EVALUATION OF THE HYDROGEOCHEMISTRY OF THE YAK TUNNEL LEADVILLE, COLORADO THROUGH THE USE OF THE GEOCHEMICAL COMPUTER PROGRAM, MINTEQ

By

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ABSTRACT

Site investigations conducted by EPA (1987a) indicate that approximately 80 percent of the cadmium and zinc in California Gulch, which flows into the Arkansas River, is from the Yak Tunnel. California Gulch is a tributary of the Arkansas River. The quality of the Yak Tunnel discharge is primarily influenced by the oxidation of sulfide minerals, mainly pyrite, within unsaturated bedrock drained by the tunnel. The Yak Tunnel discharge is characterized by low pH and high concentrations of heavy metals.

The hydrogeochemistry of the Yak Tunnel system was evaluated through the use of the geochemical, equilibrium program, MINTEQ. The model was used to predict resultant changes caused by plugging selective portions of the Yak Tunnel.

Results fo this study indicate that selective plugging of the upper portion of the Yak Tunnel will significantly enhance the water quality of the Yak Tunnel effluent due to the reduction of metal loadings. he speciation of the chemical constituants, however, will not change substantially. Results also provided excellent insight into the mobility of iron in the system. Because of the assumption that equilibrium is attained, the model overestimated the precipitation capability of cadmium.

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Chapter 1

BACKGROUND

Introduction

The Yak Tunnel is a 4-1/2 mile drainage system that intercepts groundwater flow from numerous mines in upper California Gulch and Upper Evans Gulch. The tunnel is located on the California Gulch Superfund site near Leadville, Colorado. The California Gulch site was listed on the National Priorities List (NPL) of uncontrolled hazardous waste sites in September 1983 on the basis of previous studies of the area, indicating significant heavy metals contamination in the California Gulch surface water. It is currently ranked 75th of the 703 sites on the NPL List. The site is located in the Leadville Mining District near Leadville, Colorado approximately 100 miles southwest of Denver (See Figure 1.1). The Yak Tunnel's portal is located about a mile southeast of Leadville.

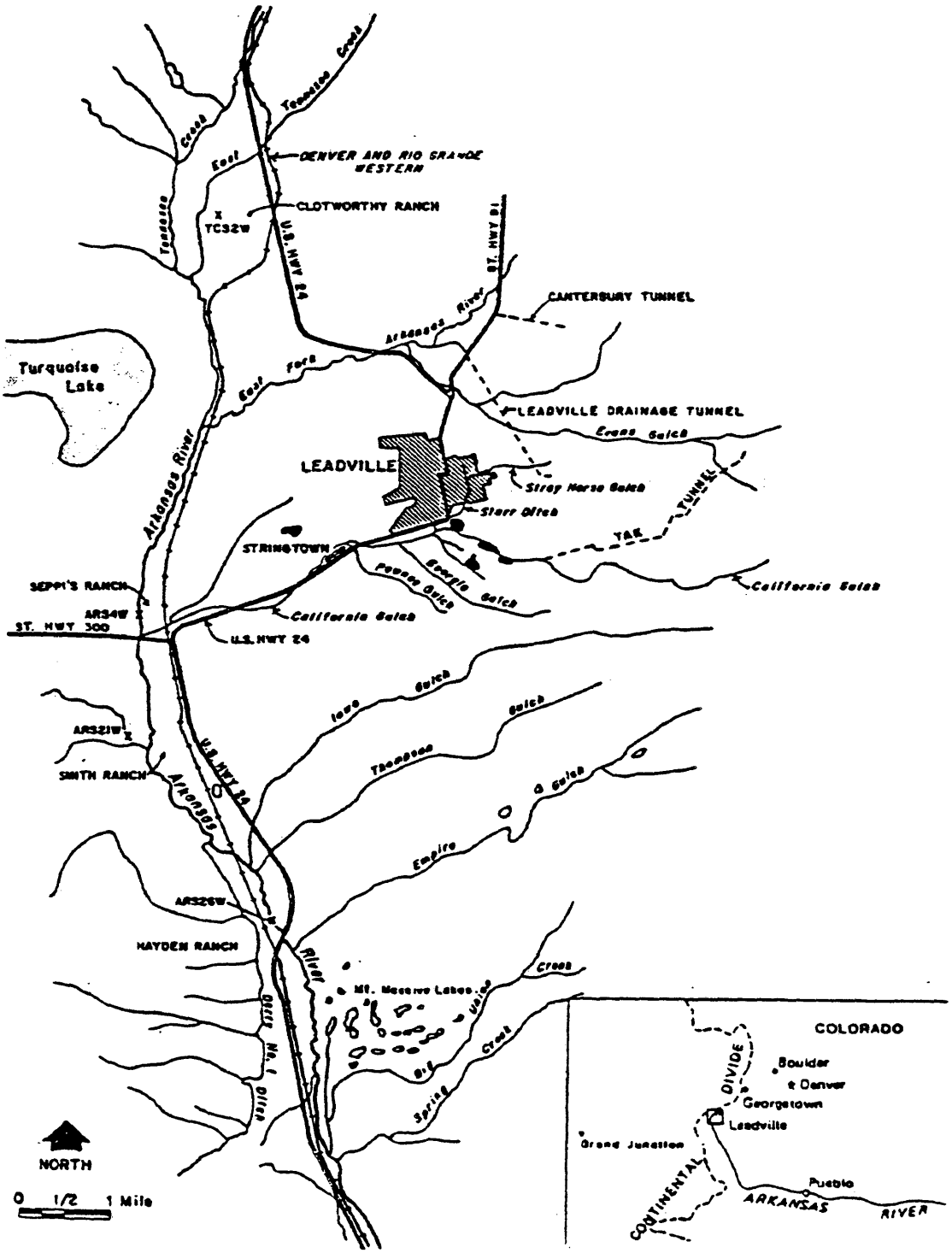
The tunnel was constructed to facilitate dewatering of existing mines, exploration for new ore bodies, ventilation access, and ore transport. An extensive system of laterals connects mine working to the tunnel and enhances its drainage capacity.

Site investigation activities conducted by the Environmental Protection Agency (EPA) (1987a) indicate that 80 percent of the cadmium and zinc in the California Gulch

Figure 1.1

LOCATION MAP OF STUDY AREA
CALIFORNIA GULCH SUPERFUND SITE
LEADVILLE, COLORADO

SRK (1986a)


Tennessee Creek
East
Tennessee
Creek
DENVER AND RIO GRANDE WESTERN
CLOTWORTHY RANCH
T9S R82W
U.S. HWY 24
ST. HWY 91
CANTERBURY TUNNEL
Arkansas River
Turquoise Lake
East Fork
LEADVILLE DRAINAGE TUNNEL
Evans Gulch
LEADVILLE
Arkansas River
Strop Horse Gulch
Starr Office
TUNNEL
YAK
STRINGTOWN
Pennsylvania Gulch
Georgia Gulch
California Gulch
SEPPI'S RANCH
AR34W
ST. HWY 300
California Gulch
U.S. HWY 24
Iowa Gulch
AR32W
SMITH RANCH
U.S. HWY 24
Arkansas
Empire
AR32W
HAYDEN RANCH
River
Mt. Massive Lakes
Creek
Union
Creek
Big
Spring
Creek
Divide
NORTH
0 1/2 1 Mile
COLORADO
DIVIDE
Boulder
Denver
Georgetown
Leadville
Grand Junction
CONTINENTAL
Pueblo
ARKANSAS
RIVER

waters are from the Yak Tunnel. The quality of the Yak Tunnel discharge is primarily influenced by oxidation of sulfide minerals, mainly pyrite, within unsaturated bedrock drained by the tunnel. This results in the release of high concentrations of metallic ions to solution and an increase in acidity. The Yak Tunnel discharge is characterized by low pH (high acidity) and high concentrations of iron, zinc, lead, copper, cadmium, and manganese. Flow from the tunnel acts as a point source discharge into California Gulch.

As part of the feasibility study in the California Gulch Superfund site investigation process, EPA has studied the remedial option of plugging selective portions of the Yak Tunnel to reduce the loading of metals to California Gulch and raise the water table to a sufficient level to limit the oxidation of sulfide minerals. This study entails the evaluation of the hydrogeochemistry of the Yak Tunnel and through use of the equilibrium model, MINTEQ, qualitatively predicting the results of selectively plugging portions of the Yak Tunnel.

Boundaries of Study Area

The area drained by the Yak Tunnel defines the areal boundaries for this thesis. This area is bounded on the east by the crestline of the Mosquito Range at an altitude of almost 14,000 feet. The western boundary is the Arkansas River Valley at an altitude of just under 10,000 feet. The

northern limit of the study is the northern catchment boundary of Evans Gulch and its tributaries. The southern limit of the study area is the drainage divide between California and Iowa Gulches (See Figure 1.2).

History of the Yak Tunnel

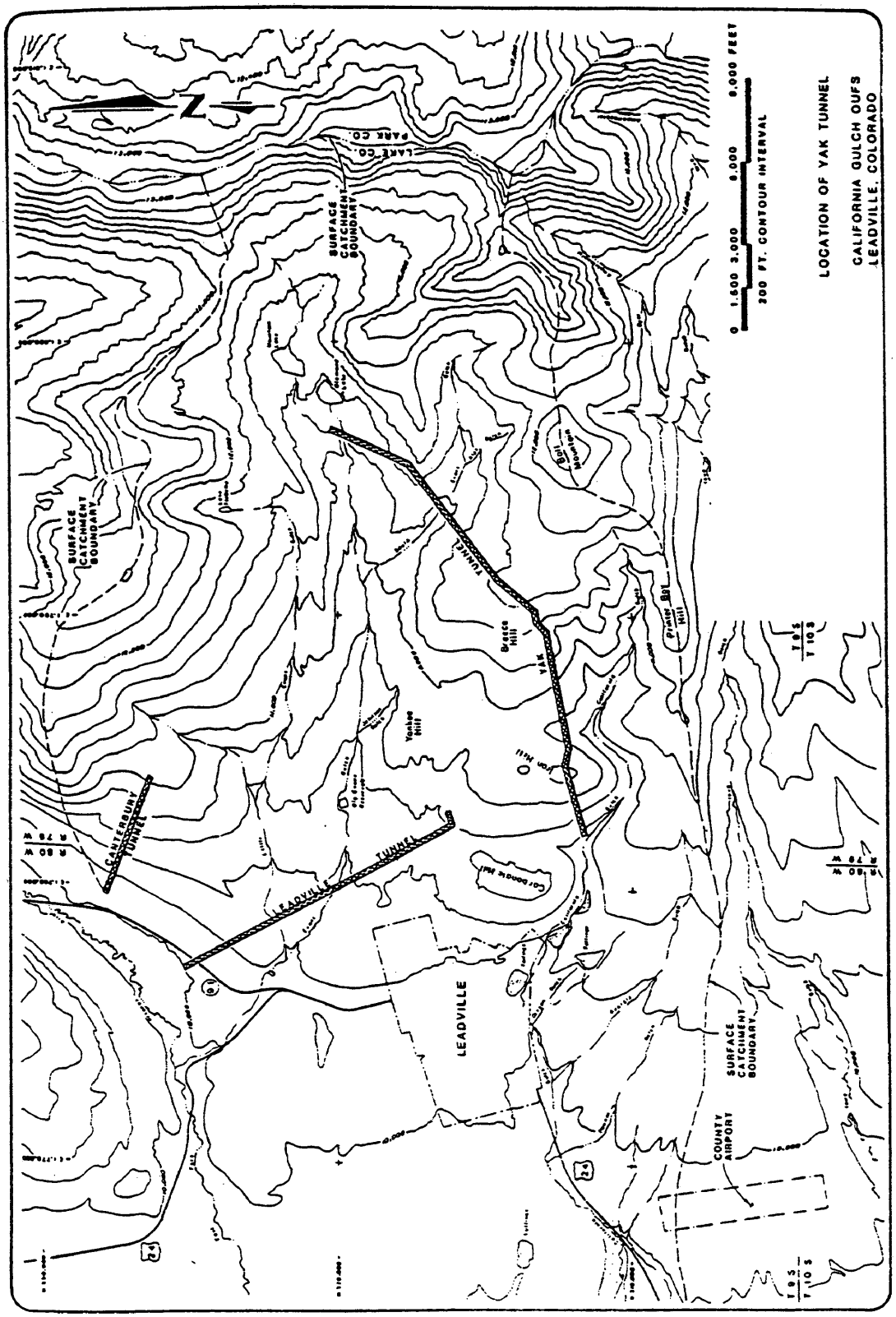
The Yak Tunnel was started in 1885 at an elevation of 10,330 feet above mean sea level (AMSL) by A.A. Blow to drain the Iron Hill mines (SRK 1986a). The tunnel was so successful, it was extended several times.

The initial development and subsequent extension of the Yak Tunnel corresponded to the major underground mining period in the Leadville area in the early 1880's to the early 1920's (Emmons et al., 1927). During this period of time, hundreds of individual mines were operated and 18 million tons of ore were treated (Emmons, et al., 1927). Since the 1920's, production has been sporadic with less than two million tons of ore extracted (SRK, 1986a). Emmons et al., (1927), identified 1,329 shafts, 155 tunnels, and 1,628 prospect holes in the Leadville district having an estimated aggregate length of 75 miles. Six years after the tunnel was opened, a concentration mill was constructed outside the portal. In 1894, when the tunnel was 4,000 feet long, it was purchased by Mining, Milling and Tunnel Company. The tunnel continued to be extended until,in 1904, it was 2 miles long and reached the Ibex No. 4 Mine. By

Figure 1.2

LOCATION OF THE YAK TUNNEL
LEADVILLE, COLORADO

SRK (1986a)


N
LOCATION OF YAK TUNNEL
CALIFORNIA GULCH OUFS
LEADVILLE, COLORADO
0 1,600 3,000 6,000 9,000 FEET
200 FT. CONTOUR INTERVAL
SURFACE CATCHMENT BOUNDARY
LAKE CO.
PARK CO.
CANTERBURY TUNNEL
LEADVILLE TUNNEL
YAK TUNNEL
LEADVILLE
COUNTY AIRPORT
Yankee Hill
Breece Hill
Printer Boy Hill
Iron Hill
Evans Gulch
California Gulch
T 9 S
T 10 S
T 10 S
T 11 S

1909, the tunnel reached the Resurrection No. 2 Mine and was 3.5 miles long. The major part of the tunnel was completed in 1912 when it reached the Resurrection No. 2 workings (McLaughlin Engineers, 1981). By mid-1913, an extension of the tunnel branched off into the Big Evans amphitheater area. Other extensions were built draining the Horseshoe Mine, Ruby Mine, North Mike Mine, South Mike Mine, Resurrection No. 1 Mine, Black Cloud Mine through Irene Bol 2, White Cap Mine, and Diamond Mine (State of Colorado, 1986).

