A WATER HANDBOOK FOR METAL MINING OPERATIONS

by

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Colorado Water

Resources Research Institute

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by

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ABSTRACT

This completion report is a handbook that operators
of metal mines can use to understand how the various sub-
stances originate in mine water and what can be done to
eliminate or control their occurrence. The introductory
chapters review the chemical weathering reactions of rock-
forming, and ore minerals, and the environmental standards
that apply to drinking water and mining and milling effluents.
Then there is a discussion of how various physical factors
such as ore petrology, groundwater hydrology, and type of
ore occurrence can affect the quality of mine drainages.
This chapter is based on extensive investigations of
mine drainages within the Front Range of Colorado. A plan
for analysis of mine waters that emphasizes understanding
the chemical nature of the water is established. Finally
suggestions for water maintenance are made based on the
chemistry of the water and the analysis schedules. An
appendix is a manual of common methods of analysis which
emphasizes how to conduct successful tests in the environ-
ment of a mining operation.

INTRODUCTION

The object of this report is to provide a description of the chemistry of water draining from mining operations. A knowledge of the chemistry of the water should yield an understanding of how the constituents in the water came to be. From this understanding, one can determine the source of the water and what the first methods of treatment should be for the effluents from a mining operation. Most of the examples used in this handbook are from metal mines. All of our studies have been done in the Front Range Mineral Belt of Colorado. So the handbook particularly pertains to mines that are working complex sulfide ore deposits.

The chemical nature of mine drainages is the first topic to be developed. Emphasis in this section is placed on relating the contituents in the water to the weathering of the ore body. Then, the aspect shifts to how physical factors such as the type of ore deposit or the availability of water affect the chemistry of the water. With the development of a scientific basis for the water quality, a monitoring scheme which can test for alternate types of water is proposed. Finally, suggestions are made for abatement of any environmental problems.

The Environmental Protection Agency has published a number of reviews (1, 2, 3, 4, 5) on mine effluents. The emphasis in these documents is on abatement technology of an industrial effluent. This handbook considers the water

constituents as natural products of the weathering of minerals. If the nature of these weathering reactions is more understood, then perhaps control procedures which limit those reactions can be used. Abatement methods which stop the pollution from occurring will decrease the need for waste water treatment facilities for a mining operation. Many of the abatement procedures which are suggested in the EPA documents (2) are the same as those which are suggested here, the difference being that the scientific basis for those procedures will be more fully explained in this guide.

Besides the EPA documents, other texts and reviews have been used for background information. The general texts by Stumm and Morgan (6) and by Hem (7) are useful summaries of the properties and chemistry of water. Reviews specific to mine drainages that are of interest are those by Wentz (8), Moran and Wentz (9), and the American Water Resources Symposium, No. 18 (10). Some of the results of the studies on Front Range Mine drainages have already been published (11, 12).

The analytical procedures that have been used in this research have been those suggested in the Standard Methods Manual for Water and Wastewater (13) or the U.S. Geological Survey water analysis manual (14). The methods of collection and analysis specific to mine drainages have already been published (15). Monitoring procedures will be discussed in a later section and the analyses required to do that monitoring will be more fully explained in that section.

THE CHEMICAL NATURE OF MINE DRAINAGES

THE WEATHERING OF ROCKS

Rocks exposed at the earth's surface are subjected to alteration by the chemical, physical or biological processes. This is called weathering, and chemical weathering is most important here. This section on weathering processes is a summary of what is found in Garrels and McKenzie (16) and Krauskopf (17).

The species in typical rain water and the dissolved species in typical river water for North America are shown in Table I (16). The constituents added between the rain and the river must come from the earth's crust. They are primarily derived from the weathering of the minerals in rocks. The reactions of minerals with air and water are certainly diverse; a study of the different types of igneous rocks, sediments and soils will confirm this. However, some useful generalizations can be made about weathering reactions. The outline below categorizes the most important reactions and provides useful examples (16):

A. Congruent Reactions - all the products are soluble in water

    1. Simple Salts - simple dissolution

$$NaCl_{(s)} \rightleftarrows Na^+(aq) + Cl^-(aq) \tag{1}$$

    halite

$$Ca \cdot SO_4 \cdot 2H_2O_{(s)} \rightleftarrows Ca^{2+}(aq) + SO_4^=(aq) + 2H_2O \tag{2}$$
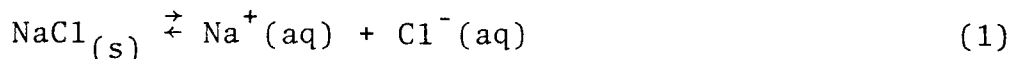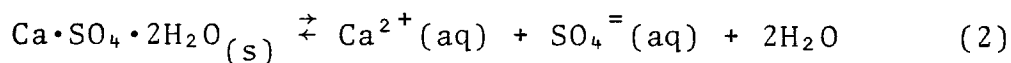
    gypsum

Table I. Dissolved Constituents in Some Natural Waters.
(Units are in mg/1 unless stated)

	Rain Water	River Water	Coal Mine Drainage	Metal Mine Drainage
Location	Menlo Park, Calif.	Mississippi @ New Orleans	Avg. for Acid Drainage	Argo Tunnel Colorado
Reference	(16)	(16)	(1)	(35)
SiO_2	0.29	6.7		48
Al			43	24
Fe		0.04	268	190
Mg	0.37	42		150
Ca	0.79	12		320
Mn			7.3	90
Cu				6.3
Zn			1.5	44
Cd				0.15
Pb				0.10
Na	2.0	25		22
K	0.25	2.9		3.4
As				0.20
HCO_3^-	4.0	132		
CL^-	3.43	30		
$SO_4^=$	1.39	56	2370	2270
pH	5.7	7.5	4.0	2.5
cond.[a]		421		3110

Cond.[a] = conductivity in μmho/cm

2. Carbonate Minerals - reactive dissolution

$$CaCO_{3(s)} + CO_{2(g)} + H_2O \rightleftarrows Ca^{2+} + 2HCO_3^- \qquad (3)$$

calcite

or $CaCO_{3(s)} + HCO_3^- + H^+ \rightleftarrows Ca^{2+} + 2HCO_3^- \qquad (4)$
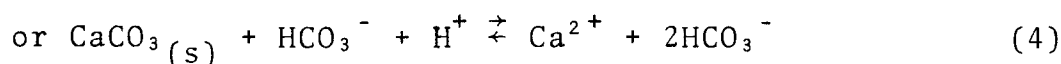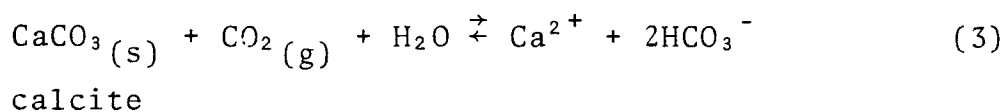
In this case, reactants in the weathering came from the water or air.

3. Quartz - reactive dissolution

$$SiO_{2(s)} + 2H_2O \rightleftarrows H_4SiO_{4(aq)} \qquad (5)$$

quartz

$$SiO_{2(s)} + H_2O + OH^- \rightleftarrows H_3SiO_4^- \qquad (6)$$
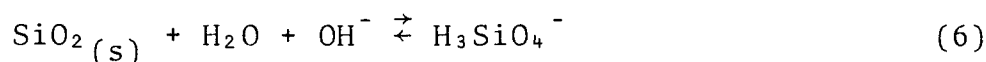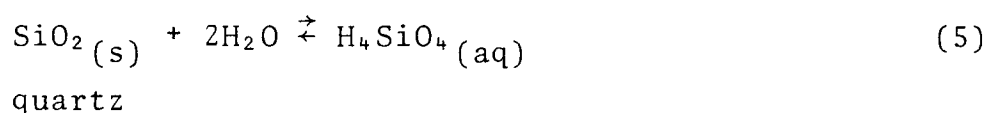
B. Incongruent Reaction - solid residues are deposited as products

1. Simple silicates - congruent or incongruent

$$Mg_2SiO_{4(s)} + 4CO_{2(g)} + 2H_2O \rightarrow 2Mg^{2+} + 4HCO_3^- +$$
$$H_4SiO_{4(aq)} \qquad (7)$$

Mg-olivine

or
$$Mg_2SiO_{4(s)} + 4CO_{2(g)} + 2H_2O \rightarrow 2Mg^{2+} + 4HCO_3^- +$$
$$SiO_{2(s)} \qquad (8)$$
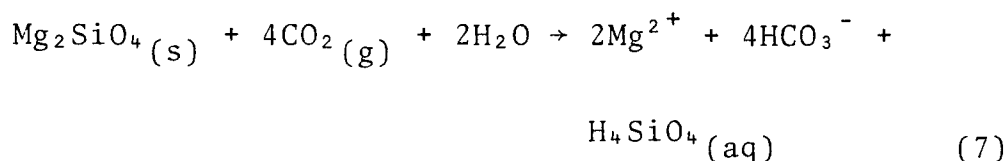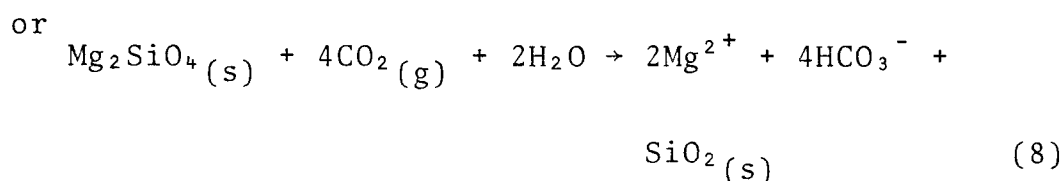
2. Alumino Silicates - deposition of clay

$$2\ NaAlSi_3O_{8(s)} + 2CO_{2(g)} + 11H_2O \rightarrow Al_2Si_2O_5(OH)_{4(s)}$$

albite   kaolinite

$$+ 2Na^+ + 2HCO_3^- + 4H_4SiO_4 \qquad (9)$$
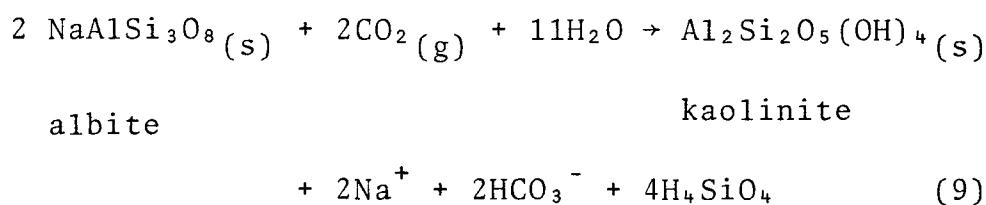
C. Oxidation - Reduction Reaction

1. Iron Silicates - dissolution to Fe(II)

$$Fe_2SiO_4 + 4CO_2 + 2H_2O \rightarrow Fe^{2+} + 4HCO_3^- + SiO_{2(s)} \qquad (10)$$
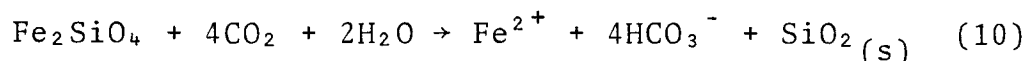
Fe - olivine

2. Iron Carbonate - dissolution to Fe(II)

$$FeCO_3 + CO_{2(g)} + H_2O \rightleftarrows Fe^{2+} + 2HCO_3^- \qquad (11)$$
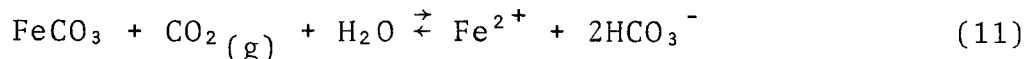
siderite

In reactions 10 and 11 the iron is not oxidized; the oxidation is shown in reaction 12.

3. Oxidation of Fe(II) to Ferric hydroxide

$$Fe^{2+} + \tfrac{1}{2}O_{2(g)} + H_2O \rightleftarrows FeO \cdot OH_{(s)} + H^+ \qquad (12)$$

goethite
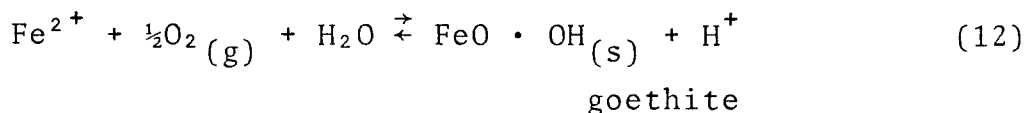
4. Pyrite: Oxidation of sulfide to sulfate

$$FeS_2 + 7/2\ O_{2(g)} + H_2O \rightarrow Fe^{2+} + 2SO_4^= + 2H^+ \qquad (13)$$
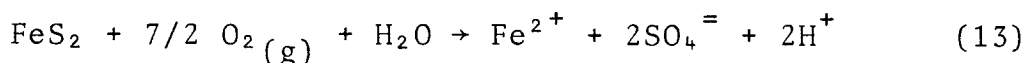
pyrite

The above reactions provide an excellent summary of what occurs as water falls as rain, percolates through the soil and rocks, discharges to the rivers and then to the seas. Some conclusions should be made about the above summary. The dissolution of carbonates as shown in reaction 4 consumes hydrogen ions in acidic waters. The dissolution of quartz as shown in reaction 6 consumes hydroxide ions in basic waters. Since quartz and carbonates are ubiquitous on the earth's crust, natural water is usually buffered between a pH of 5 to 9. Dissolved constituents such as Fe^{2+}, Ca^{2+}, Na^+, K^+, HCO_3^- and $SO_4^=$ occur naturally in water and are essential to human health.

Many of the reactions are equilibrium reactions which
are capable of being easily reversed. For example, if the
concentration of silicic acid in water becomes too high,
reaction 5 will go to the left causing the deposition of
quartz. For the case of Fe and Al, these ions are tied up
as solid residues in clays and oxides and their concentra-
tions in natural waters are ultimately quite low. Examples
of this are reactions 9 and 12. This is why there are only
minor amounts of Fe and Al dissolved in rivers as shown in
Table I. Most problems with natural waters arise when water
weathers formations which contain a unique mix of minerals
and this water is needed before the ultimate weathering
reactions have occurred.

THE WEATHERING OF ORE MINERALS

The Primary Reactions

In the summary of weathering reactions listed above,
iron minerals are listed separately. The primary reason for
this is because iron exists as Fe(II) in many igneous minerals,
but the ultimate weathering product is iron (III) hydroxide.
The weathering takes place in two steps. First the release
of Fe(II) occurs as shown in reactions 10 and 11, then the
Fe(II) is oxidized to iron (III) hydroxide, as shown in
reaction 12. The hydroxide product can occur in forms other
than the goethite shown in reaction 12 and accounts for the
different orange-red and yellow deposits seen around mine
adits. A key feature of reaction 12 which distinguishes it

from the other weather reactions is that it generates hydrogen ions making the water more acidic. The other weathering reactions work towards buffering the water; reaction 12 works in the opposite direction. Precipitation of goethite will keep the water at a pH of around 5 rather than 7 (6, 8, 16).

Pyrite is a mineral which contains Fe(II) and sulfur as $S_2{}^{2-}$. The weathering reaction 13 shows that $S_2{}^{2-}$ is oxidized to $SO_4{}^{=}$ when pyrite dissolves. Hydrogen ions are also released when this reaction occurs. In addition, it is found that Fe(III) will also react to dissolve pyrite.

$$FeS_2 + 14\ Fe^{3+} + 8H_2O \rightarrow 15\ Fe^{2+} + 2SO_4{}^{=} + 16\ H^+ \qquad (14)$$
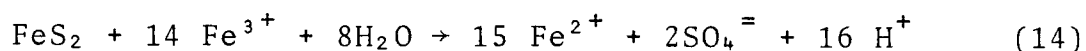
The complete model for the dissolution of pyrite was proposed by Stumm and Morgan (6) and is shown below:
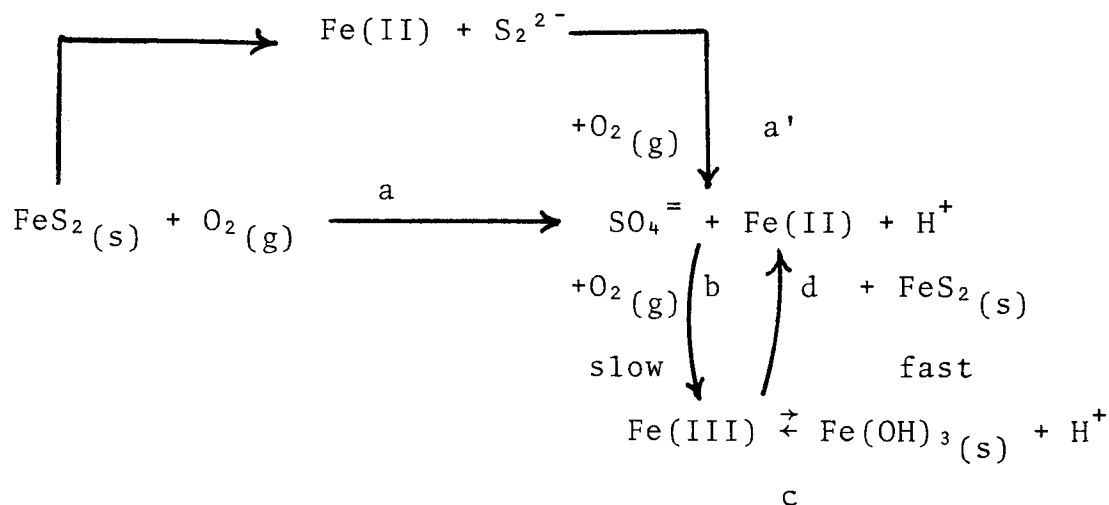
The immediate results of this weathering mechanism are two possible types of water:

A. Fe(III) water of a pH about 5 which is in association with Fe(OH)$_3$ sediment.

B. Fe(II) sulfate water of a pH of 3 or less.

A typical example of Fe(III) water (type A) is that draining the peripheral zone of the Central City Mining District as shown in Table II. Fe(II) and $SO_4^=$ water (type B) is shown by the water from the central zone as shown in Table II. In mine drainages from the Front Range of Colorado the lowest pH is 2.2; Nordstrom [18] found pH values as low as 1.0 for metal mine drainages in Northern California.

