THESIS

URANIUM IN SITU SOLUTION MINING AND GROUNDWATER QUALITY AT THE
GROVER TEST SITE, WELD COUNTY, COLORADO

Submitted by

Kenneth S. Wade

Department of Earth Resources

In partial fulfillment of the requirements

for the Degree of Master of Science

Colorado State University

Fort Collins, Colorado

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COLORADO STATE UNIVERSITY

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WE HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER OUR SUPERVISION

BY _ Kenneth S. Wade _____

ENTITLED _ Uranium In Situ Solution Mining and Groundwater Quality at _

_ the Grover Test Site, Weld County, Colorado _____

BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF

_____ Master of Science _____

Committee on Graduate Work

Frank G. Ethridge

C. Gerald Warren

_____

Tommy B. Thompson
Advisor

ABSTRACT OF THESIS

URANIUM IN SITU SOLUTION MINING AND GROUNDWATER QUALITY AT THE
GROVER TEST SITE, WELD COUNTY, COLORADO

Regional groundwater studies in Weld County, Colorado reveal
groundwater patterns which coincide with known uranium roll front
deposits. It is postulated that alteration produced by oxygen and
uranium-bearing water moving through the Fox Hills, Laramie, and
White River Formations produced a zone of high total dissolved
solids (TDS) $NaSO_4$ water which changes to low TDS, $NaHCO_3$ water as
the oxidation-reduction front is approached. Processes which could
affect such changes are: hydrolysis of feldspars, cation exchange
with clays, oxidation of pyrite, and bacterial reduction of sulfate.

The study of mineralization, solution mining, and restoration
of the Grover uranium roll front deposit, Sec. 24, T. 10 N., R.
62 W, Weld County, indicated the following points.

Reduction of uranium is directly or indirectly related to re-
ducing bacteria associated with organic material. Natural ground-
water associated with mineralized areas of the Grover aquifer is
suitable for only limited agricultural uses because of radium-
226, molybdenum, selenium, and iron contained in it. Restoration,
using TDS reduction by reverse osmosis and chemical treatment of
mined aquifer waters, reduced TDS to below baseline, but elevated
levels of radionuclides, molybdenum, ammonia, nitrate, and
selenium remain, though not reducing the groundwater utility.
The insitu mining process, using recycled leach solutions,

required little groundwater withdrawal, but overproduction, during

restoration produced potentiometric drawdown.

Kenneth S. Wade
Earth Resources Department
Colorado State University
Fort Collins, Colorado 80523
Fall, 1980

ACKNOWLEDGMENTS

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I. INTRODUCTION

The purpose of this study was to examine the mineralized Grover Sandstone aquifer at the Grover Test Site and determine what effects insitu solution mining would have on groundwater quality and quantity.

The Grover Test Site is situated in the east central portion of Section 24, T. 10N., R. 62W., Weld Co., Colorado, about 4 miles southwest of the town of Grover. It lies at about 5,040 feet above sea level on flat lying to gently rolling topography. The test site is in the Crow Creek drainage, a tributary to the South Platte River. Access is by county road going 14 miles north of State Highway 14 from Briggsdale, Colorado.

Uranium roll front mineralization was discovered in the Grover area in 1970 (Reade, 1976). Reserves are estimated to be 1,007,000 lbs. with an average grade of 0.14 percent eU_3O_8 at a cutoff grade of 0.05 percent. Because of the low grade and tonnage, Wyoming Mineral Corporation, Lakewood, Colorado, initiated a pilot solution mining test at the Grover Test Site. Various leach solutions and restoration techniques were used beginning June, 1977 and ending February, 1979.

Baseline water quality data were obtained from the Water Quality Control Division of the Colorado Department of Health. The Department of Health was the permitting agency and required Wyoming Mineral Corporation (WMC) to submit weekly reports concerning water quality and to meet specific restoration standards. Drill cores and geophysical logs provided information about lithology, structure, depositional environments, alteration, and mineralization associated with the roll

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front system. A coordinated regional study provided information concerning stratigraphy and depositional environments. See Figure 1 for locations of the Grover Site and regional study areas.

On June 18th, 1979, after the conclusion of the pilot project, water samples from the mined aquifer were analyzed in this study to determine the affects of mining and restoration on groundwater quality.
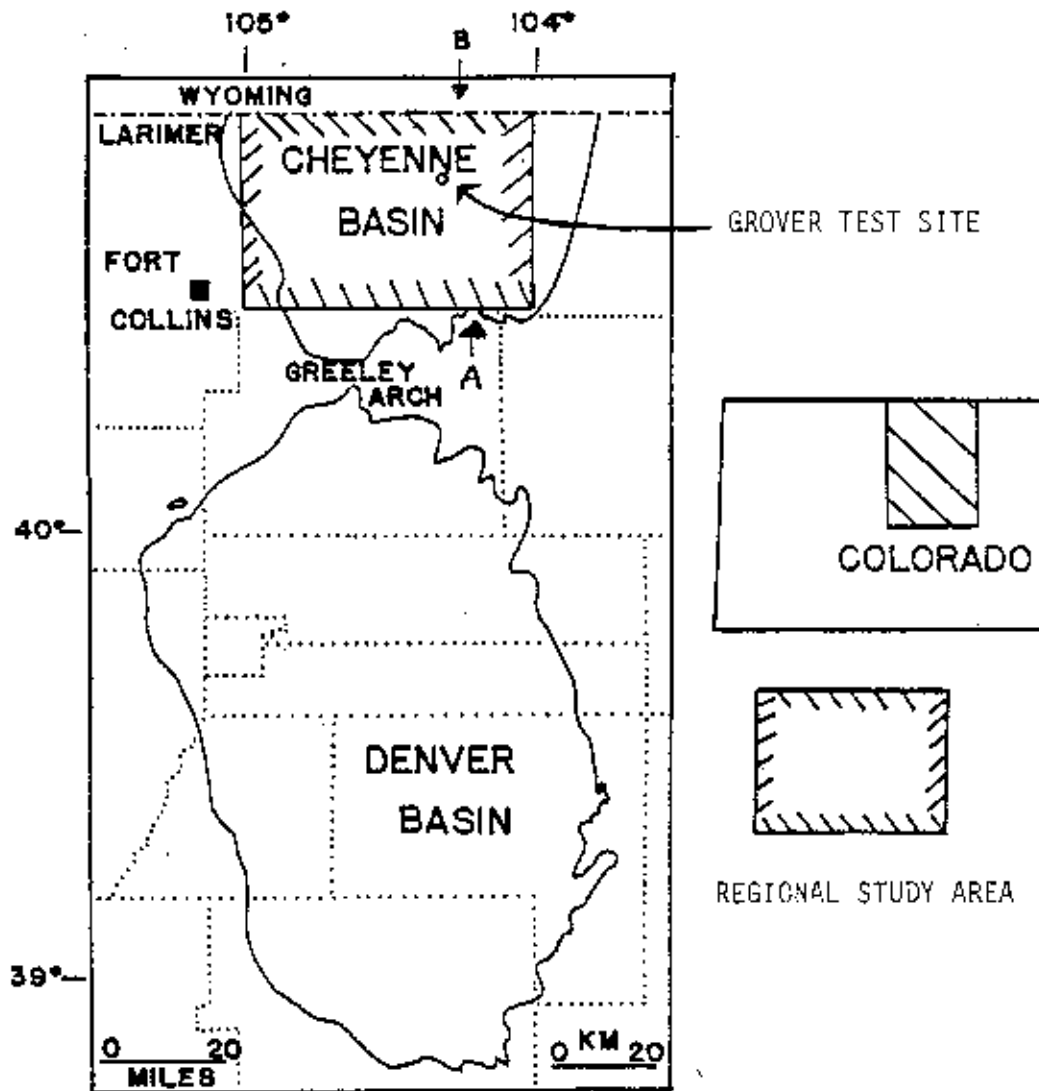
Figure 1. Location of the Grover Test Site, regional study area, and structural features. Cross section AB is found in Figure 3.

II. REGIONAL GEOLOGY AND HYDROLOGY

A. Stratigraphy

The geologic units in the area are Mesozoic and Cenozoic in age (Table 1). From the oldest to youngest these consist of: the Upper Cretaceous Pierre Shale, Fox Hills, and Laramie Formations; the Oligocene White River Group; the Pliocene Ogallala Formation; and Quaternary alluvial deposits (see Figures 2 and 3 for map and cross section of regional geology).

The Pierre Shale consists of 6,600 feet of dark gray to black marine shales with minor siltstones and sandstones. Its poor aquifer characteristics and depth limit the use of this unit as a groundwater source in the area.

The overlying Fox Hills Formation contains the Keota and Buckingham Sandstones of industrial nomenclature. (It) THE SANDSTONE consists of 200 to 450 feet of tan to brown, fine- to medium-grained sandstone with increasing amounts of black sandy shale toward the bottom. It has been interpreted by Harvey et al. (1980) to consist of stacked wave-dominated deltaic lobes. It is a reliable water producer, yielding 20 to 100 gpm of $NaHCO_3$ and $NaSO_4$ type waters with total dissolved solids ranging from 400 to 2000 mg/l. It hosts the Keota uranium roll front deposit which may shortly be mined by an insitu solution method.

The Laramie Formation is the host of the uranium mineralization which was the subject of the pilot leach mining project. It contains the Grover, Porter Creek and Sand Creek sandstones of industrial nomenclature. The "Fox Hills" unit is the name used by Wyoming

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Table 1. Rock units in study area (after Weist, 1964).

| ERA	SYSTEM	SERIES	GEOLOGIC UNIT	THICKNESS (feet)	LITHOLOGY
Cenozoic	Quaternary	Recent and Pleistocene	unconsolidated alluvial deposits	1-120	gravel, sand, silt
	Tertiary	Pliocene	Ogallala Formation	0-180	clay, silt, sand and gravel with local coarse basal conglomerates
		Oligocene	White River Group Brule Formation Chadron Formation	100-700	clayey, ashy siltstone, sandstone and conglomeratic channels.
Mesozoic	Cretaceous	Upper Cretaceous	Laramie Formation contains: Sand Creek, Porter Creek, Grover Sandstones	1100-1500	interbedded sandstones, siltstones and shales. Carbonaceous and pyritic.
			Fox Hills Formation contains: Keota and Buckingham Sandstones	200-450	sandstone and shale
			Pierre Shale	6600	dark gray and black marine shales

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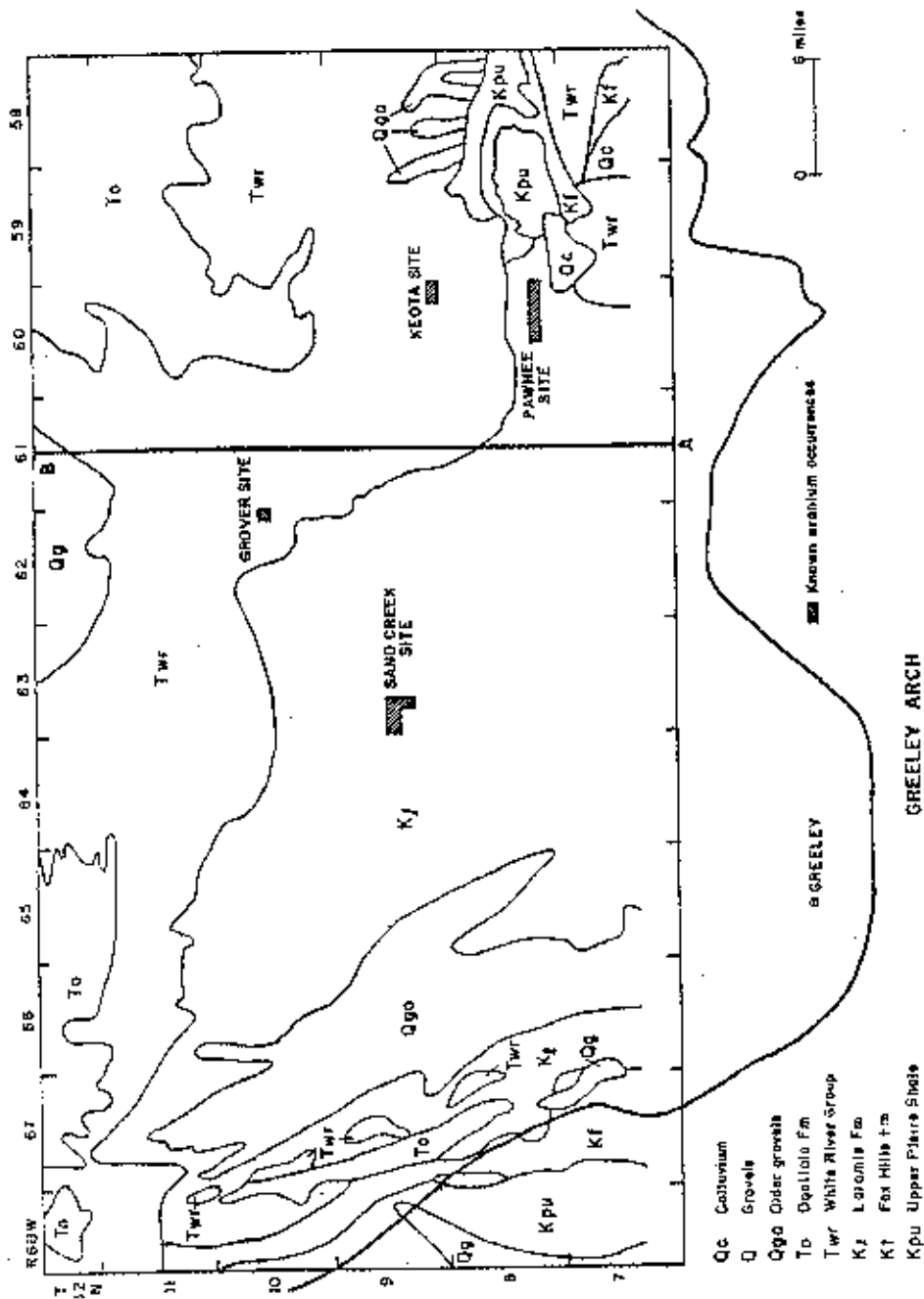
Figure 2. Geology of regional study area. (From Tweto, 1979). Cross section AB found in Figure 3.
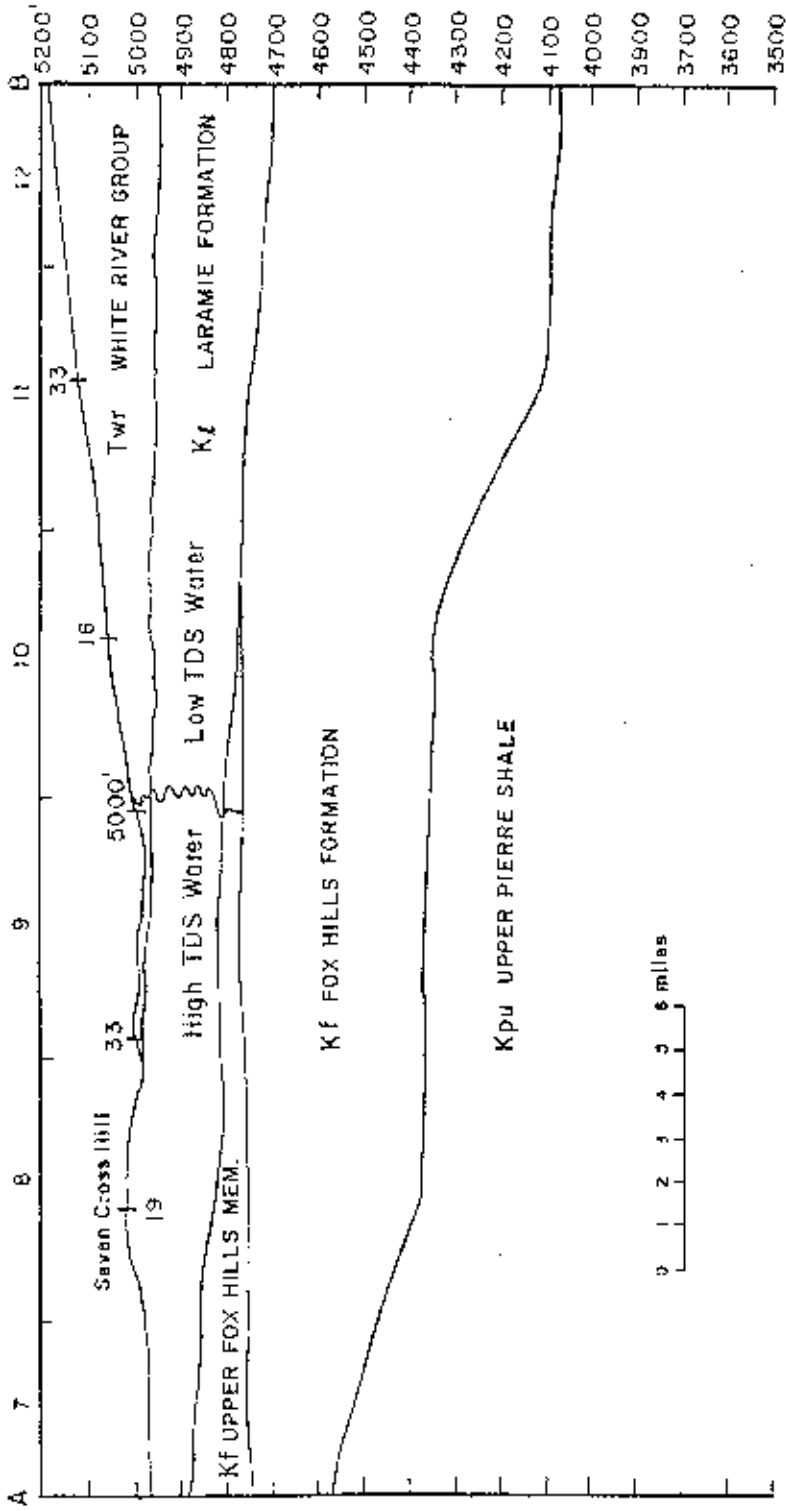
Figure 3. Cross section AB along R61W from T7N to T12N, from Ethridge et al (1979) and Iweto (1979). Cross section is located on Figure 2.

Mineral Corporation (WMC) for a thin sand layer 250 feet below the Grover Sandstone. Stratigraphic correlation using electric logs indicates this unit is contained within the Laramie Formation.

The Laramie consists of 1,100 to 1,500 feet of interbedded sandstones, shales and siltstones which consist of upward fining and occasional upward coarsening, delta and alluvial plain sandstone bodies (Kirkham, 1980). The sand beds are 10 to 90 feet thick. Coal beds up to 5 feet thick are found in the lower 400 feet.

The Porter Creek Sandstone is composed of 2 to 3 sandstone beds totaling about 40 feet in thickness. It is a near surface unit at the test site which is marked by goethite-stained grain coats and intense feldspar alteration.

The Grover Sandstone, the locus for the Grover solution mining test, varies from a thickly bedded to laminated sandstone with numerous clay partings. Some small scale, high angle crossbeds were found. It totals about 50 feet thick at the site. The Grover contains clay lenses and intraclasts, organic partings with plant debris, coal laminae up to 1 cm thick, and asphaltic layers. Mineralization was associated with the organic-rich layers. Calcite replacement was noted in one sample and a layer of calcareous mud showing cone-in-cone structure was found, but overall little calcite was found. This is reflected in the low calcium content of the Grover groundwater.

