

A WATER HANDBOOK FOR METAL MINING OPERATIONS

by

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Colorado Water

Resources Research Institute

Completion Report No. 113

**Colorado
State
University**

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Completion Report

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ABSTRACT

This completion report is a handbook that operators of metal mines can use to understand how the various substances 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 environment 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 constituents 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

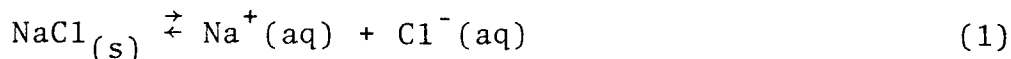
THE WEATHERING OF ROCKS

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).

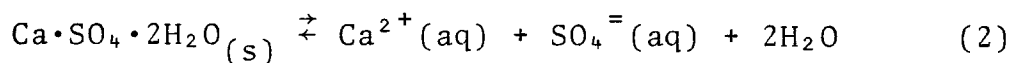
The species in typical rain water and the dissolved species in typical river water for North America are shown in Table I (16). The constituents added between the rain and the river must come from the earth's crust. They are primarily derived from the weathering of the minerals in rocks. The reactions 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



halite



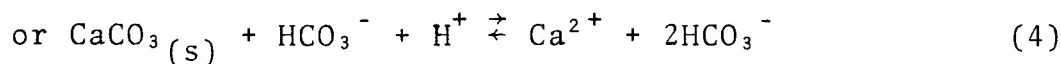
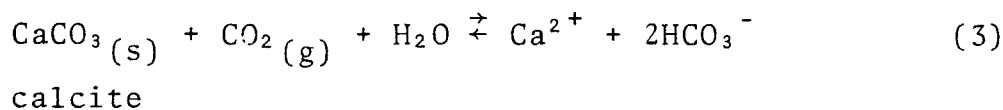
gypsum

Table I. Dissolved Constituents in Some Natural Waters.
(Units are in mg/l 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

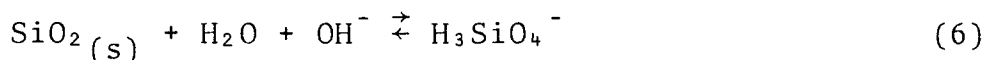
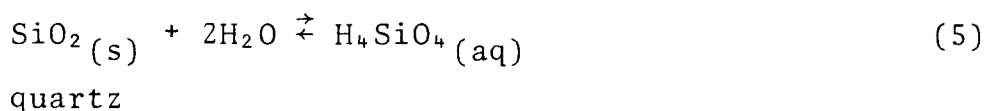
Cond.^a = conductivity in $\mu\text{mho/cm}$

2. Carbonate Minerals - reactive dissolution



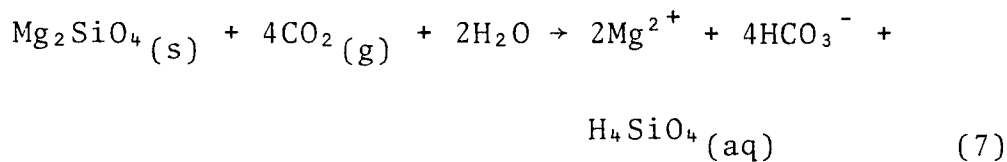
In this case, reactants in the weathering came from the water or air.

3. Quartz - reactive dissolution

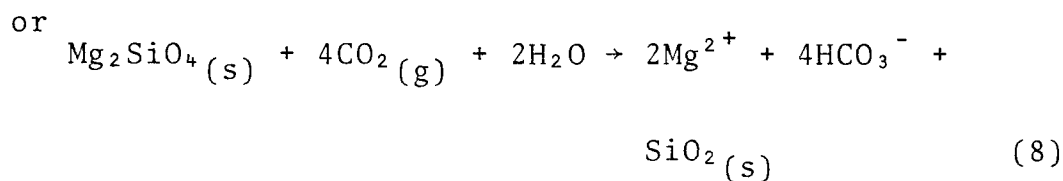


B. Incongruent Reaction - solid residues are deposited as products

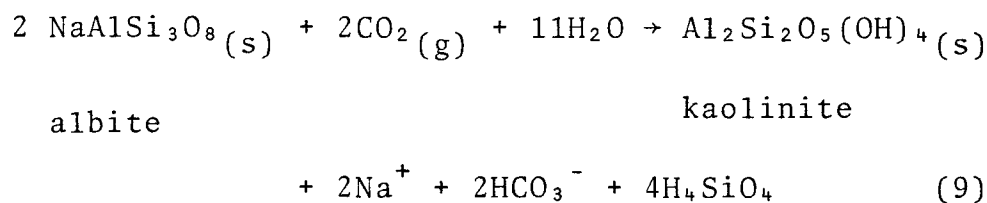
1. Simple silicates - congruent or incongruent



Mg-olivine

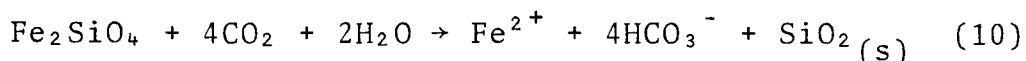


2. Alumino Silicates - deposition of clay



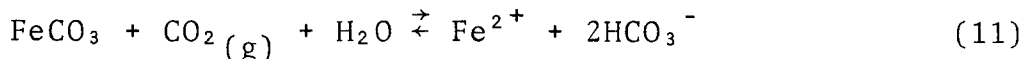
C. Oxidation - Reduction Reaction

1. Iron Silicates - dissolution to Fe(II)



Fe - olivine

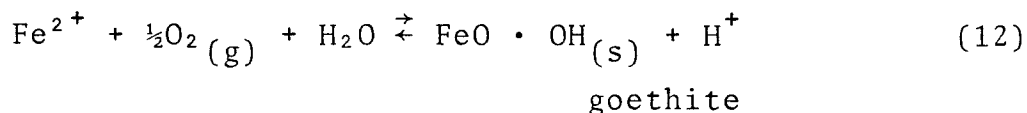
2. Iron Carbonate - dissolution to Fe(II)