To summarize, drainages from mines will contain dissolved species in the water due to the typical weathering reactions. These are likely to be Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, and SiO_2. If the water is in contact with iron minerals, it can be acidic with a pH of about 5. If it is in contact with pyrite, it can contain large amounts of Fe(II) and $SO_4^=$ and can have a pH of below 3. Note that as the water changes from river water to Type A to Type B the primary constituents change from those normally found in natural waters to those found in an industrial type of water. Nevertheless, the dissolved species in all the waters were derived from the weathering of natural minerals. Also, given time to proceed to the ultimate products, mine water will purify to river water. This fact is the basis behind most methods of mine effluent clean-up.

The Secondary Reactions - Other Sulfides

The weathering of pyrite will contribute Fe(II), $SO_4^=$, and H^+ to a ground water aquifer, but this does not explain the occurrence of other dissolved metals such as Cu, Zn, Cd,

Table II. Dissolved Constituents in Waters of the Central City Mining District.

| | MINE EFFLUENTS | | | SURFACE WATERS | |
	Central Zone	Intermediate Zone	Peripheral Zone	Nevada Gulch	Virginia Canyon
SiO_2	50-70	40-70	20-40	-	60-100
Al	25-100	n.d.	n.d.	-	50-80
Fe	200-700	2-170	0.5-4	0.5	2.4-36
Mg	150-260	80-120	30-100	30	110-130
Ca	240-360	140-300	40-300	55	170-210
Mn	90-120	20-40	1.0-5.0	8	54-68
Cu	6-60	0.1-5	<0.01-0.11	2.5	6.7-14
Zn	60-400	7-100	0.3-8	40	60-90
Cd	0.2-2.9	<0.01-0.3	<0.01-0.04	0.25	0.03-0.04
Pb	0.1-0.5	<0.01-0.20	<0.01-0.06	0.17	≈0.10
Na	10-23	14-27	6-25	8	14-23
K	1.4-3.5	4.8-7.6	3.0-5.1	3	1.7-2.9
As	0.2-7	<0.001 0.01	<0.001	<0.001	<0.003
$SO_4^=$	2300-4000	900-1300	240-800	1000	≈1600
pH	2.1-2.7	4.0-6.0	5.4-6.9	3.7	2.6-3.3
cond[a]	3100-6500	1420-2100	400-1495	550	2300-3000

cond[a] - conductivity in μmho/cm.

Pb, Mn and As. These metals will typically be included in other sulfides such as chalcopyrite $(Cu, Fe)S_2$, galena PbS, sphalerite ZnS, arsenopyrite FeAsS, enargite Cu_3AsS_4 and tennantite $(Cu, Fe, Zn, Ag)_{12}As_4S_{13}$. The information concerning the dissolution of these minerals is not as complete as that for pyrite, probably because they aren't common in coal. Some information can be gained from hydrometallurgy and solution mining studies (19, 20). Also, Wentz (8) has a good summary of the possible weathering reactions for these minerals.

In all these minerals, the anions of sulfur and arsenic will be oxidized by oxygen. The key to the dissolution is whether the anion is a complex sulfo salt, such as FeS_2, FeAsS, $(Fe, CU) S_2$, or Cu_3AsS_4, or a simple sulfide such as FeS, Ag_2S, PbS or ZnS. In the former case, the dissolution makes the water acidic; for example:

$$2FeAsS_{(s)} + 13/2O_2 + 3H_2O \rightarrow 2Fe^{2+} + 2SO_4^= + 2H_2AsO_4^- + 2H^+ \quad (16)$$
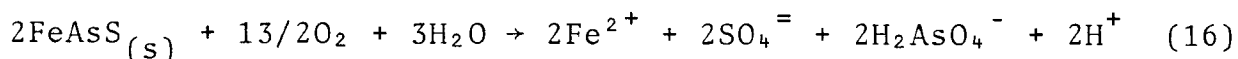
In the case of simple sulfides, no hydrogen ions are released upon dissolution; for example:

$$PbS_{(s)} + 2O_2 \rightleftharpoons Pb^{2+} + SO_4^= \quad (17)$$
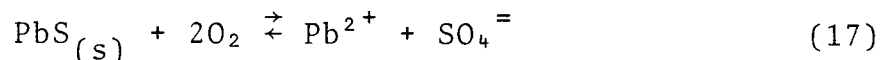
So complex sulfo minerals weather to produce acidic waters but simple sulfides do not produce acidic drainage.

Once the pH of the water has become low enough, congruent dissolution reactions of the simple sulfides are also possible.

$$PbS_{(s)} + H^+_{(aq)} \rightleftharpoons Pb^{2+}_{(aq)} + HS^-_{(aq)} \quad (18)$$

$$HS^- + 2O_2 \rightleftharpoons SO_4^= + H^+ \quad (19)$$
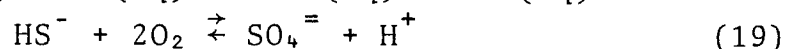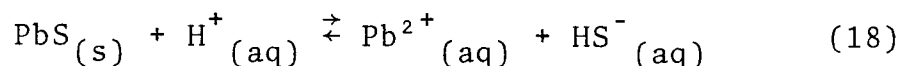
Combining the two steps gives the same as reaction 17. The hydrogen ions catalyze or speed up the dissolution reaction 17 without being consumed. Such secondary weathering reactions are of great importance in establishing the water quality. Iron dissolved in water is more of a nuisance and can be tolerated to a fairly high concentration as seen in the drinking water standards listed in Table I. In contrast, Cd, As, Pb and Ag are quite toxic and have low maximum permissible concentrations in drinking water.

High levels of iron will not remain dissolved in surface waters for very long because the pH has to be at an uncommonly low value of 3 or lower to keep mechanism 15 from proceeding to the precipitation of $Fe(OH)_3$. Is this true for the other base metals dissolved in water? Unfortunately, some metal such as Zn, Cd and Mn can remain dissolved in water even when the pH is raised to values around 7. Boyles and co-workers (21) performed studies which show quite well the relation of pH to dissolved metal concentration. They increased the pH of Argo Tunnel mine drainage by controlled increments from its initial value of 2.8 to pH=8. At each step an analysis was done of the metals still dissolved in the water. Their results are reproduced in Figure 1. The important point to note here is that Fe is precipitated from the water quite early but the other base metals stay dissolved. The conclusion is that precipitation of iron from the water does not imply that mine effluents are of
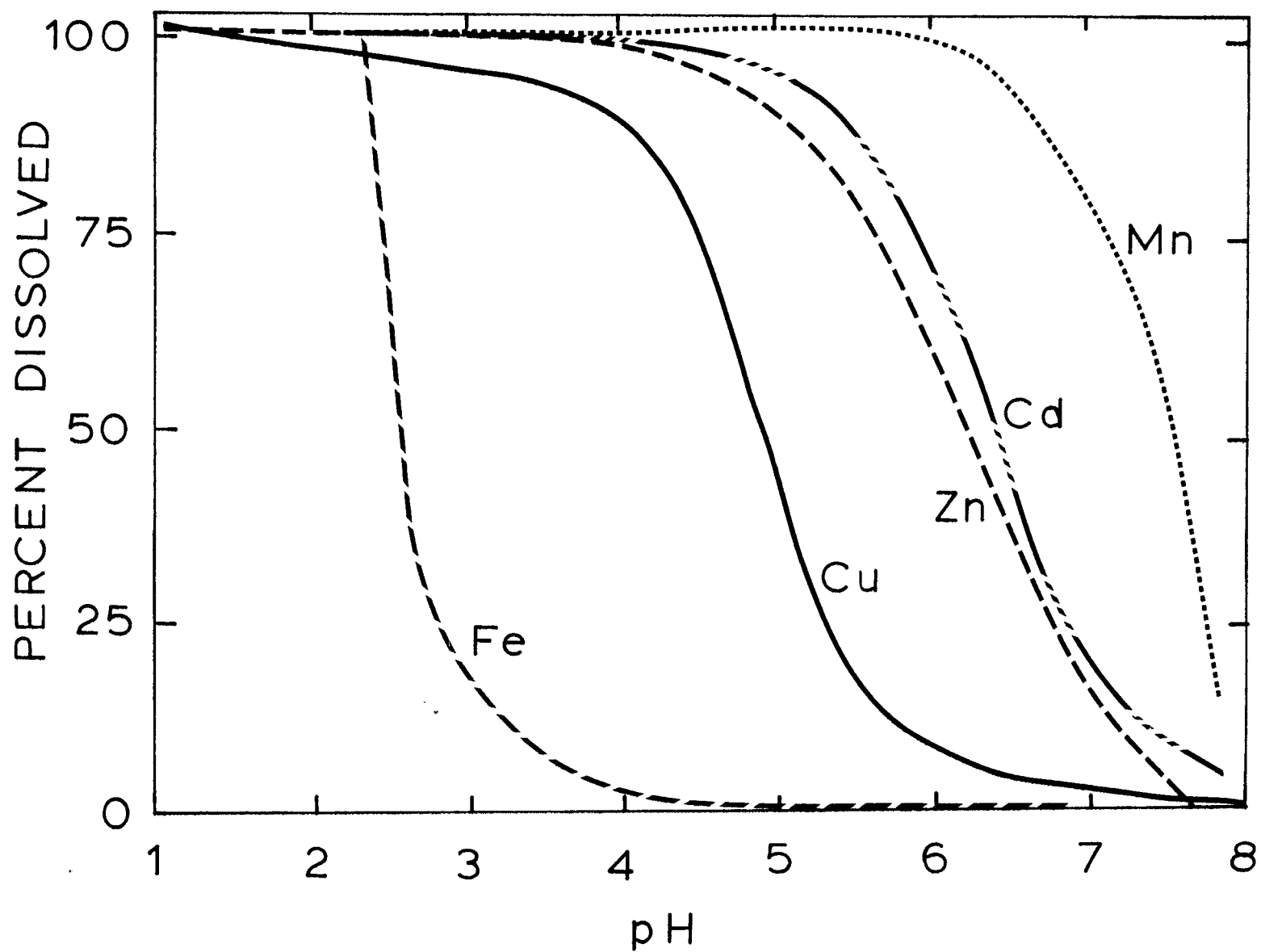
FIGURE 1. HEAVY METAL BEHAVIOR AS A FUNCTION OF PH IN ARGO WATER.

high quality. In other tests on the Argo Tunnel drainage
it was found that Pb and Ag are removed from the drainages
of low pH's comparable to those for the removal of Fe(21).

Microbes and Catalysis

The pyrite oxidation model shown in reaction 15 requires
the attack of gaseous O_2 on solid FeS . This type of reaction
is usually very slow. Indeed, Singer and Stumm (22) have
found that Step a in the model is so slow that usually
Fe(III) dissolves the pyrite through step d. Nevertheless,
O_2 is needed for the weathering of pyrite to occur and, as
Wentz (8) explains, this oxidation has to take place more
rapidly than it does under sterile laboratory conditions.
In waters of low pH and high concentrations of Fe and $SO_4^=$,
it is generally accepted that microorganisms accelerate
the weathering of FeS_2 by O_2 (6, 8, 23). The bacteria are
aerobic (need oxygen to live), chemoautotropic (derive
their nourishment from chemical reactions of inorganic com-
pounds), acidophilic (can live only in waters of low pH),
and are found in soils throughout the world. There is con-
fusion in the literature over the proper designation of the
bacteria because different microbiologists found the bacteria
operating in various localities. Some of this confusion has
been resolved in recent reviews (24, 25). A summary of the
important types appears below:

A. Thiobacillus ferrooxidans: Gains its primary nourishment
    by catalyzing the oxidation of Fe(II) to Fe(III). It can

catalyze the oxidation of elemental sulfur and $S_2O_3^=$ species to $SO_4^=$. It doesn't appear to attack $S_2^=$ or $S^=$. Ferrobacillus microorganisms were previously known (24, 26), but recently it was concluded that they were the same as Thiobacillus ferrooxidans. These bacteria work at pHs between 2 and 3.5.

B. Thiobacillus thiooxidans: Gains its primary nourishment by catalyzing the reaction of all sulfur species $S_2^=$, $S^=$, SO, $S_2O_3^=$ to $SO_4^=$. It is uncertain whether it can catalyze Fe(II) to Fe(III). The organism can catalyze the oxidation of sulfide minerals such as CuS and ZnS. It functions best at pH's between 3.5 and 2.0.

There has been much discussion concerning which species actually catalyzes pyrite oxidation. Dugan (24) has recently found that neither T ferrooxidans nor T thiooxidans alone is effective in the attack on pyrite in coal and that mixed cultures worked the best. Probably both species are present in severe mine drainage situations. There is also much discussion over whether other species are catalyzing reactions above a pH of 3.5 (8, 26). It appears that other bacteria are really effective only in special situations and that the above two species are most important in mine drainage situations (6, 8, 23). It has been shown that these organisms increase the rate of pyrite oxidation by over a thousand times the abiotic rate (6, 8, 23). Once Fe(III), $SO_4^=$ and H^+ are released, these species are also powerful catalysts for the weathering of other sulfide minerals (11).

SUMMARY OF WEATHERING

The dissolution of minerals to produce waters of high $Fe(II)$, $SO_4^=$, and H^+ contents and the recovery of the water to natural conditions are probably as follows:

A. In a rock with relatively low amounts of carbonate minerals and relatively high amounts of pyrite, the pyrite somehow dissolves, producing regions in which the water is below pH 3.5 and contains $Fe(II)$. Oxygen has to be supplied for the dissolution.

B. Bacteria begin to thrive in an environment caused by Step A and catalyze the reaction of O_2 with FeS_2 producing more dissolved $Fe(II)$ and $SO_4^=$ and maintaining the pH between 2 and 3. Oxygen has to be supplied for this Step B and the pH has to be within 2 to 3 for effective catalysis by microorganisms.

C. If other base metal sulfides are present, their dissolutions are accelerated by the joint action of the bacteria, H^+ ions, $SO_4^=$ ions, and the iron species.

D. When the water starts flowing above ground, the action of bacteria and O_2 oxidize $Fe(II)$ to $Fe(OH)_3$ and the pH is raised above 3.5. Most of the Fe is precipitated as well as Ag and Pb. Other base metals and $SO_4^=$ persist dissolved in the water. The pH of the water rises to 5-6 at this point.

E. Interaction with CO_2 and carbonate minerals raises the pH of the water to 7-8 and the other base metals are removed from the water. Sulfate remains dissolved

in the water if the concentration is not too high. By this step, the water should have eliminated the effects of being in contact with ore minerals.

MINE EFFLUENT POLLUTION

Just what is pollution and what concentration levels
constitute a problem? Neither question has a unique answer.
An operational definition of pollution is something that is
harmful and unwanted at a certain time and place. Mine
effluents are unwanted in the particular operation that is
being employed. If an operation switched to solution mining
or added a mill, the water might be quite useful. The con-
centration levels that constitute a problem relate to the
harmfulness of the water. In this area, there are three
answers and all of them are subject to revision.

HEALTH STANDARDS

The traditional approach to defining harmfulness is to
compare the concentration of the constituents in the water
against water that is fit to drink. Up to 1975, the U.S.
Public Health Service had defined recommended limits and
maximum permissible concentrations for drinking water.
These are listed in Table III.