The Grover Sandstone is a salt- and pepper-colored fine-grained rock composed of well-sorted, angular to subrounded, friable grains of quartz (48%), volcanic rock fragments (12%), clay balls (12%), plagioclase (6%), orthoclase (5%), microcline (3%), chlorite (2%), organics (2%), various clay (allophane, kaolinite, montmorillonite),

alteration products of the other grains, biotite (1%), muscovite (1%), and traces of pyrite. The modal percentages were calculated using a 500 point count of a typical section from the reduced zone. Using the classification of Dott (1964), the rock would be labeled a lithic arenite with equal proportions of sedimentary and volcanic lithic fragments (Figures 4a and 4b).

The detrital material is grain supported and true matrix is less than 1%. Magnetic susceptibility tests indicate less than 0.052% Fe_3O_4 equivalent is present (Appendix I). Detrital magnetite and ilmenite might be expected in the unaltered sediment as indicated by Reynolds and Goldhaber (1978) for the South Texas foll fronts, but since the rocks sampled at Grover were within 50 feet of the front any original detrital magnetite may have been altered to limonite or reduced to pyrite.

X-ray analysis of clay fractions of the Grover Sandstone indicate the most abundant minerals present were quartz, kaolinite, sericite, and mixed lattice illite-montmorillonite (Appendix II). Next in abundance were illite, montmorillonite, and microcline. Smaller amounts of chlorite, nacrite, and halloysite were detected. No clay zoning was found from samples across the roll front.

Diagenetic effects consisted of varying degrees of feldspar argillization, breaking and deformation of micas, deformation of clay balls into pseudomatrix, and the formation of brown-stained clay coats surrounding detrital grains.

Sieve analysis indicates the Grover Sandstone is a well sorted, fine grained sand with a symmetrical but leptokurtic grain size distribution (Appendix III). Porosity determined by bulk density
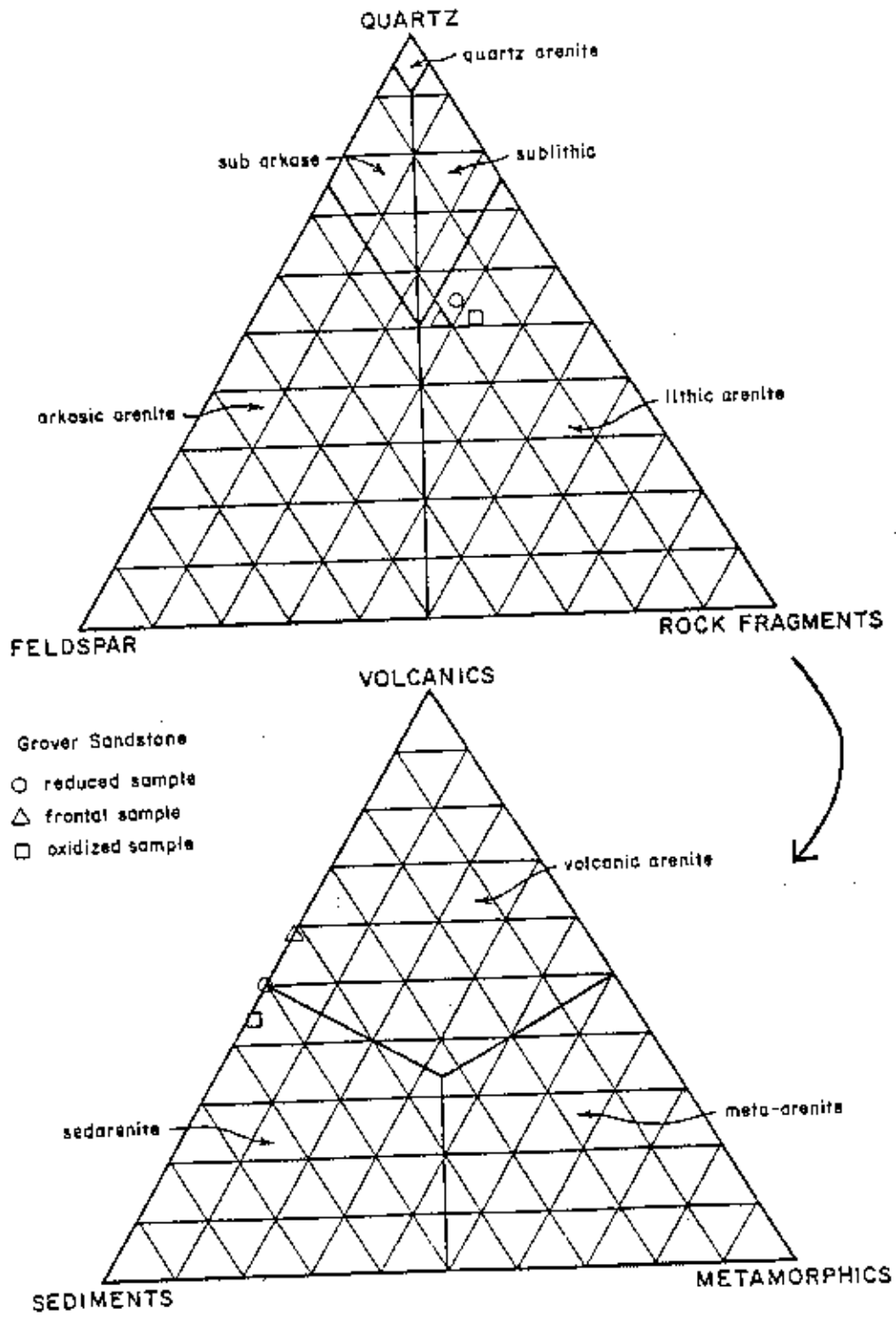
Figure 4a.   Classification of the Grover Sandstone (Dott, 1964).

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Constituent	% in oxidized zone	% in frontal zone	% in reduced zone
quartz	60	61	51
microcline	0.5	0.8	3
orthoclase	3	3	5
plagioclase	2	4	6
muscovite	0.7	1	1
biotite	2	0.8	1
chert	1	2	2
volcanic fragments	14	11	13
clay balls and pseudomatrix	14	13	12
plant fragments	1	0.8	1
chlorite	0.26	0.25	2
carbonate	0.26	0.5	0.25
porosity	28	32	28

Figure 4b. Modal Analysis of oxidized, frontal, and reduced sections of the Grover Sandstone. Determined from 500 point counts of each section.

measurements of 7 samples gave an average value of 33 percent, with values ranging from 28 to 37 percent. The density of the solids was found to be 2.55 g/cm^3 (Appendix IV). Measurements on three thin sections of 500 counts apiece gave porosity values of 28, 28, and 32 percent.

Reade (1976) interprets the Grover to be a fluvial channel sand. His sand isopach map suggests a meandering channel (Figure 5). However, the coarsening upward sequence indicated by electric logs would suggest a prograding crevasse splay may be the depositional environment. Ethridge et al. (1979) interpreted the Laramie to consist of delta plain deposits.

The depositional environments of the Laramie seem similar to those described by Galloway (1978) for the uranium mineralized Gueydan fluvial system of the Catahoula Formation, Texas. He identified crevasse splays, flood plains, coastal lake as well as fluvial channel facies.

Laramie wells produce low to moderate quantities of $NaHCO_3$ and $NaSO_4$ type water with total dissolved solids varying from 300 to 1300 mg/1 (Kirkham, 1980).

The Laramie Formation is truncated by an angular unconformity (Figures 2 and 3) which is locally exposed as an erosional surface (and elsewhere) covered by Oligocene and younger sediments (Weist, 1964).

The Oligocene White River Group is a fluvial deposit consisting of the Upper and Middle Oligocene Brule Formation and the Lower Oligocene Chadron Formation. The Brule consists of 200 to 500 feet

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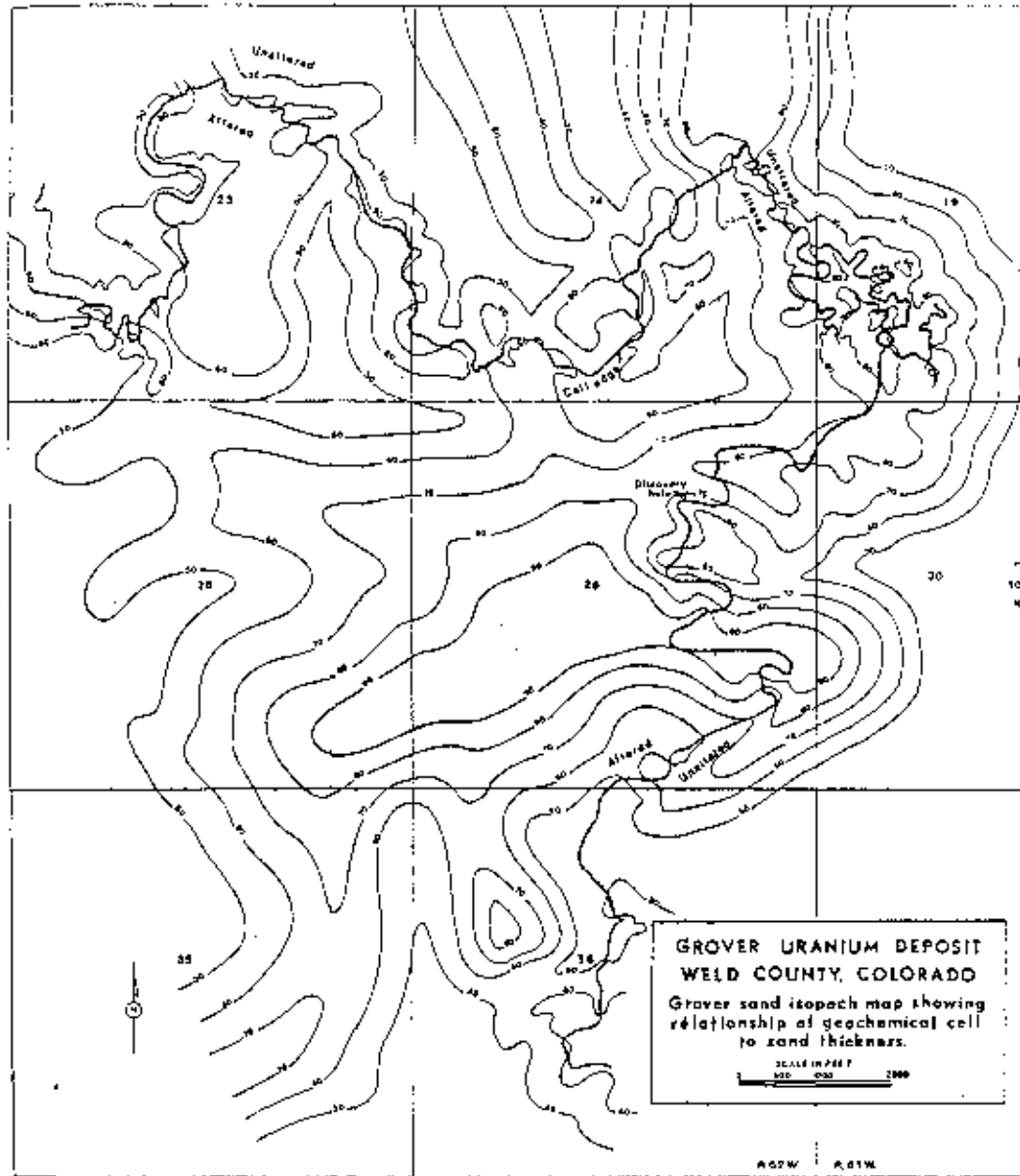
Figure 5. Grover sand isopach map showing relationship of geochemical cell to sand thickness (from Reade, 1976).

of clayey, blocky, ashy siltstone and montmorillontic claystone, with
conglomerate- and sandstone-filled calcite-cemented channels developed
on the Laramie paleosurface. These channels may be localizers of the
uranium-bearing solutions which produced the roll fronts in the under-
lying Laramie and Fox Hills Formations (see Figure 6). The fluvial
channels provide moderate to large quantities of $NaHCO_3$ water with a
TDS around 320 mg/l and $NaSO_4$ water with a TDS around 800 mg/l. The
Pliocene Ogallala Formation consists of 0 to 180 feet of clay, silt,
sand, and gravel with local deposits of coarse conglomerate. Ogallala
deposits are found north of the test site and their hydrologic charac-
teristics are not covered in this study.

Quaternary alluvial deposits in the region yield as much as
1,500 gpm of irrigation water.

B. Structural Geology

The Grover Site lies in the southern end of the Cheyenne Basin
where the sediments are dipping at low angle to the north (Figure 1).
The Cheyenne Basin is to the north of the Denver Basin, separated
from it by the Greeley Arch. The deepest part of the Cheyenne Basin
is beneath Cheyenne, Wyoming, where the Precambrian rock lies more
than 7,000 feet below sea level. The basin is a doubly-plunging
asymmetrical syncline with its axis offset to the west. The dips on
the west are steep but are gentle to the north, east, and south
(Weist, 1964).

It seems likely the basins were developing during and after
Laramide time, producing thicker Laramie deposition in the center of
the basin. The Tertiary sediments must have been deposited after the
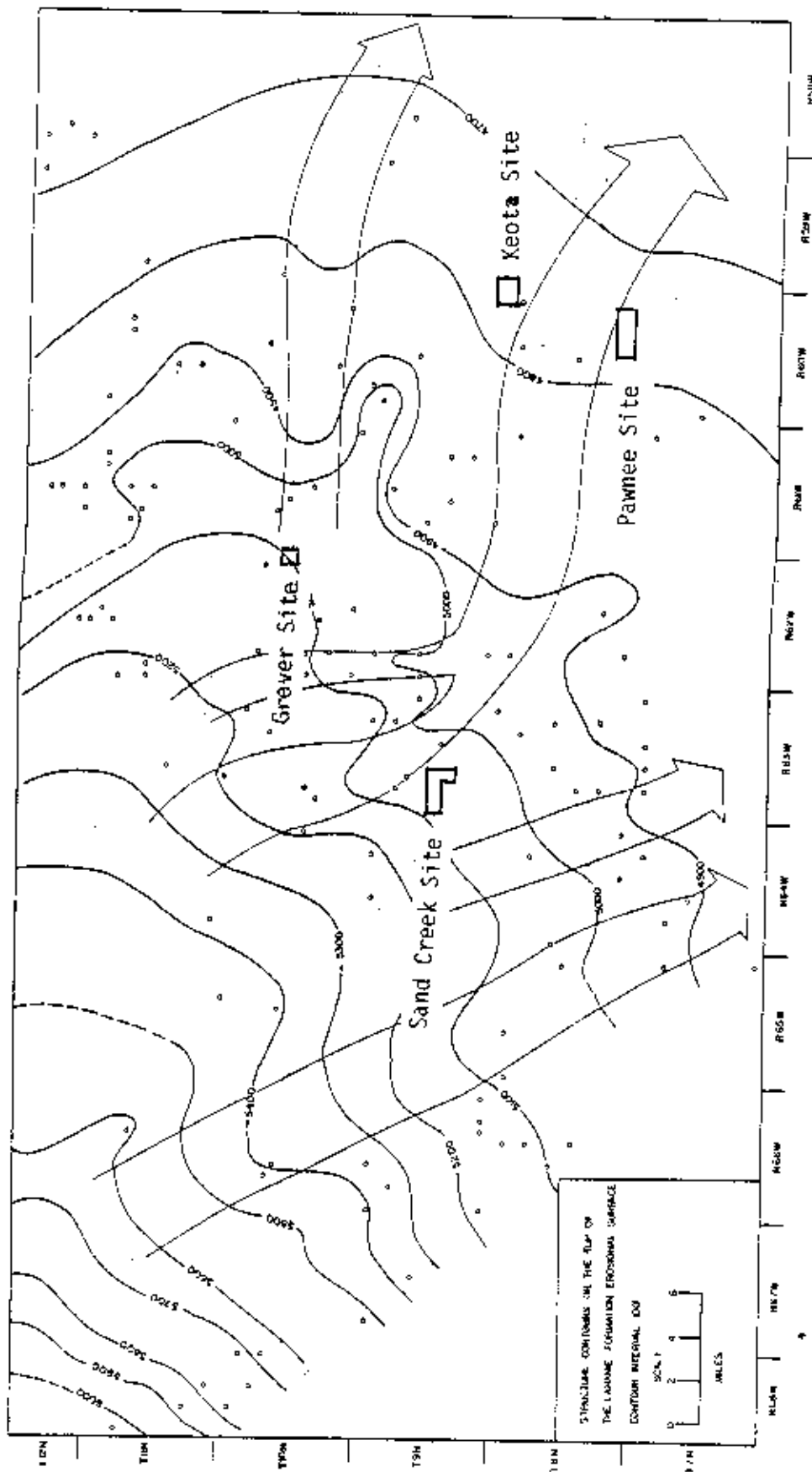
Figure 6. Paleotopography of sub-Oligocene surface, Cheyenne Basin, Colorado with locations of known uranium mineralization. Arrows indicate inferred major drainage valleys (from Ethridge, et. al., 1979).

basins had formed. The formation of the Greeley Arch is probably penecontemporaneous with Laramie deposition, but the Tertiary sediments have been stripped from the arch making it difficult to be more precise in dating the deformation.

C. Regional Groundwater Hydrology

Hydraulic gradient data by Kirkham (1980), Reade (1976), Wyoming Mineral Corporation (1976), and Wacinski (1979) indicate the potentiometric surface dips to the south-southeast with gradients varying from over 30 feet per mile north of the test site, to less than 10 feet per mile south of the site (see Figure 7). Recharge probably occurs in the Tertiary-capped highlands to the north and west and discharge to the Platte River to the south. Average annual precipitation is about 11 inches (Wacinski, 1979). The decrease in hydraulic gradient to the south may be due to upward deflection of the groundwater against aquatards and aquacludes rising on the Greeley Arch. The abundance of springs in this area is evidence of such activity.