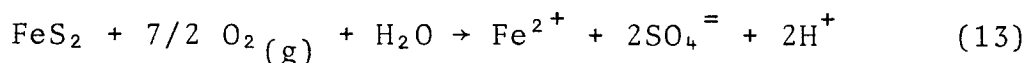
siderite

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



4. Pyrite: Oxidation of sulfide to sulfate



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 $\text{SO}_4^{=}$ 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 concentrations 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.

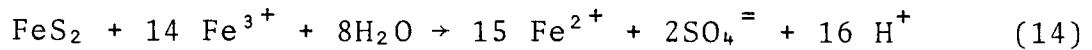
THE WEATHERING OF ORE MINERALS

The Primary Reactions

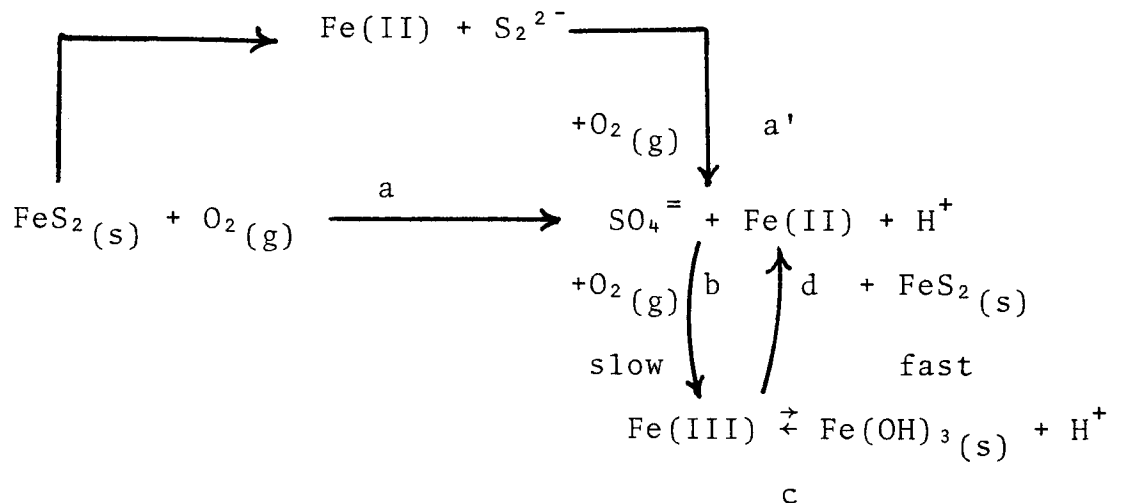
In the summary of weathering reactions listed above, iron minerals are listed separately. The primary reason for this is because iron exists as Fe(II) in many igneous minerals, but the ultimate weathering product is iron (III) hydroxide. The weathering takes place in two steps. First the release of Fe(II) 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.



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,

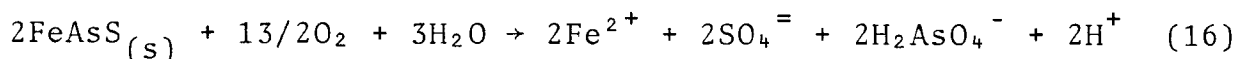
Table II. Dissolved Constituents in Waters of the Central City Mining District.

	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

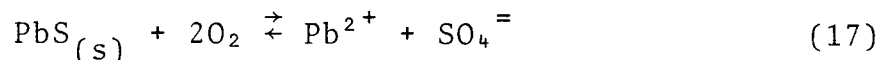
cond^a - conductivity in $\mu\text{mho/cm}$.

Pb, Mn and As. These metals will typically be included in other sulfides such as chalcopyrite $(\text{Cu, Fe})\text{S}_2$, galena PbS , sphalerite ZnS , arsenopyrite FeAsS , enargite Cu_3AsS_4 and tennantite $(\text{Cu, Fe, Zn, Ag})_{12}\text{As}_4\text{S}_{13}$. 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 , $(\text{Fe, Cu})\text{S}_2$, 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:

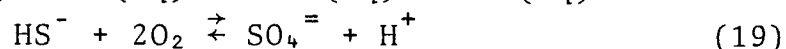
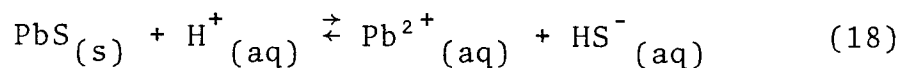


In the case of simple sulfides, no hydrogen ions are released upon dissolution; for example:



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.