In 1975, the EPA and the state governments took over
the establishment and enforcement of drinking water regula-
tions (31). They established maximum contaminant levels
(MCL) and these are also listed in Table III. Where there
is a discrepancy between the old and new drinking water
standards, research is being done to establish a maximum
concentration limit. The difference between the old and
new standards is primarily philosophical. The old standards

Table III. Environmental Standards for Water. Concentrations are in mg/l unless noted.

| Source | Drinking Water before 1975 | Drinking Water after 1975 | Suggested Criteria for aquatic life | EPA Limitations for Cu, Pb, Zn, Au, and Ag Mines | | | |
| | | | | BPCTCA[g] | | BATEA[h] | |
				30 day avg.	24 hr max.	30 day avg.	24 hr max.
Reference	(8)	(48,49)	(8)	(2)	(2)	(2)	(2)
Arsenic	$0.010^a 0.050^b$	0.05^e	1.0				
Barium	1.0^b	1.0^e	-				
Cadmium	0.010^b	0.010^e	0.010				
Chromium(VI)	0.050^b	0.05^e	0.050^d				
Cobalt	-	-	0.50				
Copper	1.0^a	1.0^f	0.01-0.02	0.05	0.1	0.05	0.10
Cyanide	$0.010^a 0.200^b$						
Iron	0.30^a	0.3^f	0.30				
Lead	0.050^b	0.05^e	0.005-0.01	0.2	0.4	0.1	0.2
Manganese	0.05^a	0.05^f	1.0				
Mercury	0.005^b	0.002^e	0.001	0.001	0.002	0.001	0.002
Nickel			0.050				
Selenium	0.01^b	0.01^e	1.0				
Silver	0.05^b	0.05^e	0.0001				
Zinc	5.0^a	5.0^f	0.03-0.07	0.5	1.0	0.5	1.0
Sulfate	250^a		250^f				
Total dissolved Solids	500^a						
pH[c]	6.0-9.0		6.5-8.5	6-9	6-9	6-9	6-9

a Recommended limit
b Maximum permissible concentration
c Hydrogen ion concentration in pH units
d Total chromium- drinking water standard is hexavalent chromium

e Maximum contaminant levels (48)
f Recommended maximum secondary contaminant levels proposed by EPA (44) and adopted by the Colorado Water Quality Control Commission (50)

g Best Practicable Control Technology Currently Available
h Best Available Technology Economically Achievable

couldn't be strictly enforced; the new standards are law and can be enforced (13).

BIOTIC STANDARDS

Another approach to defining harmfulness is to say that not only should humans be able to drink the water, but fish should be able to swim in it. The biotic concentrations suggested by Wentz (8) are listed in Table III. This dramatically changes the maximum levels of some species. In particular, Wentz (8) related how studies have shown that fish are much more susceptible to Cu and Zn dissolved in water than are humans. This is no doubt the reason why no trout are found in some streams in Colorado which are fit for drinking by humans.

EFFLUENT STANDARDS

The Environmental Protection Agency has to define concentration levels for water effluents even though the drinking water levels and the biological criteria are certain to change (1, 2). Obviously, a long term mining operation cannot function under a system which changes from year to year. Consequently, the EPA defined harmfulness in a quite different manner. The operations for treating effluents for each industry were examined for current practices and for what would be the best methods that could be economically achieved. The levels of concentration for species that result from the best current technology were designated as the current standards and they are enforced from July 1, 1977 to July 1, 1984.

These current effluent requirements are called the Best
Practicable Control Technology Currently Available (BPCTCA).
The methods which the EPA considers will best control the
harmfulness of effluents are designated as the water quality
criteria that will be effective after July 1, 1984. These
1984 standards are called the Best Available Technology
Economically Achievable (BATEA). The criteria established
by the EPA are the same for all copper, zinc, lead, gold and
silver mines and they are listed in Table III.

This EPA study and designation of effluent limitations
for the metal mining industry can be considered to be suc-
cessful because both the current and future limitations are
based on sound chemical principles. Specifically, the tech-
nology is based on the fact that natural waters will tend to
be between a pH of 6 to 9 and between those pH's most harmful
dissolved species that would come from a mining operation
will be precipitated from the water. This tendency of water
to remain between pH 6 and 9 is dictated by the buffering
effect that occurs when silicate and carbonate minerals are
weathered and dissolved. This buffering concept was explained
in the previous chapter. If sulfide minerals are weathered
and the pH of the water falls below 6, the changes in water
composition with pH are obvious as shown by the mine drainage
data in Table II and figure 1. Thus, the generation of harmful
mine effluents is caused by natural processes and, given
enough time, it can be controlled by natural processes. The
industrial control of mine effluents works on the same basis,

but the adjustment of the pH to above 6 is helped by the
addition of bases such as lime $(Ca(OH_2))$ or calcite $(CaCO_3)$.
Consequently, limits don't have to be set for Fe, Mn, Cd
or Ag. If the pH of the water is between 6 and 9, and there
are low amounts of total suspended solids, these constituents
cannot be in the water at harmful levels.

The EPA set limits on mill effluents at the same time
as mine effluents (2). In this case, the task was more
difficult. In a mill, species such as cyanide or organic
complexing agents might be added to the water to achieve
the beneficiation of the ore. These constituents, which
do not occur naturally in water, are sometimes difficult to
remove from water and may retain the base metals in the
solution. Thus, for the case of metal mills, the current
limitations are more specific and the 1984 limitations
dictate that there be zero discharge in many of the milling
categories (2).

For many people, the limitations are not bothersome,
but dealing with all the agencies which have some control
over the operation is frustrating. A good explanation of
how all the regulations operate and how the controls and
effluents are set for a particular operation is in an
article by Andrews (27). He goes through an actual example
case from start to finish to show how the EPA limitations
and the drinking water standards dictate how well the efflu-
ent from a mining or milling operation will have to be treated.

SUMMARY AND OPINION

The one thing that is certain about the Health Standards and Effluent Standards for water is that they will change. Both can affect the effluent cleanup of a mining operation. As Andrews (27) points out, if an effluent is connected to a drinking water supply, then that effluent may have to meet the drinking water standards or be of somewhat better quality than is designated by the EPA effluent criteria. What follows is opinion on how things will change.

On the matter of drinking water standards, new limits are missing for CN^- and only recommended limits are set for some constituents of secondary importance. New regulations may appear in the future that will set limits for these constituents. Sodium and molybdenum are inorganic species which are not on the list, and which may have limits set in the future. Most of the changes in drinking water regulations will occur for organic species rather than inorganic species.

On the matter of EPA effluent limitations, the course which will be taken will closely follow that which has occurred for automobile exhaust standards. That is, the EPA has probably established strict interim standards so that they can be relaxed in the future rather than make un unpopular decision to tighten regulations. Currently, new relaxed interim standards are being published for the mining and milling industry. Also, the effective data for the final BATEA limits has been extended from July 1, 1983 to July 1, 1984. However, in the end the BATEA limits will not change

much from the current values.

On the matter of state and local involvement, things can change drastically in a short time. For example, the stream into which a mine effluent flows may be upgraded to water fit for drinking water or for aquatic life. Suddenly, the mine effluent is no longer suitable and a new cleanup operation has to be devised. The only way to contend with these developments is to keep abreast of the state and local regulations. The best way to keep up to date is to stay in contact with state and local water quality offices. They should help to fairly apply the regulations to each operation.

PHYSICAL FACTORS AFFECTING DRAINAGE QUALITY

This chapter discusses how other geologic and hydrologic
factors will change the weathering reactions of the ore
minerals. Investigations within the Front Range of Colorado
have shown that at least three other parameters are important
for determining the chemistry of a drainage. These are the
ore petrology, the ground water hydrology and the physical
occurrence of the ore in the ground. Each of these will
be discussed. Much of what follows also occurs in two other
papers (11, 12).

ORE PETROLOGY VS. WATER QUALITY

In the Central City Mining District, the zones of minera-
lization have been well established (4). These zones are
shown in figure 2; and figure 3 shows the zonal distribution
of the vein forming minerals. The central zone consists
of pyrite veins and it is surrounded by a peripheral zone of
galena-sphalerite veins. The intermediate zone, which con-
tains most of the important mines, has transitional veins
that consist of minerals characteristic of the other two
zones. Wildeman and others (11) have found 8 abandoned
adits which are continuously draining, 2 in the central zone,
3 in the intermediate zone, and 3 in the peripheral zone.
The ranges in concentration of various elements for the
drainages from each zone are listed in Table II, and these
ranges highlight the zonal changes in the water chemistry.
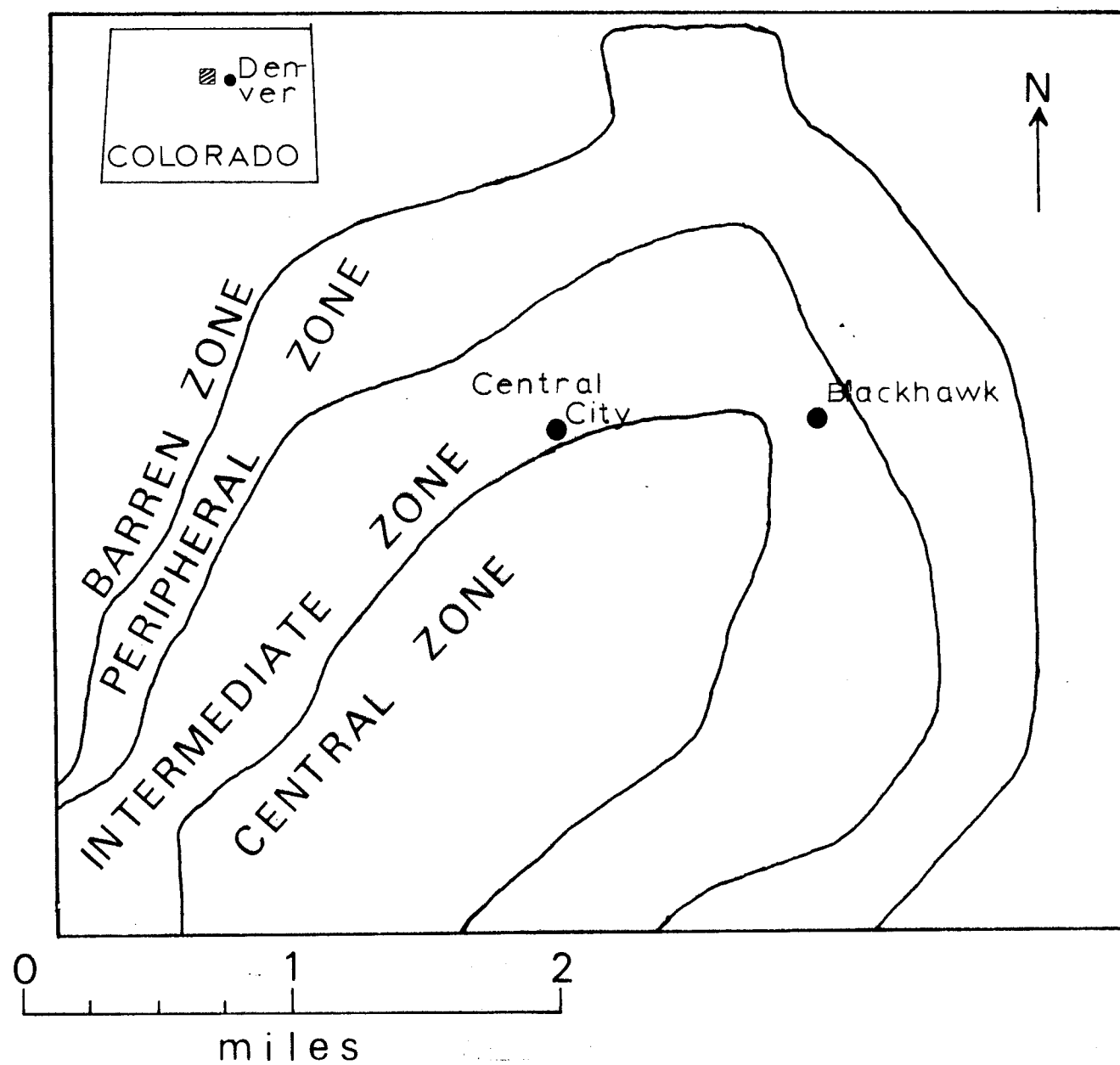
The most important conclusion that is shown by the zonal

FIGURE 2. ZONES OF MINERALIZATION IN THE CENTRAL CITY MINING DISTRICT (FROM REFERENCE 11).
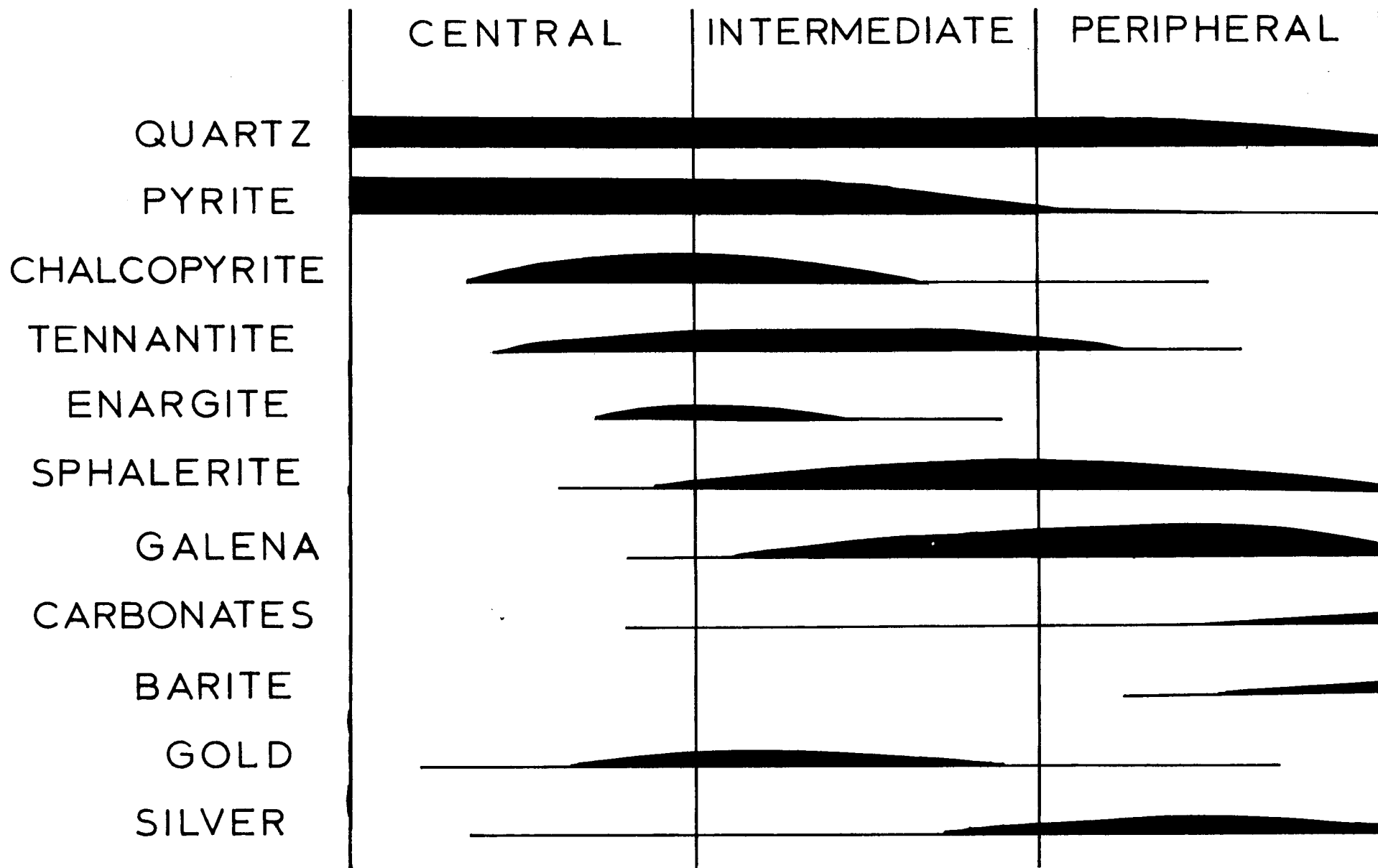
FIGURE 3. ZONAL DISTRIBUTION OF THE VEIN FORMING MINERALS IN CENTRAL CITY (FROM REFERENCE 11).

variation of the drainage is that the highest concentrations
of Zn, Cd, and Pb occur in the central zone even though
sphalerite and galena, the ore minerals which concentrate
these elements, occur in greatest abundances in the inter-
mediate and peripheral zones. The impact of this conclusion
is increased when it is coupled with the observation that
mines of greatest economic importance occur in the inter-
mediate zone or on the margin of the central zone (11).
Thus, there is not necessarily a correlation between the
economic grade of an ore extracted from a mine and the harm-
fulness of the water draining from a mine. On the other
hand, there is a direct correlation between the abundance
of pyrite in the veins and the harmfulness of the water
draining from the mine and it is felt that this is an
important parameter for determining the harmfulness of
drainages from base metal deposits.