Regional groundwater data were obtained by Kirkham (1980) and used to prepare maps which showed variations in water quality (Figures 8, 9, and 10). Waters from the White River, Laramie, and Fox Hills aquifers were sampled. There is a marked decrease in total dissolved solids (TDS) from south-southwest to north-northeast. Since the limit of high TDS water coincides with the position of known uranium roll front deposits it seems likely the elevated TDS may be a product of oxidizing uranium-bearing waters which have moved to the north-northeast (Figures 8, 9, and 10). Alteration effects, such as
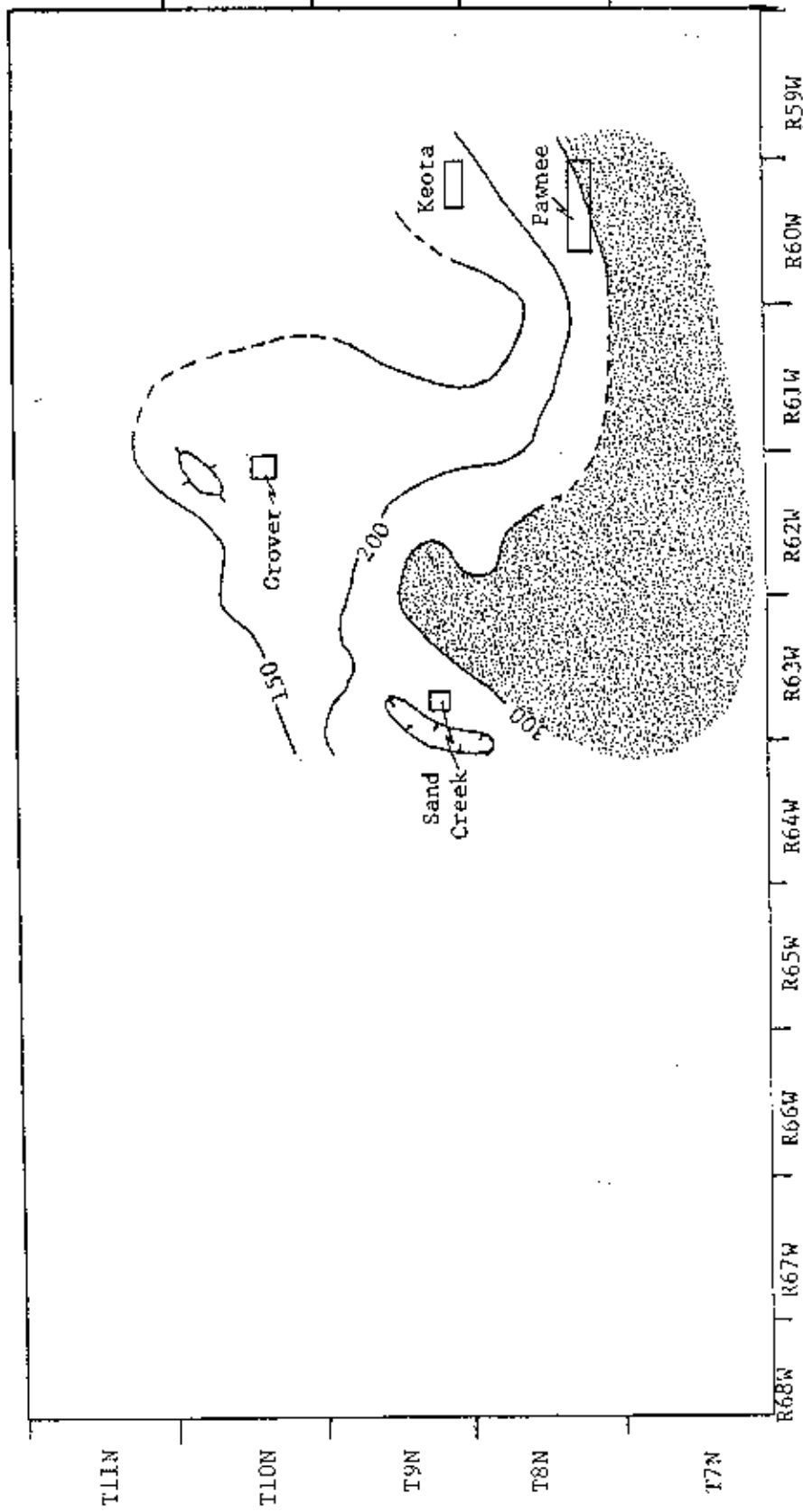
Figure 8. Isopleths of CO_3 + HCO_3 (mg/l) in the Laramie Formation. Location of the four mineralized areas indicated by rectangles. Stippling indicates concentrations greater than 300 mg./l. (from Thompson, 1980).
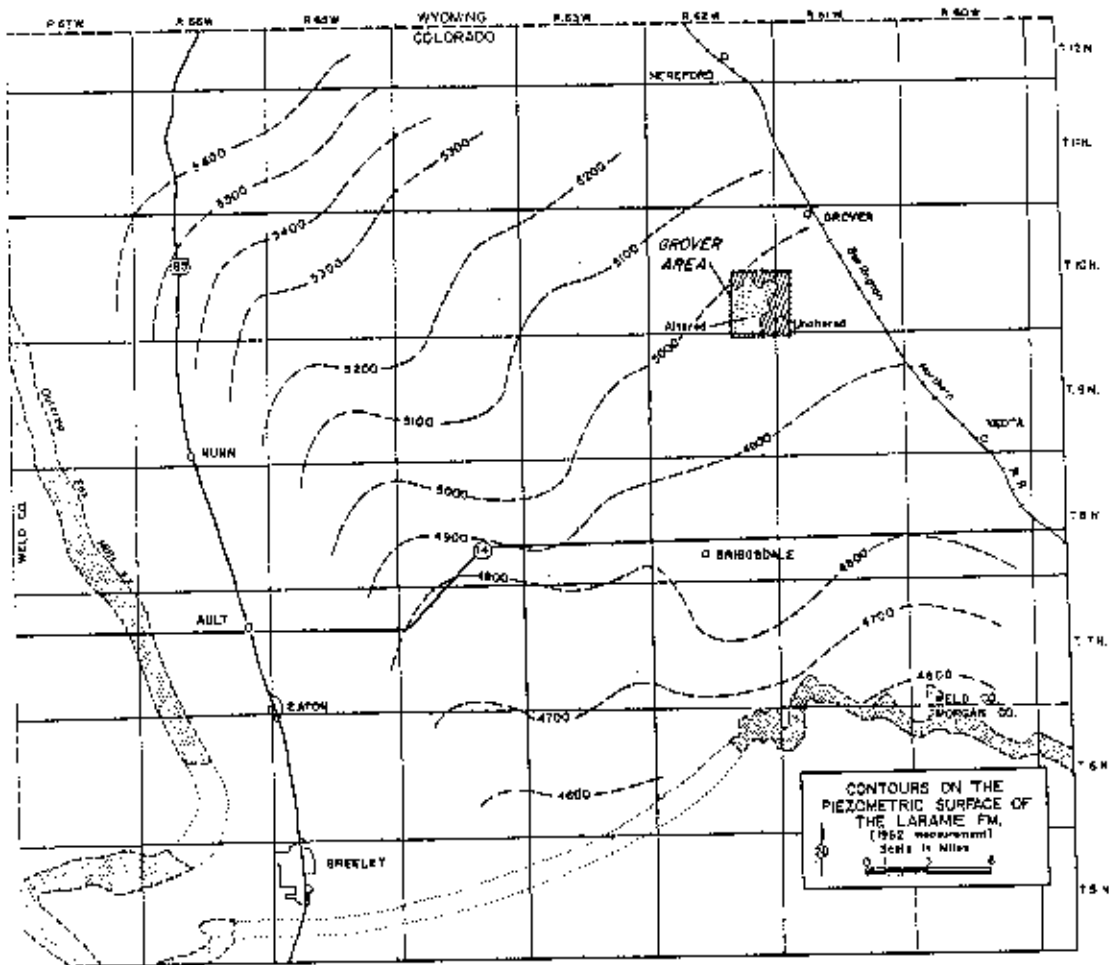
Figure 7.   Contours on the piezometric surface of the Laramie
            Formation (from Reade, 1976).
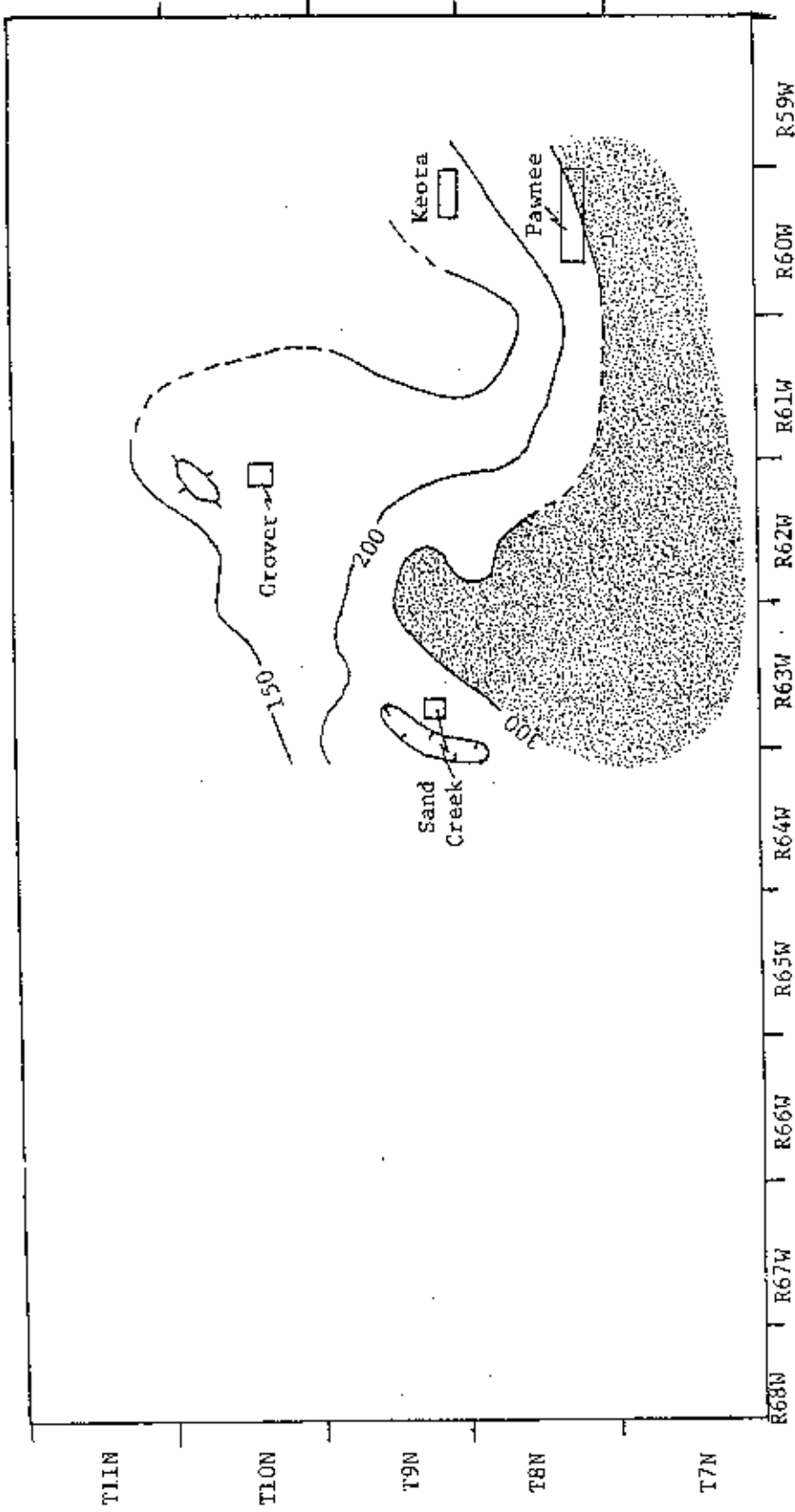
Figure 8. Isopleths of $CO_3 + HCO_3$ (mg/l) in the Laramie Formation. Location of the four mineralized areas indicated by rectangles. Stippling indicates concentrations greater than 300 mg./l. (from Thompson, 1980).
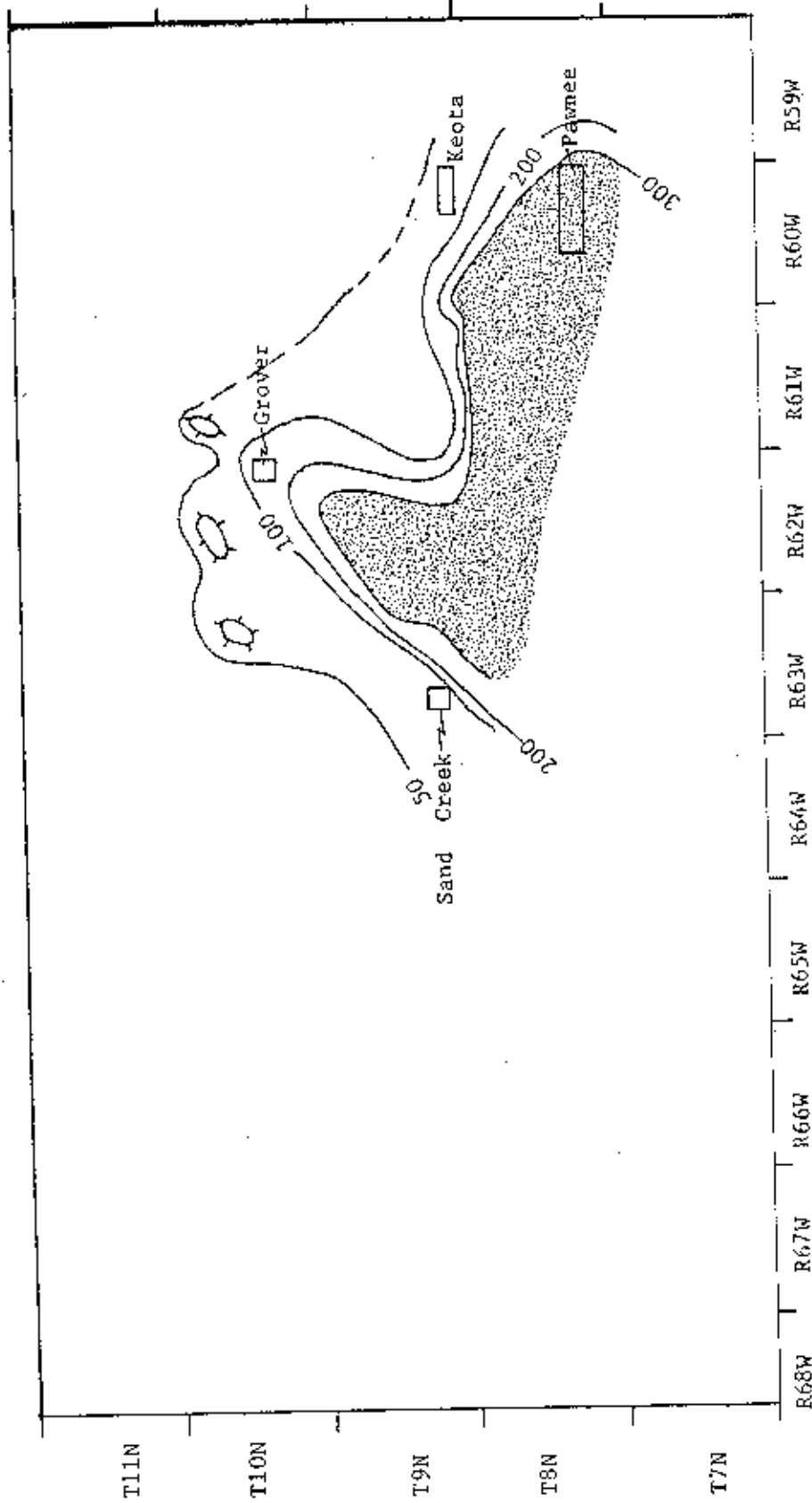
Figure 9. Isopleths of Cl + SO$_4$ in the Laramie Formation. (Contour interval 100 mg/l except for 50 contour) Location of the four mineralized areas indicated by rectangles. Stippling indicates concentrations greater than 300 mg./l. (from Thompson, 1980).

SOUTH

NORTH

High TDS Water
(NaSO₄)

Low TDS Water
(NaHCO₃)

paleochannels

recharge area

White River Group

Laramie Formation

increasing Na
decreasing
Ca,Mg,Cl,U

NaSO₄

High TDS
(450-3000 mg/ℓ)

Fox Hills
Formation

oxidation

increasing Mg,Ca
decreasing Na

uranium
mineralization

reduction

NaHCO₃

Low TDS
(300-450 mg/ℓ)

Indicate groundwater
flow lines
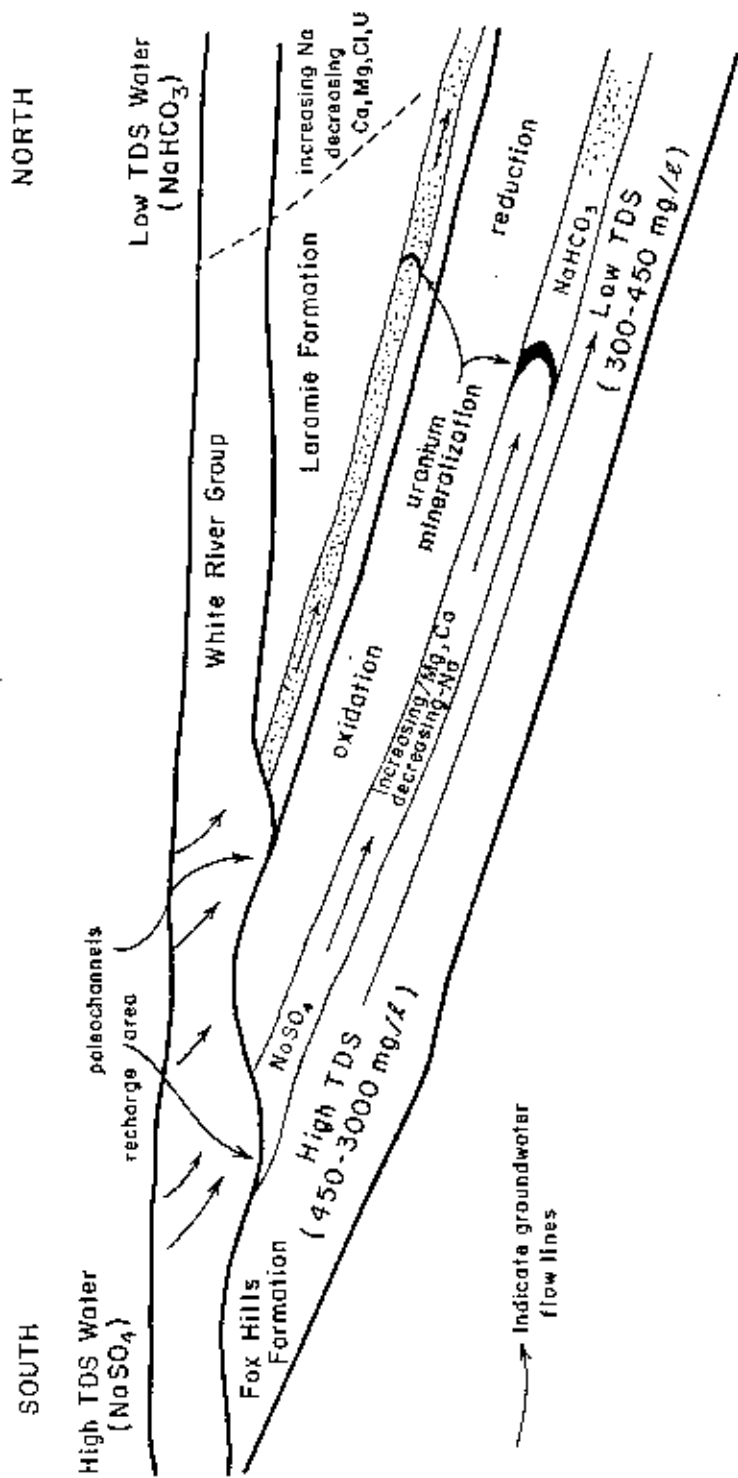
Figure 10. Schematic cross section showing vertical and horizontal changes in water quality produced by paleo-groundwater flow of oxidized uranium-bearing waters moving to the north. Later changes in physiography, possibly the incision of the high plains by the Platte River, has reversed the flow to the south.

feldspar destruction and oxidation of diagenetic pyrite and ferro-magnesium minerals could be the source for the increased TDS found to the south. The situation is made more complex by the later reversal of groundwater flow to its present southerly direction. Though this would slow the alteration processes, the alteration products already formed could supply material to the groundwater until equilibrium conditions are reached.

Because of the large variations in TDS, the groundwaters were separated into low and high TDS groups for analysis (Table 2).

It is noted the high TDS waters of all three formations are of the $NaSO_4$ type, while the low TDS waters are of the $NaHCO_3$ type. These trends are seen on the Piper diagrams of Figure 11. The steady increase in SO_4^{-2} to the south may be due to diagenetic pyrite having been oxidized to sulfate. The breakdown of feldspars to clay would contribute potassium, sodium, and calcium to the groundwater. Some calcium and sulfate may be introduced locally by dissolution of gypsiferous sediments.