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 $\text{Fe}(\text{OH})_3$. 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

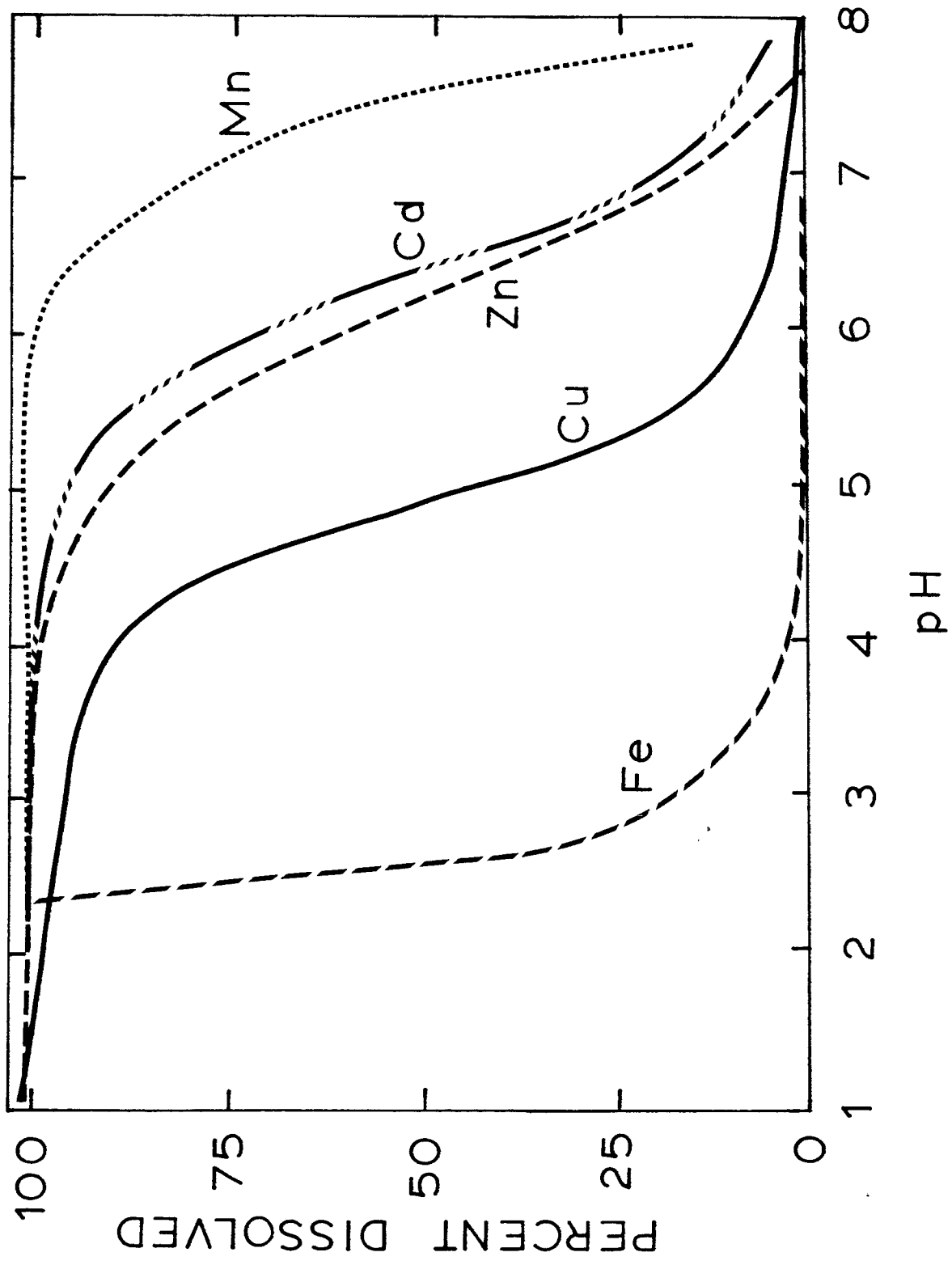


FIGURE 1. HEAVY METAL BEHAVIOR AS A FUNCTION OF PH IN ARGO WATER.

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 compounds), acidophilic (can live only in waters of low pH), and are found in soils throughout the world. There is confusion 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 $\text{Fe}(\text{OH})_3$ 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 concentration 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 regulations (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	
Reference	(8)	(48,49)	(8)	30 day avg.	24 hr max.	30 day avg.	24 hr max.
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 dis- solved 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 successful because both the current and future limitations are based on sound chemical principles. Specifically, the technology 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 ($\text{Ca}(\text{OH})_2$) 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 effluent 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 an unpopular decision to tighten regulations. Currently, new relaxed interim standards are being published for the mining and milling industry. Also, the effective date 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 mineralization 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 contains 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