What the results show is a confirmation of the sulfide
mineral weathering scheme that was summarized previously.
For some reason, it is necessary to oxidize the pyrite first.
Its dissolution will lower the pH of the water so that biologi-
cal catalysts can operate. Also, the Fe(III), HSO_4^-, and H^+
catalyze the dissolutions of the other sulfides. So the
primary criterion relating petrology to water quality is
the abundance of pyrite.

Na, K, Mg, and Ca are normally considered as the major
metal constituents in water. The zonal variation in concen-
tration of these cations is much less severe than those of

the base metals and in the case of Na and K there appears to
be no variation. The concentration ranges of the major
metals in ground water samples taken from the Central City
District show the same tight spread. It was found that
these concentrations of Na, K, Mg, and Ca correlate well
with the abundances of these elements in the wall rocks which
are normally found along faults and veins in the Central
City District (3). This suggests the relative amounts of
these major metals in the water is a reflection of the compo-
sition of the more important rock units in the mining dis-
trict and the way in which these rocks weather.

In summary, they are two sources for the chemical con-
stituents in a mine effluent. The base metals and $SO_4^=$
are derived from the vein minerals and the abundance of py-
rite in the veins is important in controlling the levels of
these metals in the mine effluent. The source of the major
metals is the wall rock and the composition of the host rock
determines the abundances of these constituents in the mine
drainage.

GROUND WATER HYDROLOGY VS. WATER QUALITY

Describing the mechanisms for ground water recharge
can become quite complex and relating this to water chemistry
adds another dimension to the difficulty. However, studies
in Pennsylvania on the water chemistry of springs issuing
from carbonate terrains have generated two simple models
for ground water systems and these can be treated as end
members for all recharge systems (28, 29). The two aquifer

models are termed the conduit flow system and the diffuse
flow system; and they are diagrammed in figure 4.

The conduit system has the water recharge localized
in a few feeder pipes which may be faults or conduits
formed by rock dissolution. The flow from the feeder
pipes can be turbulent and the water may carry a load of
suspended solids. The water chemistry of conduit systems
responds to changes in the precipitation and the seasons.
Discharge rate, temperature, pH, conductivity, and elemental
abundances all change with the above two variables. The
residence time for the water in the system is on the order
of days, and the primary changes in the water chemistry of
the aquifer can be related to the increase in the discharge
rate following precipitation. Springs feeding from limestone
caves are good examples of conduit aquifer systems.

In the diffuse aquifer system, the water recharge is
by seepage through small faults and voids and intergranular
spaces. The movement of the water is slow and it is usually
clear. The water chemistry shows little response to changes
in precipitation and the seasons; all the parameters vary
little throughout the year. The residence time of the water
in the system is measured in months. When the discharge
rate does rise a bit during the spring runoff, the abundances
of the constituents in the water may increase rather than
decrease, as if the aquifer were flushing trapped water from
its many small pores. A sandstone or glacial moraine aquifer

DIFFUSE FLOW
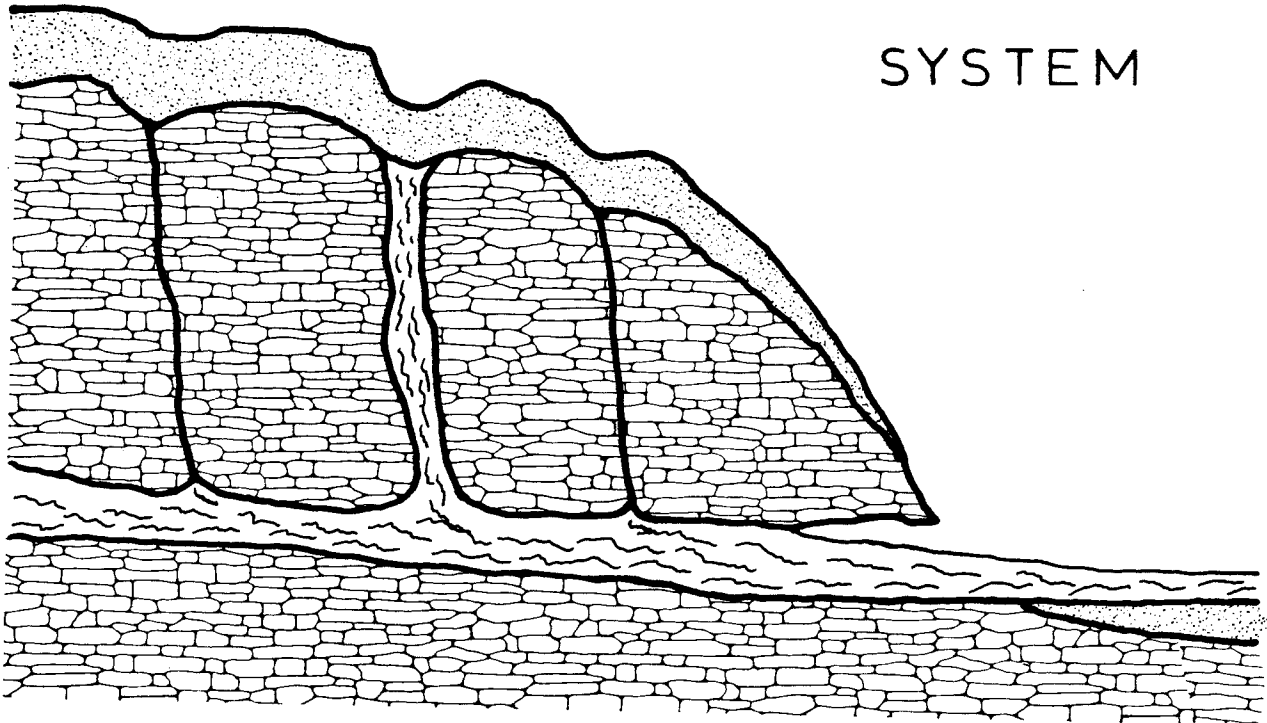## SYSTEM
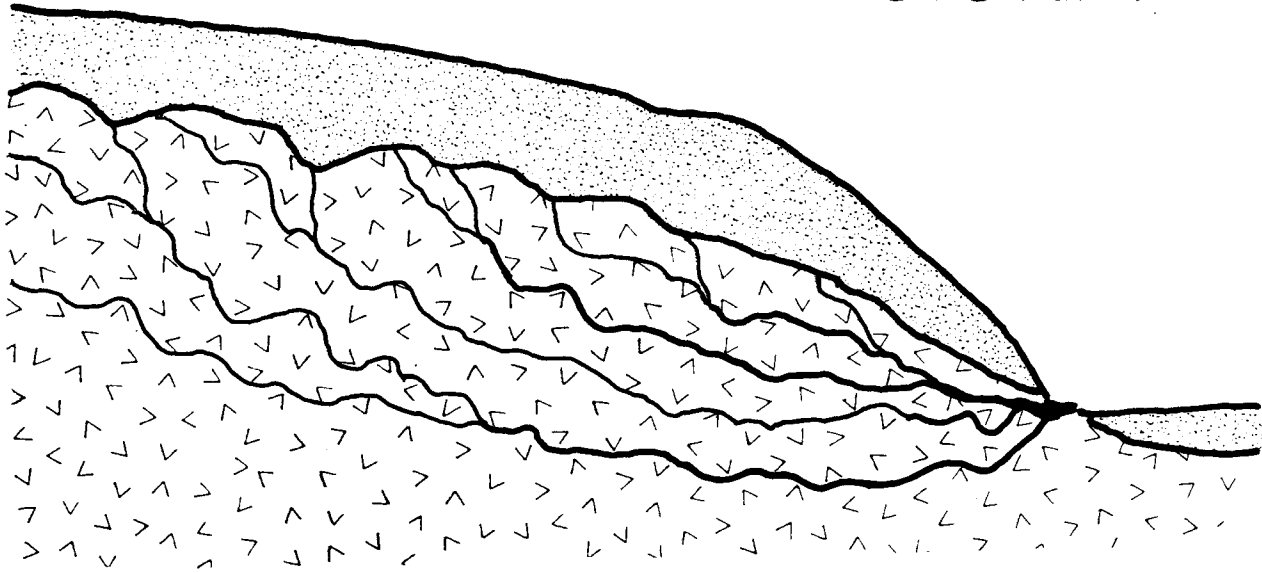
CONDUIT FLOW
SYSTEM

FIGURE 4. DIAGRAM OF THE CONDUIT AND DIFFUSE
AQUIFER MODELS.

is a good example of the diffuse type. Table IV summarizes
the differences between the diffuse and conduit ground water
systems.

From 1974 through 1977, 7 representative mine drainages
from 4 different mining districts in the Front Range of
Colorado have been monitored on a seasonal basis. All of
these mines fit the diffuse flow system. Five other mine
drainages in the Front Range have been monitored on a semi-
regular basis, and the water chemistry in these drainages
changes little from sample to sample. It appears that most
mine effluents in Colorado are fed from diffuse aquifer sys-
tems (9, 11, 12). Indeed, if a conduit aquifer were en-
countered in a mine, the high discharge rate from a point
source would be obvious.

Now if the effluent follows the diffuse aquifer system,
then the chemistry of the water is highly predictable.
This makes possible the establishment of uniform monitoring
and treatment procedures. The chemistry of the effluent
from the Argo Tunnel has been studied extensively for a
long period of time. The variation in discharge has been
investigated by Wentz for the 1976-77 period (30).   In
figure 5 are plotted the average discharge rate from the
tunnel for each month, the average discharge rate for nearby
Clear Creek and the amount of precipitation for each month
for the area. The tunnel discharge is the most constant of
these three. Figure 6 is a plot of the specific conductance
corrected to 25°C and concentrations of Fe, Mn, Na, and Cd

Table 4. Differences Between Diffuse and Conduit Aquifers.

| DIFFUSE	CONDUIT
1. No response to climato-logical changes.	1. Responds to climatological changes.
2. Little fluctuation in flow.	2. Obvious fluctuations in flow.
3. No suspended solids in the water.	3. Carries suspended solids at times of high runoff.
4. Water temperature may not change over the year.	4. Water temperature will change as expected with the seasons.
5. Parameters indicative of concentration such as conductivity and hardness do not change with the climate.	5. Parameters indicative of concentration such as conductivity and hardness show obvious changes with storms and runoff.
6. Specific concentrations of ions show little change with the climate.	6. Specific concentrations of ions show obvious changes with storms and runoff.
7. Residence time of months for the water in the aquifer.	7. Residence time of days for the water in the aquifer.
8. No diurnal changes.	8. No diurnal changes.
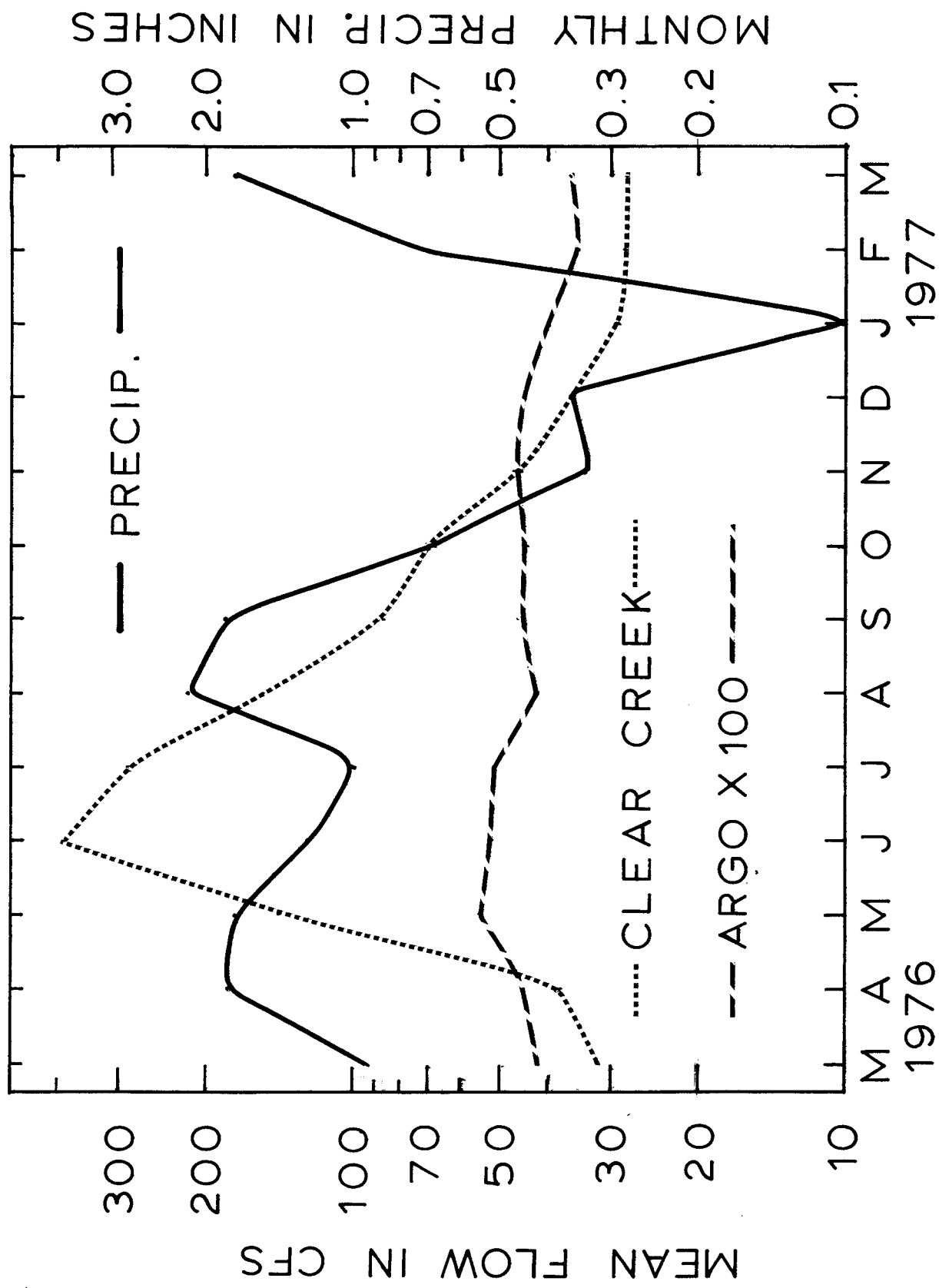
FIGURE 5. DISCHARGE AND FLOW RATES AND PRECIPITATION AT THE ARGO TUNNEL.
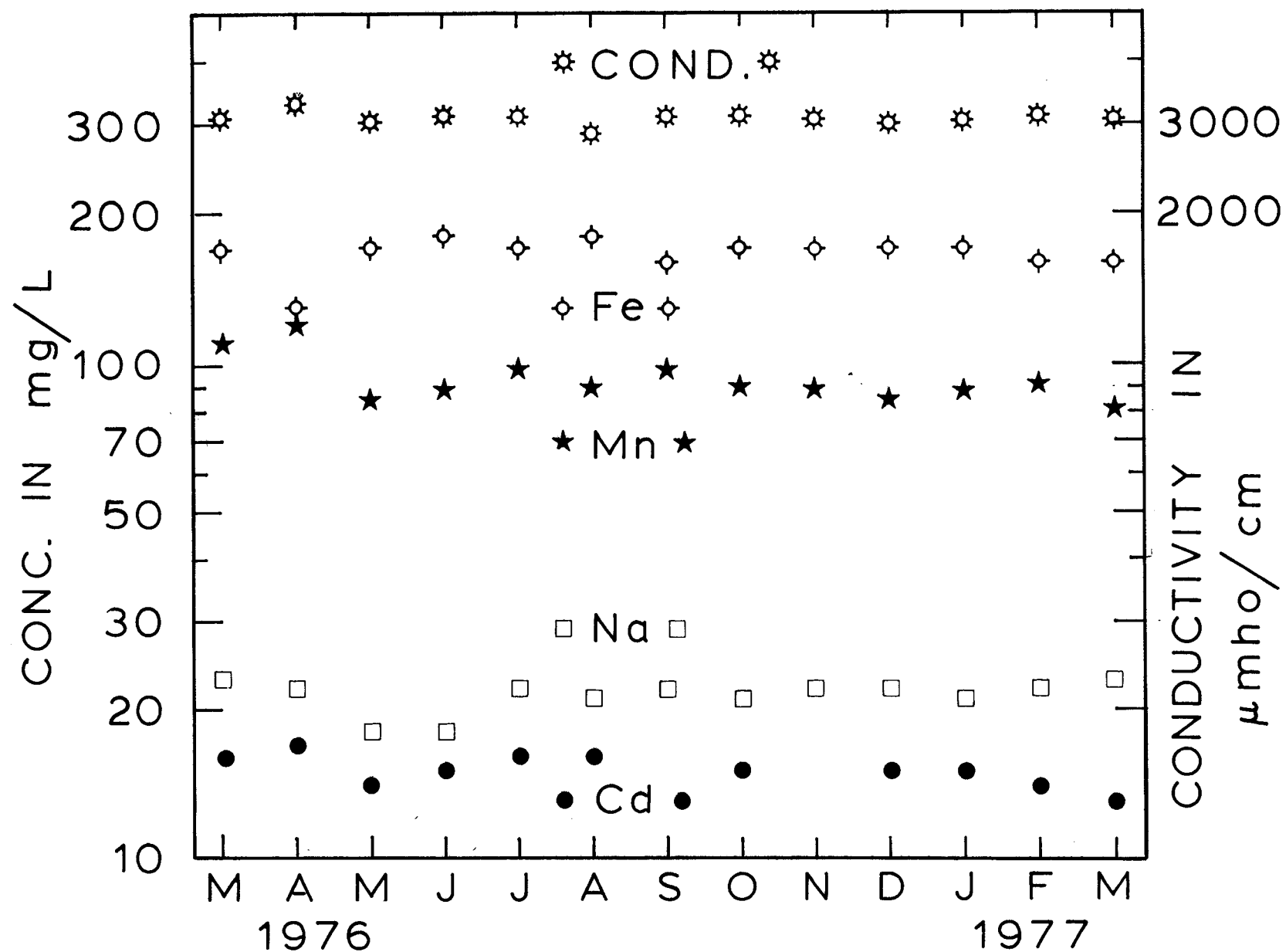
FIGURE 6. MONTHLY VALUES OF THE CONDUCTIVITY AND CONCENTRATIONS
OF IONS IN THE ARGO EFFLUENT.

in the Argo Tunnel discharge water. All this data is taken
from the study by Wentz (30). The regularity of parameters
is remarkable for a natural system. In contrast, Shuster
and White (28) found variations of over ±50% in specific
conductance and concentrations within a few days for conduit
aquifer springs issuing from limestone formations in Penn-
sylvania.