Since groundwater flow is now reversed to the south it would be expected that waters low in TDS and oxygen would replace the high TDS waters and cause reduction of sulfur and iron. The lack of this may indicate the flow reversal occurred recently, or that mixing of the groundwater during reversal still preserves much of the original TDS distribution. Hem (1970) notes that because of the slowness of sulfur oxidation and reduction reactions, especially without bacterial aid, the sulfur may remain in non-equilibrium forms for long periods. This could explain why sulfate may remain in the altered high TDS

Table 2. Water of low and high TDS groups from regional data of
         Kirkham (1980).

a) LOW TDS WATER:

CONSTITUENT	WHITE RIVER	LARAMIE	FOX HILLS
TDS (mg/l)	313	340	460
CO_3+HCO_3 (mg/l)	195 (40%)*	160 (27%)	260 (34%)
Cl (mg/l	21 (8%)	20 (6%)	15 (3%)
SO_4 (mg/l)	35 (10%)	40 (9%)	30 (5%)
Mg (mg/l)	8 (8%)	5 (4%)	1.5 (1%)
Ca (mg/l)	11 (7%)	30 (16%)	4 (2%)
Na+K (mg/l)	48 (27%)	85 (39%)	150 (54%)
TYPE	$NaHCO_3$	$NaHCO_3$	$NaHCO_3$

b) HIGH TDS WATER:

CONSTITUENT	WHITE RIVER	LARAMIE	FOX HILLS
TDS (mg/l)	796	1290	1930
CO_3+HCO_3 (mg/l)	195 (13%)	300 (13%)	320 (9%)
Cl (mg/l)	20 (2%)	150 (11%)	15 (.1%)
SO_4 (mg/l)	300 (27%)	450 (25%)	950 (34%)
Mg (mg/l)	15 (5%)	30 (7%)	110 (15%)
Ca (mg/l)	55 (12%)	105 (14%)	185 (16%)
Na+K (mg/l)	210 (40%)	255 (30%)	350 (26%)
TYPE	$NaSO_4$	$NaSO_4$	$NaSO_4$

*percents are calculated from meq./l.

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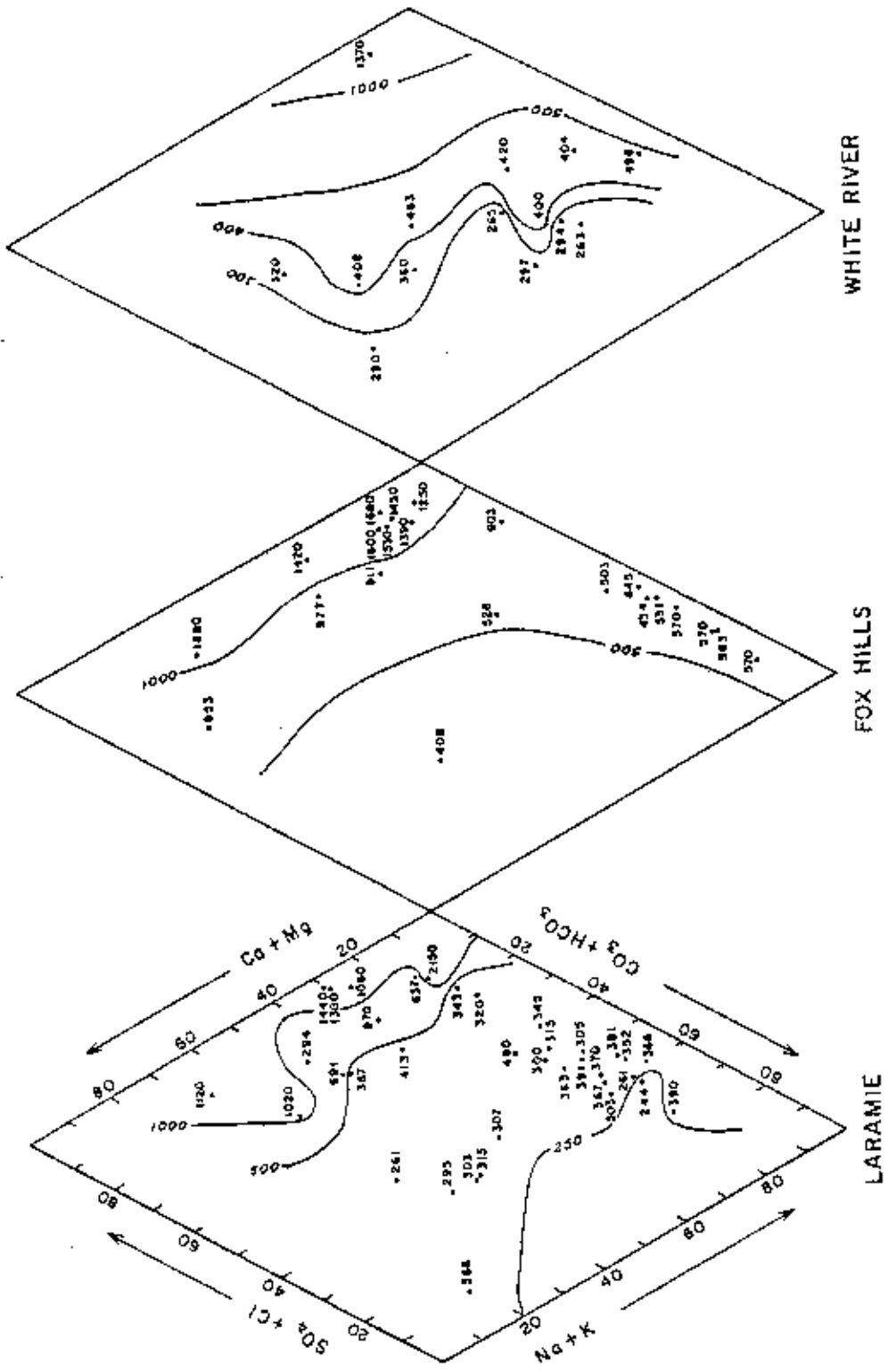
Figure 11. A comparison of water quality and TDS (total dissolved solids) for the Laramie, Fox Hills, and White River groundwaters (data from Kirkham, 1980). TDS contours are in mg./ℓ.

area even after reversal of flow would tend to produce reducing conditions.

It is noted in the low TDS group that the relative amounts of Mg^{+2}, Ca^{+2}, and SO_4^{-2} decrease and $Na^+ + K$, HCO_3^-, and TDS increase from the upper to lower aquifers. These changes could be due to intrinsic characteristics of each aquifer such as original pore fluid or mineralogy. Hall (1976), in his study of the Lower Cretaceous Hosston and Hensel Sandstones of North-Central Texas, found that $CaMgHCO_3$ waters correlated with the Hensel fluvial system, while the $NaHCO_3$ and *SODIUM BICARBONATE* $NaSO_4$ waters correlated with the Hosston delta system. The rock *SODIUM SULFATE* units in the Grover study area show similar facies changes in that the two upper units are fluvial while the lower is interpreted to be deltaic (Ethridge et al., 1979). However the water chemistry differs in that the deltaic Fox Hills contains less SO_4^{-2} than the upper fluvial units.

Another mechanism for explaining the changes in groundwater chemistry would be that as the water moves down dip from recharge areas it would change by equilibrating with the aquifer environment. Such changes have been described by Hagmaier (1971) for waters moving through aquifers of the Powder River Basin, Wyoming. Recharging groundwaters would tend to contain Ca^{+2} and Mg^{+2} leached from soils by organically-derived acids. They would also contain dissolved oxygen. As the waters moved through the aquifer the pH would be buffered by hydrolysis of feldspars and reactions with carbonates. The Ca^{+2} and Mg^{+2} could be precipitated as carbonates or preferentially absorbed by clays or zeolites. Na^+ and K^+ would be released in exchange.

SO_4^{-2}, derived from oxidation of diagenetic pyrite or gypsiferous sediments could be reduced as H_2S or pyrite by _Desulfovibrio_ bacteria associated with detrital organic material. The TDS would increase with dissolution of aquifer materials until equilibrium was reached. Large variations in water quality result, depending on the length of time and distance the water had traveled from its recharge area. Such variations are shown on the Piper diagrams in Figures 11 and 12. The variations may also be due to mixing of waters from different aquifers.

The water quality distribution is further complicated by the gross changes produced by the oxidation fronts which were described previously. When examining the high TDS group it is found that HCO_3^- and Na^+ decrease and SO_4^{-2}, Mg^{+2}, and Ca^{+2} increase from the upper to lower aquifers (Table 2). The oxidizing effects of the alteration front must be responsible but the mechanism responsible for the upper to lower changes is unclear.
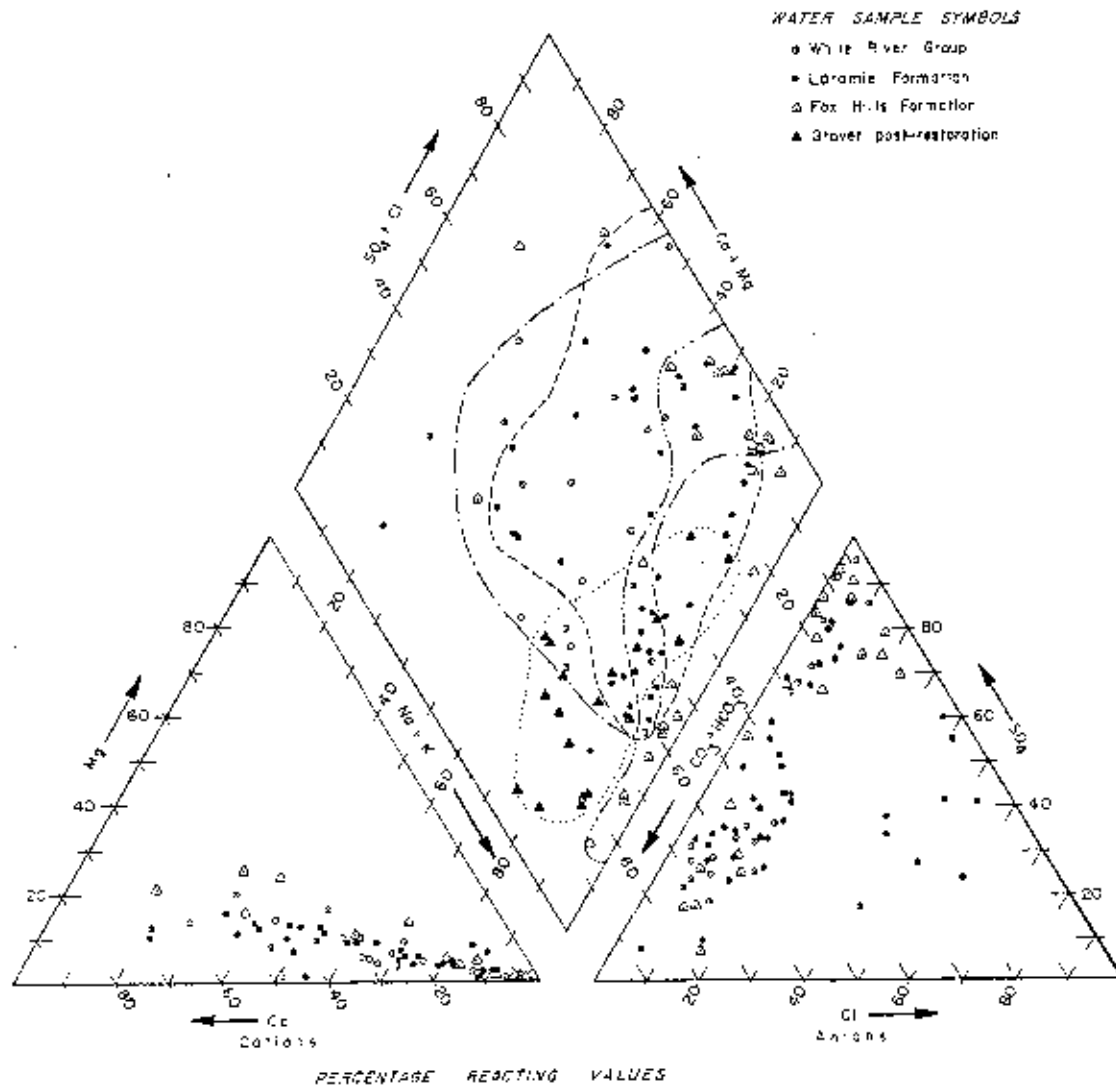
Figure 12.   Piper trilinear diagram of relative water qualities
             (from Thompson et al., 1980).

III. THE GROVER TEST SITE

A. Uranium Mineralization

Roll front type uranium mineralization has been described by: Dahl and Hagmaier (1974) in the Powder River Basin, Wyoming; Harshman (1972) in the Shirley Basin, Wyoming; and by Galloway (1978) in south Texas. The roll front deposit at Grover seems to most closely resemble the Powder River, Wyoming occurrences. They share similar organic and pyritic-bearing host rocks, uranium sources, and possible uranium precipitation mechanisms. The Grover deposit is smaller and of lower grade with 1,007,000 lbs at 0.14 percent eU_3O_8 versus 2.0×10^{10} lbs at 0.1 to 0.3 percent in the Highland area of the southern Powder River Basin. The low grade and tonnage make Grover amenable to solution mining while the Wyoming deposits are largely mined by open pit methods.

The tuffaceous White River Formation is the postulated source for the uranium at Grover (Reade, 1976). In the pH range of normal groundwater, uranium is soluble only as the oxidized +6 uranyl ion. The +4 reduced uranous ion is insoluble. The uranyl ion readily forms complexes with carbonate and bicarbonate ions. At a pH of 7, and containing 600 mg/l total carbonate, the water can hold 10 times as much uranium than when no carbonate is present (Hagmaier, 1971). The total carbonate content of the altered zone high TDS Laramie water is about 300 mg/l, but this decreases to 160 mg/l in the low TDS group which borders the postulated regional oxidation-reduction front which localizes the uranium roll deposits. The decrease in carbonate concentration may play a roll in uranium precipitation by decreasing its solubility.

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Therefore, it is likely that groundwater recharge through the uranium-bearing tuffaceous White River Group, oxidized and complexed the uranium and transported it downdip. Paleochannels developed on the Laramie may have localized flow and infiltration. As the oxidizing water contacted diagenetic pyrite, ferric iron and sulfate were produced. The iron was probably adsorbed by montmorillonitic clays as found by Harshman (1972), in the Shirley Basin where they would substitute for +3 aluminum ions. The clays would also tend to adsorb Ca^{+2} and Mg^{+2} and release Na^{+} and K^{+}. This would occur because interlayer replaceable cations in the smectites satisfy a charge imbalance so the higher valence elements are preferentially absorbed. Nine samples of Grover Sandstone were analyzed for cation exchange capability (CEC) and found to average 8.5 meq/100 g (Appendix XI).

The sulfate could be reduced by Desulfovibrio bacteria associated with the plentiful organic material found in the Laramie as suggested by Hagmaeir (1971):

$$2H^{+} + SO_4^{-2} + CH_4 \rightleftharpoons H_2S + CO_2 + 2H_2O$$
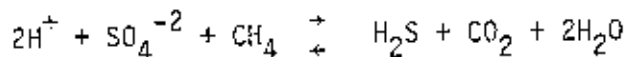
The H_2S could then reduce the uranium thus precipitating it as follows:

$$H_2S + 4UO_3 \rightleftharpoons 4UO_2 + 2H^{+} + SO_4^{-2}$$
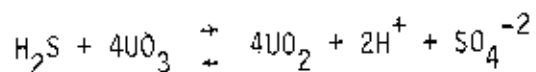
It can be seen that H_2S would be an effective precipitation mechanism in that four uraninite molecules are produced for every hydrogen sulfide molecule consumed. Dahl and Hagmaier (1974) propose that oxidation of diagenetic pyrite may produce sulfite which in turn disproportionates

to sulfate and hydrogen bisulfide. It is the hydrogen bisulfide which then reduces the uranium. In this way the need for the organics and associated bacteria needed for H_2S generation is eliminated. The high organic content of the Grover Sandstone leaves the H_2S reducing mechanism as tenable, and it is buttressed by the association of organic material with mineralization. Organic rich layers, composed of leaf fragments or asphaltic material were mineralized by Yb, V, Pb, La, and Mn, as well as uranium (Appendix V, samples 24G1c-217 and PG2R-220).

Sulfate reduction can be utilized to precipitate calcite as follows:

$$CaSO_4 + CH_4 \rightleftarrows CaCO_3 + H_2S + H_2O$$
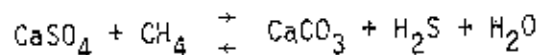
Again, organically derived methane is utilized to reduce the sulfur.

These mechanisms set up a geochemical cell whose form and rate of movement is controlled by the rate of flow of oxidizing groundwater and availability of reductants. Once a redox boundary is established it continues to be mobilized as oxidizing waters moving downdip consume reducing materials. The uranium is concentrated as the uranium-bearing waters continue moving through the system. This is evidenced by the high vanadium content of sample G24-212. The uranium and other mineralizing elements are absent but undoubtedly accompanied the vanadium before the sample was oxidized.

The physical characteristics of fluid flow through the aquifer determines the shape of the roll form. The classic mineralized roll front is portrayed as a C shape with the center of the C pointing downdip. This reflects the greater conductivity of the center of the aquifer with boundary effects slowing flow at the margins. Warren

et al. (1980) have used physical and chemical inputs to develop computer models of roll front shapes.

The Grover rolls vary from 10 to 30 feet vertically with tails running several times that updip. The deposit also contains stacked rolls where the rolls are separated by thin shale partings.

The permeability of the host sediment influences mineralization. Reade (1976) (see Figure 5) shows that mineralization is localized where the sand body thins or where it is constricted. Weak mineralization also occurs along sand-shale interfaces. Mineralization in areas of low permeability can cause small pockets of mineralization to be left stranded updip and surrounded by oxidized ground. The affects of dissolved oxygen transport and its relation to ore body geometry are discussed by Granger and Warren (1979).

Alteration of the Grover Sandstone due to the mineralization episode can be discerned, with the intensity decreasing from the oxidized to reduced ground. The alteration is summarized in Figure 13. Many roll fronts elsewhere, have distinctly colored alteration patterns in which the oxidized material has a yellowish-orange to reddish color due to limonitic and hematitic staining while the reduced ground remains gray or tan. Even with the use of color charts no marked change in color was found to be associated with oxidized or reduced ground at Grover.