Two other major tunnels were built in the area. In 1921 the Canterbury Tunnel was constructed (State of Colorado, 1986). This tunnel dewaters mines under Fryer Hill and the northern sections of Iron and Carbonate Hills. This tunnel contains relatively good quality water and is used today as part of Leadville's municipal water supply. In 1943, construction of the Leadville Mine Drainage Tunnel was begun by the Bureau of Mines (State of Colorado, 1986). The tunnel (11,299 feet long), was completed in 1952.

In 1983, as a result of an administrative order from the Colorado Department of Health, connection to the Irene Shaft and the laterals of the Black Cloud Mine leading to the Yak Tunnel were sealed. Although closed to public access, the tunnel still provides drainage for the abandoned mine workings connected with the tunnel.

Physical Description of the Yak Tunnel

The Yak Tunnel is approximately 17,800 feet long from the portal in California Gulch at an elevation of 10,333 feet AMSL (State of Colorado, 1986). The distal end of the tunnel lies 800 feet below the surface, 400 feet northeast of Resurrection No. 2 (Luke, 1978) at an elevation of 10,400 feet AMSL (SRK, 1986a). There are about 65,000 feet of interconnected drifts and laterals directly connected to the Yak Tunnel. The average slope of the tunnel is about 0.4 percent (SRK 1986a). Within the past 25 years, maintenance of the tunnel has been sporadic. Deterioration and collapse of support timbers has recently led to substantial maintenance problems (ASARCO, 1983).

Mining Areas of the Leadville Mining District

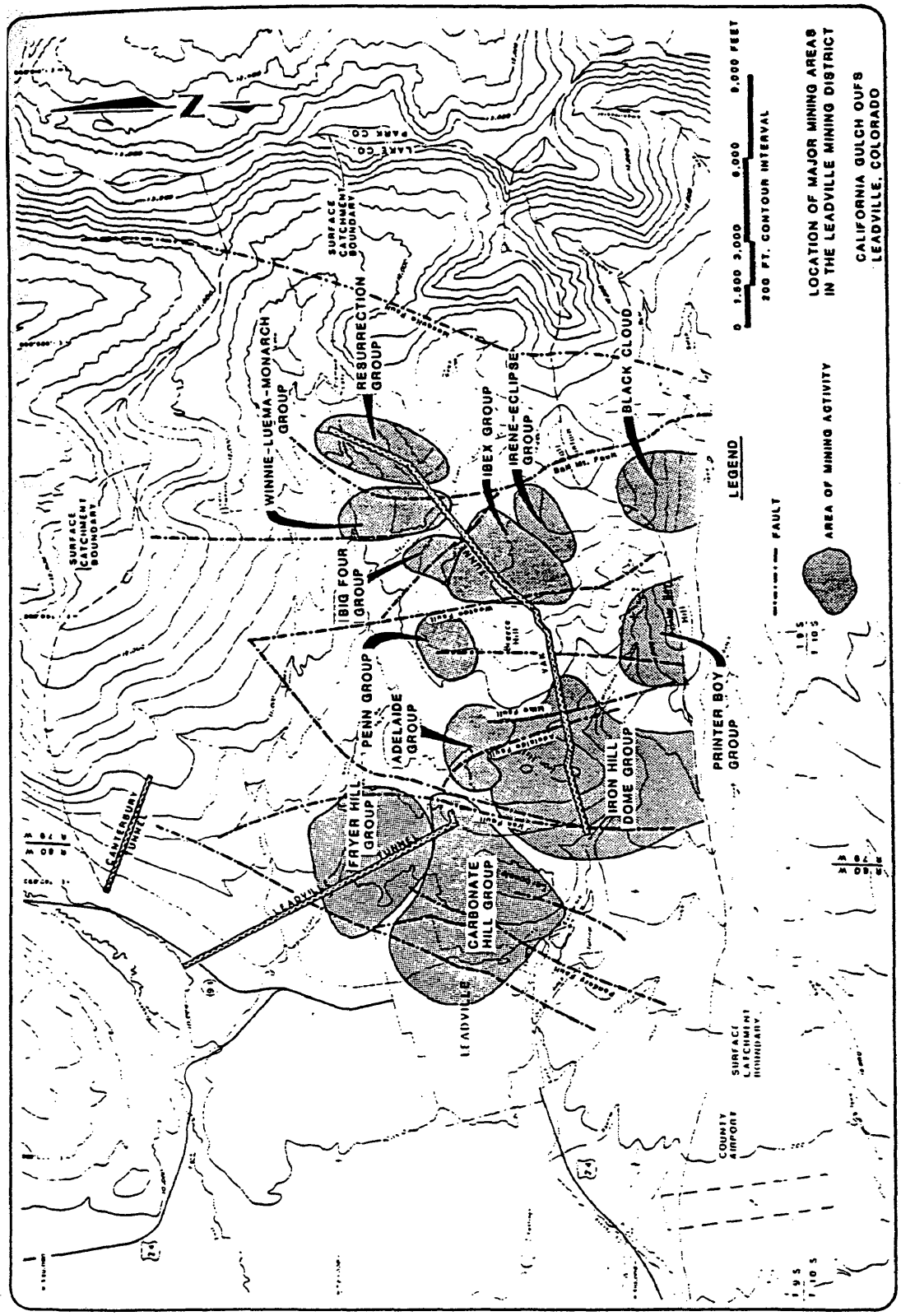
Principal mining areas of the Leadville mining district are illustrated in Figure 1.3. These areas can be divided into four major areas (SRK, 1986a). These areas comprise the: 1) Iron Hill, Dome and Adelaide workings, 2) the Carbonate Hill workings, 3) the Ibex, Irene, Resurrection, Big Four and Winnie-Leuma groups, and 4) the Penn group (SRK, 1986a).

Iron Hill/Adelaide Park/Dome Hill Group. These workings contain the largest and most extensively

Figure 1.3

LOCATION OF MAJOR MINING AREAS
IN THE LEADVILLE MINING DISTRICT
LEADVILLE, COLORADO

SRK (1986a)


N
SURFACE CATCHMENT BOUNDARY
WINNIE-LUEMA-MONARCH GROUP
RESURRECTION GROUP
IBEX GROUP
IRENE-ECLIPSE GROUP
BLACK CLOUD
BIG FOUR GROUP
PENN GROUP
ADELAIDE GROUP
FAYER HILL GROUP
CARBONATE HILL GROUP
IRON HILL DOME GROUP
PRINTER BOY GROUP
CARTERBURY TUNNEL
LEADVILLE
COUNTY AIRPORT
LEGEND
FAULT
AREA OF MINING ACTIVITY
0 1,500 3,000 6,000 9,000 FEET
200 FT. CONTOUR INTERVAL
LOCATION OF MAJOR MINING AREAS IN THE LEADVILLE MINING DISTRICT
CALIFORNIA GULCH OUFS
LEADVILLE, COLORADO

interconnected group of mines in the area drained by the Yak Tunnel.

Ibex/Big Four Group. The Ibex group is a major set of mines bounded by the Weston Fault, Colorado Prince Fault and breccia pipes. The group consists of a large number of working that are likely to be well-connected. Total mine workings in 1925 were reported to be in excess of 50 miles (Nobel, 1986).

Irene/Eclipse Group. This mine group was developed in the late 1950's and 1960's to develop deep ores located in the down-faulted block between the Weston and Ball Mountain Faults. The groups connect directly to ASARCO's operating Black Cloud Mine in Iowa Gulch and is connected to the Yak Tunnel by laterals. The group is also likely to be connected with the Ibex group.

Winnie-Luema/Monarch/Resurrection Group. This group consists of three independent mining areas that were interconnected through laterals from the Yak Tunnel, as well as workings at other levels. The Resurrection group is the largest set of these workings and was exploited at a shallow depth in Little Evans Gulch.

Geology of the Study Area

The complex geology of the Leadville Mining District has a significant impact on groundwater movement. Precambrian

crystalline rocks underlie the Leadville mining district. In this area, these rocks are schist, gneiss, and granite. Overlying the Precambrian rocks are several sedimentary rock formations of the Paleozoic Era ranging in age from Cambrian to Pennsylvanian. From oldest to youngest, these formations are the Sawatch quartzite (Cambrian Period), Peerless shale (Cambrian), Manitou dolomite (Ordovician), Chaffee Formation (Devonian consisting of the Parting quartzite and the Dyer dolomite), the Leadville dolomite (Mississippian) and the Weber Formation (Pennsylvanian, interbedded sandstone and shale). The limestones and dolomites of the Leadville area are extremely fractured and have been subjected to karst development processes that created solution channels in the rocks (Emmons et al., 1927). The karst solution features are most extensively developed in the Leadville limestones, and are filled with dolomite breccia, dolomite sand, black chert breccia, black shale, and grey clay from overlying rock units (SRK, 1986a).

The Precambrian and Paleozoic rocks were intruded during the Late Cretaceous and Tertiary Periods by igneous rocks consisting of three distinct porphyries. The earliest of these, called the White porphyry, is found in thick concordant masses, and is granodioritic in composition. The Gray porphyry group, which also tends to occur concordantly, varies in composition from granodiorite to quartz monzonite. The major intrusive, the Johnson Gulch

porphyry, commonly formed dikes along faults, and is granitic to quartz monzonitic (Behre, 1953).

The outstanding structural features, in the Leadville mining district are faults. Several periods of faulting have occurred in the region. Faulting during the Tertiary period is associated with the intrusion of igneous rocks of the Grey porphyry group and subsequent mineralization (Emmons et al., 1927 and Behre, 1953). Intensive fracturing associated with these faults played a dominant role in the emplacement of igneous intrusion, location of the ore, and oxidation of the sulfide minerals (Behre, 1953). The faults are superimposed on a regional monocline striking generally north or northwest and dipping to the east (Behre, 1953). The upthrown sides of the faults are usually to the east, resulting in the separation and offset of the sedimentary rocks into a series of east-dipping blocks in a stair-step configuration (Behre, 1953). Many of the major faults have well-developed "gouge" zones consisting of clayey crushed rock material (Emmons et al., 1927) that was formed as a result of the shearing and compressive forces acting at the time of displacement. The presence of fault gouge zones has resulted in significant groundwater level differences on opposite sides of major faults, and led to large inflows being encountered when the gouge layer of a fault zone was penetrated during mining (Emmons et al., 1927).

Mineralization of the Leadville Mining District

The primary ores of the Leadville Mining District are believed to have been deposited by magmatic solutions, associated with the intrusion of the Johnson Gulch porphyry (Behre, 1953). Three factors appear to be of paramount importance in ore localization: large structures such as folds and faults that directed the flow of solution, the nearness of intrusive rocks that served as sources or ponding agents for the solutions, and the permeability, solubility, and other pertinent properties of the particular country rock in which the ore was deposited (Behre, 1953). The source of magmatic solutions appears to be centered around the Breece Hill stock, but the location and the arrangement of ore bodies is controlled by structural features, notably the reverse faults (Emmons et al., 1927).

Premineral fractures, once opened, remain as planes of weakness, even if cemented with ore. If the region is subjected to renewed stresses, it is very likely that the fractures such as fissures may be reopened after partial or complete cementation by the ore (Behre, 1953). This process of recurrent opening and shattering probably accounts for the larger ore bodies found in some premineralization reverse faults (Behre, 1953). The principal sulfide minerals, which constitute the primary ore bodies include pyrite (iron sulfide), sphalerite (zinc sulfide) and galena (lead sulfide) (Emmons et al., 1927). Other minor sulfide

minerals include chalcocite (copper sulfide) (Emmons et al., 1927).

The ore bodies of the central Leadville district may be classified according to form as either "veins" or "fissure" types found principally in siliceous rocks, or replacement deposits or "blanket" deposits associated with carbonate rocks (SRK, 1986a). Pyrite is the principal ore mineral in the veins and fissures and also in many of the replacement bodies in limestone (SRK, 1986a). It is found densely intergrown with galena or sphalerite or both. Pyrite is also found in replacement bodies and disseminated in limestones, sandstones, quartzites and porphyries. Galena, sulfide of lead (PbS), is one of the most widespread ore minerals in the Leadville district. Because of the insolubility of its oxidation products, crystals of galena are highly resistant to chemical change even in the zone of strongest oxidation (Behre, 1953). In many deposits, galena is the only primary sulfide remaining after a long period of oxidation (Behre, 1953). Sphalerite is the only important primary zinc mineral (Behre, 1953). It is commonly intergrown with pyrite or with galena and is much more abundant than galena. Chalcocite (Cu_2S) is commonly a product of secondary sulfide alteration where chalcopyrite or other copper sulfides are present in the primary ore (Behre, 1953).

Most of the ore of Leadville has been extracted from "blanket" type deposits that tend to follow the dip of the sedimentary rock units. These "blanket" deposits have large dip dimensions (up to 2,500 ft.), smaller strike dimensions (up to 1,000 ft.) and relatively small thicknesses (SRK, 1986a).

Extent and Methods of Mining

The geometry, extent and methods of mining in the Leadville Mining District significantly influence the groundwater flow conditions in the area drained by the Yak Tunnel. It is beneficial to examine the methods of mining to determine the influence of mining on bedrock groundwater flow in the study area. The dominant mining method used in the mines drained by the Yak Tunnel is the square set with backfill (Emmons et al., 1927). In this method of mining, the mineralized zone was mined out or "stoped" (SRK, 1986a). A timbered frame was used to support the walls of the stope and was continuously enlarged as the excavation increased. The timbers also provided a working platform (SRK, 1986a). Ore was often hand sorted in the stopes so that only high grade ore was hoisted (SRK, 1986a). Much of the available space underground, including spaces between the square sets, was used for dumping of low grade ore and waste rock backfill. It is very likely that considerable backfilling of the stopes took place (SRK, 1986a).