These differences between conduit and diffuse aquifer
water are most important because they can be used to
establish the type of ground water system that prevails in
a mining operation. Such knowledge is essential for estab-
lishing a reasonably uniform procedure for maintaining water
quality. In addition, the type of water issuing from an
adit face is indicative of what is beyond that wall. So,
investigation of the changes in water over a period of time
can be used as another prospecting tool. Any piece of infor-
mation which can tell a mine operator what's behind the mine
face can be critical when it comes to determining whether
that face should be extended. The methods used to establish
the type of aquifer will be discussed in the chapter on
analytical procedures.

ORE OCCURRENCE VS. WATER QUALITY

Recent research on the chemistry of mine effluents in
the Front Range has involved the comparison of effluents in
other mining districts with those in Central City. Analyses
have been made on 4 draining adits from the Georgetown-Silver

Plume District, 5 adits from the Boulder Tungsten District, and 6 adits from the Gold Hill District. The concentration ranges of the constituents in the effluents from each district are summarized in Table V. The water chemistry of all 15 of these effluents compares with that of the Central City Peripheral Zone. Finding a mine effluent in the Front Range that is comparable in water chemistry to the Argo Tunnel which drains the Central City central zone has been quite difficult.

Why is it that the water quality of mine drainage improves considerably when leaving Central City? The ground water aquifer system is not the cause since all the effluents are of the diffuse flow type. The type of mineralization is not the cause since other adits have also bored into pyritic gold, especially in the Gold Hill District. It is felt that two other parameters have to be considered to explain these differences. The first is the occurrence of the ore body; localized veins of ore occurring in rock impervious to water is one extreme example, while ore disseminated through highly fractured rock which has a high porosity represents the other extreme. Diagrams of the vein system and the disseminated system are presented in figure 7.

The disseminated ore system allows more intimate contact of the ground water with the vein minerals and also insures a diffuse flow aquifer. The Central City District with its breccia pipe glory hole in the central zone is just such an

VEIN
ORE
SYSTEM

DISSEMINATED
ORE
SYSTEM
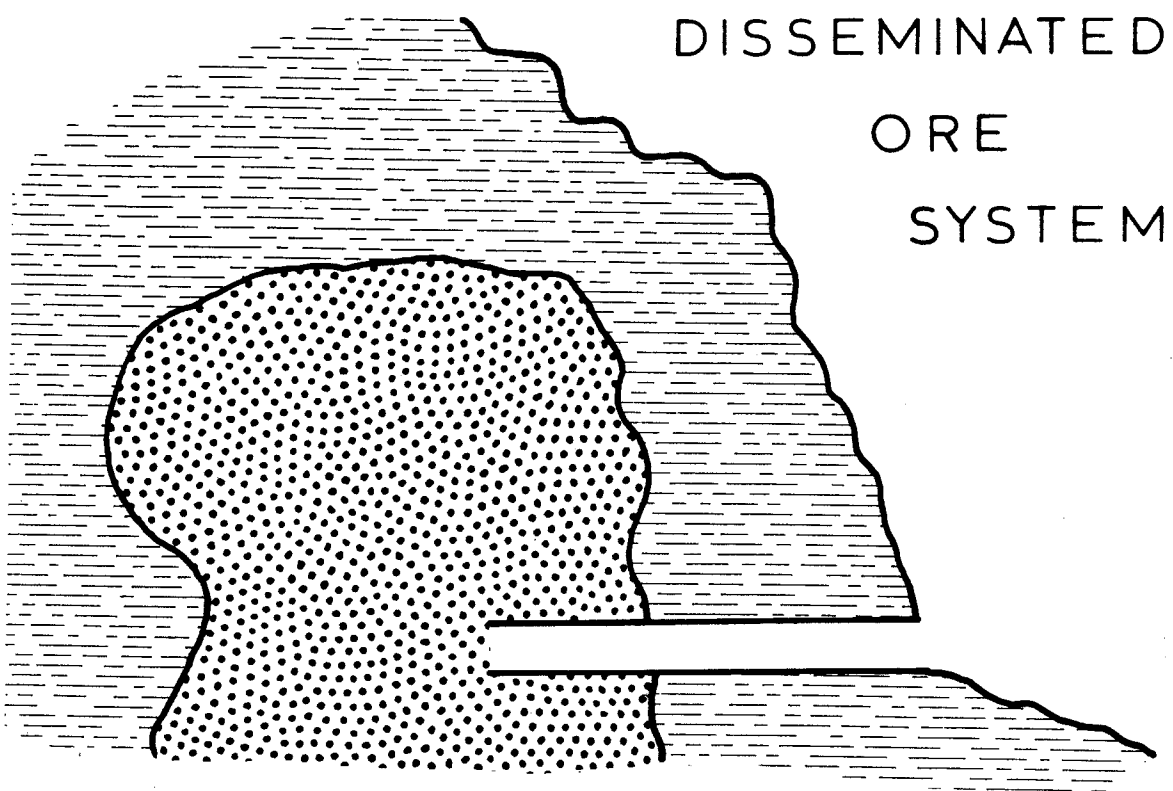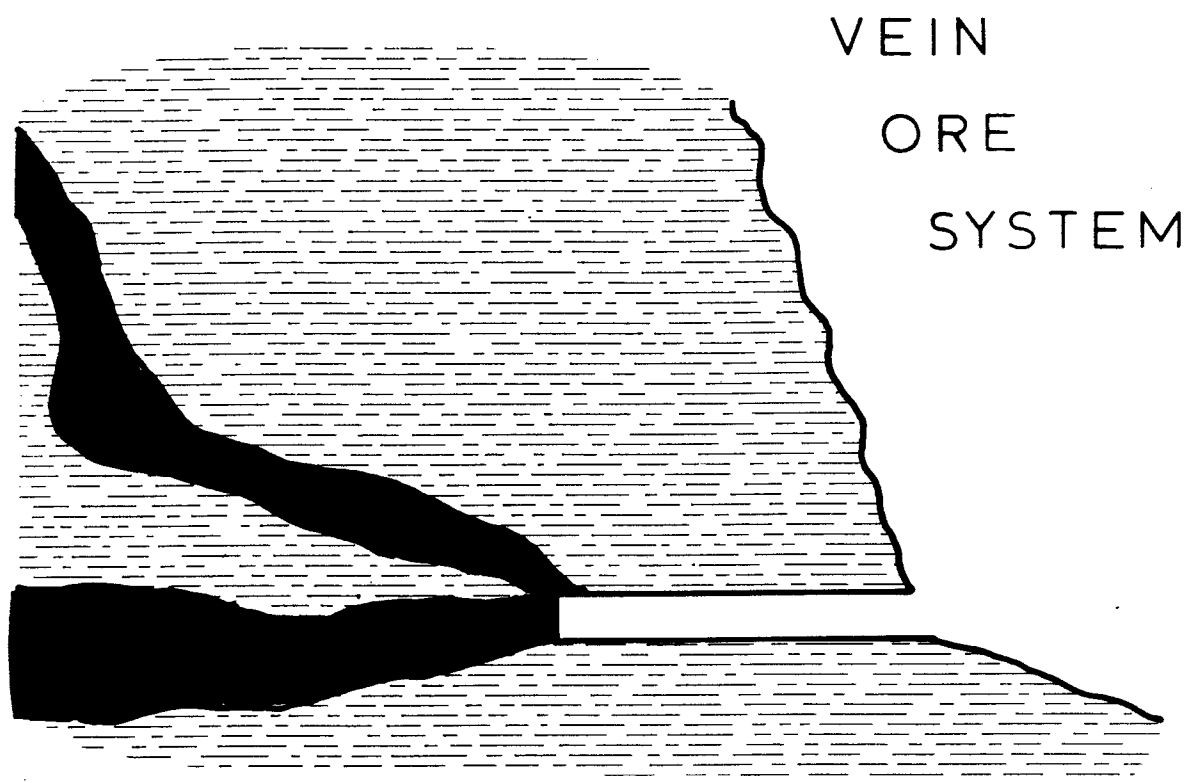
FIGURE 7. DIAGRAM OF VEIN AND DISSEMINATED ORE SYSTEMS.

Table 5. Ranges in Concentrations of the Major Elements
and Base Metals in Mine Drainages from Three
Mining Districts in the Front Range Mineral Belt
of Colorado. Pb and Cd concentrations are in
ug/1; all others are in mg/1.

	Georgetown-Silver Plume	Boulder Tungsten	Gold Hill
pH	4.4 - 7.2	5.6 - 6.7	5.5 - 7.8
Fe	0.4 - 117	0.4 - 1.7	0.4 - 4.0
Mn	0.03-3	0.03-0.4	0.03-0.38
Zn	0.1 - 70	0.03-0.09	0.08-0.9
Cu	0.1	0.2	0.5
Cd[1]	1.1 - 6.4	0.5	0.5
Pb[1]	1 - 8.5	1	1
Na	8.3 - 12.5	3 - 13	11 - 20
K	2.9 - 5.5	0.7 - 4.5	1.6 - 5.3
Mg	60 - 280	30 - 62	31 - 165
Ca	65 - 120	24 - 80	55 - 210

[1]Concentrations in ug/1.

ore body. In the Georgetown-Silver Plume District, the ore primarily occurs in veins stringing along the fractures in the granite host rock and the contact of the water with veins minerals is much less efficient.

The second parameter to be considered is the height of the water table in relation to the ore occurrence. The location of the ground water table in relation to the ore body is important because the dissolution of pyrite is an oxidation reaction.

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{=} + 4H^{+}$$
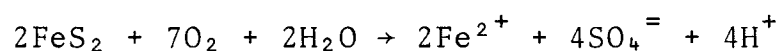
Oxygen is a necessary reactant, even when the reaction is catalyzed by bacteria. If the ore occurs below the water table, contact with air is cut off and oxidation occurs at a much lower rate. If the ore occurs above the water table, dissolution of the vein minerals is promoted. The secondary alteration of ore bodies which at some time have risen above the water table is caused by the same chemical situation.

The Argo Tunnel was built to drain the Central City District and it has been quite efficient. No natural springs occur in the district and the water table is about at the level of the Argo Tunnel with much of the disseminated ore occurring above the water table. In other mining districts in the Front Range, drainage tunnels are not as extensive and springs can typically be found nearby. This implies that the water table is higher in relation to the ore and oxidation of the vein minerals is less extensive.

Certainly many mines are operated above the ground

water table and are extracting ore from disseminated deposits.
In these cases it should be realized that mine effluents
will be more susceptible to turning into pollution problems.

SUMMARY

Two requirements are needed for a chemical reaction
to proceed. The necessary reactants have to be available,
and the encounter of these reactants to make the product
has to be reasonably rapid. The ore petrology, ground water
hydrology and ore occurrence are factors which do not change
the weathering reactions. Instead these parameters can
change so that the reactions won't proceed. In some in-
stances, a reactant is not available such as when ground
water cuts off the air supply. In other instances the speed
of the reaction is slowed such as when large crystals
in a vein are weathered as opposed to smaller crystals dis-
seminated uniformly through a deposit. Obviously, it would
be reasonable to design mine effluent operations so that
the factors which diminish the weathering of pyrite are
functioning.

ANALYSIS OF MINE WATERS

The chemical composition of mine waters has to be known first to understand the nature of the water, second to comply with state and federal regulations, and third to maintain quality control on effluent treatment operations. The usual opinion is that the chemical analyses have to be done by outside laboratories, however, this is not the case if a careful analytical program is established. If a mining operation can establish such a program, its primary benefit is a better knowledge of the operation. With that knowledge, a convincing case can be made to government agencies concerning effluent problems. The testing program suggested below is not expensive or difficult and the operators of the mine have control over the program. The chief difficulty with an analysis program is that someone will have to take care in being clean, careful and tidy in an environment where these qualities are hard to practice. The technical basis for the analysis program is given in this chapter. No descriptions of the analyses are contained in the Appendix.

THE BASIC TESTS

Are there a few basic tests that can answer most questions concerning mine effluents? Wentz (32) looked at this question by applying statistical tests to weigh the correlation between the parameters usually measured in water analyses and mine drainages that didn't meet the drinking water standards. He

found that pH and conductivity were the two most reliable parameters to indicate poor water. The next decisive tests to indicate poor quality mine drainages were the determination of the concentrations of $SO_4^=$ and Zn^{2+}. Schuster and White (28) in their study of diffuse vs. conduit aquifers found that temperature, total hardness, pH and flow varied significantly in the conduit aquifers. Of these parameters, total hardness varied the most, sometimes the change being as large as a factor of two. In a paper on implementing the EPA effluent guidelines, Robins (33) suggests that total suspended solids will be the most difficult to control. Drastic changes in precipitation and runoff can rapidly change the load of suspended solids which makes the design of control equipment difficult. From the above observations the following list of tests can be dictated:

    A. Basic Meteorological Tests

        1. Air Temperature

        2. Precipitation Amount

    B. Basic Water Tests

        1. Flow rate

        2. pH

        3. Conductivity and water temperature

    C. Basic Effluent Tests

        1. Total Suspended Solids

In the beginning of the analytical program, samples will have to be sent to outside labs for total characterization. This will be dictated by the water release permit. But, after

an on-site analytical program has been established, and the
regulatory agencies are convinced that effluent operations
are under proper control, on-site indicator tests can perhaps
be substituted for more expensive specific tests. In this
regard, the above tests should suffice in most instances.

Most of the basic tests are self-explanatory. Standard
procedures for analysis can be found in most water analysis
guides (13, 14). In the Appendix, procedural guidelines
for some of the water tests are suggested. The one test
that requires explanation is conductivity.

Conductivity of Mine Drainages

Conductivity, or specific conductance, is a numerical
expression of the ability of water to carry electrical cur-
rent. It is usually measured in micro mho/cm (μmho/cm) where
a mho is the inverse of resistance in ohm. Pure water is
a poor conductor; it has a conductivity of 0.5-4 μmho/cm. When
ions are present in the water from soluble salts or strong
acids and bases the conductivity is much higher. Natural
waters range between 50 to 1500 μmho/cm. Reviews on the
measurement of conductivity and how it varies in water can
be found in Hem (7) and in the Wastewater Manual (13).

Effluents issuing from mines typically contain ionic
species and suspended solids. They carry only minor amounts
of nonionic dissolved material such as dissolved organic
compounds. The total dissolved organic carbon in 11 mine
drainage waters in the Front Range of Colorado ranged from <1

to 5 mg/ℓ (34). Conductivity is an indicator of the dis-
solved ionic species, so its measurement is indicative of
the amount of dissolved ionic material in the water. Recent
advances in instrumentation allow portable measurements to
be made easily and precisely (see the Appendix). Thus,
conductivity is a sensitive indicator of the level of total
dissolved solids and hardness in water.