Quartz grain destruction in the form of pitted and sutured grain surfaces increases updip from the redox boundary. Very few quartz overgrowths were found, indicating quartz was being flushed from the system. Increased biotite destruction occurred updip. Biotite in reduced ground often shows subhedral crystal outlines, good cleavage,

OXIDIZED   FRONTAL   REDUCED

alteration rims: pyrite,   pyrite, Fe-chlorite
bleaching, sericitization,
argillization.
clay grain coats,
kaolinite nests

←——————————————————— increasing quartz grain dissolution

←——————————————————— increasing biotite and feldspar
                                            destruction

←——————————————————— increasing brown-stained clays

←——————————————————— increasing dissolution of organic
                                            fragments
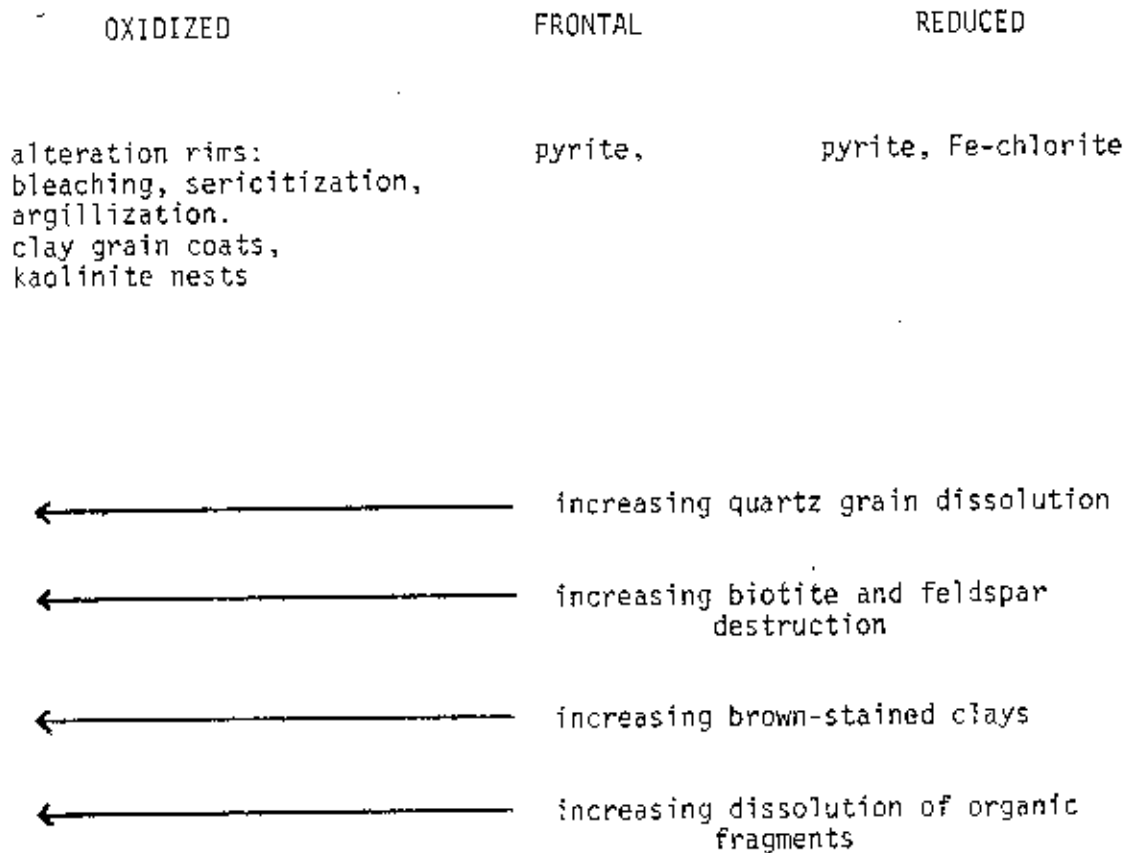
Figure 13.   Alteration effects through the roll-front.

and high birefringence. Updip these features are reduced with many grains altering to a brown-stained clay. Plagioclase and orthoclase behave in a similar fashion.

Golden brown high iron chlorite was found as a replacement or pore infilling in the reduced ground. Chlorite of any type was rare in the oxidized or frontal zone though some was found as an alteration product of biotite. Pyrite infillings of pore space were found in the front and reduced zone. The secondary nature of the pyrite was very apparent.

Spherical to oval pellets, 1.8 to 6.2 mm long were found in the reduced zone. These consisted of detrital grains of the Grover Sandstone tightly bonded by a matrix of siliceous cement. They are probably organic in origin, though perhaps an initial carbonate cement was replaced by silica. The pellets are pyritized in the frontal zone. The cement was partially or totally replaced by pyrite and some microcline and plagioclase grains were partially replaced along twin planes. The surfaces of the pellets developed a framboidal texture expressed as a sprinkling of pyrite cubes (0.1 mm). No pellets were found in the oxidized zone and are assumed to have been destroyed by the alteration associated with the mineralizing fluids.

Whole rock analysis (Appendix V) indicates an increase of iron in the front relative to the oxidized or reduced zones. The iron may be contained in the secondary pyrite, iron rich clays or chlorite. The source could be the oxidation of detrital iron oxides, biogenic pyrite, or biotite.

There is an increase in brown-stained clays updip. Some true matrix of this material was found in the oxidized zone. The staining may be a result of iron oxidation or mobilization of organic material.

An increase in clay coats was also noted in the oxidized zone. These were usually brown stained though some were sericitized. Kaolinite nests representing true matrix, and pore spaces partially lined with brown stained clay were noted. The oxidized zone was also marked by organic fragments showing a caries texture which would indicate dissolution. The clay balls show alteration rims of bleached clay, sericite, or montmorillonite.

B. Mining and Restoration Processes

Because of the low grade and tonnage, Wyoming Mineral Corporation, Lakewood, Colorado, initiated a solution mining test project at the Grover Site in the east-central part of Section 24, T. 10N., R. 62W., Weld County, Colorado. Uranium leach solutions and restoration procedures were tested in two small well fields and a single hole slug test to determine both the economics and process of the in situ mining method. All testing took place in the Grover Sandstone of the Laramie Formation. Kirkham (1979), Larson (1978), Thompson (1978), U.S. Nuclear Reg. Comm. (1978, 1978a) describes in situ uranium mining methods and related environmental concerns.

The leach solutions (lixiviants) consisted of bicarbonates of ammonia, sodium, or calcium, mixed with hydrogen peroxide. The concentration of the ammonium bicarbonate was around 5 g/l, while the hydrogen peroxide concentration was around 2 g/l. The pH was maintained at 7.5 to 9.0. The hydrogen peroxide oxidizes the uranium from the insoluble +4 to the soluble +6 oxidation states. The uranium is then complexed with the bicarbonate and the pregnant solution is pumped to the surface for processing. Some likely reactions between

the leach solution and the uranium are as follows (modified from Larson, 1978):

1. $\quad UO_2 \quad + \quad H_2O_2 \quad \rightleftarrows \quad UO_3 + H_2O \rightleftarrows UO_2^{+2} + 2OH^-$

   uraninite $\quad$ hydrogen $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ uranyl
   $\quad\quad\quad\quad\quad$ peroxide $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ ion

2. $UO_3 + H_2O + 3(NH_4)_2 CO_3 \rightleftarrows (NH_4)_4 UO_3(CO_3)_3 + 2NH_4OH$

3. $UO_3 + 2NH_4HCO_3 \rightleftarrows (NH_4)_2 UO_3(CO_3)_2 + H_2O$

4. $UO_3 + 2NH_4HCO_3 + (NH_4)_2CO_3 \rightleftarrows (NH_4)_4 UO_2(CO_3)_3 + H_2O$
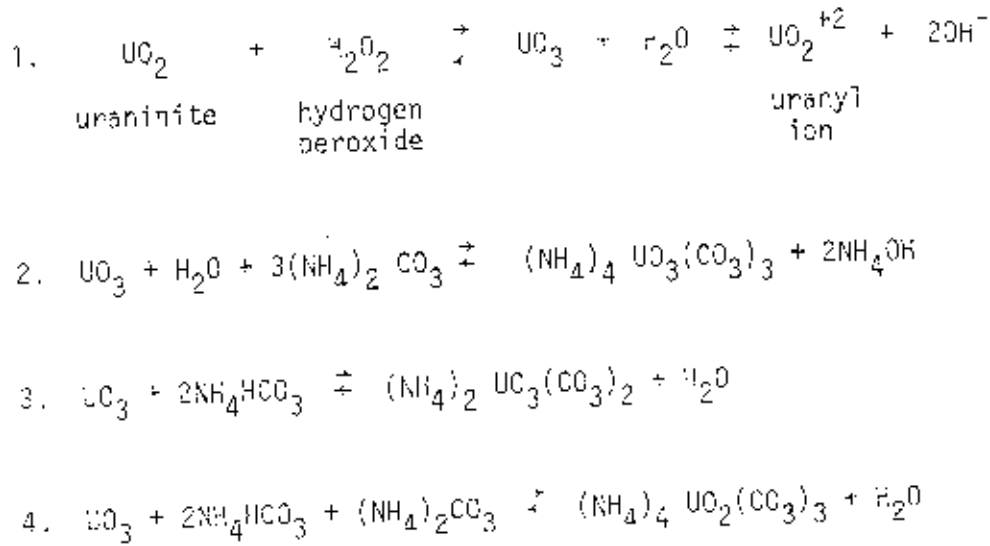
Some of the ammonia, sodium, or calcium originally combined with the bicarbonate is left behind. After the uranium is stripped, the solution is regenerated with makeup leach chemicals, its pH adjusted, and reinjected into the leach field.

A slug test undertaken in February, 1977, consisted of injecting 4,000 gallons of ammonium bicarbonate leach into a single hole. After 24 hours 4,000 gallons of fluid was recovered and analyzed. To test groundwater sweeping as a restoration technique, 16,000 additional gallons were pumped and analyzed. These data (WMC,1979) are found in Table 3. It can be seen that levels of U_3O_8 and NH_4 remain elevated after restoration.

AMMONIUM

Table 3.   Grover slug test (WMC, 1979).

PARAMETER	PREMINING	POSTMINING*	POST-RESTORATION
NH_4^+(mg/1)	1.0	740	20
HCO_3^-(mg/1)	192	2310	205
SO_4^{-2}	29	40	35
Ca^{+2}	6	23	1
Cl^-	6	13	8
U_3O_8	1	100	6

* Samples taken at midpoint of slug recovery

Well Field I (WFI) began leach operations with an ammonium bicar-bonate-hydrogen peroxide lixiviant in June of 1977 and terminated in September of 1977 (Figure 14). WFI consisted of 3 five spot well patterns in which the corner wells were injected with the leach solu-tion. The wells were screened for 4 to 12 feet at the mineralized intervals. The pregnant leach fluids were recovered at production wells in the center of each pattern. The field is 40 feet wide and 120 feet long.

Well Field II (WFII) began operation with the same lixiviant in October, 1977 and terminated in December, 1977. Calcium bicarbonate-hydrogen peroxide leach was then used from February, 1978 to April, 1978. In May, 1978, slug testing, using sodium bicarbonate-hydrogen peroxide was carried out in WFII.

Restoration procedures for both fields consisted of clean water recycle, chemical treatment with $CaCl_2$, and residual total dissolved solids (TDS) reduction. The first and last processes are essentially the same in that well field waters, polluted with leach chemicals and mobilized metals, are pumped through two reverse osmosis units in series, removing most of the TDS, and then being returned to the leach field. In this way only a small bleed stream is lost from the reverse osmosis units. The clean water recycle was started on May 13, 1978 and con-cluded on July 5, 1978, when the NH_4^+ level had equilibrated at 160 mg/l.

The chemical treatment began on July 6th, 1978 and ended on September 7, 1978. During this time, high concentrations of $CaCl_2$ were pumped through the well fields. The high Ca^{+2} concentration caused the NH_4^+ adsorbed on the clays to be replaced by the Ca^{+2}. The NH_4^+ was removed above ground by air stripping as ammonia.
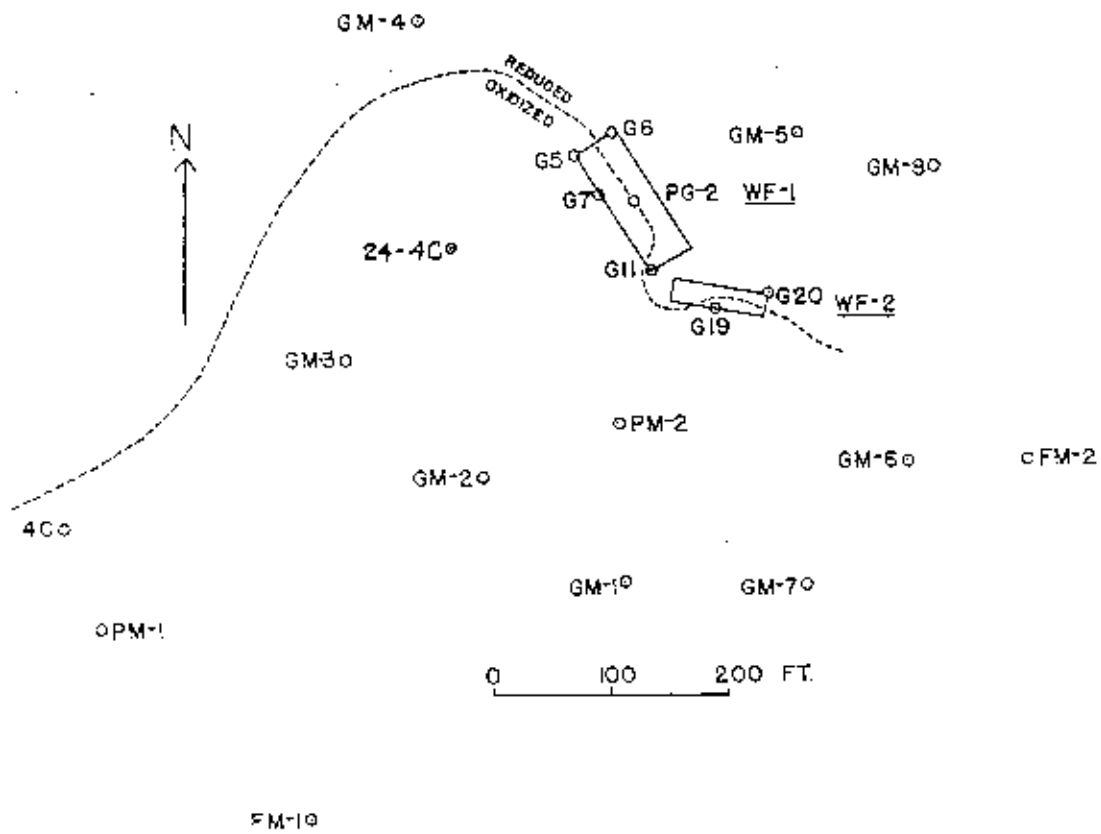
Figure 14. Monitor and leach field sample well locations, Grover
test site, Cheyenne Basin, Colorado. (Sec. 24, T10N,
R62W).

The TDS reduction began on September 8, 1978 and ended on February 28, 1979, when TDS levels dropped below baseline values. Overpumping of the well fields was carried out for six weeks during this process and is reflected on a delayed drawdown in the Grover Monitor wells of up to 17 feet. During the entire mining procedure a net production excess was maintained to help keep leach fluids from migrating outside of the well fields.

The goal of restoration was to reduce TDS to within 10 percent of baseline and return the water quality to all possible uses prior to mining (WMC, 1978a).

C. Water Quality Monitoring

Horizontal migration of leach fluids out from the well fields was monitored by the Grover Monitor Wells (GM, Figure 14). These wells encircled the well fields and were screened in only the Grover Sandstone (Figure 15). Vertical migrations were monitored by the Porter Creek Monitor Wells (PM), which were screened in the sandstone unit overlying the Grover, and by the "Fox Hills" Monitor Wells (FM), which were screened in a sandstone unit underlying the Grover. Weekly analyses of waters from the monitor wells were made by WMC.

Averages of the water quality constituents from the weekly monitor well analyses are presented in Table 4. These are believed to reflect the true character of the groundwaters since no leach excursions were detected. The wells sample water from both sides of the roll front, but not directly from mineralized frontal material.

The waters at the Grover Site are similar to the low TDS waters differentiated in the regional study (Table 2a). The Grover waters are

NORTH ———————————————————————— SOUTH

FT

50 —

PORTER CR. SAND

100 —

150 —

200 — GROVER SAND   ROLL FRONT, MINERALIZED

REDUCED, UNALTERED   OXIDIZED, ALTERED

250 —

300 —

350 —

        0   50   100

                   FT.

400 —

450 —

"FOX HILLS"

500 —
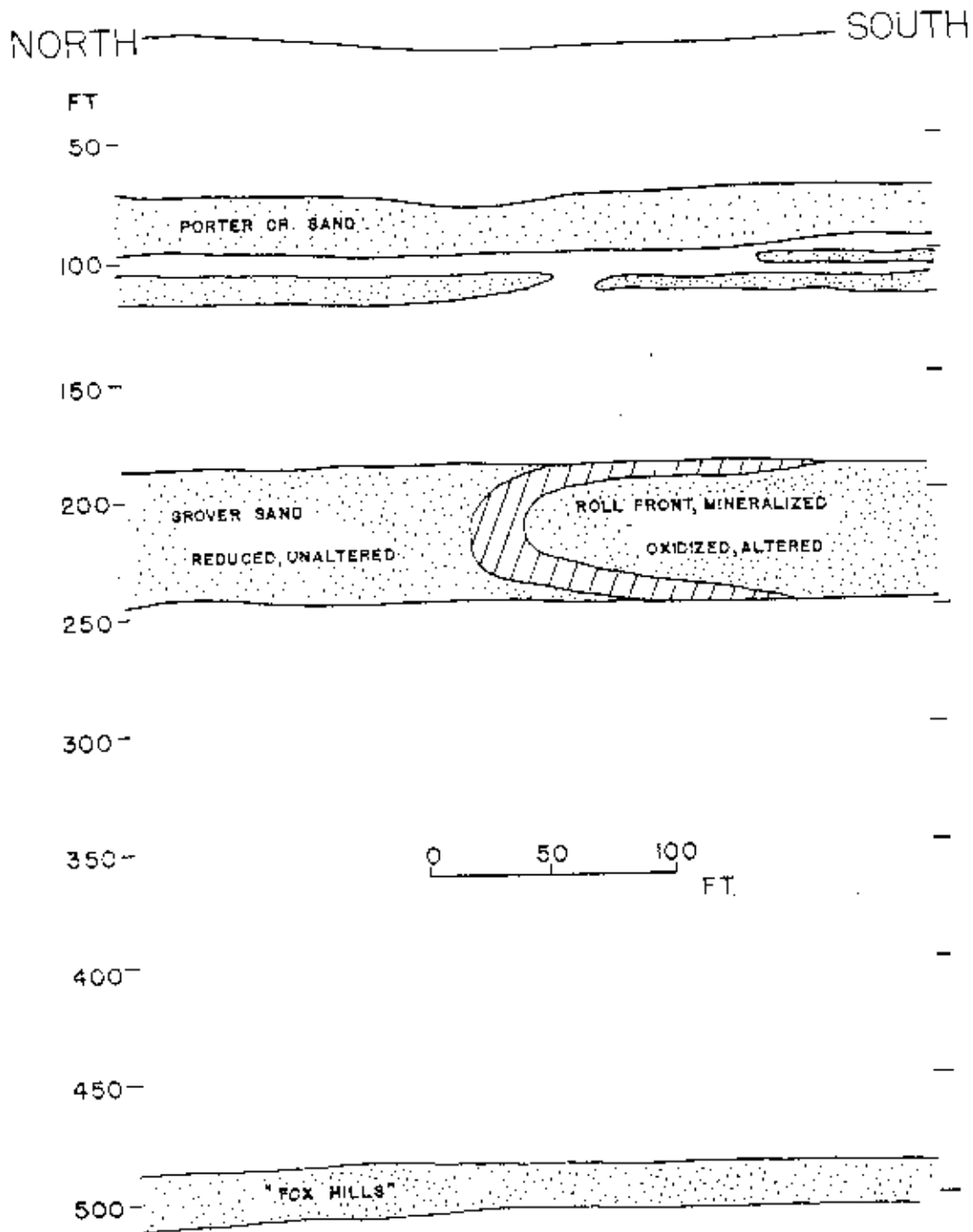
Figure 15. Cross section of Porter Creek, Grover, and "Fox Hills" sands, Grover Test Site, Cheyenne Basin, Colorado.

