CELLS
  С
         C(3,J) = A1 + C(1, J+1) - A2 + C(1, J) + A3 + C(1, J-1) - A4 + C(2, J)
         C(4,J) = B1 + C(1,J) + B2 + C(2,J)
         IF (C(1,J).GT.C(2,J)/EQ) C(3,J)=A1+C(1,J+1)-A5+C(1,J)+A3+C(1,J-1)
         IF (C(1,J).GT.C(2,J)/EQ) C(4,J)=C(2,J)
     50 CONTINUE
  С
         COMPUTATION FOR LAST CELL
  С
  С
         C(3+N)=(A1-A5)+C(1+N)+A3+C(1+M)
         C(4 \cdot N) = 0 \cdot 0
  С
         COMPUTATION FOR MASS FLUX OUT
  С
  С
         FMOUT=FMOUT+V*POR*DELT*(C(1,N)+D*FLOAT(N)*C(1,1))
  С
  С
         PRINT RESULTS FOR TIME STEP
  С
         IF (MOD(I,NPRNT).NE.0.) GC TO 80
  С
         MASS BALANCE COMPUTATIONS
  С
  С
         D0 55 J=1+N
         THASS=TMASS+DELX+POR+(C(3,J)+C(4,J))
      55 CONTINUE
  С
         RESID=THASSI-THASS-FHOUT
  C
         WRITE AND PLOT OUTPUT
  С
  С
         WRITE (6,60) TIME, TMASS, RESID
  С
      60 FORMAT (//,6HTIME =,F10.2,10X,12HTOTAL MASS =,E10.3,10X,
        123HMASS BALANCE RESIDUAL =,E10.3)
         WRITE (6,70) (C(3,J),J=1,N)
         WRITE (6,70) (C(4,J),J=1,N)
      70 FORMAT (10X,10F10-2/(12X,10F10-2))
80 CONTINUE
  С
   IF (MOD(I,NPLOT).NE.0..AND.I.NE.NPRNT) GO TO 86
        DO 82 J=1,N
```

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```
XARRAY(J)=FLOAT(J)+DX
      BARRAY(J)=C(4,J)/(CINT+EQ)
      CARRAY(J)=C(3,J)/CINT
   82 CONTINUE
      XARRAY(N+1)=0.0
      BARRAY(N+1)=0.0
      CARRAY(N+1)=0.0
      XARRAY(N+2)=0.2
      BARRAY(N+2)=0.25
      CARRAY(N+2)=0.25
С
С
      CALL PLOT(0.,-5.,-3)
      CALL LINE (XARRAY, BARRAY, N, 1, 0, 2)
      CALL PLOT(0.,5.,-3)
      CALL LINE(XARRAY+CARRAY+N,1,0,2)
С
С
C
   86 CONTINUE
С
С
      UPDATE CONCENTRATIONS FOR NEXT TIME STEP
С
      DO 90 J=1,N
                                .
      C(1,J)=C(3,J)
      C(2,J)=C(4,J)
      IF (C(3,J).LE.CHAX(J)) GO TO 90
      CMAX(J)=C(3,J)
      TMAX(J)=TIME
   90 CONTINUE
  100 CONTINUE
С
С
      WRITE AND PLOT MAXIMUM MOBILE PHASE CONCENTRATION
С
      WRITE (6,105)
  105 FORMAT (10X,29HMAXIMUM SOLUTE CONCENTRATIONS,//)
      WRITE (6,70) (CHAX(J),J=1,N)
      WRITE (6,70) (TMAX(J),J=1,N)
С
      DO 110 J=1.N
      CARRAY(J)=CMAX(J)/CINT
  110 CONTINUE
С
      CALL LINE (XARRAY, CARRAY, N, 1, -1, 14)
C
      CALL PLOT(0.,0.,999)
С
     STOP
      END
```