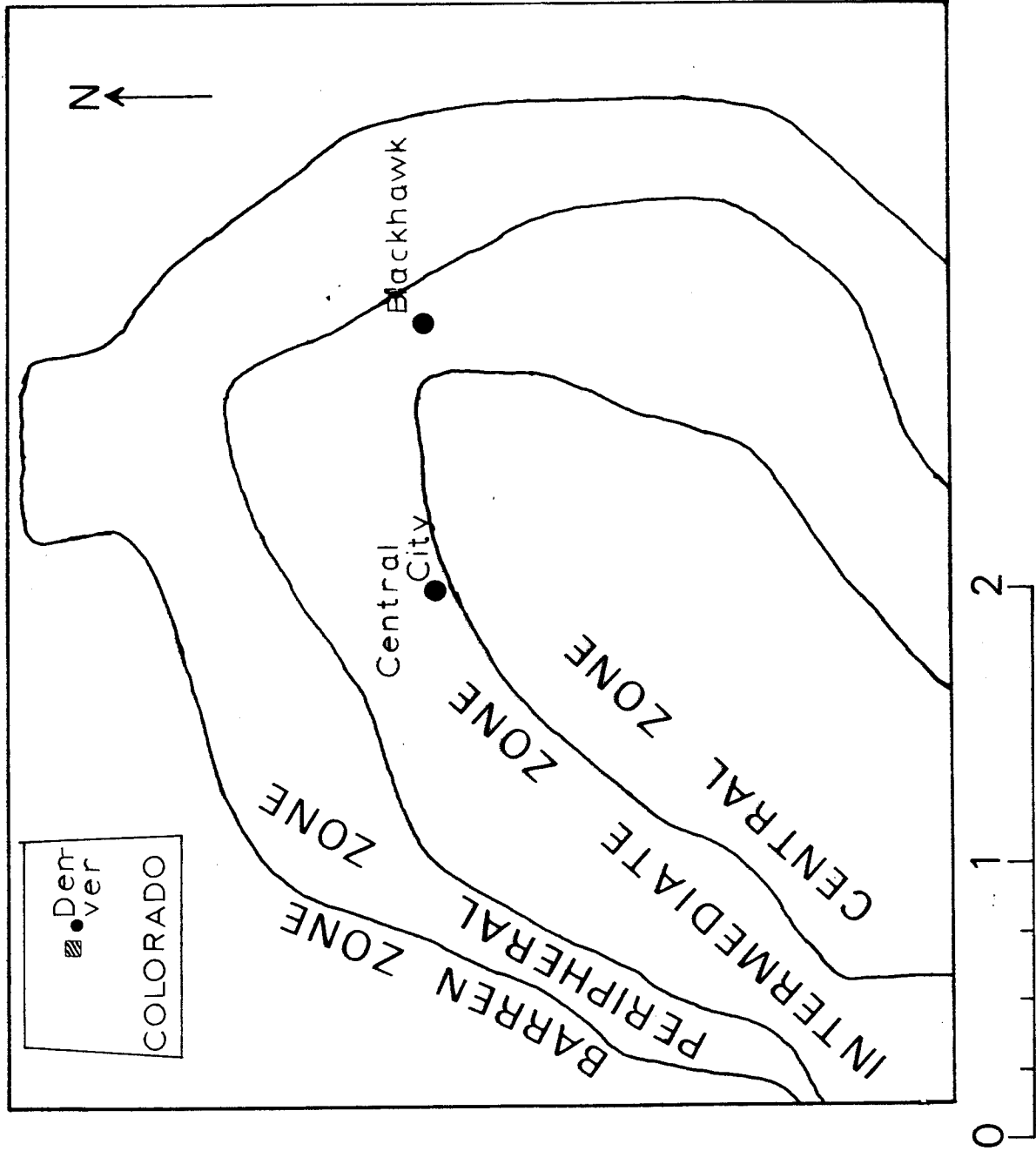


FIGURE 2. ZONES OF MINERALIZATION IN THE CENTRAL CITY MINING DISTRICT (FROM REFERENCE 11).

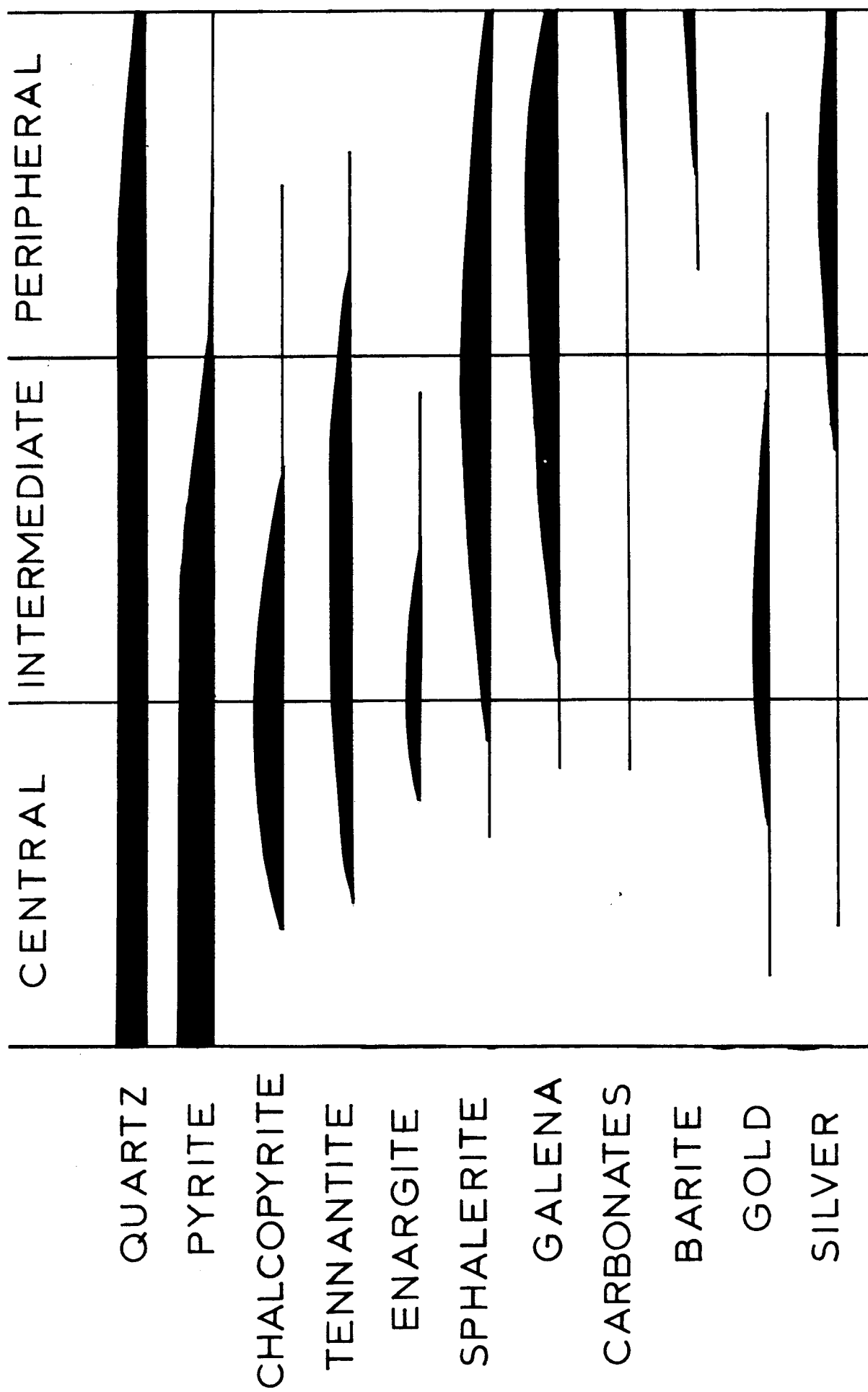


FIGURE 3. ZONAL DISTRIBUTION OF THE VEIN FORMING MINERALS IN CENTRAL CITY (FROM REFERENCE 11).