Hem (7) suggests that typically the relation between
conductivity and total dissolved solids follows a simple
straight line relation

$$K \ A = S$$

where K is conductivity in micro mho/cm, S is total dissolved
solids in milligrams per liter and A is some conversion fac-
tor between 0.5 and 1.0. The variability of the conversion
factor A usually renders this equation useful for making only
estimates. But Hem (7) goes on to show that in particular
situations, the relation holds true to the extent that total
dissolved solids and major element concentration can be
estimated with conductance measurements to better than 5%.
Ramirez (35) has shown that for mine drainage effluents which
have $SO_4^=$ as the dominant anion, the conductance is an excel-
lent indicator of total dissolved solids, and iron and sulfate
concentrations. To do this, certain procedures have to be
followed.

The first detail that should be resolved for good con-
ductivity data is that the parameter changes with temperature.
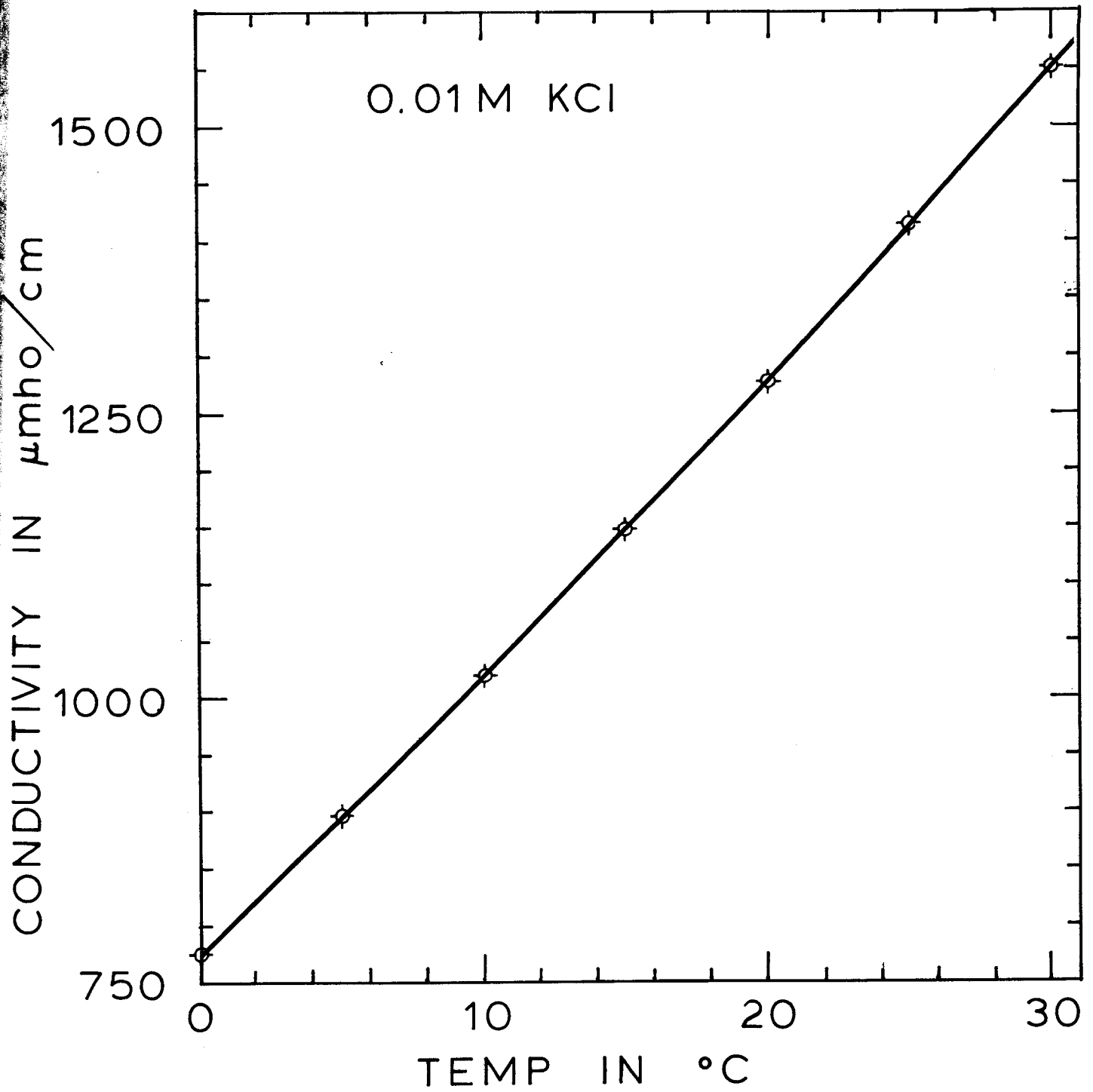Figure 8 is a plot of conductance versus temperature for a

FIGURE 8. CONDUCTIVITY VERSUS TEMPERATURE
OF A KCL SOLUTION.

0.01 mole/liter solution of KCl. The change is about 2% for every 1°C change. Consequently, conductivities are corrected to a standard 25°C. This can be done by taking the measurement at 25°C, or also by using a correction factor based on the specific conductance of KCl at various temperatures (see the Appendix). The next requirement for extended use of conductivity data is that total dissolved solids and complete cation and anion analyses be performed on the waters so that correlations can be made with the conductivity data. This procedure for a Front Range mine effluent is described below. A similar study was made by McWhorter and coworkers (36) on mine drainages in Colorado.

The analyses of Argo water from Spring and Summer 1978 are given in Table VI. They represent a complete elemental analysis; the only important anion is $SO_4^=$. Conductivity at 25°C, total dissolved solids determined as a sum of anions and cations, and total dissolved solids determined by analysis (14) closely correlate. In fact, Ramirez (35) found that for mine drainage waters there is alomst a perfect 1:1 correlation between conductivity at 25°C expressed in μmho/cm and total dissolved solids expressed in mg/ℓ. Figure 9 is a summary of his results for waters varying from pH's between 2.5 and 7.0 (35). The results have two implications:

    1. In a gross sense conductivity and pH will give a sensitive indication of the load of dissolved ions in mine drainge waters. This is usually enough to point out problem areas.

Table VI. Concentrations of dissolved species in Argo Tunnel water in 1977 and 1978. Concentrations are in mg/ℓ; conductivities are in μmho/cm; TDS is total dissolved solids in mg/ℓ.

Date	Na	K	Mg	Ca	Al	SiO$_2$	Mn	Fe	Cu	Zn	Cd	Pb	SO$_4^=$	pH	cond	T°C	cond @25°C	TDS
7/13/77	22	3.2	110	308	-	-	87	202	4.9	38	0.15	0.10	-	2.75	2590	15	3190	-
3/13/78	22	3.4	112	330	-	-	87	200	3.7	37	0.11	0.07	-	2.60	2430	15	2994	-
5/11/78	22	3.4	112	324	23	86	103	180	4.1	43	0.14	0.05	2214	2.5	2680	16	3229	3118
5/19/78	22	3.1	112	315	23	80	103	177	4.1	43	0.16	0.06	2235	2.6	2700	15	3326	3121
5/25/78	22	3.2	115	315	26	86	118	197	5.2	52	0.20	0.10	2415	2.4	2890	15	3560	3360
6/1/78	21.5	2.8	114	300	26	87	123	236	5.5	52	0.22	0.15	2392	2.6	2910	15	3580	3364
6/7/78	21.8	2.6	116	300	27	90	123	241	5.9	53	0.20	0.14	2433	2.5	2970	16	3578	3365
6/15/78	21	2.6	119	294	28	92	123	252	6.1	52	0.18	0.11	2528	2.7	3020	16	3639	3521
6/22/78	21	2.7	122	280	28	96	128	263	6.6	55	0.20	0.10	2540	2.5	3000	16	3615	3546
6/29/78	20.5	2.7	122	300	29	97	130	263	7.1	54	0.18	0.16	2462	2.5	3000	15	3696	3491

2. In a specific situation, if the composition of the
    water is well known, conductivity will be a good
    indicator test of changes in concentration of
    specific elements.

The second conclusion needs more explanation. Figure
10 is a graph of conductivity vs. concentration for Fe,
Cd, Zn, and Na for the Argo Tunnel data in Table VI. For
those cations that are primarily derived from the sulfide
minerals, the changes in concentration correlate well with
conductivity. For those elements that are derived from
the rock forming minerals, the concentration doesn't
change at all. Consequently, when the compositional changes
in the water are well known, there is an excellent chance
that conductivity will serve as a good indicative test
of concentration changes.

TESTS FOR THE NATURE OF THE WATER

In this area there are two objectives for the tests:

1. Is the water of an acid mine drainage type or is
    it weathering more typical types of rock?

2. Is the aquifer a diffuse or conduit type?

To answer the first question tests of pH and conductivity
should be mde. Acid mine water of poor quality will have a
pH below 3 and a specific conductance above 2000 μmho/cm at
25°C. A pH of 4-5 and specific conductance of 1000-2000 is
suspect. If the pH is between 6 and 9 and the specific con-
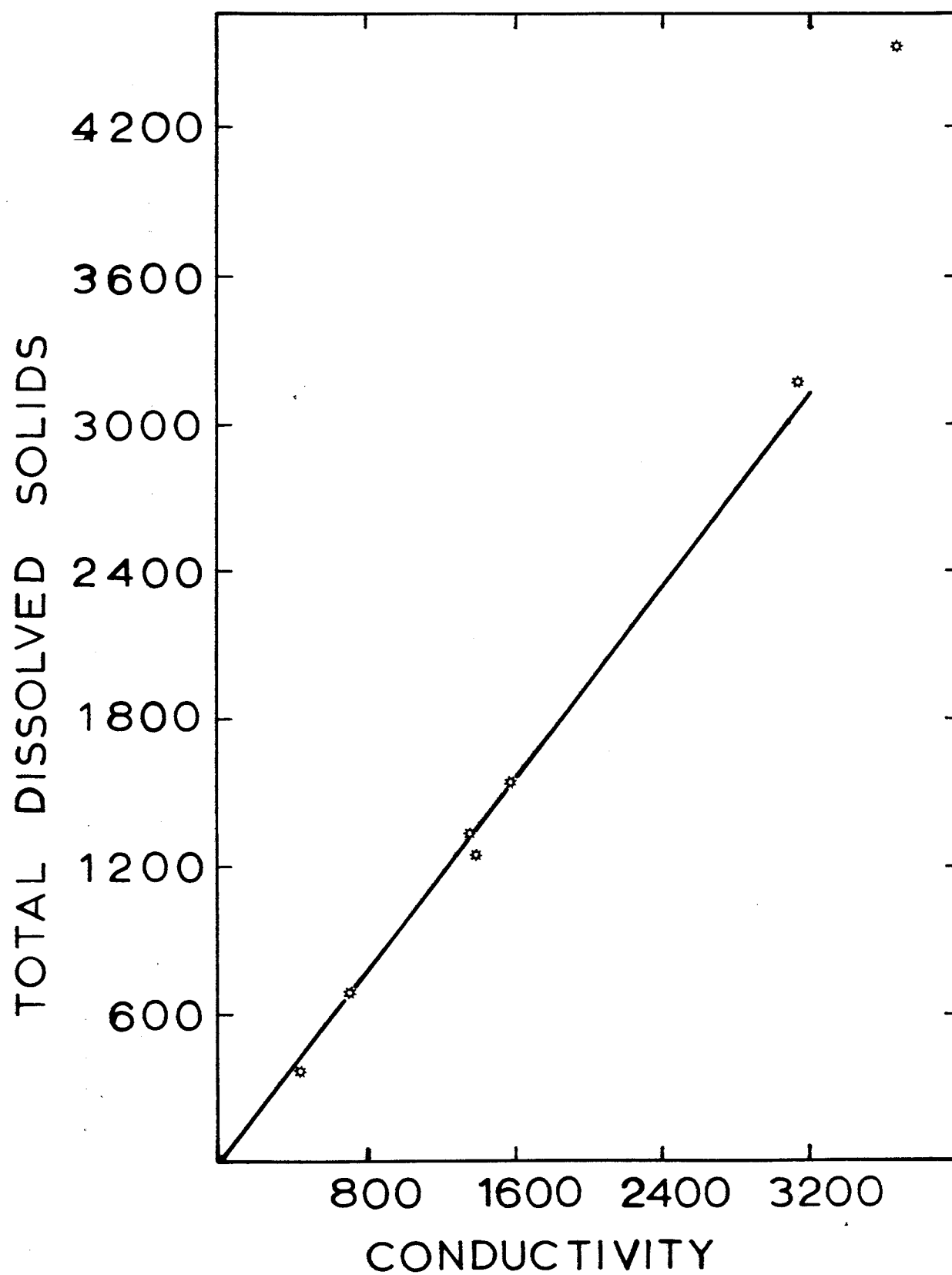ductance is below 1000 the water probably has not weathered

FIGURE 9.   DISSOLVED SOLIDS (MG/L) AS A FUNCTION OF THE
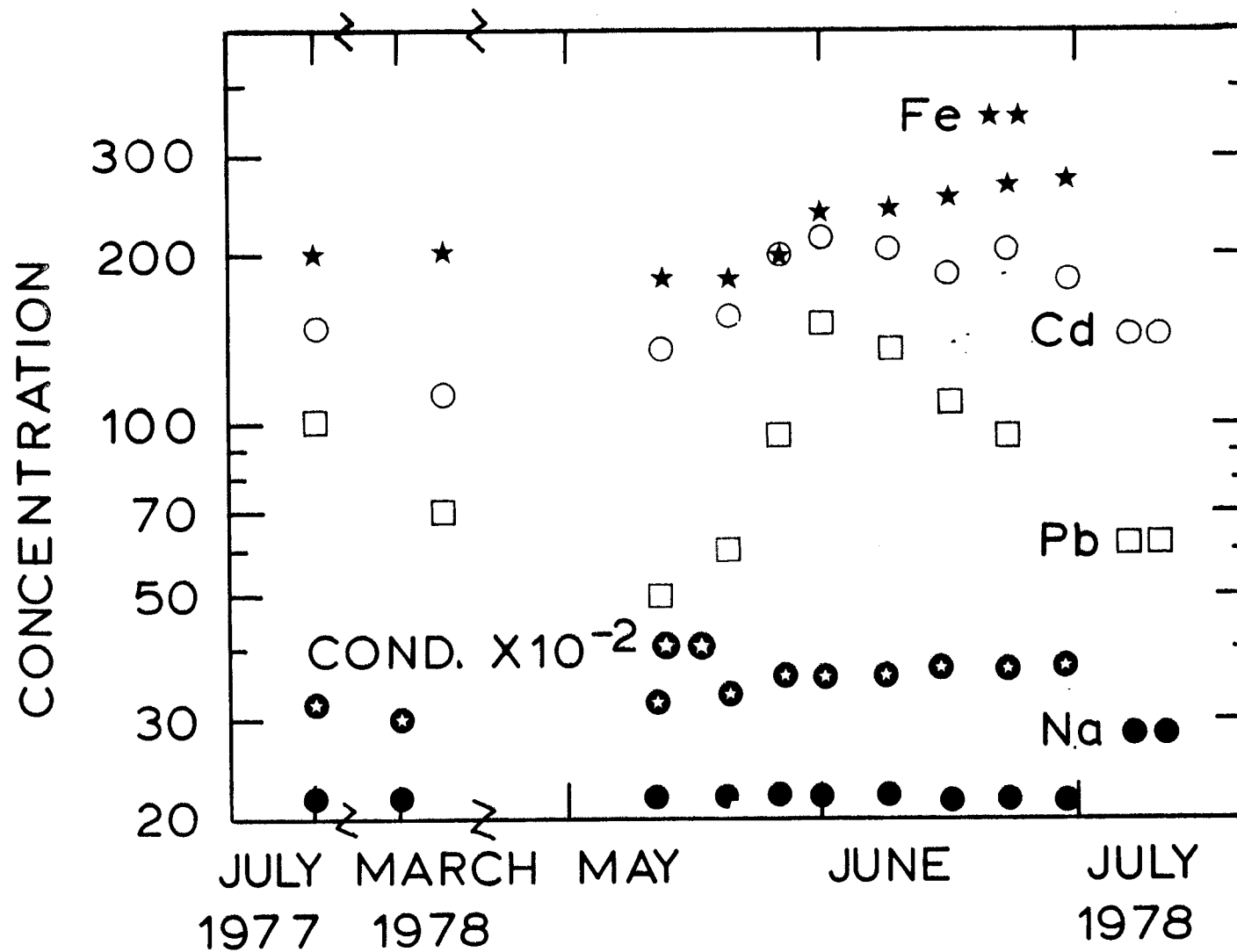
CONDUCTIVITY (MICROMHOS/CM) FOR MINE EFFLUENTS.