Deeper ore bodies were accessed by shafts. The smaller ore bodies, being more difficult to locate, often required considerable mine development (SRK, 1986a). The near-surface blanket ore bodies were generally accessed by declines driven from the surface and intersecting along the contact between the ore zones and the overlying porphyry (Emmons et al., 1927). Mine development associated with fissure ore bodies was generally limited compared with the development of the blanket ore bodies (SRK, 1986a).

It is beneficial to assess the void space within the Yak Tunnel drainage to enable prediction of the rise in the water table resulting from the plugging of the Yak Tunnel in selected locations. There is limited production and mine map data available to assess stope volumes, mine development volumes, and potential void spaces (EPA, 1987b). The stopes, which are probably backfilled with broken rock, still have void space. SRK (1986a) estimated that potential void space in the stopes is 60 percent of the estimated stope volume. This total void space in the stopes has been estimated to vary from 47 to 63 million cubic feet (SRK, 1986a). Further consolidation, because of subsidence within the larger stopes, could conceivably decrease the void space an additional 25 percent. The estimated void space accounting for backfilling and consolidation is between 35 and 47 million cubic feet (SRK, 1986a).

Similar to stope volume assumption, SRK (1986a) assumed that 50 percent of the void space in the development areas has been lost through backfilling and collapse. A development area void space of 20 to 27 million cubic feet has been calculated (SRK, 1986a).

Based on Emmons et al. (1927) data, SRK (1986a) estimated that approximately 75 percent of the mining activity took place above the elevation of the Yak Tunnel. Void space above the level of the Yak Tunnel is estimated at 41 to 56 million cubic feet.

Hydrogeology of the Yak Tunnel Drainage

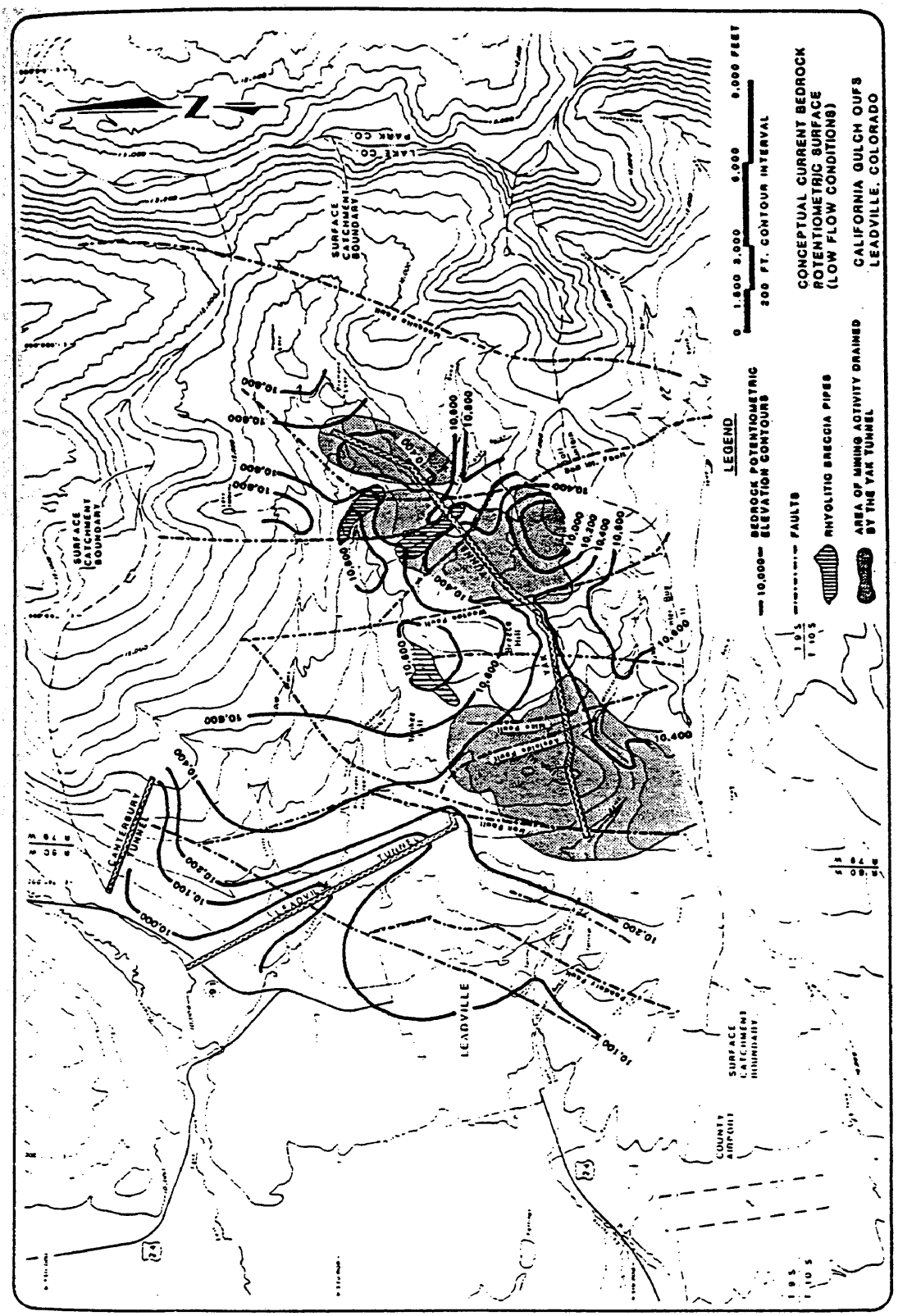
Bedrock groundwater in the Leadville Mining District occurs in granite, quartzite, limestone, sandstone, and porphyry dikes. Faulting and associated fracturing significantly influences the hydrogeologic characteristics of the bedrock units, as well as the overall groundwater flow paths (SRK, 1986a). The faulting and vertical offset of different formations have caused the rocks to be hydrologically interconnected. Thus, groundwater behaves as a single hydrologic unit. The Yak Tunnel acts as a horizontal well that drains this groundwater.

The present configuration of the groundwater table, based on relatively few data points, is probably similar to that depicted in Figure 1.4. This interpretation (SRK, 1986a) considers the effects of interconnected mine

Figure 1.4

CONCEPTUAL CURRENT BEDROCK
POTENTIOMETRIC SURFACE
(LOW FLOW CONDITIONS)
LEADVILLE, COLORADO

SRK (1986a)


N
LEGEND
0 1,000 2,000 4,000 6,000 FEET
200 FT. CONTOUR INTERVAL
10,000 BEDROCK POTENTIOMETRIC ELEVATION CONTOURS
FAULTS
RHYOLITIC BRECCIA PIPES
AREA OF MINING ACTIVITY DRAINED BY THE YAK TUNNEL
CONCEPTUAL CURRENT BEDROCK POTENTIOMETRIC SURFACE (LOW FLOW CONDITIONS)
CALIFORNIA GULCH OUFS
LEADVILLE, COLORADO
SURFACE CATCHMENT BOUNDARY
LAKE CO
PARK CO
LEADVILLE
YAK TUNNEL
LEADVILLE TUNNEL
CHALK CREEK TUNNEL
10,800
10,600
10,400
10,200
10,100
10,000

workings, drainage of the mine workings by the tunnels reduced permeability across fault zones that probably have not been penetrated by mine workings, and major areas of active recharge. It also is based on probable average permeabilities of the bedrock units, and water balance considerations using the documented flows (ASARCO, no date; and U.S. Bureau of Reclamation, 1979) within the Yak Tunnel and Leadville Tunnel.

Recharge. Recharge to the bedrock aquifer in the Leadville Mining District is controlled primarily by precipitation, topography and certain bedrock outcrops which have not been affected by mining (SRK,1986a). Increased recharge may occur on a local basis from surface water flows and alluvial underflow due to the undermining of the creek areas. Evidence for this occurrence is the relatively high seasonal inflows in the White Cap lateral of the Yak Tunnel which drains mining areas under California Gulch (ASARCO, no date). The rhyolytic agglomerate intrusive pipes in the area are an important potential recharge conduit to the groundwater system because of the locally higher permeability, the occurrence of the rock in vertically extensive pipes, and the outcrop of the pipes in low lying drainages (SRK, 1986a). Recharge to the Resurrection Group and Ibex-Irene Group occurs from the direct infiltration of surface waters in the headwater areas of Evans and South

Evans Gulches (SRK, 1986a). Much of this recharge is probably through the Josie and Ollie Reed rhyolite breccia pipes, which directly underlie these gulches.

The mining-related activities in the Leadville Mining District have probably altered the areas of recharge to the groundwater system. Most of the recharge to the bedrock system occurs during the snowmelt period. This assertion is supported by the evidence of an increase in discharge from the Yak Tunnel following snowmelt periods as compared to the weighted average flow for the same time period (See Figure 1.5). In addition, this rapid response of the Yak Tunnel's discharge to an increase in recharge to the system reflects the rapid movement of groundwater through the mined areas (SRK, 1986a). Recharge to the northern workings in the Iron Hill group is from lateral groundwater (EPA, 1987B).

Influence of Faults. Faulting and associated fracturing significantly influences the hydrogeologic characteristics of the bedrock unit, as well as the overall groundwater flow paths.

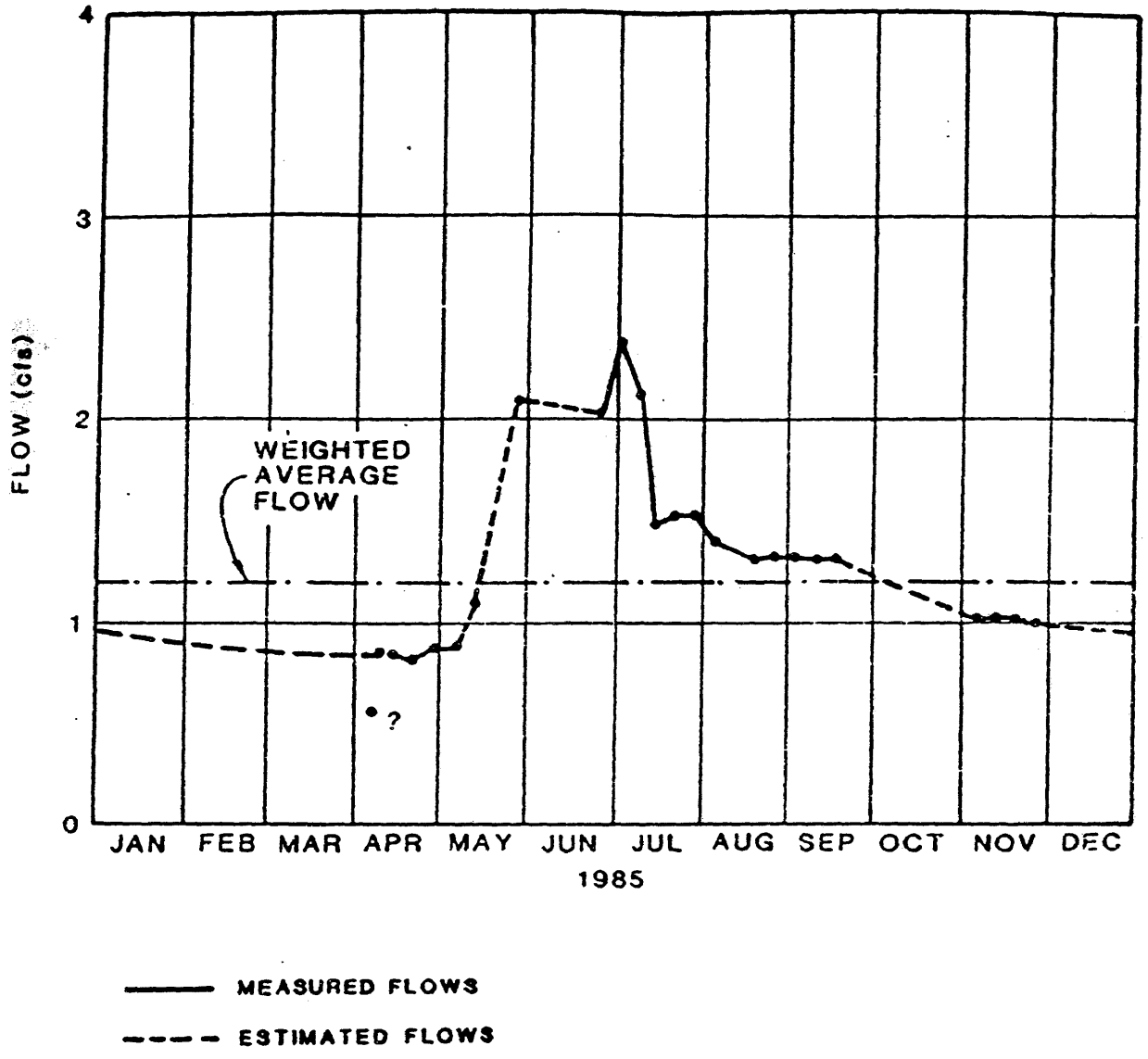
Most of the faults in the Leadville Mining District trend north-south. The hydrogeologic characteristics of the major fault zones tend to enhance groundwater flows that parallel the fault planes, and restrict flows across the fault planes (Emmons et al., 1927).