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 intermediate 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 intermediate 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 harmfulness 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 biological 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 concentration 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 composition of the more important rock units in the mining district and the way in which these rocks weather.

In summary, they are two sources for the chemical constituents in a mine effluent. The base metals and $\text{SO}_4^{=}$ are derived from the vein minerals and the abundance of pyrite 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

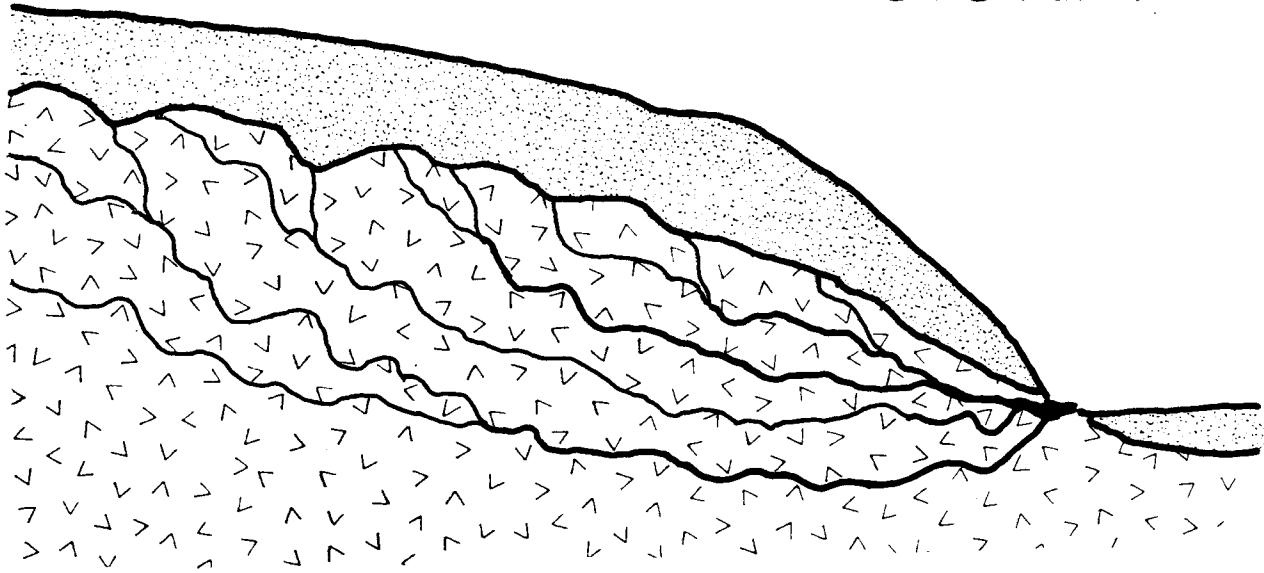
Describing the mechanisms for ground water recharge can become quite complex and relating this to water chemistry adds another dimension to the difficulty. However, studies in Pennsylvania on the water chemistry of springs issuing from carbonate terrains have generated two simple models for ground water 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