FIGURE 10. CONDUCTIVITY AND CONCENTRATIONS OF FE, CD, PB, & NA AS A FUNCTION OF TIME FOR ARGO TUNNEL WATER.

sulfide minerals. Any water that is suspicious should be
sampled for more complete analyses. If the water is flowing
outdoors, then aquatic life will also be a clue. Acid mine
water will usually kill vegetation except for certain algae
in the water. Other water will support grasses and flowers
along the banks. The color of the water can sometimes be
deceptive. Water of a pH of 3 can be almost colorless,
while water of a pH of 5 flowing over red/orange sediment
can appear to be much worse than expected.

To answer the question of aquifer type will take intui-
tion, and a long period of observation. The characteristic
of the two aquifer models is shown in Table IV. Flow is the
primary physical observation, the consistency of the flow in
a diffuse aquifer is remarkable. On the other hand a conduit
aquifer will react to changes in precipitation and to the
spring thaw and runoff. A stake in the stream bed is all
that is needed to observe variations in flow of 50% or more.
Observations for a week to 10 days after a wet period are
most important. The primary chemical test is conductivity
and temperature. For a conduit aquifer, large amounts of
precipitation or runoff will dilute the ground water and
conductivity and temperature will drop. Also, the water may
carry more suspended material. For a conduit aquifer, a
large amount of precipitation or runoff may change the flow
but if it does, the concentration is likely to increase
because ground water that has been in contact with rock
for long periods of time will be flushed out. The effect

can be seen for the Argo Tunnel results in Table VI and in
Figure 10. The samples were taken over the Spring runoff
period to test for variations in concentration with flow.
Measurement of flow, conductivity and temperature every week
during the spring recharge is a good way to determine the
type of aquifer.

The reasons for knowing the type of aquifer are quite
important. For any diffuse aquifer, the flow will be con-
stant and the worry of overwhelming treatment facilities
will be minimal. For conduit aquifers, the danger of over-
whelming treatment equipment or having a mine flood is quite
real. Conduit aquifer water is probably unnecessary since
diversion procedures could probably be used on the surface
above the mine to limit the amount of water entering the
aquifer. The flood of the Idorado Mine near Silverton,
Colorado in the Spring of 1978 is an example of damage by
a conduit aquifer which could possibly have been averted.
If the aquifer type is known, then more is known about the
earth around the mine. Such knowledge not only helps to
control water problems but adds to the knowledge needed for
where to open the next adit.

TESTS FOR COMPLIANCE TO REGULATIONS

The water discharge permit dictates how often discharge
water has to be analyzed and for what species analyses have
to be made. The important point to understand is that such
a discharge permit is a flexible contract. If the operator

can show that he has been conducting careful and regular tests of the water, then the analyses dictated in the permit can be changed. If a change in the analytical schedule can be made, then conductivity as an indicative test for effluent levels is the best candidate.

Other than conductivity, pH measurements should be made. This test is indicative of the concentration levels of many base metal ions and can be used as an essential test that effluent quality is being maintained. Presently, there is no substitute test for suspended solids so this is also necessary.

If a mining operation is dealing only with diffuse aquifer water and if the chemical composition of the water has been studied for a reasonable length of time, then for routine compliance pH, conductivity and suspended solids should be the only necessary tests. Total chemical analyses or analyses for compliance should be necessary only a few times a year. The burden of eliminating more stringent analyses lies on the operator showing that he understands the nature of his mine water and also understands how to perform the needed analyses.

TESTS FOR MAINTAINING QUALITY CONTROL

A water effluent treatment system should be considered like any other industrial chemical process. As such, it should conform to the principles of process engineering (37). To be successful, monitoring of the output has to be performed

so that information can be fed back to the input so that proper adjustments can be made to improve the process. The classic process engineering diagram shown in Figure 11 summarizes these principles.

The requirements on monitoring for effective feedback are:

1. That the measured properties respond rapidly to changes in the input parameters.

2. That the measured properties accurately reflect the key reactions that occur in the chemical process.

3. That the properties be easily and rapidly measured even to the point of automated readings.

In processes involving water, pH and conductivity usually are the most reliable feedback monitors. Since the key reaction in most effluent treatment processes is neutralization of the acid water with an appropriate base, monitoring pH to provide input feedback is obviously essential. Monitoring the conductivity will provide information on whether too much base has been added. In addition, both pH and conductivity can be easily measured and readily automated. This is especially true for conductivity where the equipment is typically easier to maintain than pH meters. Again, complete chemical analyses of the output stream are necessary to better understand the water treatment process. But again, once the process is understood and under control, routine monitoring can be accomplished with conductivity and pH and
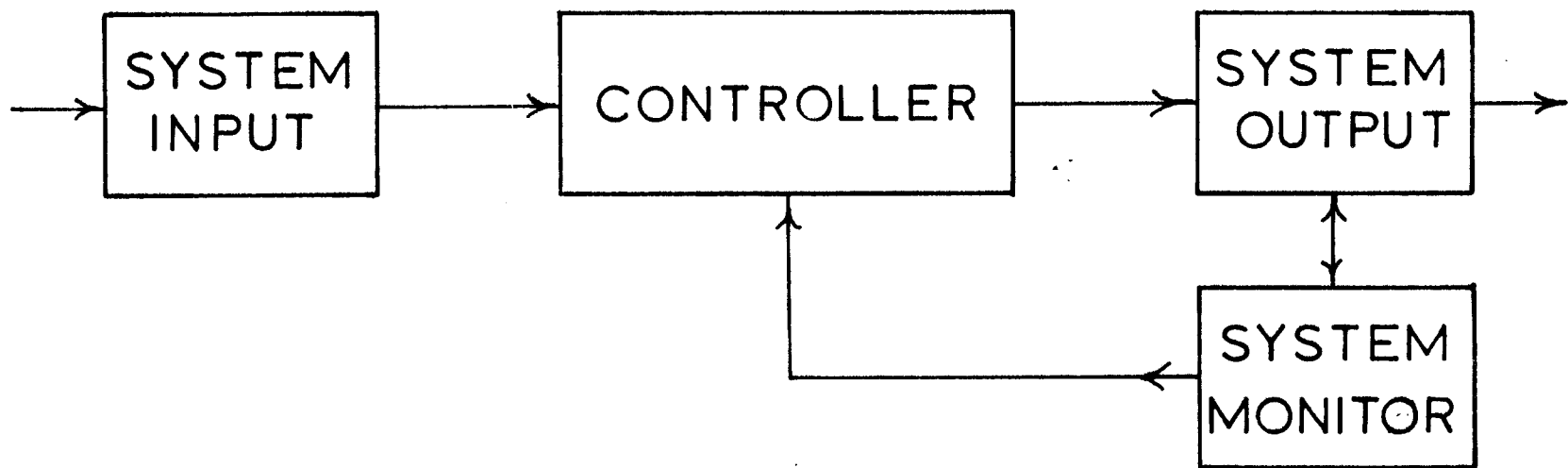
FIGURE 11. DIAGRAM OF A TYPICAL PROCESS SYSTEM
CONTAINING A FEEDBACK LOOP.

specific tests will be needed only occasionally.

SUMMARY

The primary point to this analytical section is that analyses should be made to know the chemistry of the water, and not just to comply with effluent limitations. If this is done, then the types of weathering reactions and the type of ground water aquifer can be established. For processing wastewaters, the same complete knowledge is necessary. In this case, indicative analyses such as pH and conductivity can often replace specific analyses if the water has been well characterized.

SUGGESTIONS FOR WATER MAINTENANCE

For mining operations, the maintenance of water is
fairly straightforward. Most of the obnoxious constituents
can be precipitated from the water by raising the pH. This
is the primary method of treatment which is suggested for
metal mining operations by the EPA (1). The next step in
most operations is the removal of suspended solids by settling.
These two processes are already well developed and only minor
suggestions are made in this chapter for treatment of process
water. Because of this good background of process method,
this chapter stresses using the understanding of water
chemistry to decide what water to process. Many mines are
located in areas where the construction of extensive treat-
ment ponds is difficult and expensive. Also, the indiscriminant
addition of lime to all the water effluents can be costly.
Some waters don't have to be treated and other waters can
become much more obnoxious if they accumulate in the wrong
areas. Knowledge of the water chemistry should allow the
separation of good water from bad and this can help con-
siderably in reducing the amount of effort involved in water
treatment.

The general suggestions which will be developed are:

1. Try to stop conduit aquifers from penetrating a
   mine by sealing the surface sources.

2. Separate conduit aquifer water from diffuse aquifer
   water since typically the conduit water does not

need treatment.

3. Keep water from rock which promotes acid mine
   drainage and divert it if possible to places which
   will control acid mine drainage.

In general then, the stress here is on separation,
diversion, and other methods of control besides the brute
force addition of lime coupled with waiting for settling to
occur. In this regard, Hyatt (38) has prepared an excellent
article outlining techniques that can be tried to make water
effluent treatment more manageable. His article primarily
deals with mill wastes and in this division of the ore
dressing industry many of the BATEA limits for 1984 are for
zero discharge to be maintained. Hyatt points out that
natural waters from the ground or the air that find their
way into the process will have to be treated as if they
were coming from the process. Obviously, diversion and
separation techniques have to be considered to keep process
operations from being controlled by the whims of nature.

WATER IN UNDERGROUND OPERATIONS

Water from conduit aquifers should be kept from under-
ground operations as much as possible. This water has a
direct connection from the surface to the tunnels and this
situation makes the water a nuisance and perhaps dangerous.
The flow can vary greatly with precipitation and spring
runoff so control of the amount of conduit aquifer water is
difficult. At best, it can cause intermittent flooding; at

worst, it can cause severe flooding or cave-ins. Furthermore, once this water penetrates the underground workings it has the potential of weathering ore minerals to create acid mine drainage.

Penetration by surface waters can often be traced by the use of dyes added to the water. Once this has been done, reclamation procedures can be attempted on the surface. Diversions by flumes or conduits or the construction of dams to hold water back are all potentially useful projects. Trexler and coworkers (39) have published a study done on the Bunker Hill Mine near Kellog, Utah in which surface water aquifers were substantiated and recommendations were made for improvements. This article makes a nice case study of how to reclaim surface water from underground operations.

For waters that are already present underground, the primary consideration is separation. If conduit aquifer water cannot be eliminated, it should be separated from the other waters and piped directly to the surface for discharge. This water should be of similar quality as the surface water. There is a good chance that it doesn't have to be treated if it can be shown by careful analyses that it is just fugitive surface water. If there is appreciable conduit aquifer water, a separate discharge system would pay for itself in reduced treatment costs.

For waters that are in the category of acid mine drainage, again the primary maintenance consideration is separation. Here, the separation is from better quality waters and from

ore minerals in the bedrock and in tailings so that the water will not deteriorate to a worse condition. Separation can be by conduits and flumes; plastic pipe should be used to eliminate corrosion. If the underground workings contain carbonate rock, then consider the alternative of diversion of the water to this area. The weathering reactions for carbonate minerals discussed under rock weathering will keep the water from further deterioration. In addition, contact with carbonates should raise the pH of the water in the same way as the use of lime. Separation from ore bearing rock to places that are neutral or that can naturally cleanse the water should reduce the maintenance effort needed at the surface.

WATER IN ABOVE-GROUND OPERATIONS

In above-ground operations the important consideration is the diversion of all rainfall and snowmelt away from working areas. If this water invades the mining property, then the operator is responsible for its maintenance. If this water penetrates tailings piles, then it can weather sulfide minerals and become an effluent of poor quality. An article by Herricks and coworkers (40) shows how plans can be made to control surface waters. They emphasize how the location of surface operations can be used to promote good water management.

A problem that often occurs is the mixing of waters with tailings from abandoned mines or waters from abandoned mines with recent tailings. This should definitely be avoided.

If sulfur and iron oxidizing bacteria are present, their most likely habitat will be in abandoned mines and tailings. It takes on the order of years for the biological catalysts to operate at peak efficiency. In active operations, their effect can be reduced by not allowing water to remain in contact with sulfide minerals. In abandoned operations, the microbiologic organisms can work to their greatest extent. Mixing abandoned and active residues will allow the biologic weathering of sulfides to increase in the current refuse.

PROCESS WATER

For this category of water, the operations of neutralization and settling which are currently used in the industry are reasonable. However, some recent observations on what happens upon addition of base to the water may help to make these processes more efficient. There are some properties of the hydroxide precipitates that are formed which can affect how well the water is cleaned. These properties have only recently been investigated (41, 42, 43), so that an explanation of how they affect the removal of heavy metals from waters is in order.

The raising of the pH of water causes the formation of heavy metal hydroxide precipitates which settle from the water. Figure 1 shows the sequence of removal as the pH is raised. There are also two other mechanisms for removal of heavy metals, specifically, adsorption of ions onto the surfaces of solids and occlusion of ions into the structure

of newly formed precipitates. These processes enable the removal of heavy metal cations even though the pH may not be high enough to cause removal through precipitation. Diagrammatic reactions for the three processes are shown below:

1. $M^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow M(OH)_2 \downarrow$ Precipitation

2. $2M^{2+}_{(aq)} + $ Adsorption

3. $M^{2+}_{(aq)} + $ Occlusion
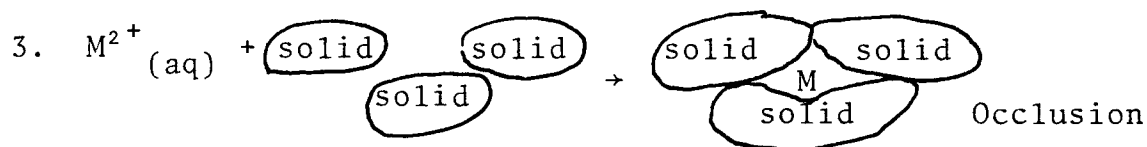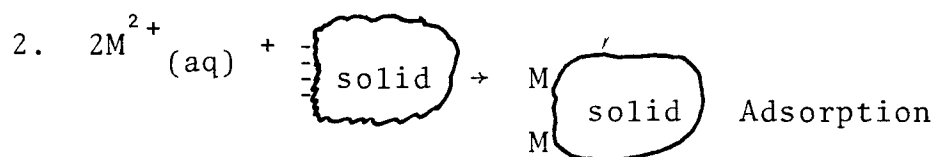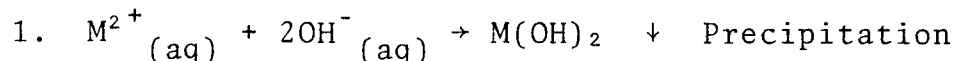
For adsorption and occlusion to be significant processes, the solid particles have to be small so that they possess high relative surface areas. In natural waters, the hydroxides of aluminum, silicon, manganese and iron form colloidal sized precipitates. These gelatinous solids have been found to have a high propensity for adsorbing and occluding other ions (6, 17). Since Mn and Fe are present in mine drainage systems it has been speculated that the hydroxides of these two metals have been just as important to the removal of cations such as Pb^{2+}, Cd^{2+}, Zn^{2+}, Ag^+, and Cu^{2+} as the precipitation of the respective hydroxides (43, 44). Of the two processes, adsorption appears to be more important than occlusion (43, 44). A discussion of the adsorptive capacities of Mn and Fe hydroxides and how this relates to process waters

follows.

The diagrammatic reaction for adsorption shows an impor-
tant feature of the process. The surface of the solid is
charged and the force of attraction of the ion for the solid
surface is electrostatic in nature (45). Now the amount of
surface charge as well as the sign of the charge can be changed
by changing the conditions of precipitation or by strongly
adsorbing some other ions onto the surface of the solid. For
hydroxide precipitates in water, the pH of the system strongly
dictates whether the surface is positive or negative. At
low pH's, H^+ ions are strongly adsorbed and the hydroxide
surface is positive; at high pH's an excess of OH^- ions occur
on the surface and thus it is negative. The pH at which the
surface changes from positive to negative is called the iso-
electric point (45). For manganese oxide precipitates, the
isoelectric point is at about a pH of 2, whereas for iron
hydroxide precipitates, the isoelectric point varies between
pH 5 and 9 (41, 44). What this means is that if a tailings
pond suspension is at pH of about 6, then Mn hydroxides have
a negative surface and Fe hydroxides have a positive or neutral
surface. Consequently, Mn oxides will more strongly adsorb
trace metal cations than will Fe oxides. This situation
has been substantiated by the recent studies of trace metal
associations with Fe and Mn oxides (41, 42).

What this implies regarding the removal of obnoxious
cations from mine and mill waters is that one cannot rely on

the precipitation of Fe hydroxide in mine water and the
adsorption of all other cations onto the Fe hydroxide sur-
face. For adsorption to be effective, the water should con-
tain appreciable Mn if the pH is below 7, or else the pH
should be close to 8 to allow precipitation and adsorption
by Fe hydroxides.