In addition, faulting enable various rock layers to become vertically hydrologically connected. Faulting allows

Figure 1.5

YAK TUNNEL DISCHARGE
DURING 1985

SRK (1986a)


4
3
2
1
0
FLOW (cfs)
WEIGHTED AVERAGE FLOW
?
JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC
1985
MEASURED FLOWS
ESTIMATED FLOWS

effective bypass of lower permeability units which would normally restrict the movement of groundwater (SRK, 1986a). On the other hand, many of the major faults in the Leadville Mining District including the Iron/Mikado and Weston faults have well developed "gouge" zones consisting of clayey crushed rock material (Emmons et al., 1927). These faults provide resistance to groundwater movement from east to west. The low permeability of the gouge material tends to restrict the flow across the fault plane. This feature resulted in significant groundwater level differences on opposite sides of major fault zones prior to mining (Emmons et al., 1927). Upon penetrating the clayey gouge layer in a fault, miners often reported encountering large amounts of water flowing into the drifts or shafts in which they were working (Emmons et al., 1927). Although the Iron and Mikado faults have been penetrated and extensively mined, there is evidence to suggest that these faults still provide a reasonable barrier to lateral groundwater flows across the fault zones (SRK, 1986a).

Significant differences in water level elevation in shafts on opposite sides of these faults were recorded by the U.S. Bureau of Mines in 1944 (Turk and Taylor, 1979).

Mine Activity Influence. As stated previously, the geometry, extent and methods of mining in the Leadville area significantly influence the groundwater flow conditions in the area drained by the Yak Tunnel (SRK, 1986a). Mining

activities have probably significantly altered the natural hydrogeologic characteristics of the bedrock units, and the overall groundwater paths (SRK, 1986a). The major hydrologic effect of mining in the Leadville district was the cross-cutting of faults by drifts and shafts during mining operations (Emmons et al., 1927). The natural hydraulic conductivity of the gouge material associated with fault zones is probably in the order of 10^{-7} to 10^{-6} cm/sec (0.1 to 1 ft/yr), which is a typical range for clayey material (Freeze and Cherry, 1979). It is assumed that penetration of the fault zones by mining activities and the extensive mining of the gouge material has probably significantly increased the overall hydraulic conductivity across the fault zones to within the range 10^{-6} to 10^{-5} cm/sec (1 to 10 ft/yr) (SRK 1986a). In addition, the sinking of numerous access and exploration shafts has probably increased vertical hydrologic connection between the slightly dipping lithologic units (SRK, 1986a). These shafts penetrate low permeability rock units that would normally restrict vertical groundwater flow. The extensive mine workings have increased hydrologic connection with the major mining areas and in some cases possibly between mining areas. This is due to both direct removal of material as well as subsequent fracturing of overlying bedrock (SRK, 1986a). Conversely, backfilling of waste material within the workings and subsequent compression of excavated areas

as a result of subsidence tends to reduce the effect of mining activities (SRK, 1986a).

The increased drainage caused by the construction of the mine works and the Yak Tunnel has led to a general lowering of the water table, resulting in exposure of additional sulfide minerals to oxygen that were previously below the water table (SRK, 1986a). The relatively high permeability of these mined areas would result in reasonably uniform water level elevations (EPA, 1987b).

Currently, the only substantial active mining operation in the Yak Tunnel drainage is the Black Cloud Mine. It has been estimated by EPA (1987b) that 60 percent of the bedrock groundwater in the Yak Tunnel drainage is intercepted by the Yak Tunnel and 30 percent of the bedrock groundwater flows is discharged from the Black Cloud Mine. A major portion of this discharge is water that flows from the Irene workings. The Irene workings, however, during the period of time of ASARCO's measurements (1973 and 1975), discharged directly into the Yak Tunnel. If operations at the Black Cloud Mine were to cease, it is predicted that most of this water would be discharged through the Yak Tunnel. Currently, only 10 percent of the groundwater is not intercepted by mine workings.

Contribution of Mine Groups to Yak Tunnel

The Yak Tunnel connects three distinct and separate groups of mines within the California Mining District (ASARCO, 1983). Beginning at the portal, the first group of mines is the White Cap-Cord group located in California Gulch and on Iron Hill. The second group is the Ibex-Irene group located on Breece Hill and Mine in Iowa Gulch and is connected to the Yak Tunnel. The third group of mines at the end of the tunnel is the Resurrection-Diamond group located in Evans Gulch. The amount of flow and relative contribution of flow to the Yak Tunnel is illustrated in Figure 1.6.

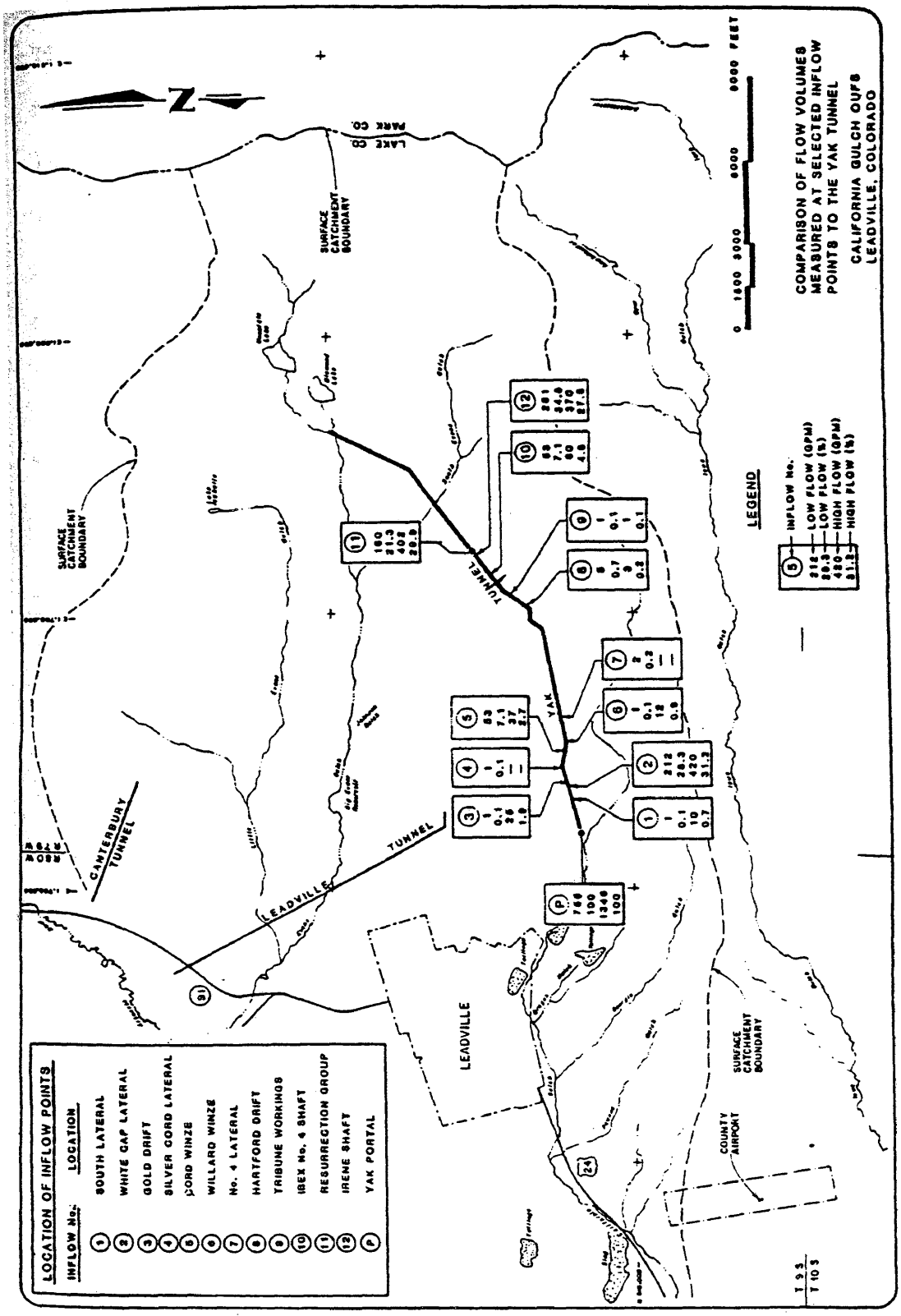
Resurrection. Drainage from the Resurrection mine contributes to the Yak flow at its head. The ore reserves in the Resurrection mine exist wholly within the Leadville Dolomite and lie above the groundwater level (Hydro-Search, Inc., 1986). The pH of the Yak head flows is significantly higher than the pH of the Yak portal discharge.

Flow measurements by ASARCO (no date) in October 1973, indicate that 32 percent of the Yak Tunnel flow is contributed from the Resurrection Mine Group. Although metal concentrations of water from Resurrection drainage do not exceed EPA limits for Drinking Water Standards except for manganese, because of the high flows, this drainage provides a significant loading of metals to the Yak Tunnel.

Figure 1.6

COMPARISION OF FLOW VOLUMES
MEASURED AT SELECTED INFLOW POINTS
TO THE YAK TUNNEL

SRK (1986a)


LOCATION OF INFLOW POINTS
INFLOW No. LOCATION
1 SOUTH LATERAL
2 WHITE CAP LATERAL
3 GOLD DRIFT
4 SILVER CORD LATERAL
5 CORD WINZE
6 WILLARD WINZE
7 No. 4 LATERAL
8 HARTFORD DRIFT
9 TRIBUNE WORKINGS
10 IBEX No. 4 SHAFT
11 RESURRECTION GROUP
12 IRENE SHAFT
P YAK PORTAL
LEGEND
INFLOW No.
LOW FLOW (GPM)
LOW FLOW (%)
HIGH FLOW (GPM)
HIGH FLOW (%)
COMPARISON OF FLOW VOLUMES MEASURED AT SELECTED INFLOW POINTS TO THE YAK TUNNEL
CALIFORNIA GULCH OUTS
LEADVILLE, COLORADO
0 1500 3000 6000 9000 FEET
SURFACE CATCHMENT BOUNDARY
CANTERBURY TUNNEL
LEADVILLE TUNNEL
YAK TUNNEL
LEADVILLE
COUNTY AIRPORT
LAKE CO.
PARK CO.
T 9 S
T 10 S

Ibex-Irene. According to ASARCO (1973, 1975) there is negligible flow from the Irene group into the Yak Tunnel. The Ibex group contributes flow to both the Yak Tunnel and the Irene group of workings (SRKa, 1986). In several locations the Ibex workings are connected to the Irene workings (ASARCO, map; as cited by EPA 1987b). Active dewatering of the Irene mines has made these workings act as a collection basin rather than a discharge to the Yak Tunnel (SRKa 1986). The Irene workings drain to ASARCO's Black Cloud mine (EPA, 1987b).

Iron Hill Group. The southern Iron group workings have large discharges (200+ gpm) to the Yak Tunnel and show significant increases in discharge (400+ gpm) during the Spring runoff period (EPA, 1987b). The volume of discharge and seasonal variation is too large to be attributable to lateral groundwater flow. It is probably attributable to direct infiltration of California Gulch surface flows (EPA, 1987b) and related groundwater underflows into these mined areas (EPA,1987b).

Water Quality

The Yak Tunnel provides 75 to 85 percent of the heavy metal load to the Arkansas River through California Gulch (EPA, 1987a). Degradation of groundwater drained by the Yak Tunnel can be attributed to be the result of the mining and

dewatering operations, and, to a certain extent, the Yak Tunnel itself, which caused the water table in the vicinity of the Yak Tunnel drainage to be lowered. The effect of lowering the groundwater table was to allow free oxygen to come into contact with sulfide deposits. One of the most prevalent sulfide minerals in the Leadville mining district is pyrite (FeS_2). This mineral oxidizes to form insoluble iron hydroxides ("yellow boy"), which quickly precipitate out of solution, and the production of acidic and sulfate-rich waters.

The oxidation of iron sulfides in mining areas results in release of high concentrations of metallic ions to solution and an increase in acidity. The efluent resulting from this geochemical process is commonly referred to as "acid mine drainage." The water quality of the Yak Tunnel effluent is significantly impacted as a result of this geochemical process. The Yak Tunnel discharge is characterized by low pH (high acidity) and elevated concentrations of iron, zinc, lead, copper, cadmium and manganese. Oxidation of other sulfide minerals such as sphalerite (ZnS) and galena (PbS) release minor amounts of zinc and lead into the water, although they do not contribute to the production of acidity (HRS, 1984).

The oxidation of iron sulfide has been studied extensively. The basic process of the oxidation of iron sulfide results in iron going into solution and sulfuric

acid being produced in a self-propagating cycle. The chemical reaction for this process is described as follows:

Initiator reaction:

pyrite + oxygen + water -> ferrous ions + sulfate + acidity

Propagation Cycle:

oxygen + ->ferric iron<-->ferric oxides + acidity-> + pyrite

Initiator reaction:

$$FeS_2 + 7/2\ O_2 + H_2O + Fe^{2+} + SO_4^{-2} + 2H^+$$

Propagation cycle:

$$Fe^{2+} + 1/4\ O^{-2} + H^+ = Fe^{3+} + 1/2\ H_2O$$

$$FeS_2 + 1/4\ Fe^{3+} + 8\ H_2O = 15\ Fe^{2+} + 2\ SO_4^{-2} + 16\ H^+$$

$$Fe^{3+} + 3\ H_2O = Fe(OH)_3 + H^+$$

In the initiator reaction, sulfur is oxidized to sulfate generating hydrogen ions and releasing Fe^{2+} (ferrous iron) into solution (Forstner and Wittmann, 1981). This oxidation process may be accomplished either directly by atmospheric oxygen or by the simple dissociation of pyrite in solution, followed by oxidation by aqueous oxygen (Stumm and Morgan, 1970). Ferrous ions are then oxidized to produce ferric ions in the first step of the propagation cycle.

In the initial stage of the cycle, the natural alkalinity of the water is sufficient to prevent ferric iron

from remaining in solution. Insoluble ferric oxides are produced and precipitated forming the characteristic yellow sediment known as "yellow-boy." The formation of ferric oxides, however, is accompanied by a release of hydrogen ions, which causes the pH to decrease. When the pH has dropped enough to allow ferric iron to remain in solution, the second step of the propagation cycle begins. Ferric iron, a strong lixiviant and powerful oxidizing agent, assumes the primary role in the oxidation of pyrite (Garrels, and Thompson, 1980). Ferric is reduced to ferrous iron to produce more sulfate and acidity, and then is reoxidized to ferric iron, propagating the cycle.