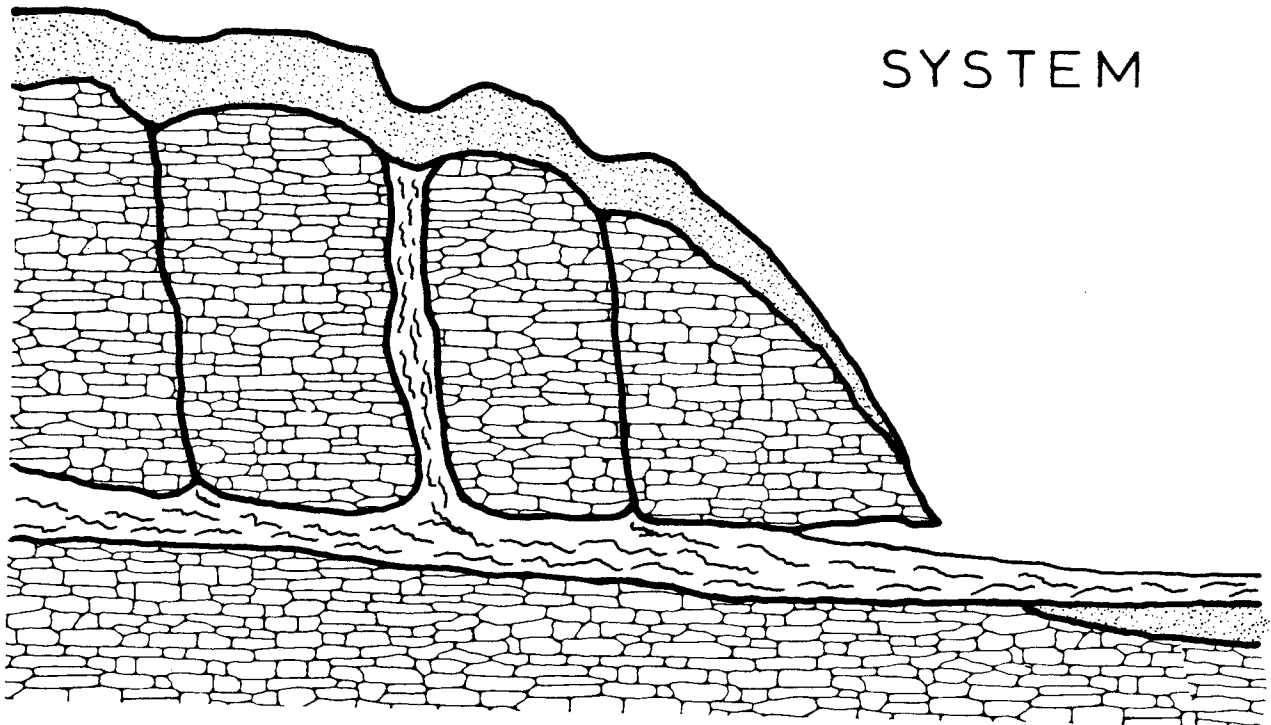


FIGURE 4. DIAGRAM OF THE CONDUIT AND DIFFUSE
AQUIFER MODELS.

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 systems (9, 11, 12). Indeed, if a conduit aquifer were encountered 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.

<u>DIFFUSE</u>	<u>CONDUIT</u>
1. No response to climatological 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.

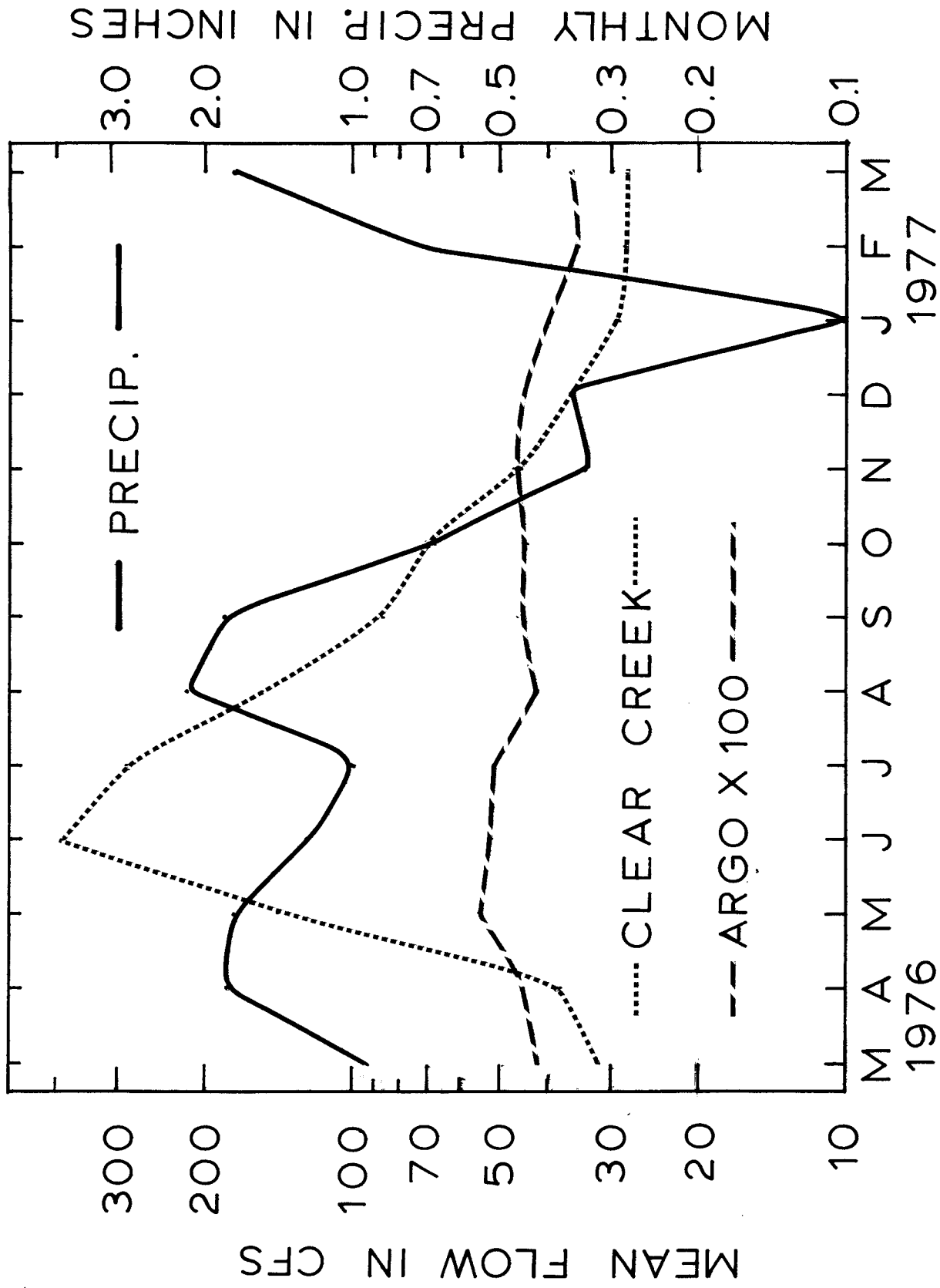


FIGURE 5. DISCHARGE AND FLOW RATES AND PRECIPITATION AT THE ARGO TUNNEL.