Table 4. Water quality at the Grover Site from weekly monitor well data. (percents calculated from meq/l)

CONSTITUENT	PORTER CREEK	GROVER	"FOX HILLS"
TDS mg/l	315	390	460
HCO_3 mg/l	156 (30%)	251 (44%)	300 (44%)
Cl mg/l	8 (3%)	7 (2%)	9.5 (2%)
SO_4 mg/l	43 (11%)	40 (8%)	7.0 (1%)
Mg mg/l	10 (10%)	3 (2%)	.4 (.02%)
Ca mg/l	20 (12%)	5.2 (3%)	3.3 (2%)
K+Na mg/l	68 (36%)	80 (42%)	126 (51%)
U mg/l	.02 - .27	.01 - .11	.02 - .05
Type	$NaHCO_3$	$NaHCO_3$	$NaHCO_3$

of the NaHCO$_3$ type though the Porter Creek contains significant amounts of SO$_4^{-2}$, Mg^{+2}, and Ca^{+2}. This makes sense in that the Grover Site is at the northeastern edge of the postulated regional alteration-oxidation front.

There are changes in the water quality of the three units which are seen when comparing water from the different aquifer depths. Mg, SO$_4$, Ca, and U decrease, while TDS, HCO$_3$+CO$_3$ and Na increase from the upper to lower unit (Table 4). Possible explanations for these changes were discussed in the section on regional groundwater hydraulics and quality. The argument for the equilibrium adjustment mechanism is made stronger here because of the decreased likelihood of major facies changes over this section of the Laramie Formation, especially since the chloride percentage remains fairly constant. The higher uranium content in the Porter Creek is understandable since the Porter Creek is a more oxidizing near surface environment in which uranium is more soluble.

WMC compiled baseline water quality data by sampling recovery wells G-1, G-2, and G-3 of WFI during June of 1977. Four samples were taken from each well prior to mining and the results averaged. The baseline data are presented in Table 5, column 4 (WMC, 1979).

Since the baseline water is taken from the most intensely mineralized section of the Grover Sandstone it has distinctive characteristics. These characteristics were found by comparing the water sample constituents with some normal ground and surface water limits suggested by Hem (1970) (Table 6).

The Ra-226 and possibly the lead are decay products of uranium-235. The elevated aluminum value may be due to feldspar destruction. Significant amounts of Cu, V, Se, Fe, Mo, and Pb were also found to be

Table 5. A comparison of studied groundwaters with Colorado and EPA standards.

Constituents	Gruver[1]	Porter Creek[2]	Tux Hills[3]	Well Field 4 (baseline)	Well Field 5 1 and 11 Post-restoration	Colorado Domestic Water	Colorado & EPA Agricultural Std.	EPA Livestock Std.
Radium 226 pc/l	23.6	--	0.85	13.4	130	5	--	5
Gross Alpha pc/l	67.3	--	76	177	1300	--	--	--
Conductance mmho/cm	488	473	672	701	861	--	--	--
TDS (hct)	647		332	295	210	--	2000-6000	3000
Alkalinity mg/l	168	141	215	154.7	66	--	--	--
NH3 N mg/l	3.4	--	0.6	0.25	2.7	0.5	--	--
NO3 N mg/l		--	--	1.4	8.1	10	100	--
Uranium mg/l	0.04	0.13	0.035	0.0086	0.17	5[6]	--	--
Calcium mg/l	5.5	20.4	3.3	9.1	14.3	--	--	--
Magnesium mg/l	1.6	--	0.48	1.1	2.0	--	--	--
Sodium mg/l	81	88.7	126	85.2	55.6	--	--	--
Potassium mg/l	26	--	2.6	4.4	3.70	--	--	--
Bicarbonate mg/l	257	150	300	79	77.5	--	--	--
Carbonate mg/l	22	--	16	4.31	12 (max)	--	--	--
Sulfate mg/l	49.5	44	7.0	38.3	26.3	250	--	--
Chloride mg/l	7.3	8.3	9.4	7.0	14.6	--	--	--
Fluoride mg/l	0.32	--	0.39	0.7	0.32	1.4-2.4	1	2
Silica mg/l	10.8	--	9.0	5.45	7.7	--	--	--
Molybdenum mg/l		--	--	0.02	0.08	--	0.01-0.05	--
Iron mg/l	0.5	--	0.068	0.7	0.5 (max)	0.3	5	--
Selenium mg/l	--	--	--	0.01	0.25 (max)	0.01	0.02	0.05
Vanadium mg/l	--	--	--	0.03	0.03	--	0.1	--
Boron mg/l	10.8	--	0.138	0.3	5.2 (max)	--	0.75	--
Hardness	24.7	63	16	--	--	--	--	--
Sodium Adsorption Ratio (SAR)	7.08	4.19	17.3	7.12	3.84	--	--	--
Ph	7.38	6.04	7.4	8.45	8.2	--	--	--
Gross Beta pc/l				15.23	55.3	--	--	--

1, 2, 3, data averaged from weekly analytical reports filed by WMC with Colorado Dept. of Health

4- from Groundwater Status Report of WMC filed with Colorado Dept. of Health

5-Averages of analyses made by Skyline Labs and CSU for this study

6-proposed by EPA

7-from WMC

Table 6. Comparison of mineralized Grover water with normal
          occurrences.

CONSTITUENT	NORMAL RANGE OR LIMIT	GROVER BASELINE
Al	0.10 (mg/1)	0.538 (mg/1)
Cu	0.0064 (mg/1)	0.020 (mg/1)
Fe	0.0056-.56 (mg/1)	0.70 (mg/1)
Pb	0.004 (mg/1)	0.020 (mg/1)
Mo	0.010 (mg/1)	0.020 (mg/1)
Ni	0.10 (mg/1)	0.20 (mg/1)
Zn	0.10 (mg/1)	0.040 (mg/1)
B	0.2 (mg/1)	0.10 (mg/1)
V	0.10 (mg/1)	0.030 (mg/1)
U	0.0001-.010 (mg/1)	0.086 (mg/1)
Ra-226	1 pc/1	13.4 pc/1

associated with uranium mineralization in the Shirley Basin roll front deposits (Harshman, 1972). High boron values are found in many groundwaters in the region but do not seem to be related to uranium mineralization.

D. Groundwater Hydraulics

The Grover Sandstone is bounded by claystones on top and bottom, producing a confined aquifer with artesian pressure (WMC, 1976). There is a pressure head of about 200 feet or 85 psi on the top of the sandstone unit. According to tests conducted by WMC (1976), the Porter Creek and Grover Sandstones are not hydraulically connected.

As noted in the regional section, the hydraulic gradient of the Grover Site should be around 28 feet per mile to the south-southeast (Reade, 1976). A potentiometric map prepared by WMC (1976) indicates a gradient of about 22 feet per mile to the south. Using the Grover Monitor Well water levels recorded over a one year period, a series of potentiometric maps of the Grover aquifer were prepared for this study. The results indicate a gradient of 26.9 feet per mile southward.

WMC conducted a pump test at well 24-4c, located 140 feet west-southwest of Well Field I (Figure 14) on April 7, 1976 which gave a permeability (hydraulic conductivity) of 1.5 darcy (1,330 ft/year). Core tests indicate permeabilities of 2-8 darcy. The pump tests gave a storage coefficient of about 0.00011. The permeability was found to be anisotropic, with the major axis of transmissivity oriented NW-SE or parallel to the roll front. This may be an artifact of the roll front geometry with the mineralization in some way reducing water movement.

In order to calculate the seepage velocity (the true rate of ground-water movement through the aquifer), the porosity of the sediment must be determined. WMC (1976) reported that Core Laboratories, Inc. found the porosity to average 38 percent among 14 samples. In this study porosity was determined by bulk density and thin section point count measurements. The bulk density study indicated a value of 33 percent (Appendix IV). Thin section study, consisting of three 500 point count samples, gave values of 28, 28, and 30 percent. The thin section study probably gives the best value since the clays and fine grained alteration products in the sediment seem to absorb water, thus giving an inflated value for the void space as determined by the bulk density study.

Using the hydraulic gradient (i) and hydraulic conductivity (K), the darcy velocity (q) is calculated using Darcy's Law:

$$q = Ki$$

Using a K = 1,330 ft/yr and i = 26.9 ft/mile to the south,

$$q = 6.78 \text{ ft/yr to the south}$$

Using a porosity (∅) of 0.30, the seepage velocity (Vs) is calculated as follows:

$$Vs = \frac{q}{\emptyset} = \frac{6.78}{0.30} = 22.6 \text{ ft/yr to the south}$$

Using sieve analysis of the Grover Sandstone (Appendix III) and the Fair-Hatch equation (Fair and Hatch, 1933), another value for the hydraulic conductivity (K) was determined to be 3,760 ft/yr, giving a darcy velocity of 19.15 ft/yr and a seepage velocity (Vs) of 63.8 ft/yr. The same porosity value of 30 percent was used. Appendix XII gives the procedure for this determination. The hydraulic conductivity

as calculated by the Fair-Hatch method is sensitive to changes in porosity. This dependent relationship is plotted on a graph in Appendix XII. The graph shows that in order for the Fair-Hatch equation to predict the same value for K as found by the WMC pump test, the porosity of the Grover Sandstone would have to be 22 percent.

Using the seepage velocities of 22.6 and 63.8 ft/yr it is calculated it would take 7.5 and 2.7 years respectively, for the solutions moving from the leach field under the natural hydraulic gradient to intercept the nearest monitor well, 170 feet to the south. However, natural hydraulic gradients will not exist in the vicinity of the well field during in situ mining and, as a result of steeper gradients, seepage velocities will be greater.

The mining operation had little impact on groundwater quantities since only a small net production excess was maintained. No water table drawdown occurred until a six week overproduction test during restoration produced a 17 foot drawdown in the monitor wells. Since this is a confined aquifer with a total thickness of about 50 feet, a drawdown of this magnitude seems significant. There are no data available to determine if the potential level has recovered.

E. The Effects of Mining and Restoration on Groundwater Quality

The well field monitor wells were sampled prior to initiation of leach operations, begun in June, 1977, and continued until January, 1979. In that time there was no indication of mine fluid excursion. This is not surprising since the nearest downgradient monitor well would not intercept natural groundwater flow from the field for 2.7 to 7.5 years. Net excess production and the overproduction test during

restoration insured that only excursions of large magnitude or migrations along unidentified faults or solution channels could possibly be detected in the short term. Some wells in Well Field I had to be redrilled and cased. There is the possibility that leakage around the casing of the original wells may have resulted in vertical exursions, but since no excursions were detected in the "Fox Hills" or Porter Creek monitors, any such excursion was not large.

WMC tested for leach fluid excursion before restoration by drilling and sampling 4 holes about 20 feet from the well field pattern. No ammonia was detected but elevated values of total carbonate indicate the leach fluids had penetrated to that distance (WMC, 1979). The lack of ammonia migration can best be explained by cation exchange of ammonia with clays in the Grover Sandstone.

Table 7 shows the affect of solution mining on well field waters before any restoration was begun (WMC, 1978b). Before restoration, all major anions and cations increased as well as the leach target, uranium. Increases also occurred in values for barium, chromium, copper, iron, manganese, molybdenum, nickel, selenium, vanadium, ammonia, and radium-226. The pH and fluoride decreased. The changes in ammonia, bicarbonate, and pH were probably caused by direct additions of the chemical leach solution. Increases in the other constituents must be attributed to the mobilizing effects of the leach solutions.

After completion of restoration activity on February, 1979 the well fields were sealed. Water from the well fields was sampled on March 11th and April 30th by WMC and the Colorado Department of Health

Table 7. Effects of Mining on Grouhdwater Before Restoration
          (WMC, 1978).

Constituent (PPM)	WF-1 Baseline (Pre-mining)	Post-Mining Analysis	
		WF-1	WF-2
Calcium	9.1	75.8	190.0
Magnesium	1.1	22.4	32.95
Sodium	85.2	237.5	268.5
Bicarbonate	220.1	1158	1088.5
Sulfate	38.3	311	404.5
Chloride	7.0	75.5	93.0
Nitrate	1.4	5.2	3.0
Fluoride	0.7	0.1	0.1
TDS	295	728	1392
pH	8.45	8.07	7.45
Arsenic	0.01	0.01	0.01
Barium	0.03	0.16	0.15
Cadmium	0.002	0.004	0.006
Chromium	0.003	0.005	0.066
Copper	0.06	0.08	0.036
Iron	0.7	1.25	0.03
Lead	0.02	0.03	0.023
Manganese	0.02	0.16	0.64
Mercury	0.0002	0.000	0.00
Molybdenum	0.02	0.31	0.10
Nickel	0.2	0.52	0.2
Selenium	0.01	8.9	0.095
Silver	0.003	0.002	--
Zinc	0.04	0.08	0.035
Boron	0.10	0.15	0.235
Vanadium	0.03	0.3	1.87
Uranium	0.25	12.48	11.65
Ra226 (pc/l)	13.4	259.8 ± 3.9	1069 ± 9.5
Ammonia	0.086	1248	11.05

Table 8. Radiochemical parameters sampled at Grover Site by CDH and WMC (from WMC, 1979).

WELL #	DATE 1979	GROSS ALPHA, pCi/L		GROSS BETA, pCi/L		Ra-226, pCi/L	U-Nat[a], pCi/L		
		CDH-RCL	WMC	CDH-RCL	WMC	CDH-RCL	CDH-RCL	WMC[b]
PG-2	3-11	579 c 36	347 c 30	99 c 18	27 c 57	NR[d]	340 c 23	356
	4-30	499 c 34	262 c 25	92 c 19	79 c 167	13.0 c 0.6	329 c 13	350
	6-18	454 c 30	348 c 31	247 c 25	63 c 67	14.7 c 0.6	388 c 23	373
G-5	3-11	684 c 30	341 c 29	149 c 21	64 c 57	NR	149 c 10	155
	4-30	808 c 35	740 c 41	204 c 24	138 c 68	NR	219 c 9	241
	6-18	985 c 39	359 c 30	270 c 27	95 c 68	44.6 c 1.0	333 c 22	293
G-6	3-11	164 c 16	533 c 35	28 c 12	70 c 58	NR	79 c 12	121
	4-30	1176 c 43	346 c 29	163 c 23	37 c 66	20.0 c 0.7	187 c 8	201
	6-18	1058 c 41	580 c 38	213 c 38	71 c 68	18.4 c 0.7	246 c 33	241
G-7	3-11	557 c 27	94 c 15	99 c 18	0 c 56	NR	111 c 11	86
	4-30	150 c 15	141 c 18	45 c 13	0 c 65	NR	121 c 5	132
	6-18	192 c 17	156 c 20	78 c 16	19 c 67	4.6 c 0.3	162 c 10	166
G-11	3-11	106 c 17	31 c 11	14 c 10	0 c 56	NR	56 c 7	57
	4-30	61 c 13	11 c 7	19 c 10	51 c 66	2.8 c 0.3	31 c 4	23
	6-18	37 c 10	21 c 10	25 c 11	11 c 67	0.8 c 0.1	24 c 4	23
G-19	3-11	3713 c 66	2352 c 73	358 c 37	109 c 58	NR	49 c 7	52
	4-30	2430 c 57	2099 c 70	249 c 30	134 c 68	NR	56 c 4	57
	6-18	3180 c 67	2268 c 73	265 c 32	123 c 68	20.5 c 0.7	57 c 9	52
G-20	3-11	464 c 23	287 c 25	38 c 14	20 c 56	NR	11 c 1	23
	4-30	1702 c 48	965 c 47	87 c 21	32 c 66	7.0 c 0.4	51 c 5	46
	6-18	1683 c 49	1127 c 51	161 c 25	15 c 67	7.5 c 0.4	65 c 8	40

50

Table 8. Continued

a Calculated from U-chem Values; ppm U_3O_8 × 0.848 = ppm U; ppm U × 667 = U-Nat pCi/L.

b No confidence interval reported with value.

c Confidence interval for value

d Parameter NOT RUN on sample

CDH-RCL = Colorado Department of Health - Radiochemistry Laboratory

WMC   = Wyoming Mineral Corporation

(CDH). On June 18th WMC, CDH, and CSU (this study) collected additional water samples from the well fields. Table 8 shows radiochemical sampling by WMC and CDH for the three dates. There is much variation in radio-activity between wells, dates sampled, and the sampling agency. The large variation between wells is also noted in a more detailed analysis by CSU in Table 9. The spatial variations in water quality may be due to differences in thickness of ore intercepts, grade of mineralization, the degree of metal mobilization produced by the leach solutions, the degree of restoration in the area of each well, or the amount of clay or organics, which may enter into reactions with constituents in the well field water.

The variations in the radiochemical parameters (Table 8) through time often appears erratic, but wells G-5, G-6, and G-20 show a definite increase in alpha and beta activity, as well as uranium concentration, during the three months. This indicates the leach field had not reached equilibrium conditions by June 18th, 1979. These parameters are sig-nificantly higher than the baseline values and the trend indicates they are still increasing in some wells. The radionuclides mobilized by the leach solutions may have been adsorbed by clays or complexed by organic material and their concentration temporarily depressed by the clean water recycling and TDS reduction restoration methods. With the termin-ation of restoration activities these materials may release radioactive products until equilibrium is established. It is also possible that the hydrogen peroxide in the leach solution has left the well field in an oxidizing state in which uranium and other radionuclides are soluble. As new groundwater moves through the field the well field waters will become mixed and swept out by oxygen deficient water. Sulfur-reducing

Table 9. Grover Test Site Well Data of June 18, 1979.

Constituent	MILL-PKZA* 4.06±3.5	M62B NA	GSA 145±6.82	G5B NA	G5A 166±7.35	G6D NA	G7A 6.9(±4).10	G7B NA	G11A 2.02±.585	G11B NA	G14A 37±17.4	G19B NA	G20A 24.3±2.00	G20B NA	Ave. 103
Radium 226 (pc/l)															
Gross Alpha (pc/l)	314	NA	1370.	NA	920.	NA	142	NA	17.3	NA	5620.	NA	1300	NA	1398
Conductivity (mhos/cm)	620/534	620/512	280/250	285/252	300/264	330/269	245/226	260/210	600/543	580/484	190/196	225/193	260/232	260/209	361
TDS (mg/l dry)	360	285	145	185	180	140	165	145	265	220	70	130	55	140	175
pH (standard units)	7.7	7.7	7.2	7.7	8.4	7.8	8.7	0.7	7.2	7.3	6.5	6.5	8.7	7.2	8.2
Alkalinity (total as CaCO3, mg/l)	100	96	52	58	68	66	54	38	135	115	30	30	46	38	66
NH_3-N (mg/l)	7.3	8.0	2.8	2.0	11.0	0.5	1.8	1.5	0.3	0.2	0.4	0.1	1.2	0.1	2.7
NO_3-N (mg/l)	15	17	18	19	6.0	14	1.1	0.5	7.9	6.3	0.2	0.3	0.7	0.2	8.1
Uranium (mg/l)	0.44	0.38	0.32	0.28	.24	0.24	0.12	0.16	0.022	0.018	0.055	0.048	0.065	0.055	0.17
Calcium (mg/l)	12.8	12.2	10.9	13.2	11.3	11.6	15.7	73.6	38.7	34.8	4.54	4.19	10.5	5.7	14.3
Mg (mg/l)	2.50	2.50	1.17	1.33	0.76	0.92	0.36	0.46	8.1	7.8	0.45	0.45	0.1	0.21	2.0
Na (mg/l)	51	90	47	43	51	51	36	37	81	73	43	44	46	45	55.6
K (mg/l)	6.2	5.0	2.1	2.0	2.2	2.8	1.8	1.5	8.7	8.6	1.7	1.4	5.5	2.5	3.78
HCO_3 (mg/l)	120	165	64	70	80	80	52	46	165	145	36	36	30	46	77.5
CO_3 (mg/l)	<2	<2	<2	<2	<2	<2	6.0	<2	<2	<2	<2	<2	12	<2	--
SO_4 (mg/l)	46	28	12	5	8	26	4	8	32	38	40	100	24	20	26.3
Cl (mg/l)	30	28	7	5	8	7	13	7	40	26	6	7	12	9	14.6
F (mg/l)	0.44	0.4	0.25	0.2	0.2	0.2	0.23	0.2	0.3	1.0	0.15	0.12	0.16	0.16	0.32
SiO_2 (mg/l)	9.4	7.3	5.5	4.6	5.6	4.7	3.7	3.7	13	14	9.3	10.0	9.3	8.3	7.7
Mo (mg/l)	0.14	0.12	0.0/	0.064	0.035	0.066	0.038	0.043	0.025	0.032	0.13	0.1	0.21	0.09	0.08
Fe (mg/l)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.5	0.3	<0.1	<0.1	0.1
Se (mg/l)	<.02	<0.02	0.15	0.25	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	--
V (mg/l)	0.033	0.042	0.004	0.044	0.028	0.022	0.008	0.010	0.006	0.030	0.030	0.063	0.025	0.038	.03
TDS (mg/l cal)	342	315	161	161	161	199	136	120	396	354	142	141	152	144	210
Boron (mg/l)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.0	<0.1	<0.1	<0.1	0.15	0.20	--

*A denotes sample taken after two bore volumes pumped *B denotes sample taken after six bore volumes pumped
NA - not analyzed

bacteria feeding on the organic debris may also produce a reducing environment in which the radionuclides and other metals would be fixed by reduction and precipitation. It may even be possible for well field restoration to include a final treatment in which the aquifer could be returned to reducing conditions by the addition of a reductant such as hydrogen bisulfide.