The powerful oxidizing action of ferric ions may also be responsible for the release of other metals such as Cd, Cu, Pb, Zn, and Mn from their sulfide forms (Singer and Stumm, 1970; Stumm and Morgan, 1970). Ferric iron that is produced in the oxidation of pyrite, which is a major component of the ore bodies in the Leadville area, assumes the role of oxygen thereby releasing the divalent metal ion and elemental sulfur (Nordstrom et al., 1979).

In addition to the effect of pH on the reaction process, microorganisms play a significant role in the formation of acid mine drainage. The oxidation of Fe^{2+} occurs extremely slowly in the acid mine waters. Singer and Stumm (1970) have shown that the oxidation of ferrous iron is the rate determining step in the production of acid mine

waters. Were it not for the obvious presence of a catalytic agent, the formation process would essentially cease once the pH had dropped below 5. Singer and Stumm (1970) examined the effect of various catalytic agents and found that microorganisms were by far the most efficient, increasing the rate of the reaction by a factor of greater than 10^6. Without these bacterial catalysts, the oxidizing rate of Fe^{2+} in natural systems is too slow to be of any consequence in acid formation. The acidophilic iron-oxidizing bacterium Thiobacillus ferrooxidans is generally believed to be responsible for the catalysis.

T. ferrooxidans is an aerobic bacterium that thrives in a low pH environment (pH from less than 1 to a pH of 4.5). This bacterium derives its metabolic energy from the oxidation of Fe^{2+}. Thus, it self-perpetuates an environment that is suitable for its survival. Although an aerobic bacterium, T. ferrooxidans can tolerate severe oxygen deprivation.

The significance of T. ferrooxidans in the formation of acid mine drainage is that it allows the continuation of the propagation cycle by rapidly providing a steady source of Fe^{3+}, the primary oxidant of pyrite. In addition, the extreme acid environment it creates allows Fe^{3+} to remain in solution thereby facilitating the geochemical process.

According to Forstner and Wittman (1981), bacterial oxidation of other metallic sulfides such as CdS, PbS, and

ZnS may be stimulated by the presence of iron sulfide. This reaction can be characterized as follows:

Metal sulfide + 2 Fe^{3+} -->divalent metal cation + 2 Fe^{2+} + S^0

Since the presence of oxygen is essential for the initiation of the acid mine drainage geochemical process and the support of the catalyst, T. ferrooxidans, the position of the oxide/sulfide interface in relation to the water table has a major influence on the extent that oxidation and the subsequent production of acid mine drainage may take place. The oxidation depth below present ground surface varies widely in the Leadville Mining District. The reasons for this variation include geologic structures, lithology of the bedrock, form and position of the ore bodies, and the effects of glacial erosion and deposition (Emmons et al., 1927). Within the area drained by the Yak Tunnel, the major areas where extensive sulfide minerals exist above the present water table is in the Ibex/Irene and Resurrection/Winnie/Luema Mine areas and between the Mike and Weston Fault zones, and to a lesser extent, the sulfide ores exist above the present water table in the Adalaide/Iron Hill/Dome Hill group of mines.

Because of the "acid mine drainage" process occurring in the Leadville Mining District, inflow of bedrock groundwater into the Yak Tunnel is high in metals and high

in acidity. A major part of the zinc and lead concentrations in the Yak Tunnel discharge are due to the interaction of waters with carbonate minerals such as smithsonite ($ZnCO_3$) and cerrusite ($PbCO_3$), which are the principal ore minerals in the replacement deposits. Since cadmium generally substitutes for zinc, it is also released. The principal sources for manganese include gangue minerals such as mangano-siderite and jasperoid (Hydro-Search, Inc., 1986).

Water quality measurements of the inflow of water from the mine groups that are drained by the Yak Tunnel were conducted by ASARCO in October, 1973. These measurements consisted of analyzing heavy metal concentrations, pH, alkalinity, flow rates and natural chemical constituents. These data are presented in Table 1.1.

Table 1.1.

ASARCO 1973 WATER QUALITY DATA
YAK TUNNEL (Total mg/l)

Inflow Point	Cd	Cu	Fe	Pb	Mg	Zn	SO_4	Mn
South Lateral	0.10	.05	5.9	0.05	.8	1.4	190	.8
White Cap Lateral	0.18	0.06	20.0	0.05	7.0	7.6	220	7.0
Gold Drift	1.30	0.20	136.0	0.15	19.0	0.9	1100	19.0
Silver Cord Lateral	0.01	0.10	41.0	0.01	0.2	0.9	124	0.2
Cord Winze	0.08	0.10	59.0	0.01	1.5	1.9	120	1.5
Willard Winze	1.50	0.10	38.0	0.20	32.0	30.0	3600	32.0
No. 4 Lateral	0.05	0.10	19.0	0.10	1.4	3.0	190	1.4
Hartford Drift	.06	0.10	16.0	0.10	0.5	0.4	120	.5
Tribune Workings	.05	0.10	42.0	0.10	1.3	0.8	160	13.0
Ibex No. 4 Shaft	2.00	1.10	70.0	0.20	98.0	320.0	90	98.0
Resurrection Group	.20	.30	150.0	0.10	8.8	53.0	160	8.8
Irene Shaft	.30	.10	68.0	0.10	5.0	39.0	190	50.0

Variations in the water quality in the Yak Tunnel occur on a seasonal basis. Water quality data on Yak Tunnel discharge collected during 1984 and 1985 (EPA, 1987b) indicate that the highest concentrations of dissolved metals occur during the high flows following the spring snowmelt period. Measurements by ASARCO (no date) in 1973 were conducted during a low flow period in October. Flow measurements were taken by ASARCO (no date) in June, 1975, that are representative of high flow conditions. There were no water quality measurements taken at this time.

Condition of the Yak Tunnel

The condition of the Yak Tunnel has a significant influence on the present quality of the Yak effluent, the rate of flow through the tunnel and future remedial actions. In February 1983, ASARCO personnel inspected the tunnel (Johnson, C., et al., 1983). During this inspection, several areas of the tunnel were observed to have major falls of timber and/or rock. These falls were damming up flow within the tunnel (ASARCO, 1983). Timber sets were observed as being in terrible shape, and additional timber and roof cave-ins were anticipated to occur in the near future (Johnson, C., et al., 1983). In addition, there is reference to considerable layers of "slimes" on the tunnel floor due to precipitation of iron hydroxide precipitates (yellow boy), fines from backfill operations in recent times, and an accumulation of mud and debris.

Because of the acidic water conditions in the tunnel, the timber sets are susceptible to deterioration. Widespread occurrence of timbers and/or roof falls could result in large dams being formed in the tunnel or connecting laterals (EPA, 1987b). These dams could collapse, creating a surge event. Surge events are not predictable, either in occurrence or size (EPA, 1987b). A surge event occurred at the Yak Tunnel on October 22, 1985.

Tainter (1952) stated that of the first 1000 feet from the portal, approximately 53 percent was unsupported, 35 percent was supported with timber, and 12 percent supported with steel. In 1952, 18 men were involved in tunnel maintenance and were replacing timber sets with steel, where required (Tainter, 1952). They identified two long sections of poor rock conditions that required timber and steel sets. These section were located 7,000 to 8,600 feet from the tunnel portal (Tainter, 1952).

Proposed Remedial Alternative

One of the viable remedial alternatives proposed by EPA (1987b) to mitigate the problem of acid mine drainage from the Yak Tunnel is to partially plug selective portions of the Yak Tunnel and treat the remaining effluent through conventional wastewater treatment processes. The purpose of plugging the Yak Tunnel would be to reduce or eliminate the discharge of acid mine drainage. Plugging would also be

expected to raise the groundwater level in the underground mine workings, thereby inundating mineralized zones. This would, in turn, reduce the potential for acid generation. Mine plugging involves placing a concrete plug in an underground mine tunnel to block the flow of mine water. Plugs are concrete structures that are anchored into surrounding rock.

The effect of plugging is to cause the water to back up behind the plug until it finds an alternative exit route. These routes include other tunnels or vertical shafts, or flow into the regional groundwater system (SRK, 1986b). Plugging technology has been successfully used in South Africa, however, success in North America has been very site specific (SRK, 1986b).

Knowledge of the geohydrology is critical to achieving a successful plugging operation (EPA, 1987b). Failure of plugging technology occurs in two forms: (1) the concrete structure can rupture from the water pressure behind the plug; and (2) water, under increased hydrostatic pressure, will flow along fractures, fissures, and faults and eventually seep around the plug (EPA, 1987b). Plug failure occurs more commonly through the second mechanism (EPA, 1987b). Implementability and reliability of plugging is based on the effects plugging would have on the bedrock groundwater system in Upper California Gulch and Upper Evans Gulch (EPA, 1987b).

SRK (1986b) studied the technical feasibility of plugging. To be effective, plugs must be located in areas of sound, intact rock and away from interconnected mine workings which could cause flow to bypass the plug. Typical locations for plugs in the Yak Tunnel are immediately downgradient from the major groups of mine workings. Preference for selection of specific locations for the implementation of plugs should be given to reaches where rock conditions are good and which converge in a downstream direction. This will aid in providing a good seal between the rock and the plug. Previous experience with plug construction has demonstrated that the design should be based on limiting the water pressure gradient along the plug length. Usually, a value between 25 and 45 pounds per square inch (psi) per foot length of plug is selected. Because the competence at the proposed plug positions is currently unknown, it has been recommended that a value of 15 psi be used as a design constraint.

After construction, the plug must be sealed by grouting. This should be started at the interface between the rock and plug and proceed outwards from the plug in a number of stages. In most cases, a stainless steel pipe will be placed in the plug. It would be fitted with a valve at the downstream end. This pipe would be used to collect water samples, to measure the head developing behind the plug, and to reduce the water level behind the plug should this ever

be required. The use of this pipe over a very long period cannot be relied on because of potential problems with corrosion and clogging.

Several actions have been proposed to reduce or eliminate Yak Tunnel discharges. Plugging the Yak Tunnel at selected locations is an alternative that could reduce the acid and metal load to California Gulch. It would result in an increase in groundwater levels in the various mined areas drained by the tunnel behind the plugs. This would in turn reduce the amount of sulfide minerals exposed to oxidation (SRK, 1986a).

Plugging of the tunnel would not reduce the amount of recharge to the mine areas. Consequently, average annual groundwater movement in the vicinity of the mined areas would remain the same, however, due to the raising of the water table in the workings, a smaller proportion of the recharge would pass through the mine openings and sulfide zones (SRK, 1986c). A larger proportion would be forced to bypass the mined areas (SRK, 1986d). The major discharge areas for groundwater in the mined areas in the absence of the Yak Tunnel drain, would be lower California Gulch and the Black Cloud operation and to a lesser extent lower Evans Gulch (SRK, 1986d).

Continued operation of the Black Cloud Mine necessitates dewatering activities which result in local groundwater "sink" to the south of the Irene group of mines

(SRK, 1986a). Documentation obtained from ASARCO indicates that the Irene shaft is presently in direct connection with the Black Cloud so that presumably water levels in these two group of mines are at about the same level (SRK, 1986a). The partial plugging alternatives under continued operation of the Black Cloud have to consider the influences of this active dewatering.

Current consideration for selective plugging of the Yak Tunnel is being given to positioning a single plug below the Resurrection Group and below the Ibex Group, accompanied by plugs in the connecting laterals with the Irene Group to avoid direct groundwater discharges to the Black Cloud Operation.

The final water levels in the Iron Hill group of mines would be well below the oxide/sulfide interface so that generation of acid mine drainage in this area would still occur. Furthermore, the extensive workings of the Iron Hill group are probably very effective in allowing bypass of a plugged Yak Tunnel in this area.

EPA (1987b) investigated the feasibility of implementing plugs below the Resurrection and Ibex groups. One of the purposes of this study is to investigate the resultant change in water quality downgradient of the Ibex group due to plugging of the Resurrection and Ibex groups.

Plug Below Resurrection Group

A single plug placed below the Resurrection group is not projected to be very effective in reducing the volume of mine drainage to the Yak Tunnel (SRK, 1986a) mainly because it appears that there is a good potential for direct communication through the workings with the Ibex group. Even without direct communication, the relatively high permeability of the Ollie Reed breccia pipe separating the Resurrection group from the Ibex and Irene groups is likely to provide easy bypass of a Yak Tunnel plug at this location. SRK's (1986a) water balance studies indicate that the water level elevation in the Resurrection group could rise from the present assumed elevation of about 10,400 feet AMSL to about 10,550 feet. It is possible that even a relatively low projected rise of water level may have a significant influence on sulfide oxidation. The lowest shaft collar elevation is 11,000 feet AMSL, therefore it is unlikely that any point surface discharges would occur as a result of emplacement of the plug.

Plug Below Ibex Group

Plugging of the Yak Tunnel below the Ibex group would have to be accompanied by plugs in the connecting lateral with the Irene group to avoid direct groundwater discharges to the Black Cloud operation (SRK, 1986a). Continued

dewatering of the Irene workings behind these plugs due to Black Cloud operation would induce flow away from these plugs.

SRK's water balance calculations (1986a) indicate that water levels in the Ibex and Resurrection mine groups would rise between 10,650 and 10,750 feet AMSL during low flow conditions. The topography and shaft collar elevations in the Ibex and Resurrection areas indicate a minimum elevation of about 11,000 feet AMSL in Evans Gulch. Therefore, it is unlikely that surface discharge of groundwater would occur. The final projected water levels would be sufficient to inundate the sulfide zone in the Resurrection Group but not in the Ibex group where sulfides occur at relatively high elevations of about 11,000 feet AMSL.

Most of the groundwater recharging the Ibex and Resurrection groups is projected to flow to the Irene group area. This groundwater flow would bypass emplaced plugs and would eventually be discharged to Iowa Gulch by the Black Cloud dewatering operations.

Yak Tunnel flows are projected to be significantly reduced by this plugging option, however, much of this flow reduction is a result of increased discharge to the Black Cloud operation. If Black Cloud operations were to be discontinued, the absence of leakage to the Irene group would result in water levels behind the tunnel plug rising higher than under operating conditions.