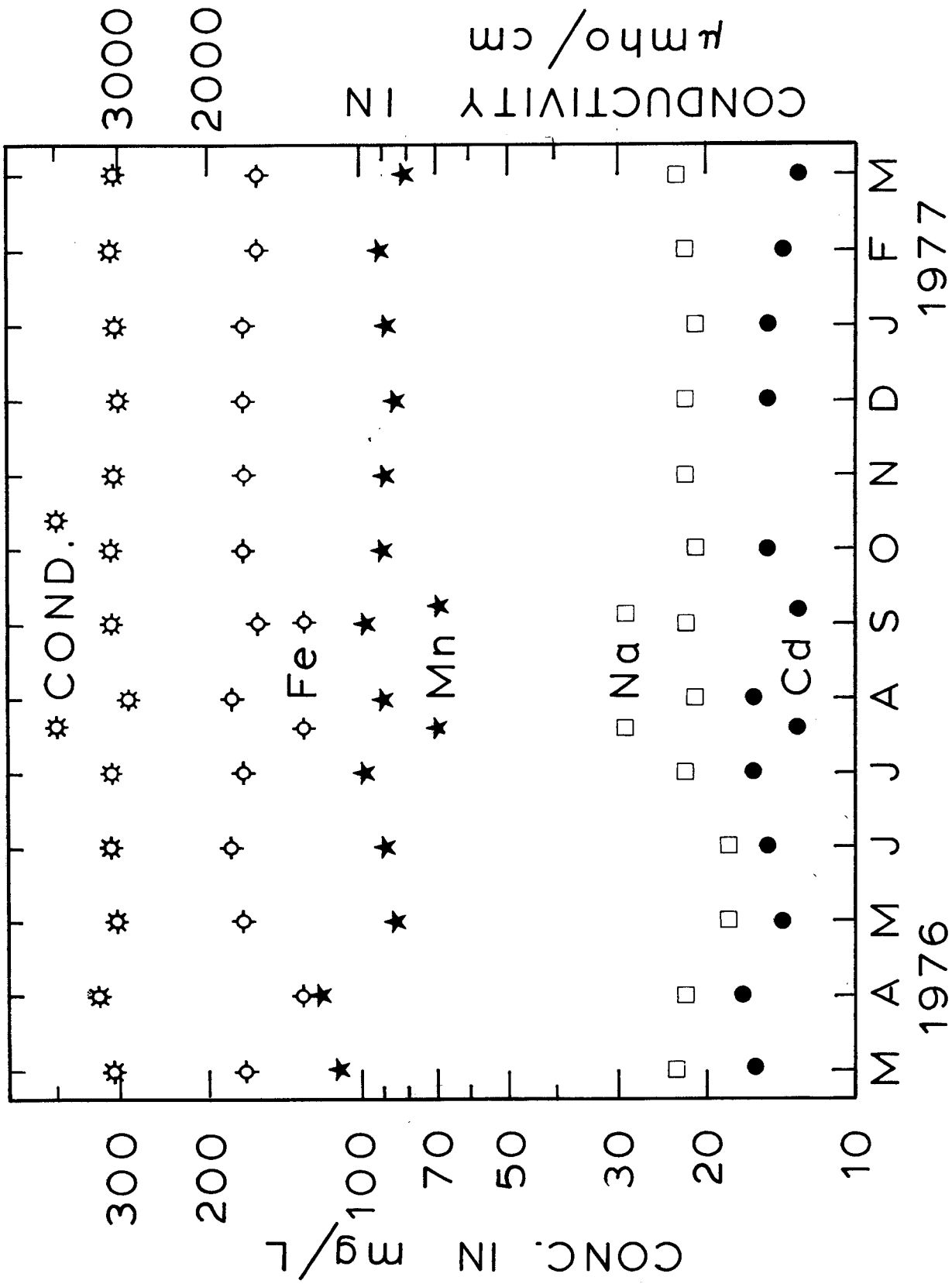


FIGURE 6. MONTHLY VALUES OF THE CONDUCTIVITY AND CONCENTRATIONS OF IONS IN THE ARGO EFFLUENT.

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 $\pm 50\%$ in specific conductance and concentrations within a few days for conduit aquifer springs issuing from limestone formations in Pennsylvania.

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 establishing 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 information 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