The water collected on June 18, 1979 by CSU was from seven leach field wells sampled after two and six well bore volumes had been pumped (Table 9). These are denoted by the letters A and B, respectively. It was thought that near well affects might be observed by sampling water after different volumes were pumped. Little difference was observed but the precision of the analyses was found to be good. The radium-226 and gross alpha samples were unfiltered and all others were filtered. Two conductivities for each sample are shown on the table. The upper number represents measurements made in the field at the time of sampling while the lower one was measured in the laboratory. Skyline Labs, Wheatridge, Colorado, did all analyses except the radium-226 and gross alpha which were done by the Department of Radiology and Radiation Biology, Colorado State University. Both radium-226 and gross alpha measured at CSU showed values higher than those analyzed by WMC and CDH. The lower values are a result of their samples being filtered and a 1 to 14 day waiting period before the gross alpha determinations were made.

Table 10 shows a comparison of the alpha activities calculated to be produced by the uranium with the gross alpha activity actually measured. A 677 pc/l was used as the alpha activity for 1 mg/l of uranium.

Table 10. Calculated uranium alpha activities.

WELL	U (mg/1)	Alpha Activity Calculated for U* (pc/1)	Measured (pc/1)
PG2A	0.44	298	344
G5A	0.32	216	1370
G6A	0.24	162	920
G7A	0.12	81	142
G11A	0.022	15	17.3
G19A	0.055	37	5620
G20A	0.065	44	1300
AVERAGE	0.17	115	1341

* 677 pc/1 was used as the alpha activity
for 1 mg/1 of uranium.

The uranium alpha activity accounts for only a small amount of the gross alpha activity. WMC feels this is due to analytical problems, but since WMC, CDH, and CSU all reported this association it seems more likely the unaccounted alpha activity may be due to unidentified daughter products of the uranium-235/lead decay series. Some expensive analytical work is needed to identify these products. Alpha radiation from the radium-226 is much too small to account for the excess alpha activity.

Total dissolved solids (TDS) were measured in the lab and a comparison was made with the calculated wet TDS, which was adjusted to dried weight. The wet adjusted TDS average was 171 mg/l which compares closely with the actual dry average of 175 mg/l. However, the balance of major cations with anions shows a consistent cation excess or anion deficiency (Table 11).

The mining restoration did not affect the character of the groundwater as far as major ions were concerned. This can be seen in Figure 16 where graphs of ion concentration compare preleach versus post-restoration waters. The shapes of the diagrams characterize the constituents while their size is proportional to the total ionic content or relative amounts of TDS. It can be seen that the TDS of the post-restoration waters has been reduced. Wells PG-2 and G11 (Table 9) show elevated values of TDS, chloride, and/or calcium. This may be a result of incomplete TDS restoration after the $CaCl_2$ treatment.

The levels of radium-226 make the Grover Monitor Well waters unsuitable for domestic or livestock use (Table 5) (Colorado Department of Health, 1979). Because of limited data, the possible uses of the

Table 11. Cation-anion balance for CSU Grover analysis

|		PG2A	PG2B	G5A	G5B	G6A	G6B	G7A	G7B	G11A	G11B	G19A	G19B	G20A	G20B
Cations	Ca^{+2}	.64	.6J	.54	.66	.56	.58	.78	.68	1.93	1.74	.23	.21	.52	.29
	Mg^{+2}	.22	.21	.10	.11	.06	.08	.03	.04	.67	.64	.04	.04	.008	.02
	Na^+	3.96	3.91	2.04	1.87	2.22	2.22	1.57	1.61	3.52	3.17	1.87	1.91	2.00	1.96
	K^+	.16	.15	.05	.06	.06	.07	.05	.04	.22	.22	.04	.04	.14	.06
	Total	4.98	4.88	2.73	2.69	2.91	2.95	2.43	2.37	6.34	5.77	2.18	2.26	2.67	2.32
Anions	HCO_3^-	1.97	1.89	1.05	1.15	1.31	1.31	.85	.75	2.70	2.38	.59	.59	.49	.75
	CO_3^{-2}	–	–	–	–	–	–	.20	–	–	–	–	–	.80	–
	SO_4^{-2}	.96	.58	.25	–	–	.54	.08	.17	.67	.79	.83	.77	.50	.42
	Cl^{-1}	.85	.79	.20	.14	.23	.20	.37	.20	1.13	.73	.17	.20	.34	.25
	Total	3.78	3.26	1.50	1.26	1.54	1.95	1.50	1.12	4.50	3.90	1.59	1.56	2.13	1.42
	Balance	1.20	1.62	1.23	1.43	1.37	1.60	-.93	1.25	1.84	1.87	.59	.61	.54	.90

37
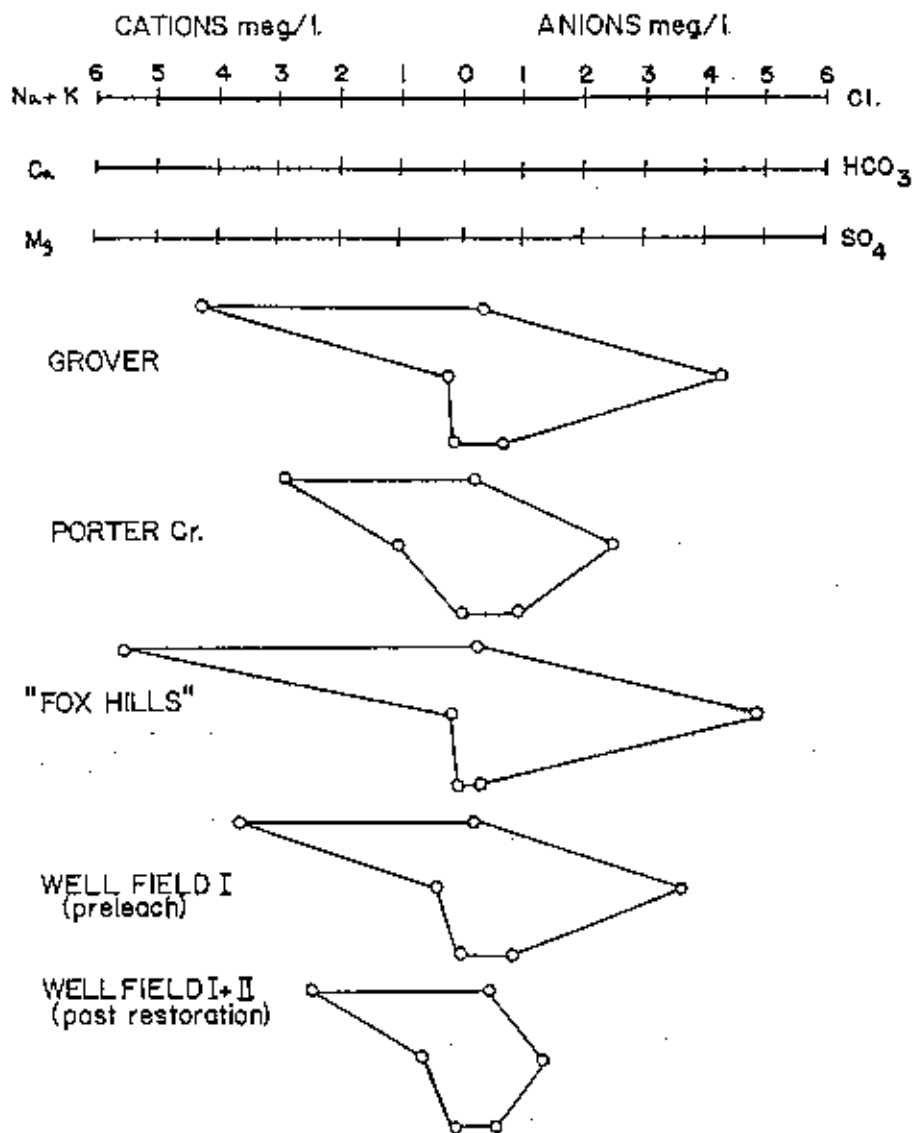
Figure 16. Waters typed by major ions, Grover test site, Cheyenne Basin, Colorado.

Porter Creek water cannot be ascertained. The "Fox Hills" has a radium 226 acceptable for domestic use but the ammonia value of 0.6 ml/g is greater than the allowable standard of 0.5 mg/l. Its sodium adsorption ratio (SAR) of 17.3 is large enough to restrict its use in some irrigation applications.

The goal of restoration was to reduce the total dissolved solids (TDS) to within 10 percent of baseline and return the water quality to all possible uses the water could be put to prior to mining (WMC, 1978a). In order to establish a baseline of water quality the three production wells of Well Field I were sampled before mining was initiated (see column 4 of Table 5). This baseline indicates the values of iron (0.7 mg/l) and radium-226 (13.4 pc/l) preclude the use of these waters for domestic use. The selenium (0.01 mg/l) is at the limit set for domestic use. The low TDS and SAR make the water suitable for irrigation, but the molybdenum content (0.02 mg/l) limits its use in certain irrigation applications. The radium-226 (13.4 pc/l) precludes its use for livestock. In conclusion, it is seen that natural waters drawn from the mineralized sands are suitable only for restricted agricultural use.

Post-restoration analysis indicates that WMC has achieved its goal of returning the aquifer waters to within 10 percent of baseline TDS. There is the possibility that the increases in selenium may further reduce its limited agricultural suitability. The water quality was degraded quantitatively by increases in levels of radionuclides, ammonia, nitrate, calcium, chloride, molybdenum, selenium, and boron, but, since the water in its natural state is of poor quality, further

degradation of its suitability for use does not occur. Of special concern though, is the large increase in radionuclide activity. There is a 10 fold increase in gross alpha, 8 fold increase in radium-226, 3 fold increase in gross beta, and the concentrations appear to be increasing in some of the wells during the 3 months following restoration. The Environmental Protection Agency is presently formulating standards for gross alpha and beta but this is difficult since no minimum threshold tolerance level for radiation exposure is known. Therefore, the standard will have to be chosen in a somewhat arbitrary fashion.

IV. CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

Waters from the Grover roll front uranium deposit are suitable
for only restricted agricultural use because of the elevated values
of radium-226, molybdenum, selenium, and iron. Restoration after in
situ mining can restore groundwater to baseline total dissolved
solids (TDS) but leaves levels of radionuclides, molybdenum, ammonia,
nitrate, and selenium elevated above premining levels. Of special
concern are the high gross alpha and beta activities for which there
are no government standards for toxic levels. Little groundwater was
consumed during the leaching, but overproduction during restoration
resulted in a significant drawdown of the potentiometric surface.

Roll front systems may be reflected in the regional groundwater
quality by the alteration of pyritic, lithic sediments as oxidizing
groundwaters create areas of increasing TDS updip from the roll
front deposits. This information may be useful in groundwater use
planning and possibly as a uranium exploration tool.

B. Recommendations

1) Wells for monitoring vertical excursions should be placed
within 20 feet of the leach field in order for vertical excursions
due to well inadequacy to be detected expeditiously.

2) Some wells for monitoring horizontal excursions should be
located down gradient such that natural groundwater flow would in-
tercept them in 2 years.

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3) Baseline water quality data should be collected from a sufficient number of leach field wells to insure a representative sample is obtained. The number required will be determined by the size of the well field, variability of water quality within the field, and sampling costs. Averaging of data should not be used alone as large variations in well response to mining and restoration makes examination of individual well response necessary.

4) A check of water table or potentiometric levels before and during the mining process should be made. Observed drawdowns should be monitored afterward to observe rebound.

5) State limits for molybdenum, gross alpha and gross beta should be established.

6) Further research should be untertaken to identify the sources of alpha and beta radiation in restored groundwater.

7) Maps of mineralized roll front areas should be made available to the Colorado Department of Health and State Engineer for groundwater use planning. This information could be provided by mineral companies as soon as roll front positions become common knowledge in industry or when mining rights in an exploration play are assured. In this way domestic or irrigation well completions in mineralized areas could be avoided.

8) Regional maps of groundwater quality in uranium mineralized areas could be prepared and used for exploration as well as groundwater use planning.

9) The possibility of using a reductant such as hydrogen bisulfide to precipitate and stabilize radionuclides and other metals mobilized by the leach fluids should be studied.

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APPENDIX I

Magnetic Susceptibility of Grover Core Samples

A Bison Magnetic Susceptibility Meter, Model 3101A, was used to measure magnetic contents of 13 samples of disaggregated Grover Sandstone. All samples indicated less than 0.05 percent Fe_3O_4 equivalent and no significant difference was found in the magnetite contents of oxidized, frontal, or reduced ground.

CALIBRATION

Fe_3O_4 Standards	Meter Reading (cgs.)
0%	0
0.5%	55.6
1.0%	108.4
2.0%	210.5

Samples	Reading (cgs)	Fe_3O_4 Equivalent
PG2R-221 (reduced)	2.4	0.020
PG2R-215 (reduced)	3.5	0.032
PG2R-226 (reduced)	3.8	0.035
PG1R-221 (reduced)	3.4	0.031
PG1R-226 (reduced)	5.6	0.052
24G1c-233 (front)	5.1	0.047
24G1c-222 (front)	5.1	0.047
24G2c-223 (front)	4.5	0.042
24G2c-235 (front)	5.7	0.053
G24-210 (oxidized)	3.4	0.031
G24-230 (oxidized)	4.1	0.038
G24-239 (oxidized)	3.6	0.033

APPENDIX II

Clay X-ray Sample Preparation

Twelve Grover Sandstone samples were disaggregated by lightly grinding the dry sample with a pestle. Sample sizes varied from 180 to 550 g. After sieving, the -325 mesh fraction was retained. These fractions varied from 5.3 to 24.3 g.

The -325 fraction was then placed in 500 ml beakers with distilled water with Calgon added as a dispersant. The Calgon concentration was 0.5 weight percent. Rubey's settling velocity for very fine silt was found to be 60 microns/sec (Krambein and Pettijohn, 1938). Since the beaker was filled with 88.9 mm of solution it would take 24.44 minutes for all the silts to settle out. The calculations are as follows.

1) $mm/sec = (60 \frac{micron}{sec}) (\frac{1mm}{10^3 \, micron}) = 0.06 \, mm/sec = $ settling rate

2) total time for settline through 88.9 mm of solution =

$minutes = (88.9 \, mm) (\frac{1 \, sec}{0.06 \, mm}) (\frac{1 \, min}{60 \, sec}) = 24.44$ minutes

After settling, the solution containing the clay fraction was decanted and the settling process was repeated. The clay fraction left in solution was checked optically, and clay separation was confirmed. The clay solutions were allowed to settle for two days and then the remaining colloid fraction decanted, leaving the clay fraction. After drying each clay sample was made into three x-ray mounts and analyzed by x-ray equipment in the Department of Earth Resources.

Results of Grover clay x-ray analysis.

		G24-223 (oxidized)	G24-210 (oxidized)	G24-230 (oxidized)	24G1c-222 (front)	24G1c-233 (front)	24G2c-223 (front)	4G2c-235 (front)	PG1R-226 (reduced)	PG1R-221 (reduced)	PG2R-226 (reduced)	PG2R-221 (reduced)	PG2R-215
Kaolinite	high	x	x	x	x	x	x	x	x	x	x	x	x
	med												
	low												
Sericite	high	x	x	x			x	x	x	x	x	x	x
	med												
	low				x	x							
Regular illite – montmorillonite CEC	high	x	x	x	x	x*	x	x	x			x	x
	med	7	21		5.3	4.5	6.5	5.4		x	x		10
	low												
Montmorillonite	high	x	x	x	x	x		x	x	x	x	x	x
	med			x			x						
	low												
Illite	high	x	x	x		x	x	x	x	x	x	x	x
	med						x						
	low												

Results of Grover clay x-ray analysis (continued).

		G24-223 (oxidized)	G24-210 (oxidized)	G24-230 (oxidized)	246IC-222 (front)	246IC-233 (front)	246C-223 (front)	246C-235 (front)	P61R-226 (reduced)	P61R-221 (reduced)	P62R-226 (reduced)	P62R-221 (reduced)	P62R-215
Chlorite	high				×	×							
	med	×	×	×			×	×	×	×	×	×	×
	low												
Nacrite	high												
	med	×	×	×	o	×	×	o	×	×	×	×	×
	low												
Halloysite	high												
	med	×	×	o	×	×	×	×	×	×	×	×	×
	low												

o = not present

APPENDIX III

Sieve Fractions for 13 Grover Sandstone Samples

Appendix III. Sieve fractions for 13 Grover Sandstone samples.

Grain Size ∅ (mm)	PG2R 221'	24G1c 222'	24G1c 233'	2462c 235'	2462c 233'	G24 230'	G24 223'	PG2R 226'	PG2R 215'	PG7R 226'	G24 210'	G24 239'	PG7R 221'	x̄ Samples	% x̄	Cumulative % of x̄
.5 (.71)	-	-	-	3.0	-	1.2	1.2	1.2	3.1	1.2	1.3	-	0.6	12.8	0.3	0.3
1.0 (.50)	-	0.3	0.3	3.0	0.7	1.5	1.4	1.7	2.4	1.5	4.8	-	0.5	18.1	0.4	0.7
1.5 (.35)	0.2*	0.6	0.4	1.3	1.1	0.8	0.8	2.7	1.4	1.8	2.6	1.5	0.6	16.0	0.3	1.0
2.0 (.25)	5.8	10.0	4.0	14.2	13.6	6.4	8.6	17.1	14.5	13.5	12.6	5.8	7.7	133.8	2.6	3.6
2.5 (.177)	30.2	93.0	10.2	51.0	131.4	28.0	37.6	120.0	150.3	110.0	115.8	8.5	72.1	950.1	18.9	22.5
3.0 (.125)	103.4	185.0	176.4	276.8	241.3	209.3	153.2	242.9	220.5	295.0	189.3	91.9	203.5	2588.5	51.1	73.6
3.5 (.088)	32.0	39.0	84.1	92.4	38.7	105.2	67.7	54.4	32.1	85.8	27.5	200.9	41.3	901.1	17.8	91.4
4.0 (.0625)	3.7	4.7	10.0	19.2	4.3	18.6	13.0	9.3	5.5	10.6	10.0	33.0	6.3	148.2	2.9	94.3
4.5 (.044)	2.3	3.3	4.7	13.8	3.5	9.6	6.4	7.6	6.0	10.0	10.7	12.0	5.3	83.2	1.6	95.9
<4.5 (.044)	5.3	9.6	9.1	24.3	10.6	19.6	13.7	17.9	16.7	22.5	22.7	18.8	13.8	204.6	4.0	99.9
Total Weight	182.9	345.5	299.2	499.0	445.2	400.0	299.6	474.8	453.5	551.9	397.3	372.5	351.7	5064.2		

*All weights in grams.