To put what was explained above into practice, reliance
on the addition of lime to raise the pH may not be enough to
lower the levels of heavy metals to safe concentrations.
The concentrations of Fe and Mn in the water are important
and the pH of the solid-water system is also a factor.
The method of addition of lime may affect the manner in which
the predominant hydroxide precipitates are formed and this
could affect their adsorption capacities. Also, aeration
may change the properties of the tailings pond system to
promote or hinder heavy metals removal. The tailings pond
operation is a place where empirical experiments may appre-
ciably change the efficiency of the operation. Parameters
that may possibly be varied are the speed and position of
where lime is added, the method of aeration, the position
of the aerators, the flow of water into the pond, and the
size of the pond.

Concerning the design and operation of water treatment
facilities for mines and mills, Hyatt (38) has analyzed
various alternatives quite nicely. He includes in his review
a summary of the EPA limitations for milling operations,
internal milling operations to be considered, controls around

and within the tailings pond, a review of different water
treatment methods, and economic estimates of how much each
treatment method costs for different sized operation. He
also suggests that the tailings pond is a good place to
conduct practical experiments to determine just which set
of procedures will work best for wastewater treatment. The
number of parameters that he suggests to vary is extensive.
Among the more interesting are ways of promoting or retarding
evaporation from the pond, ways of constructing leakage
control points rather than relying on impervious liners,
and suggestions for turbulence baffles to promote settling
efficiency.

CONCLUSIONS

These suggestions for water maintenance are not innova-
tive but neither are they costly. Hopefully, the procedures
follow an obvious problem-solving sequence:

1. Secure a complete chemical analysis of the water for
   a number of times over the course of a year. Include
   some samples collected during spring runoff.

2. At more frequent intervals (about once a week)
   determine the pH, conductivity, and total suspended
   solids in the water.

3. Assess whether ground waters are of the diffuse or
   conduit aquifer type in underground operations.

4. Block off conduit aquifers on the surface if possible.

5. Separate and divert the different water types.

6. Divert fugitive surface waters from all operations.

7. Try manipulating the conditions in the tailings pond
    to achieve the best possible treatment situation.

8. The cornerstone of this treatment method is to
    know what species are in the water and how the con-
    centrations may change over time. With this knowledge
    the type of water can be determined and the treat-
    ment can be tailored to the water type.

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APPENDIX I: ANALYTICAL METHODS

Methods comparable to those described below can be found
in all water analysis manuals (13, 14). The difference is
that the methods from manuals are authorized while the proce-
dures described below are sometimes changed from the author-
ized methods to be specifically useful to mining operations.

COLLECTION OF WATER SAMPLES

The way water is collected for analysis is perhaps more
critical than the analysis itself. It cannot be done using
any old bottle and taking any old water sample. What is
done during collection necessarily biases the analytical
results. This portion of the analytical program has to be
carefully planned. The following outlines what should be
considered.

Collection Kit

The following items are necessary:

1.   Polyethylene collection bottles 5.00 ml or 1ℓ size.

2.   250 ml polyethylene beaker

3.   Laboratory wipers such as Kimwipes

4.   Polyethylene bottle (125 ml) of reagent grade HNO_3
     diluted 1:1.

5.   Towel

6.   Field notebook

7.   Thermometer for measuring water temperature.

8.   Conductivity meter

9.   Polyethylene bottle (500 ml) of distilled or deionized

water

10.   10 ml graduated cylinder.

The following items are optional:

11.   pH test paper

12.   pH meter with two reference buffer solutions

13.   Field filter unit with air pump or N_2 tank for
      pressurized filtering.

First, it is suggested that the analyst check this list
of items with other such lists and complete his own list of
items for collection (13, 14). Second, comments are needed
about the optionality of a pH meter and field filter unit.
With regard to a pH meter, this electrochemical measurement
is technically difficult and the instrument is easily sub-
ject to environmental influences. It is best to leave the
pH meter set and take the samples to the meter as rapidly
as possible. The measurement of pH is discussed in a later
section.

Filtering Samples

Whether to filter the water or not has to be carefully
considered because this operation can bias the analytical
results. If the samples are filtered, a 0.45 μm membrane
filter should be used in a field filter unit. Such field
filter systems are now available from most scientific supply
companies. For mine drainage waters, most water is in a
low energy flow situation and the load of suspended solids
is minimal. In our studies, we have operated on the premise

that if we cannot see particulates in the water, then we
won't filter. We have tested this rule of thumb by taking
unfiltered samples and comparing them with samples that have
been filtered by various methods (35). The concentrations
of all species were the same to within 5% on all but two
cases. In one case, the water was slightly turbid and the
analyses were predictably different. In the other case, the
sample couldn't be filtered until 20 minutes after collection
and the results were different. So, if the water looks tur-
bid, filter and do it immediately. If not, filtering can be
neglected.

If the water is clean, great care should be taken to
insure that the stream is not roiled up during collection
so that suspended material inadvertantly finds its way into
the sample. Collection should be done at a pool so that as
much suspended material as possible has settled out. Also,
if a large sample bottle is placed in a stream, filling it
sometimes roils up the system. This is the reason for the
plastic beaker on the necessities list. Use it to sample
the water with little disturbance to the system.

Handling the Sample

The species in water are usually not in equilibrium
and precipitation reactions will occur if the water is left
to stand as is. Consequently, the water has to be stabilized.
For cations this is done by adding nitric acid to the sample.
The amount added is 5 ml of 1:1 HNO_3 per liter of water.

This amount of acid is sufficient to prevent precipitation of hydroxides, to kill most microbes, and to prevent adsorption onto the bottle walls.

The nitric acid is diluted because concentrated acid attacks plastic bottles. No matter how much care is taken, the acid bottle invariably leaks or spills so keep the bottle and graduate wrapped tightly in a plastic bag so leaks can be contained.

For pH measurements, bicarbonate analyses, and dissolved solids measurements, unacidified water is needed. Usually 1ℓ of sample will be sufficient for analyses on the unacidified water. For the acidified sample, collect 500 ml of water.

When taking the sample, the bottle you put it in may be dirty even though it is new. Rinse the bottle twice with a sufficient amount of the sample water to make sure any contaminants have been removed or replaced by what is in the water.

Bottles

Glass bottles are heavy and adsorb most trace metals so they are not good for inorganic analyses of water. Some plastic polymers such as polycarbonates or polyacrylics also adsorb trace metals. The best bottles to use are made of conventional polyethylene. This material is free from most inorganic contaminants and also doesn't adsorb trace metals as extensively as glass (46).

Storing Samples

For the acidified water samples which will be used for trace metal analyses, deterioration of the sample poses no problem. In our laboratory, we have stored mine drainage waters for a year in polyethylene bottles with no change in the concentration. For the unacidified water, one has to act rapidly. The water will start to react to form precipitates in the matter of an hour, especially if there is an appreciable concentration of Fe in the sample.

pH MEASUREMENTS

In our experience, the measurement of pH is technically difficult to do in the field. The primary cause for this difficulty is the measuring concept involved in a glass membrane electrode. Hydrogen ions have to flow through the membrane to complete the electrical circuit. This is not easy and consequently, a typical pH electronic circuit has an impedance of at least 10,000,000 ohm (47). This high resistance requires that the pH meter be a complex test instrument. When such an instrument is taken in the field, it has to be superbly constructed or otherwise the electronic components will be damaged. Even with a good instrument, the following problems have occurred to us more than once:

1. Moisture on the electrode jack causes intermittent shorting of the circuit.

2. Oil or rust on the electrode jack causes poor connection in the circuit.

3. Cold weather (below 15°C) causes malfunctioning of
   the meter.

4. Wind causes malfunctioning of the meter.

5. Static electricity build up on the dial face
   causes malfunction of the meter.

We have established a policy that a pH meter has to be
placed in as controlled an environment as possible, even
when it is taken in the field. Consequently, it is left in
a warm portion of the vehicle and samples are taken to the
meter for pH measurements. Only on calm, warm days do we
risk taking the pH meter to the water. For most water, the
pH measurement will not change for a half-hour. So if you
can return to the lab within that time, field pH measurements
are unnecessary.

Even in a controlled environment, a pH measurement is
not easy. The principal culprit is the glass electrode which
is easily fouled. Consider the glass electrode a necessary
evil; most water chemists would not bother with such a tem-
peramental apparatus if the measurement of pH weren't important.
The following pieces of advice should be considered:

1. Always have on hand 3 standard buffers of pH 4.00,
7.00 and 9 or 10. In some instances a faulty system will
be adequate over 3 pH units to solve problems.

2. Never trust the battery check indicator; if there
is a question, check the batteries themselves. Most portable
pH meters require a mercury cell as a constant voltage source.
These batteries tend to fail abruptly and often show failure

only under a reasonable load.

3. Always keep the electrode wet, preferably in a solution of saturated KCl. If this is not feasible, try keeping the water in the protective cup that came with the electrode.

4. The best way to use the rubber sleeve over the KCl filling hole on the electrode is to just pinch it open to the atmosphere and not slide the sleeve down. One forgets that the sleeve is down and leaves the electrode or packs it back in its box. The result invariably is a dried up electrode when a critical measurement needs to be taken. Recently, electrodes which have a KCl gel which needs no filling have been made available.

5. On a combination glass electrode, there is a hole near the tip that is filled with fiberglass or some ceramic. This hole permits electrical contact with the reference electrode inside the glass electrode. This fiber junction has to be in the solution for the electrical circuit to be completed. Solution has to flow through this hole so it has to be kept free of grease and dirt. When taking the pH of mucky water this can present a problem.

6. Always have two electrodes on hand. The only way an electrode system can be checked is to see if a good electrode system performs the way it should. As a substitute, a pH meter test instrument is available from most supply houses. It will serve the purpose of an extra electrode and is worth the cost if a laboratory has many meters.

7. The pH measurement taken is only as good as the buffers
which are used for calibration. In some instances with tablet
buffers, the solution makes an excellent nutrient for bacteria
growth. Some of the buffers which are already in solution
have a bacteriacide in them and are stable for long periods
of time. In that respect, the prepared solutions may be
worth the expense.

In summary, pH measurements take a high level of technical
expertise. There appears to be no substitute for careful
maintenance of the glass electrode and the pH meter. Save
the instruction manual on the meter and the information sheet
on the electrode. They usually contain suggestions to try
if the system is operating poorly.

CONDUCTIVITY AND TEMPERATURE

In comparison to pH measurement, modern electronic
circuit designs have made the measurement of conductivity
quite easy. The portable meters have a dial readout which
enables readings to be accurately made from 100 μmho/cm to
50,000 μmho/cm. New conductivity cells which are encased in
plastic are rugged and durable. In addition, some cells
have temperature probes built into them so both readings
can be made with the same meter. The maintenance procedures
which are suggested for the new cells are quite good. Only
once has a conductivity cell gone foul and that was because
it was being used in a solution which had an appreciable
amount of sulfide ion in it. Otherwise, the cleaning

procedures which have been suggested have allowed us to use the electrode for 4 years without replatinizing. Some suggestions concerning the measurement of conductance are given below:

1. Frequently check the accuracy of your conductivity cell by measurement of the conductance of a standard KCl solution such as that given in the instrument manual or that given in Table VII.

2. A conductivity meter and cell which can take temperature measurements is worthwhile. In most instances, it is quite difficult to make a precise temperature measurement with a thermometer. The thermistor devices will be precise. This is important since water temperature changes of ±2°C in some effluent streams are quite significant. However water temperatures is measured, it is important to use the same device and method all the time to achieve consistent results.

3. To compare conductivities of different waters, the values have to be adjusted to the same temperature. The adjustment factors given in Table VII for a 0.01M solution of KCl are suitable for this purpose.

4. When taking a conductivity reading, make sure the cell is totally immersed so that the proper solution flow and contact is maintained around the electrodes. If this is not done, the reading will typically fluctuate considerably. Also, for temperature measurements the thermistor on the probe can usually be seen on the top by the cable. Make

Table VII. 0.01M KCl conductivities in μmho/cm vs.
           temperature in °C.

Temp °C	cond	corr. to 25°C
0	776	1.821
1	800	1.766
2	824	1.715
3	848	1.666
4	872	1.620
5	896	1.577
6	921	1.534
7	945	1.495
8	970	1.457
9	995	1.420
10	1020	1.385
11	1045	1.352
12	1070	1.321
13	1095	1.290
14	1121	1.260
15	1147	1.232
16	1173	1/205
17	1199	1.178
18	1225	1.154
19	1251	1.130
20	1278	1.106
21	1305	1.083
22	1332	1.061
23	1359	1.061
24	1386	1.020
25	1413	1.000
26	1441	0.9806
27	1468	0.9625
28	1496	0.9445
29	1524	0.9272
30	1552	0.9104

certain this is immersed so that water temperatures rather than air temperatures are recorded.

NONFILTERABLE RESIDUES

For these two measurements to be made by the standard methods requires extensive laboratory equipment (13, 14). What is developed in this section are suggestions for determining these solids concentrations with less expensive equipment but the analyses require more time. Some objectives behind the solids measurements need to be explained so that the measurements can be put in proper context.

For dissolved solids, the conductivity reading is a good method of measurement, but first, the empirical relation between conductivity at 25°C and total dissolved solids levels has to be established by making measurements by both methods on the different types of waters a number of times. Note that the relationship may be different for different types of water. If there are appreciable concentrations of volatile species such as nitrates, carbonates or organics in the water, making a precise determination of total dissolved solids is difficult. For waters associated with mining operations, these constituents are usually not present so the methods used can be a little less exacting. Again, it is necessary to have a complete analysis of the water to verify that volatile species are not in appreciable concentration so that the methods used prove feasible.

In the case of suspended solids or nonfilterable residue, the concentrations are subject to compliance restrictions.

For mining operations these restrictions are between 20 and
30 mg of suspended solids in a liter of water (2, 38). This
value is so low that excellent analytical procedures will
have to be used to achieve any consistent results. In fact,
if water samples are sent out for suspended solids measure-
ments, send some replicates to check the precision of the
methods in the laboratory. At the level of 20 mg/ℓ of
suspended solids in water, an analytical laboratory needs
a balance capable of weighing to 0.1 mg and a reliable
filtering apparatus which uses 0.45 μm membrane filters (13,
14). The analysis will have to be performed in a restricted
area which is clean and free of dust. Although the U.S.G.S.
manual suggests that the correlation between turbidity and
suspended solids is subject to too many variations (13), it
may be reasonable to attempt this on a restricted basis.
The precision of the diagnostic turbidity test could
be better than the specific analysis for suspended solids.
As of now, there is no easy method to do the analysis of sus-
pended solids and the standard methods should be used.

DISSOLVED SOLIDS ANALYSIS

Most waters will carry at least 300 mg/ℓ of dissolved
salts. Waters derived from glacier melting can fall below
100 mg/ℓ. Consequently, if one liter of water is evaporated
to dryness, the residue is likely to be at least 300 mg. If
this is the case, the test can be made on a triple beam
balance if care is taken. Some precautions should be taken.

First, the container used for evaporation should have a
large surface area so that a thick cake of residue is not
formed. It appears that a thick cake retains moisture (13,
14). Also, the weight of the evaporation container should
be light and made of inert material so that it can be heated
to 180°C (350°F). An aluminum pie plate should work nicely.
They come in a 5-inch size that weighs less than 5 g, and
this size easily fits on a triple beam balance, and maintains
a constant weight.

Supplies

1. Aluminum pie plate (5-inch size)

2. Triple beam balance

3. Heat source of less than 100°C (200°F) and then 180°C
    (350°F). A regular food oven will be sufficient.

4. A filtering setup which uses Whatman No. 50 filter
    paper may be necessary if the water is turbid.

Procedure

Collect 1 liter of suspension free water or filter one
liter of water to eliminate suspended solids. The water
should be unacidified and analysis should be started within
24 hours. Evaporate the liter of water in 200 ml amounts
into an aluminum pie plate which has been preweighed to a
constant weight. Evaporation should take place in the low
temperature oven. Upon evaporation of the water, dry the
sample in the high temperature oven for 2 hours. Weigh the
plate immediately upon cooling. The weight difference

expressed in milligrams will be the total dissolved solids in mg/ℓ.

Comments

1. For mine drainages, it is necessary to begin evaporation immediately since the water is unacidified and a $Fe(OH)_3$ precipitate can start to form within 24 hours.

2. After the residue is evaporated, the analysis can be interrupted. At this point, the sample in the pie plate can be stored in a dust free area until a number of samples are ready for the 180° oven.

3. Since the pie plates will probably be purchased at the local supermarket, they may have a surface layer of organic material. Wash them and heat them to a consistent weight in the 180° oven before using them for analysis.