Projected final water level elevations are in the range of 10,800 to 10,900 feet AMSL. The rise in the water level would cause a reduction in the potential sulfide oxidation. The possibility of discharge to the surface is slight as the lowest shaft collar elevations in this area are at 11,020 feet AMSL.

With the Black Cloud operation discontinued, the major discharge area for the Ibex, Irene mines would be the Yak Tunnel downgradient from the Ibex plug. Leakage around the plug to the Yak Tunnel west of the Weston Fault is projected to be in the order of 100 gpm due to the relatively high hydraulic gradients that would be developed across the fault zone. A small increase in recharge to deep bedrock groundwater systems from the mined areas is also projected to occur under this scenario.

Combination of Resurrection and Ibex Plugs

The additional plug below the Resurrection group may reduce the seasonal water level fluctuation in the Ibex group to 20-30 feet. This may help reduce the volume of acid mine drainage generation in the Ibex group.

Chapter 2

MINTEQ

General Information on MINTEQ

The computer program MINTEQ (metal speciation equilibrium model for surface and groundwater) is used in this study to simulate water quality changes resulting from the implementation of plugs in the Yak Tunnel. MINTEQ is a thermodynamic equilibrium, geochemical model, developed for the U.S. Environmental Protection Agency (EPA) to help assess the fate of selected priority pollutant metals in aquatic systems. It combines the best features of two existing geochemical models, MINEQL (Westall et al, 1986) whose development was supported by EPA, and WATEQ3, whose development was supported by the United States Geological Survey (USGS). Information provided in this study concerning MINTEQ is based on Felmy et al., (1984). MINTEQ's mathematical structure was taken from MINEQL. The WATEQ3 features were added to this basic structure. The main features obtained from WATEQ3 are the well referenced thermodynamic data base, temperature correction of equilibrium constants using either the Van't Hoff relationship or analytical expressions for the equilibrium constants as a function of temperature, and ionic strength correction using either the extended Debye-Huckel equation or the Davies equation. MINTEQ can solve a much broader

range of chemical equilibrium problems than WATEQ3 and is much more user-oriented than MINEQL. MINTEQ has a well referenced thermodynamic data base and has added six different sorption algorithms: 1) an "activity" K_d, 2) an "activity" Langmuir equation, 3) an "activity" Freundlich equation, 4) anion exchange algorithm, 5) a constant capacitance surface complexation model, and 6) a triple layer surface complexation model. In addition, a large number of user oriented features such as the ability to handle alkalinity inputs, an initial mass of solid, and different analytical input units were incorporated.

MINTEQ can be used to find solutions to a variety of chemical equilibrium problems that would be far too cumbersome to attempt by hand. MINTEQ is versatile enough to accept a wide variety of chemical equilibrium problems and can be used to mimic conditions present in many natural or laboratory systems. Because MINTEQ is an "equilibrium" model, it can only be used to predict the distributions of chemical species in the gaseous, aqueous, and dissolved phases for systems at equilibrium. Thus, MINTEQ does not have kinetic capability. In many environmental systems the equilibrium assumption may not be valid.

The chemical equilibrium problem can be described by a set of mass balance equations, one for each component, and a set of mass action expressions, one for each species. The problem then reduces to solving the non-linear mass action

expressions with linear mass balance equations. This is commonly termed the equilibrium constant approach to the chemical equilibrium problem.

Definition of Chemical Species

The input program for MINTEQ is called PRODEFA1. It uses six types of classifications for chemical species that are used in the executable file of MINTEQ.

Type 1: Aqueous Basis Species. A "basis species" or "component" is an aqueous species that is used to define equilibria. Only "basis species" are used for reactants in a chemical reaction. Some elements, however, have more than one oxidation state and therefore also have a basis species identifier.

Type 2: Derived Species. A "derived species" is formed from a combination of two or more components.

Type 3: Fixed Species. A "fixed species" can be any species with a fixed activity. Fixed activities are commonly one of four types: 1) components present at a fixed activity, such as pH or pE, 2) solid phases which are present in infinite supply, 3) gases present at a fixed partial pressure, and 4) oxidation/reduction reactions between any two components.

Type 4: Finite Minerals. A finite mineral is one that is initially present in a finite quantity and subject to complete dissolution.

Type 5: Potential Mineral. A "potential mineral" is defined as a mineral that is not present initially, but instead may form during chemical equilibration, if the solubility product is exceeded.

Type 6: Excluded Species. An "excluded species" is an aqueous derived species, an adsorbed species, a mineral or gas that is in the thermochemical data base, but will be ignored while the equilibrium portion of the problem is being solved.

Type 7: Added or Modified Species or Chemical Equilibria. A species or chemical equilibrium that is not in the thermochemical data base, may be added by the user as a Type 7 species. Also included in this classification are species or equilibria that are already in the thermochemical data base but which have been modified for a particular problem by the user.

Aqueous Components

The aqueous phase in MINTEQ consists of chemicals fully dissolved in water. The chemistry of the aqueous phase is generally complex, because it often contains a large number

of chemical species that are in complex equilibrium with each other.

By convention, all reactions are written in terms of aqueous components. The aqueous components are the aqueous species chosen as "basis species."

Charge Balance

An aqueous solution must always be neutral, i.e., the number of positive charges of the aqueous species must equal the number of negative charges. MINTEQ does not use the charge balance equation, however, there is the option of terminating if the charge of the initial aqueous solution is unbalanced by more than 30 percent.

Carbonates

Carbonates are an integral part of aqueous problems involving geochemistry. Inorganic carbon can exist in many forms in an aqueous solution (i.e., H_2CO_3, HCO_3^{-1}, CO_3^{-2}, $CO_2(gas)$, $CO_2(aq)$, $M_x(CO_3)_4$, and $M_x(HCO_3)_4$), and contributes in a major and complex way to the chemistry of aqueous solutions. MINTEQ allows the user to introduce inorganic carbon into the problem via $CO_2(gas)$, total inorganic carbon, carbon alkalinity, or fixed carbonate $(CO_3)^{-2}$. activity.

Alkalinity

Total alkalinity is usually reported by laboratories as mg/l $CaCO_3$, i.e., the number of mg/l of $CaCO_3$ required to use up an equivalent number of milli-equivalents (meq) in titrating to a lower pH. For MINTEQ, alkalinity is expressed in terms of mg/l of CO_3^{-2}, or meq/l CO_3^{-2} which are converted into mg/l CO_3.

Redox Reactions

MINTEQ has the convention that all redox reactions are "half-cell" reactions. Hence they include the electron as one of the components. Although free electrons do not exist in perceptible quantities in aqueous solutions, the redox propensity of a solution can be expressed by the "activity" of the electron. This activity can be calculated from a redox potential or as pE (the negative logarithm of a molality).

Redox problems may arise when an element can exist in two or more oxidation states, i.e., Fe^{+3} or Fe^{+2}. Some aqueous reactions between two oxidation states are very slow and when several multivalent elements are present simultaneously, it is not guaranteed that MINTEQ will be able to predict their behavior in the aqueous phase. Instead of automatically including all the reactions in the

problem, the user is advised to designate only those reactions to be considered.

There are three ways to model redox behavior with MINTEQ: 1) fix the ratio of oxidized to reduced species by fixing the electron activity, 2) establish the total concentrations of each oxidation state for one element and implicitly fix the electron activity by the reaction, or 3) ignore the redox reaction.

Ionic Strength and Activity Coefficient Calculations

The ionic strength of an aqueous phase is obtained by summing the product of molalities of aqueous species multiplied by the square of their charges. The Davies and Extended Debye-Huckel algorithms are used by MINTEQ to calculate activity coefficients for various aqueous species.

The activity coefficient for a species is the ratio of its thermodynamic activity to its concentration. The Davies formula depends only on the charge of the ion and the ionic strength of the medium, this algorithm is only accurate at ionic strength lower than about 0.1 molal. The Debye-Huckel algorithm, however, has one extra general parameter and two ion-specific parameters.

If the Debye-Huckel parameters are not known for a given ion, MINTEQ will revert to the Davies formulation to calculate its activity coefficient. This algorithm is usually accurate up to ionic strength of about 0.5 molal.

When the concentrations of the aqueous species vary during the Newton-Raphson iterations performed by MINTEQ, the ionic strength will also vary.

Chapter 3

RESEARCH METHODOLOGY

Objective

The intent of this study is two fold: (1) to evaluate the hydrogeochemical characteristics of the Yak Tunnel under current conditions, and (2) to evaluate the resultant hydrogeochemical changes as a result of implementing one of EPA's proposed remedial actions to emplace plugs below the Resurrection and Ibex groups. This study uses the computer program MINTEQ to evaluate the thermodynamic behavior of the current Yak Tunnel chemical system and will be used as a tool to predict changes in the hydrogeochemistry of the Yak Tunnel of the remedial alternative. The program calculates saturation states of the aqueous solution with respect to various mineral phases and equilibrium distribution of various species of metals.

Input Parameters

The input data consist of chemical species, temperature, pH,and Eh (or pE). The chemical data to be used in the simulation are based on analytical measurements taken by ASARCO in October, 1973. The October, 1973 measurements are representative of low flow conditions. No information exists on the accuracy of ASARCO data, however,

it does appear to be consistent with flow and water quality measurements conducted by EPA (1987a). Analytical results for concentrations for heavy metals for the ASARCO October, 1973 data represent total concentrations. They are the only data available that allows the relative contribution by flow and quality of the various mined areas drained by the Yak Tunnel.

The concentrations of chemical constituents to be input into MINTEQ are based on the following calculations:

1st Step: Determine Total Loading to the Tunnel. The total loading of chemical constituents to the tunnel is based on the product of the chemical concentrations and the rate of flow into the tunnel based on ASARCO October, 1973 data. The loading of the inflow points to the tunnel have been calculated based on October, 1973 data collected by ASARCO. These data are representative of steady-state conditions in the Yak Tunnel.

2nd Step: Prediction of Yak Tunnel Portal Flow Subsequent to Plugging. It is necessary to predict the flow of water within the Yak Tunnel subsequent to plugging. For the purposes of this study, the total flow is equivalent to the sum of the flow measurements at inflow points below the proposed plugging location below the Ibex Group.

3rd Step: Calculation of Chemical Concentrations Prior to Equilibrium. The chemical concentrations to be input

into MINTEQ have been determined by dividing the total loads to the Yak Tunnel (Calculated in Step 1) by the predicted Yak Tunnel portal flow rates.

These mass balance calculations are based on the assumption that the chemical constituents behave conservatively. In addition, the calculations do not take into consideration the precipitation of chemical constituents under super-saturation conditions.

Derived Input Parameters. The ASARCO (no date) October 1973 data did not provide information on oxidation potential, and sodium and calcium concentrations. The pH of the system was based on field measurements conducted by EPA in November, 1985 (EPA, 1987a). It should be noted that the pH did not vary considerably except for the June, 1985, (See Table 3.1) sampling event (EPA, 1987a). This deviation during the spring snowmelt period may be attributed to increased inflows into the Yak Tunnel from the White Cap lateral. During this time period, inflows of highly acidic water from the White Cap lateral approximately double in magnitude of discharge.

Table 3.1.

pH OF YAK TUNNEL DISCHARGE

Sampling Event	pH
November 1984	6.0
March 1985	6.1
June 1985	3.2
September 1985	6.2
November 1985	5.8

Concentrations of sodium and calcium remained constant even during the June, 1985, sampling event.

The necessity of having calcium and sodium as input parameters was two fold. First, an estimate of these major cations was necessary to provide an accurate cation-an ion balance, thus facilitating convergence of the MINTEQ model. Second, it provided information on calcium and sodium speciation and possible precipitation of these cation complexes.

The oxidation potential of the system was based on the ratio between the ferrous-ferric redox couple measured during the March 1985, and September, 1985, EPA sampling events. The use of ferrous-ferric in determining the oxidation potential in an acid mine drainage environment has been substantiated by Nordstrom et al., (1979). The data collected by EPA and the determination of Eh of the system are presented in Table 3.2.

Table 3.2.

OXIDATION POTENTIAL OF YAK TUNNEL DISCHARGE

Sampling Event	Fe^{2+}(mg/l)	Fe^{3+}(mg/l)	Eh(mV)
March, 1985	1.30	.88	.73
September, 1985	6.20	.90	.69

Although the ratio of the redox couple varies between measurements, the resulting Eh calculations do not change considerably. To determine the influence of error in the

analytical measurement of ferrous and ferric constituents, computer simulations were conducted for both oxidation potentials. The input data for computer simulations by MINTEQ are presented in Table 3.3.

Table 3.3.

INPUT DATA FOR MINTEQ SIMULATION OBTAINED FROM MASS BALANCE CALCULATIONS OF ASARCO 1973 DATA

	Current Conditions (mg/l)	Plugging (Ibex, Resurrection) (mg/l)
Cd	.375	.165
Cu	.256	.069
Pb	.08	.045
Fe	72.3	27.9
Mg	70.7	30.4
Mn	16.8	5.9
Zn	55.5	6.4
SO_4	183.0	214.0
Ca	80.0	80.0
Na	1.4	1.4
pH	6.0	6.0
Eh(mV)	.69	.69
Alkalinity	97.1	95.1

Computer Simulation

The calculated chemical concentrations from the mass balance calculations detailed above were input into PRODEFA1, which is an interactive program built to help users develop an input data file for MINTEQ. PRODEFA1 makes activity guesses for the entered components and converts all input concentrations to molal concentrations.

MINTEQ was used in this study to predict the resultant water quality of the Yak Tunnel subsequent to plugging the Yak Tunnel below the Ibex Group. The use of MINTEQ enabled the prediction of precipitation of metals in solution in the form of inorganic metal complexes, the equilibrium distribution of various species of metals and the role of complexation in relation to the solubility of a chemical constituent.

Precipitation. The utilization of MINTEQ enabled the prediction of the tendency of a solid phase to precipitate once the plugging is implemented. The thermodynamic tendency of a solid phase to precipitate or dissolve depends upon the Saturation Index (S.I.). The Saturation Index is the logarithmic ratio of the Ion-Activity Product of dissolved constituents of a solid phase at disequilibrium over the equilibrium constant (solubility product at a given temperature) for the compound. The S.I. is calculated by the following expression:

$$S.I. = \text{Log } (IAP/Keq)$$

If the S.I. is positive for a solid phase, the solution is supersaturated with respect to that specific compound, so, the solid species has a tendency to precipitate. Conversely, if the S.I. is negative (<0), then the solid species has a tendency to dissolve.