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Appendix III. Grain size distribution of the Grover Sandstone from a composite of 13 samples.
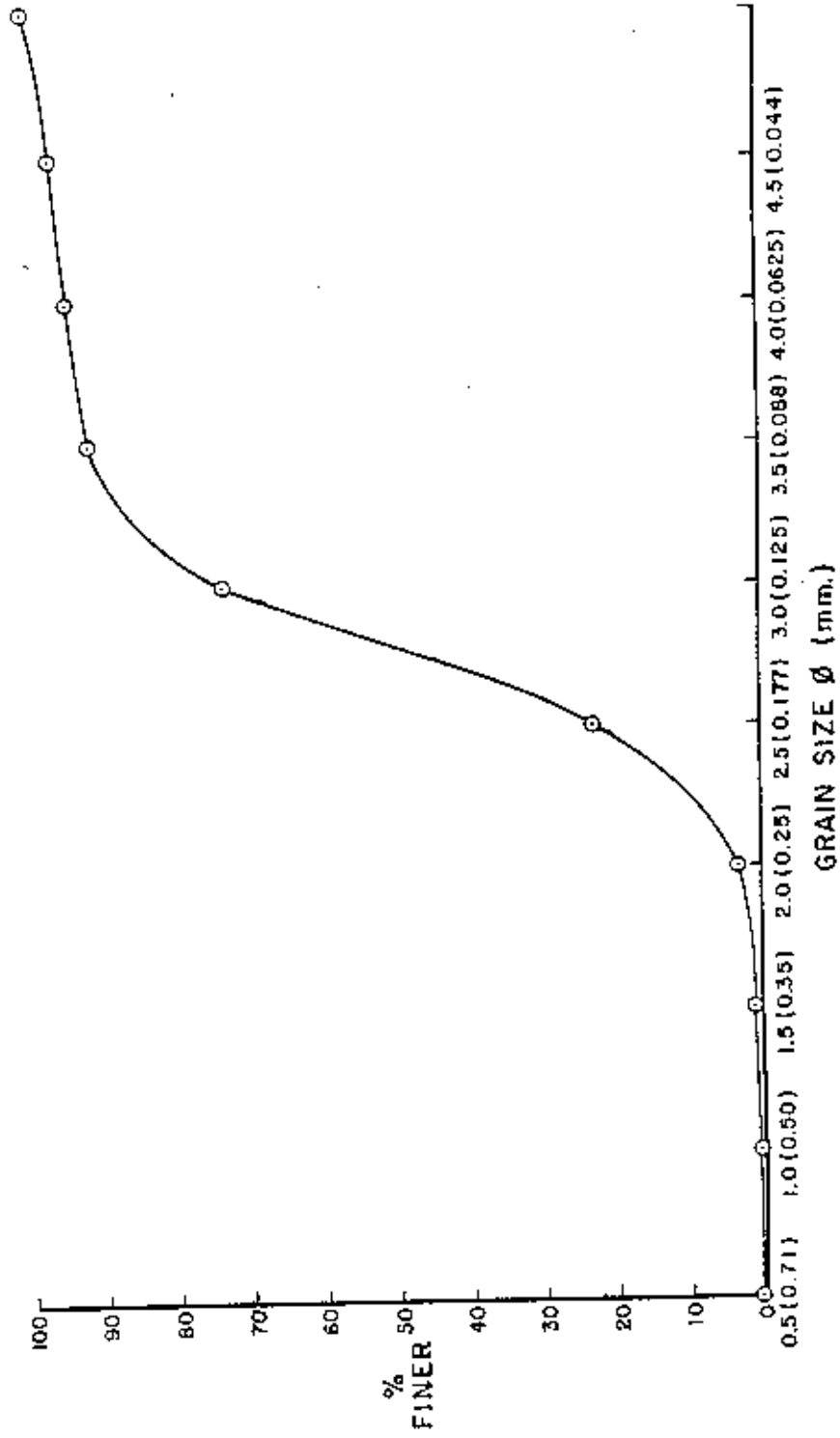
<u>MEDIAN</u> $(\phi 50) = 2.80 \; (\approx .15 \text{ mm}) = $ fine sand (Wentworth) size class

<u>MEAN</u>

(Dx)

$$\frac{\phi 90 + \phi 80 + \phi 70 + \phi 60 + \phi 50 + \phi 40 + \phi 30 + \phi 20 + \phi 10}{9}$$

$$\frac{3.38 + 3.10 + 2.95 + 2.90 + 2.80 + 2.70 + 2.60 + 2.47 + 2.25}{9}$$

$$= \phi 2.79 \; (\; .15 \text{ mm})$$

<u>SORTING</u>

(So)

$$\frac{\phi 90 + \phi 80 + \phi 70 - \phi 30 - \phi 20 - \phi 10}{5.3}$$

$$\frac{3.38 + 3.1 + 2.95 - 2.60 - 2.45 - 2.25}{5.3}$$

$$= .40 \; = \text{well sorted}$$

(well sorted according to Briggs (1977) ranges
from .35 - .50)

SKEWNESS $= \dfrac{\phi 84 - \phi 50}{\phi 84 \quad \phi 16} - \dfrac{\phi 50 - \phi 10}{\phi 90 \quad \phi 10}$ $= -.01 \; = $ symetrical

(Sk)

$$\frac{3.18 - 2.80}{3.18 - 2.38} - \frac{2.80 - 2.25}{3.38 \quad 2.25}$$

KURTOSIS $= \dfrac{\phi 90 - \phi 10}{1.9(\phi 75 - \phi 25)}$ $= 1.19 = $ leptokurtic

(Kg)

$$\frac{3.38 - 2.25}{1.9(3.05 - 2.55)}$$

APPENDIX IV

BULK DENSITY MEASUREMENTS OF GROVER SANDSTONES

DRILL HOLE	HEIGHT* (inches)	MASS (g)	BULK VOLUME (cm^3)	VOLUME OF ROCK (cm^3)	POROSITY (ϕ)	DENSITY OF SOLIDS
PG2R	1.8	303.5	181.6	118	35	2.57
PG2R	3.2	517	322.8	210	35	2.46
24G1c	1.9	315	191.7	123	36	2.56
24G1c	2.3	426	232.0	168	28	2.58
24G1c	1.75	315	176.7	112	37	2.58
G24	3.0	433	302.7	205	32	2.50
G24	2.35	289	237.1	165	30	2.58

* radii ~ 1.4 inches   Averages: 33.3%   2.55

1) Bulk volume of sample found using height (h) and radius (r) of core.

$$Bulk\ Volume = \pi r^2 h$$

2) Rock volume found by submersing core in water and measuring cm^3 of water displaced.

3) Calculate porosity (ϕ) as follows:

$$\phi = \frac{bulk\ volume - volume\ of\ rock}{bulk\ volume}$$

4) Density of solid material found as follows:

$$density\ (d) = \frac{mass\ (g)}{volume\ of\ rock\ (cm^3)}$$

RESULTS: Mean of porosity ϕ value = 33.3%
and mean density = 2.55 g/cm^3

Appendix Y. Semiquantitative 6-step spectrographic analysis of Grover Sandstone samples (analyzed by U.S. Geological Survey).

Sample / Element	G24-212	G24-223	average of oxidized samples	2461c-217	2461c-222	2461c-233	2462c-223	2462c-235	average of frontal samples	PG2R-215	PG2R-220	average of reduced samples
Fe %	0.7	1.0	0.85	5	0.7	1	1.5	1.5	1.94	1.0	5	3.0
Mg %	0.1	0.2	0.15	0.2	0.2	0.15	0.3	0.2	.20	0.3	0.15	0.23
Ca %	0.3	0.2	0.25	0.5	0.15	0.15	0.2	0.2	0.24	0.2	0.3	0.25
Ti %	0.15	0.15	0.15	0.2	0.15	0.2	0.2	0.2	0.19	0.15	0.2	0.18
Mn (ppm)	100	70	65	200	70	70	70	100	102	70	300	185
B (ppm)	20	20	20	20	L	20	20	20	~20	L	20	L to 20
Ba (ppm)	500	1000	750	300	1000	700	1000	1000	800	1000	500	750
Be (ppm)	1.5	N	-	1.5	N	N	N	N	-	N	L	-
Co (ppm)	7	5.0	6	L50?	L	L	L	L	L	L	L50?	1 to L50
Cr (ppm)	50	15	32.5	50	15	15	20	20	24	15	20	17.5
Cu (ppm)	10	5.0	7.5	15	5	5	7	30	12.4	5	15	10
La (ppm)	N	N	N	50	N	N	N	N	-	N	50	N to 50
Mo (ppm)	N	N	N	L	L	N	L	N	N	N	N	N
Nb (ppm)	N	N	N	L	L	L	L	L	L	L	7	L to N
Hf (ppm)	5	5	N	7	5	5	5	5	L	5	30	6
Pb (ppm)	N	15	5	50	20	20	20	10	~20	15	5	22.5
Sc (ppm)	L	L	L	10	L	L	L	L	~L	150	100	L to 5
Sr (ppm)	100	150	125	150	100	70	150	150	124	30	1500	125
V (ppm)	700	160	430	1000	300	30	700	300	412	15	150	765
Y (ppm)	15	15	15	20	20	20	15	15	18	70	200	82.5
Zr (ppm)	150	200	175	100	100	700	150	500	310	?	3	135
Al %	2.0	7	4.5	3.0	5	5	7	7	5.4	0.7	0.3	5.0
Na %	0.7	0.7	0.7	0.5	0.7	0.5	0.7	0.7	0.62	3	1.5	0.5
K %	3	3	3	2.0	3	2	3	3	2.6	10	7	2.25
Ga (ppm)	7	7	7	15	10	5	3	7	9.4	1	15	8.5
Yb (ppm)	2	2	2	10	1.5	3	.3	2	3.9	N	7000	6
U (ppm)	N	N	N	7000	N	~100	N	~100	0 to 7000	N	200	N to 7000
Gamma (cps)/100g	~100	~100	~100	300	150	~100	150	100 to 300	100 to 300	100	150	150
CEC (meq/100g)	21	7.0	14	12	5.3	4.5	6.5	5.4	6.74	10.0	4.4	7.2
Notes:	contains bedded organics	clean sand		asphaltic	clean sand with thin organic layer	clean sand	clean sand with plant fragments			clean sand with plant fragments	thick organic layers	

[1] CEC - Cation Exchange Capacity in milliequivalents/100g
N - below limit of detection
L - detected, but below level of determination or value shown

[2] High uranium values mask Co

APPENDIX XI

CATION EXCHANGE CAPACITY (CEC) OF THE GROVER SANDSTONE

SAMPLE	CEC (meg/100g)
G24-212	21.0
G24-223	7.0
24G1c-217	12.0
24G1c-222	5.3
24G1c-233	4.5
24G2c-223	6.5
24G2c-235	5.4
PG2R-215	10.0
PG2R-220	4.4
average	8.5

The CEC for the dominant clays found in the Grover Sandstone are listed below (Carroll, 1959):

Clay	CEC(meg/1)
Kaolinite	3-15
Illite	10-40
allophane	≈ 70
montmorillonite	70-100

Since clay minerals constitute about 20% of the Gover Sandstone and the sandstone averages 8.5 meg/100g for CEC, the effective CEC for the clays must be 42.5 meg/1. This indicates there is a significant amount of clay with high CEC because kaolinite, a clay with low CEC, makes up a large portion of the clay fraction. The thin section and X-ray analysis indicates the high CEC clays present are mixed lattice illite-montmorillonite and allophane with lesser amounts of montmorillonite.

The exchange capacity of the sandstone explains the need for chemical treatment with $CaCl_2$ during restoration to replace the adsorbed ammonium ion.

APPENDIX XII

COMPUTING PERMEABILITY OF GROVER SANDSTONE UISNG THE FAIR-HATCH EQUATION

AND A COMPOSITE OF 13 SIEVE ANALYSES

The Fair-Hatch equation (Fair and Hatch, 1933) determines the permeability of a sediment using the measured values of grain size distribution, porsosity, and estimates for packing and roundness coefficients for the particular sediment. Fluid flow is assumed to be laminar.

$$k = m \frac{1}{\left[\frac{(1-\phi)^2}{\phi^3} \left(\frac{SF}{100} \sum \frac{P}{dm} \right)^2 \right]}$$

m = packing factor (near 5 for most sands)

ϕ = Porosity

SF = shape factor, 6 (spheres) to 7.7 (angular)

p = % of grains between d_1 and d_2

k = intrinsic permeability

dm = $\sqrt{d_1 d_2}$; d_1 and d_2 = grain size limits in mm.

Utilizing a composite of 13 Grover Sandstone sieve analyses a cumulative grain size distribution was calculated and curve plotted. Using this data the following calculations were made:

% (p)	d_1 (mm)	d_2 (mm)	dm = $\sqrt{d_1 d_2}$	P/dm
0.4	0.71	0.50	0.596	0.67
0.3	0.50	0.35	0.418	0.72
2.6	0.35	0.25	0.296	8.78
18.9	0.25	0.177	0.210	90.00
51.1	0.177	0.125	0.149	342.95
17.8	0.125	0.088	0.105	169.52
2.9	0.088	0.0625	0.074	39.19
1.6	0.0625	0.044	0.052	30.77

$\sum$ = 682.60

Using m = 5, = .30, SF = 7.2, $\frac{P}{dm}$ = 682.60 the equation can be completed as follows:

$$k = \cfrac{1}{5 \left[\frac{(1-.30)^2}{(.30)^2} \left(\frac{7.2}{100} (682.6) \right)^2 \right]}$$

$$k = 4.56 \times 10^{-6} \text{ mm}^2 = 4.56 \times 10^{-8} \text{ cm}^2$$

Finding hydraulic conductivity (K) from intrinsic permeability (k).

$$K = \frac{k\gamma}{\mu} \qquad\qquad \gamma = \text{density } (980 \text{ dyne/cm}^3)$$

$$\mu = \text{viscosity } (1.23 \times 10^{-2} \text{ dyne-sec}^{-2} \text{ at } 54^{\circ}F)$$

$$K = \frac{(4.56 \times 10^{-8} \text{ cm}^2) (980 \text{ dyne-cm}^3)}{1.23 \times 10^{-2} \text{ dyne-sec}^{-2}}$$

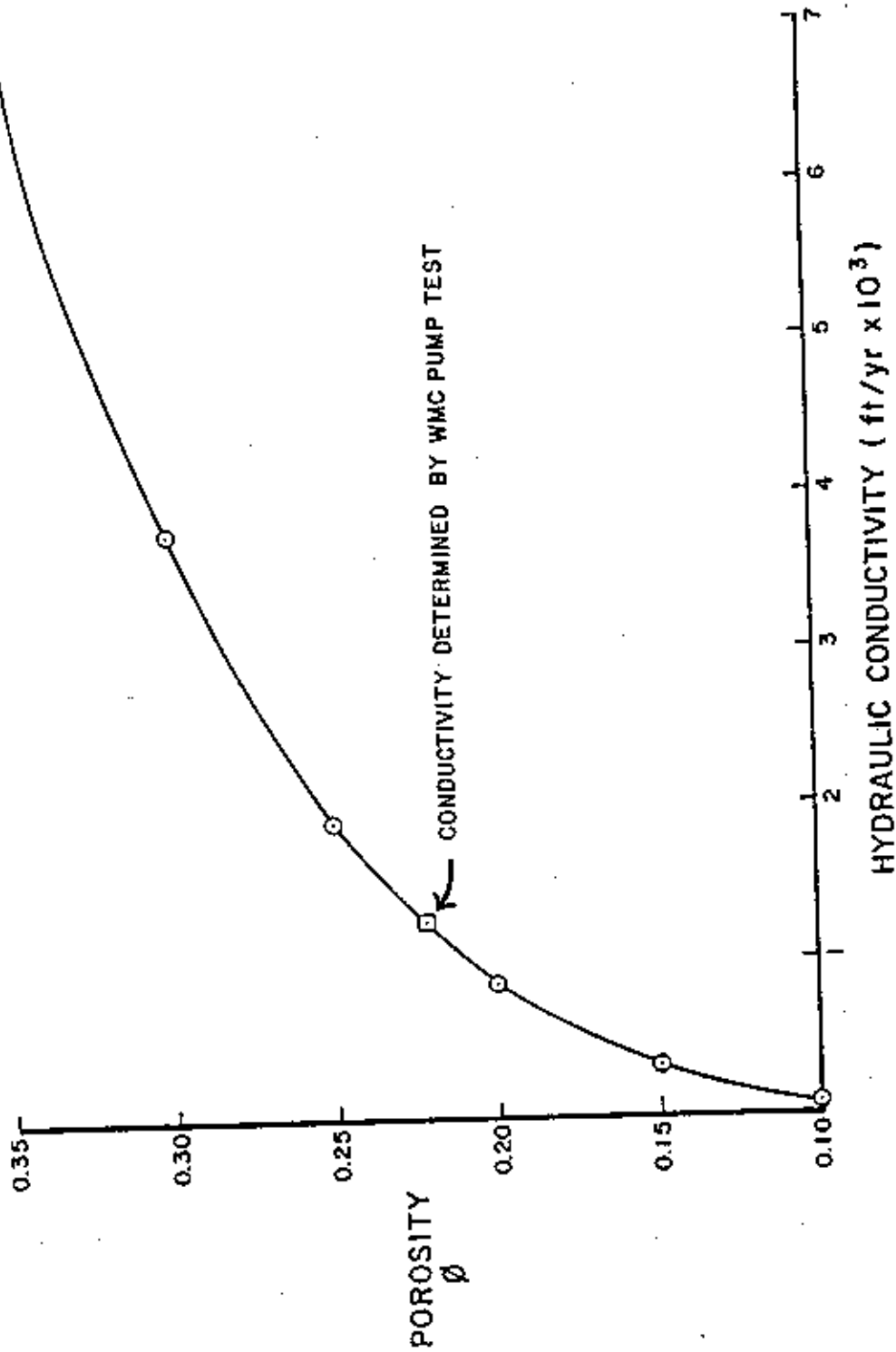$$K = 3.63 \times 10^{-3} \text{ cm/sec} = 3.76 \times 10^3 \text{ ft/yr}$$

Using the hydraulic condictivity (k) and hydraulic gradient (i) the Darcy flow velocity (q) is found. The gradient was determined using potentiometric maps constructed at the Grover Test site.

$$q = Ki$$
$$= (3.76 \times 10^3 \text{ ft/yr}) (26.9 \text{ ft/}5280 \text{ ft})$$
$$= 19.15 \text{ ft/year}$$

The seepage velocity (V_s) is calculated using the Darcy velocity (q) and porosity ($\emptyset$):

$$V_s = \frac{q}{\emptyset}$$

$$V_s = \frac{19.15}{0.30} = 63.8 \text{ ft/yr}$$

Appendix XII. Hydraulic conductivity predicted by the Fair-Hatch equation for the Grover Sandstone as porosity($\emptyset$) is varied.