Through the calculation by MINTEQ of the Saturation Index, one can predict the thermodynamic tendency of metals in solution to precipitate in the form of inorganic metal complexes.

Ion Complexation

The application of MINTEQ enabled the prediction of equilibrium distribution of various species of metals under current condition and subsequent to the partial plugging alternative. The Tunnel effluent is a metal enriched, sulfate water. Because of the thermodynamic tendency to complex, when waters have large sulfate concentrations, sulfate complexes are normally quite important (Freeze and Cherry, 1979).

The chemical analysis of chemical constituents indicate the total concentration of the constituents, but not in the form in which the constituents occur in the effluent. Some constituents are present almost entirely in the simple ionic form. Other ions, such as calcium and magnesium, are present in the ionic forms, Ca^{+2} and Mg^{+2}, and inorganic ion associations such the uncharged (zero-valence) species, $CaSO_4$, $CaCO_3$, $MgSO_4$, and $MgCO_3$ and the charged associations, $CaHCO^{3+}$ and $MgHCO^{3+}$. These charged and uncharged associations are known as complexes and can greatly enhance the solubility of a chemical constituent.

The complexes form because of the forces of electrical attraction between the ions of opposite charges. The chemical constituent input parameter for MINTEQ is equivalent to the total dissolved concentration of an inorganic species C(i) and can expressed as:

C(i) = Sum C (free ion) + Sum C (inorganic complexes).

Testing of the Applicability of MINTEQ to Geochemically Modeling the Yak Tunnel System

The applicability of the MINTEQ geochemical computer simulation in this system was tested by comparing values predicted from MINTEQ to the observed concentration in the present system. From this comparison, one can determine the extent to which the assumption that equilibrium conditions are present.

Specifically, the ability of MINTEQ to predict precipitation of metals and the increase in solubility due to complexing was tested.

Evaluation of Remedial Alternatives

Since SRK (1986a) has deemed a sole plug below the Resurrection Group technically non-beneficial, this study will only concentrate on the plugging alternatives that block flow upgradient from directly below the Ibex Group. For the purpose of this study, it is assumed that the

resultant effluent quality of the Yak Tunnel would be the same for the option of only plugging directly below the Ibex Group as well as directly below the Resurrection Group. Data obtained by ASARCO (no date) for October, 1973, will be used for the evaluation of the proposed remedial alternative through the geochemical equilibrium simulation by the computer program MINTEQ.

Chapter 4

RESULTS AND DISCUSSION

Evaluation of Present Conditions

To assess the applicability of the use of MINTEQ in evaluating the hydrogeochemistry of the Yak Tunnel, present condition were simulated and compared against analytical results obtained by EPA (1987a). As stated previously, computer simulations were conducted for oxidation potentials that corresponded to both ferrous-ferric redox couple ratios taken by EPA. Results of the computer simulation did not vary considerably between different oxidation potentials. For the purpose of simplification, only results that represent an oxidation potential of the system of 0.71 mV will be presented when displaying results of MINTEQ simulations.

Comparison of Analytical Results. A comparison of chemical constituent concentrations based on mass balance concentrations and concentrations based on equilibrium simulation through the use of the equilibrium geochemical program MINTEQ, is provided in Table 4.1. In addition, analytical concentrations for sampling conducted by EPA (1987a) are also provided in this table. As might be expected, mass balance concentrations compare reasonably well with EPA data for mobile chemical constituents such as

manganese, zinc and magnesium. In comparison to EPA November, 1985 data, Concentrations derived by mass balance calculations show a 2 percent increase for magnesium, 16.6 percent decrease for zinc and 17 percent decrease in manganese. Based on this comparison, one may conclude that the data acquired by ASARCO in October 1973, is of reasonable quality. Mass balance concentrations do not compare well for iron, cadmium and sulfate with respect to the results of the EPA analysis. The results obtained for iron through use of MINTEQ provide a much better assessment than mass balance calculations because of the allowance for precipitation of the iron minerals, magnetite and siderite.

Table 4.1.

COMPARISON OF CONCENTRATIONS FOR THE YAK TUNNEL EFFLUENT (Mass Balance Calculations Based on ASARCO, 1973 data)

CURRENT CONDITIONS

	EPA November 1985 Data	Mass Balance	MINTEQ Simulation
Cd	.270	.375	.066
Cu	.265	.26	.26
Pb	Undetected	.08	.08
Fe	5.36	72.3	33.5
Mg	69.0	70.7	70.7
Mn	20.5	16.8	16.8
Zn	65.9	55.5	55.5
SO_4	578.0	182.9	182.9
Flow (l/min)	1,870	1,840	1,840

* Corrected for flow from Irene 1330 lateral

Precipitation. Based on the MINTEQ calculations, three minerals reach supersaturation and precipitate out of solution under current conditions. These minerals are magnetite (Fe_3O_4), siderite ($FeCO_3$), and otavite ($CdCO_3$). The magnitude of precipitation of these minerals is provided in Table 4.2. The minerals hematite (Fe_2O_3), rhodochrosite ($MnCO_3$), smithsonite ($ZnCO_3$) and $ZnCO_3$, - $1H_2O$ are close to saturation in the Yak Tunnel system with a saturation index of greater than -1.0. The actual occurrence of precipitation of these minerals in the Yak tunnel was not verified in this study. In order to verify these results, the identification of minerals through the use of x-ray diffractometry is necessary.

Table 4.2.

YAK TUNNEL PRECIPITATES
(Based MINTEQ Simulation of ASARCO
1973 data)
Current Conditions

Mineral	Concentration
Magnetite	1.09×10^{-4} moles
Otavite	2.63×10^{-7} moles
Siderite	2.56×10^{-4} moles

Based on observed results, cadmium is reasonably mobile in the Yak Tunnel aqueous system. MINTEQ calculations indicate, however, that under equilibrium conditions, cadmium tends to precipitate in the form of the mineral otavite.

Compared to most other heavy metals, cadmium is relatively mobile in the aqueous environment. However, otavite has a low solubility product. This mineral tends to precipitate in waters of relatively high alkalinities. The solubility of cadmium in water is usually inversely related to the pH value and amount of organic material present. Since the Yak Tunnel aqueous system is slightly acidic and is void of organic material, one would expect cadmium to be mobile. Yet, due to the high alkaline loadings, under equilibrium conditions, cadmium tends to precipitate based on MINTEQ calculations. The discrepancies between MINTEQ calculations and observed results may be attributed to the insufficient residence times of cadmium in the Yak Tunnel aqueous system.

Speciation. Chemical analysis of chemical constituents indicate total concentration of constituents but not the form in which the constituents occur in water. Constituents can be present in simple ion form, or in charged and neutral complexes. Toxicity of metals in solution is related to the form in which it occurs. In most instances, the element is most toxic in its free ionic form.

The complexes form because of the forces of electrical attraction between the ions of opposite charge. Geochemical simulations through the use of MINTEQ provide information on the chemical form in which the elements are present in

solution. This is extremely useful in the assessment of water quality of metal laden waters.

Recent studies of the upper Arkansas River have found the aquatic system significantly impacted downstream of the California Gulch confluence due to heavy metal contamination (LaBounty et al., 1975). The population of fish, dominated by brown trout (Salmo trutta), is severely reduced downstream of the confluence (State of Colorado, 1986). This observation has been attributed to heavy metal concentrations which reach lethal levels and to long-term exposure to heavy metals which reduces the reproductive capacity of trout (State of Colorado, 1986). The heavy metals of principle concern in the Arkansas River are zinc and cadmium. Concentrations for both metals exceed Federal Aquatic Life Criteria standards downstream of the California Gulch - Arkansas River confluence. Because of the importance of complexing in sulfate dominant waters, such as the Yak Tunnel effluent and the deleterious effects of heavy metal contamination in the Arkansas River, it is beneficial to examine the role of complexation in the Yak Tunnel effluent.

As one might expect, based on MINTEQ calculations, sulfate forms complexes readily (31 percent complexed). A substantial amount of cadmium and zinc is present in a complexed form. In the current Yak Tunnel system, 23 percent of the cadmium and 20 percent of the zinc in solution are complexed. Although these elements are not

biologically available in their complex form, once the Yak Tunnel effluent is diluted with waters of less sulfate concentrations, such as the Leadville Sewage Treatment effluent and the Arkansas River, these metals may become biologically available in their ionic form.

Input Data Evaluation. Because of the comparison of mobile chemical concentrations based on mass balance calculations and EPA (1987a) data, one may conclude that the ASARCO October 1973, data are of reasonable quality. In addition, the cation/anion balance was within acceptable limits (13 percent).

The oxidation potential of the system was based on the analysis of the ferrous-ferric redox couple taken at the portal of the Yak Tunnel by EPA (1987a). Nordstom et al., (1979) in an acid mine drainage environment found that 77 percent of the oxidation potential values determined by the ferrous-ferric redox couple fall within +/- 30 mV of those measured with a platinum electrode. According to this study, the largest source of error in determining the oxidation potential in a system using the ferrous-ferric redox couple is the analytical data. The next largest source of error seems to be the adequacy of the activity coefficients and stability constants. Although there are differences in analytical measurements conducted by EPA, the oxidation potential derived from the different sampling events does not differ substantially. Thus, this input

parameter is not considered a significant source of error in this study.

Another input parameter was the pH concentration of the aqueous system. This input parameter was based on four separate sampling events. The pH did not substantially vary (5.8 - 6.2) for EPA sampling events except during the spring snowmelt sampling period (June 1985). As cited above, the cation/anion balance for the MINTEQ simulation, with the inclusion of pH, was within reasonable limits. If the estimation of pH deviated substantially from actual conditions, there would be a substantial cation/anion imbalance.

Based on EPA (1987a) data, seasonal variations of analytical concentration do not substantially vary except during the spring snowmelt period. Thus, ASARCO October 1973, data, along with the derived input parameters may be considered valid in representing the water quality of the Yak Tunnel effluent, except during spring snowmelt periods. The Yak Tunnel system changes dramatically during the spring snowmelt period. Most of the recharge to the bedrock system occurs during this period. Increased recharge occurs of a local basis from surface water flows and alluvial underflow due to undermining of the creek areas. This results in high seasonal inflows from the White Cap lateral into the Yak Tunnel. Yak Tunnel inflows from the White Cap lateral are significantly degraded in comparison to other inflow points.

Thus, during spring snowmelt periods, due to increase discharge from the White Cap lateral, the Yak Tunnel effluent tends to be extremely acidic (i.e., pH 3.2). Because of significant hydrological and geochemical change in the Yak Tunnel system during the spring snowmelt period, the analytical concentrations of chemical constituents presented in this study are not representative of conditions during the spring snowmelt period.

Evaluation of Methodology. The results obtained through the use of MINTEQ in this study are based on the assumption that equilibrium conditions within the Yak Tunnel have been attained. The equilibrium state is a state of maximum stability which a closed physicochemical system proceeds by irreversible processes (Stumm and Morgan, 1970). When the reaction rates of the system are very fast in relation to the residence time in waters, the equilibrium assumption can be considered valid. If reaction rates are comparable or slower than the residence time in waters, however, this assumption is not reasonable. According to Langmuir and Mahoney (1986), homogeneous reactions occurring within waters are generally very fast, with half times of seconds or less and so can be considered in equilibrium. On the other hand, reactions between the water and minerals such as precipitation/dissolution (a heterogeneous reaction) have half-times usually of days to tens of years or more. In addition, a substantial degree of error is

inherent within the equilibrium models such as MINTEQ through the use of thermodynamic constants obtained through laboratory measurements that vary by orders of magnitude between different researchers and may not be indicative of natural conditions.

Despite these inaccuracies, equilibrium models have great value because of their capability for establishing boundary conditions on the chemical processes (Freeze and Cherry, 1979). Differences between observed hydrogeochemical conditions can provide insight into the behavior of the system and at a minimum can provide a quantitative framework with which appropriate questions can be posed (Freeze and Cherry, 1984).

Results from MINTEQ simulations indicate that otavite, a cadmium carbonate mineral, precipitates out of solution. Mass balance calculations indicate that cadmium loadings into the Yak Tunnel are greater than measured values at the portal. Although this discrepancy could be attributed to analytical error, it is probably related to the precipitation of otavite. MINTEQ results appear to overestimate the magnitude of precipitation. This observation may be related to the possibility that equilibrium has not been reached concerning this reaction. Results from MINTEQ calculations do not take into account kinetics or rates, of chemical reactions. Many chemical reactions which are thermodynamically favorable may not

occur to an appreciable extent due to kinetically imposed constraints (i.e. precipitation/dissolution reactions).

MINTEQ is only accurate in predicting speciation and precipitation/dissolution of a very well defined system that may not be reflective of actual conditions. Although many of the parameters used in this study were reasonably defined, parameters such as biologically mediated reactions that may potentially impact the water quality of the Yak Tunnel system were not taken into consideration.

Influence of Sorption. To assess the transport and fate of metals in the Yak Tunnel hydrogeochemical system, the influence of sorption was investigated in this study. In a water/sediment system, dissolved substances have a tendency to partition themselves between the solution and the mineral grains and other solids present. This partitioning is called sorption. Based on the observed "yellow boy" in the Yak Tunnel, it was determined that amorphous iron oxyhydroxide should be considered as the sorbing solid (sorbent) in this system. The ability for the sorption of metals onto iron oxyhydroxides is greatly dependent upon the pH of the system, since the pH of the system influences the surface charge of the sorbent. The surface charge results from the adsorption of H^+ or OH^- groups onto surface sites which have unsatisfied bonds or broken bonds (Langmuir and Mahoney, 1986).

In this study, the transport of zinc and cadmium were assessed. These two metals are of concern because the Federal Aquatic Life Criteria standards for these metals are exceeded below the California Gulch - Arkansas River confluence. The sorption of these two metals onto amorphous iron oxyhydroxides was measured by Benjamin and Leckie (1981) as a function of pH.

According to their study, at metal ion concentrations of 5×10^{-5} M and a pH of 6.0, cadmium does not sorb and less than 10 percent of zinc sorbs onto the amorphous iron oxyhydroxide. Based on this information, it appears that sorption is not a significant influence on the attenuation of cadmium and zinc in the Yak Tunnel hydrogeochemical system.

Evaluation of the Ibex and Resurrection Remedial Plugging Alternative

The intent for emplacing plugs below the Resurrection and Ibex groups is to reduce loadings of metals from the distal portion of the Yak Tunnel. Mass loading calculations of the proposed remedial action are compared to current values of metal loadings in Table 4.3.

In addition, the resultant chemical concentrations based on mass balance calculations and MINTEQ simulations subsequent to plugging are presented in Table 4.4 and compared with EPA results (1987a).

Table 4.3.

COMPARISON OF LOADINGS OF PROPOSED REMEDIAL ACTION WITH PRESENT CONDITIONS (Based on ASARCO 1973 Data)

	Current Conditions (mg/min)	Plugging (Ibex, Resurrection) Plugs (mg/min)
Cd	696	173
Cu	475	72.8
Pb	147	47.9
Fe	134,000	29,200
Mg	131,000	31,900
Mn	31,100	6,160
Zn	103,000	6,640
SO_4	339,000	224,000

Table 4.4.

COMPARISON OF 1985 YAK TUNNEL CONCENTRATION DATA WITH CONCENTRATIONS OBTAINED FROM MINTEQ SIMULATION OF EPA's PROPOSED REMEDIATION (Plugging of Ibex and Resurrection Groups)

	EPA (mg/l) November 1985	MINTEQ (mg/l) Simulation
Cd	.270	.057
Cu	.265	.069
Pb	Undetected	.045
Fe	5.3	15.6
Mg	69.0	30.4
Mn	20.5	5.9
Zn	65.9	6.4
SO_4	578.0	214.0
Flow (l/min)	1,870.0	840.0

Water Quality. In comparison to concentrations for of metals in the Yak Tunnel effluent under current conditions (based on ASARCO October 1973 data, Table 4.1) and predicted concentrations of metals as a result of the proposed selective plugging remedial alternative, all concentrations of metals will decrease subsequent to remediation. Zinc

will decrease 94 percent, manganese 64 percent, iron 42 percent (based on MINTEQ results), copper 63 percent, and magnesium 56 percent.

The reduction of metals is principally attributed to the cessation of inflow for the Ibex No. 4 Shaft and the Resurrection Group. Although inflow from the Ibex No. 4 Shaft contributes only 10 percent of the current Yak Tunnel discharge volume, loadings of metals (Mg, Mn, Cd, Cu, and Zn) from this inflow point are significant. In addition, under current conditions, the Resurrection Group is a major source of iron and zinc loading to the Yak Tunnel.

Speciation. Based on MINTEQ, the speciation of the metals in the resultant Yak Tunnel effluent will not appreciably change (< 1 percent) subsequent to the proposed selective plugging remedial alternative. Although it is anticipated that the percentile distribution of metal species will remain constant, the amount of biologically available metals, in their ionic form, will decrease with the reduction of loading.

Precipitation. Based on MINTEQ, the minerals magnetite and otavite reach supersaturation and precipitate (See Table 4.5). The minerals hematite (Fe_2O_3), siderite ($FeCO_3$), rhodochrosite ($MnCO_3$), smithsonite ($ZnCO_3$), $ZnCO_3$, 1 H20 are near saturation with saturation indexes of greater than -1.0.

Table 4.5.

YAK TUNNEL PRECIPITATES
(Based on MINTEQ Simulation of
ASARCO 1973 Data)

Plugging Scenario

Mineral	Concentration
Magnetite	7.08×10^{-5} moles
Otavite	9.07×10^{-7} moles

Hydrogeologic Evaluation. This study assumes that there is no bypass of the plugs in the Yak Tunnel. Once plugs are emplaced below the Resurrection and Ibex groups there is an indication that there will be bypass of the plugs. Because of the possibility of direct communication of the Resurrection group with the Ibex group and the relatively high permeability of the Ollie Reed breccia pipe separating these two groups, there is a likelihood of easy bypass of the plug below the Resurrection plug (SRK, 1986d). Furthermore, the emplacement of a plug below the Ibex group accompanied by plugs in connecting laterals with the Irene group will probably result in an increase of groundwater discharge to the Black Cloud workings (SRK, 1986d). It is predicted that the emplacement of plugs below the Resurrection and Ibex groups will cause 20 gpm to bypass the plugs and flow into the Yak Tunnel below the Ibex group. The quality of this water that may bypass the plugs will probably be better than under current conditions due the

inundation of sulfide deposits in these groups as the groundwater level rises subsequent to plugging.

Because of the rapid and unpredictable variations and changes during the spring snowmelt period, the resultant water quality of the Yak Tunnel subsequent to plugging cannot be quantified. During this time period, flows from the White Cap lateral into the Yak Tunnel of poor quality would significantly increase, whereas, there would be limited inflow from waters upgradient due to plugging. Thus, one would expect that the resultant water quality of the Yak Tunnel effluent would be exacerbated by the plugging alternative during the spring snowmelt period.

Overall, it appears that the emplacement of plugs below the Ibex and Resurrection groups will significantly reduce the loadings of metals and the resultant concentrations of metals. The speciation of the chemical constituents, will not change substantially. Results of the analysis of the plugging alternative through the use of the equilibrium program MINTEQ, indicate that many of the same water-mineral reactions that occur under present conditions (i.e. precipitation of magnetite) will also occur subsequent to plugging.

Chapter 5

CONCLUSION

In this study, the relative hydrogeochemical characteristics in the Yak Tunnel under current conditions, and resultant hydrogeochemical changes subsequent to selective plugging (one of EPA's proposed remedial alternatives) were evaluated, using the computer chemical equilibrium program, MINTEQ. This study, however, did not evaluate the Yak Tunnel system during the spring snowmelt period due to (1) insufficient data, (2) inability to predict hydrologic variations, and (3) inability to predict resultant changes in water quality.

The major inaccuracies associated with this program are: (1) MINTEQ calculations do not take into account kinetics or rates of heterogeneous chemical reactions, (2) many of the thermodynamic constants used in MINTEQ calculations may not be accurate or indicative of natural conditions, and (3) results from MINTEQ are only accurate in for a very well-defined system and may not be reflective of actual conditions. Despite these inaccuracies, the use of this program proved valuable for (1) establishing boundary conditions on the chemical processes, (2) predicting homogeneous reactions, (3) providing insight into hydrogeochemical conditions through identifying differences between observed conditions.

Under current conditions, the Yak Tunnel discharge is characterized by low pH (high acidity) and high concentrations of iron, zinc, lead, copper, cadmium and manganese. In this effluent, complexation of metals plays a significant role. thirty-one percent of the sulfate, 23 percent of the cadmium and 20 percent of the zinc are present in complexed form in the Yak Tunnel system. Iron, in the Yak Tunnel system, tends to precipitate readily. Although MINTEQ results indicate that otavite ($CdCO_3$) precipitates readily under current conditions, observed analytical results do not confirm this occurrence. This discrepancy may be attributed to a long reaction rate in comparison to the residence time of the effluent. Due to the acidic nature of the Yak effluent, it appears that sorption is not a significant influence regarding the attenuation of the principal metals of concern, cadmium and zinc.

Due to the cessation of flow into the Yak Tunnel from the Ibex No. 4 Shaft and the Resurrection Group, selective plugging of the upper portion of the Yak Tunnel will significantly reduce the loading of metal constituents to the lower portion of the tunnel. As a result, the water quality of Yak Tunnel effluent will be significantly enhanced. Based on ASARCO 1973 data, subsequent to the subject remediation, concentrations of metals in the Yak Tunnel will be reduced by the following percentages: 94 percent reduction of zinc, 64 percent reduction of

manganese, 42 percent reduction of iron, 63 percent reduction of copper and 56 percent reduction of magnesium. Although the loadings of metals to the tunnel will significantly decrease, the speciation of the metals will remain constant. Although the reduction of iron will be significant, it is predicted that iron will continue to precipitate subsequent to selective plugging.

REFERENCES CITED

ASARCO, no date. Yak Tunnel water quality and quantity; flow rates for 12 locations along the Yak Tunnel, October 20, 1973 and June 24, 1975 and percent of total. Contains individual water samples for 1973 summary above, pH, temperature, review of results.

ASARCO, 1983. Some Facts Concerning the Yak Tunnel. Unpublished. Wallace, Idaho.

Ball, J.W., E.A. Jenne and M.W. Cantrell. 1981. WATEQ3: A Geochemical Model with Uranium Added. U.S. Geological Survey Open File Report 81-1183.

Behre, C.H. Jr. 1953. Geology and Ore Deposits of the West Slope of the Mosquito Range. U.S. Geological Survey Professional Paper 235.

Benjamin, M.M., J.O. Leckie. 1984. Multiple-Site Absorption of Cd, Cu, An, and Pb on Amorphous Iron Oxyhydroxide. Hournal of Colloid and Interface Science, volume 79, No. 1: 209-221.

EPA, 1987a. Remedial Investigation California Gulch-Yak Tunnel.

EPA, 1987b. Feasibility Study, Yak Tunnel Operable Unit.

Emmons, S.F., J.D. Irving, and G.F. Loughlin. 1927. Geology and Ore Deposits of the Leadville Mining District, Colorado. U.S. Geological Survey Professional Paper No. 148.

Felmy, A.R., D.C. Girvin, and A. Jenne. 1984. MINTEQ - A Computer Program For Calculating Aqueous Geochemical Equilibria. EPA-600/3-84-032, PB54-157148, U.S. Environmental Protection Agency, Athens, Ga.

Forstner, U., and Wittman, G.T.W. 1983. Metal Pollution in the Aquatic Environment. Springer-Verlag, New York, New York.

Freeze, A.R. and J.A. Cherry. 1979. Groundwater. Prentice-Hall, Inc. Englewood, Cliffs, New Jersey.

Garrels, R.M. and M.E. Thompson. 1960. Oxidation of pyrite by iron sulfate solutions. Amer. Journ. Sci., Bradley Volume, 258-A: 57-67.

HRS Water Consultants. 1984. Hydrogeological Evaluation of the Yak Tunnel and California Gulch. Lakewood, Colorado.

Hydro-Search, Inc. 1986. Water-Quality Modeling Study Yak Drainage Tunnel Leadville District, Leadville, Colorado. Golden, Colorado.

Johnson, C., et al., 1983. "Yak Tunnel Inspection Trip," February 23, 1983. Field notes by ASARCO staff members.

LaBounty, J.F., J.J. Sartoria, L.D. Klein, E.F. Monk, and H. A. Salman. 1975. Assessment of Heavy Metals Pollution in the Upper Arkansas River of Colorado. U.S. Department of the Interior, Bureau of Reclamation, Denver, Colorado.

Langmuir, D. and J. Mahoney, 1986. Chemical Equilibrium and Kinetics of Geochemical Processes in Ground Water Studies. Canadian/American Conference on Hydrogeology, Pratical Applications and Ground Water Geochemistry. (B. Hitchon and E.I. Wallick, eds.). National Well Water Association, Worthington, OH.

Luke, J. 1978. A brief history of the Yak Tunnel. Mountain Diggings 8(1):20. LCCCA, Leadville, Colorado.

McLaughlin Engineers. 1981. Colorado Inactive Mine Drainage Water Quality and Impact Abatement. Preliminary Engineering Report. Prepared for the Division of Mined Land Reclamation, Colorado Department of Natural Resources, Denver, Colorado.

Noble, A., 1986. California Gulch Project, Yak Tunnel Connections and Geology.

Nordstrom, D.K., E.A. Jenne, and J.W. Ball. 1984. Redox equilibria of iron in acid mine waters in E.A. Jenne (ed.). Chemical Modeling in Aqueous Systems. American Chemical Society Symposium Series No. 93.

SRK (Steffen, Robertson and Kirsten). 1986a. Technical Memorandum No. 11001/01, California Gulch Operable Unit Feasibility Study - Yak Tunnel Geologic, Mining and Hydrologic Study. Prepared for CH2M Hill, December 1986.

SRK (Steffen, Robertson and Kirsten). 1986b. Technical Memorandum No. 11001/04, California Gulch Operable Unit Feasibility Study - Yak Tunnel Plug Design. Prepared for CH2M Hill, December 1986.

SRK (Steffen, Robertson and Kirsten). 1986c. Technical Memorandum No. 11001/03, California Gulch Operable Unit Feasibility Study - Yak Tunnel Rehabilitation and Maintenance. Prepared for CH2M Hill, December 1986.

Singer, P.C., and W. Stumm. 1970. Acid mine drainage: the rate determining step. Science 167: 1121-1123.

State of Colorado. 1986. Yak Tunnel/California Gulch Remedial Investigation, February 28, 1986.

Stumm, W. and J.J. Morgan, 1970. Aquatic Chemistry. Wiley-Interscience, New York, New York. 583 pp.

Tainter, S.L. 1952. Ibex-Sunday Area, Leadville, Colorado, Yak Tunnel. Memorandum for Mr. D.J. Pope, Salt Lake City, Utah, June 9, 1952.

Turk, J.T. and G.J. Taylor. 1979. Appraisal of Ground Water in the Vicinity of the Leadville Drainage Tunnel, Lake County, Colorado. U.S. Geological Survey on Open File report 79-1538. Lakewood, Colorado.

U.S. Bureau of Reclamation, 1979. Study of Effects on Plugging the Leadville Drainage Tunnel. Special Report, September 1979, U.S. Bureau of Reclamation Lower Missouri Region.

Westall, J.C., J.L. Zachary, and F.M.M. Morel. 1986. MINEQL, A Computer Program for the Calculation of Chemical Equilibrium Composition of Aqueous Systems. Tech. Note 18, Dept. of Civil Eng., Massachusetts Institute of Technology Cambridge, Massachusetts.