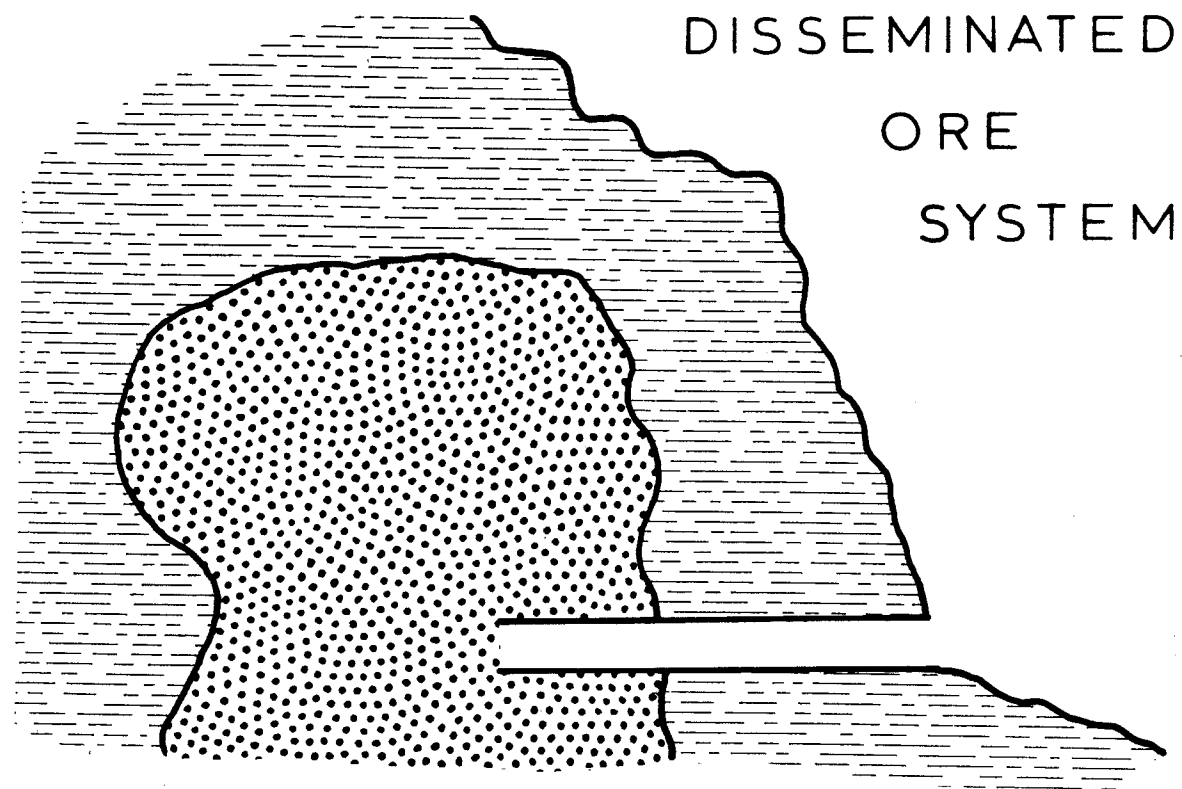
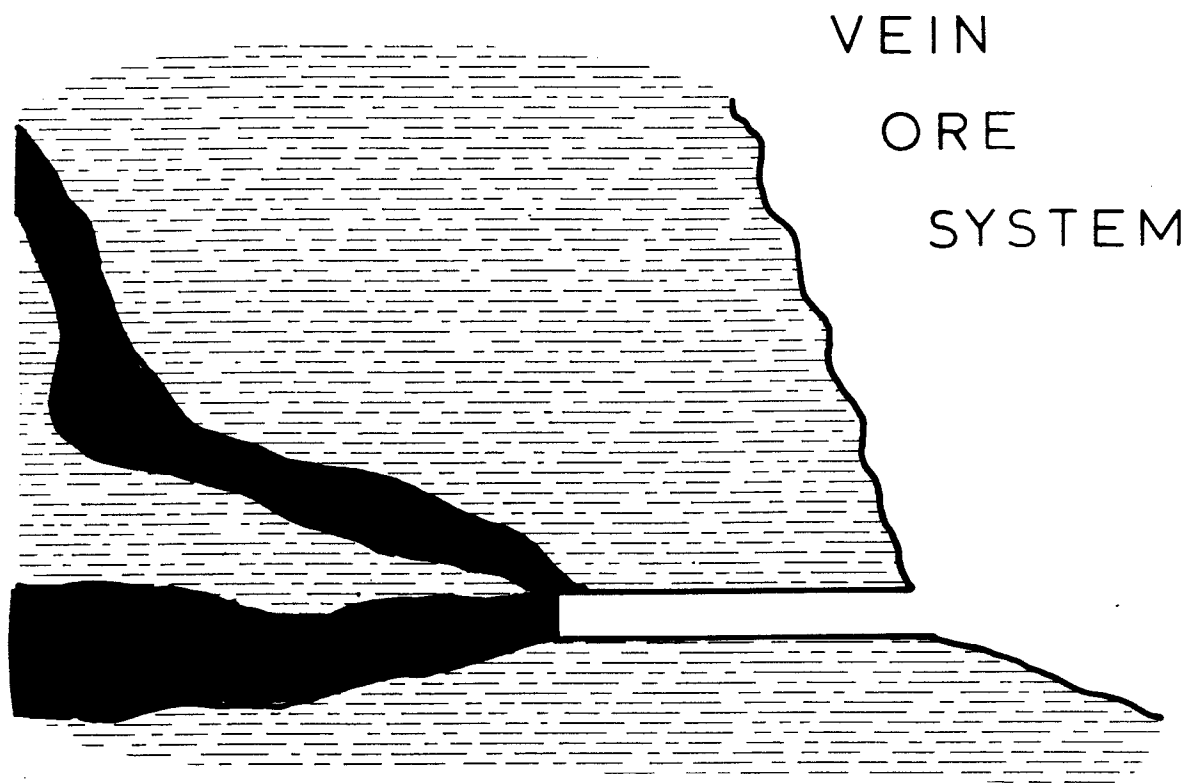


FIGURE 7. DIAGRAM OF VEIN AND DISSEMINATED ORE SYSTEMS.

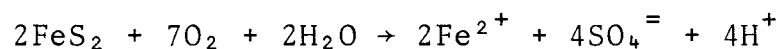
Table 5. Ranges in Concentrations of the Major Elements and Base Metals in Mine Drainages from Three Mining Districts in the Front Range Mineral Belt of Colorado. Pb and Cd concentrations are in ug/l; all others are in mg/l.

	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

¹Concentrations in ug/l.

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.



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 instances, 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 disseminated 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 current. It is usually measured in micro mho/cm ($\mu\text{mho/cm}$) where a mho is the inverse of resistance in ohm. Pure water is a poor conductor; it has a conductivity of 0.5-4 $\mu\text{mho/cm}$. 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 $\mu\text{mho/cm}$. 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 dissolved 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 factor 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 excellent 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 conductivity data is that the parameter changes with temperature. Figure 8 is a plot of conductance versus temperature for a

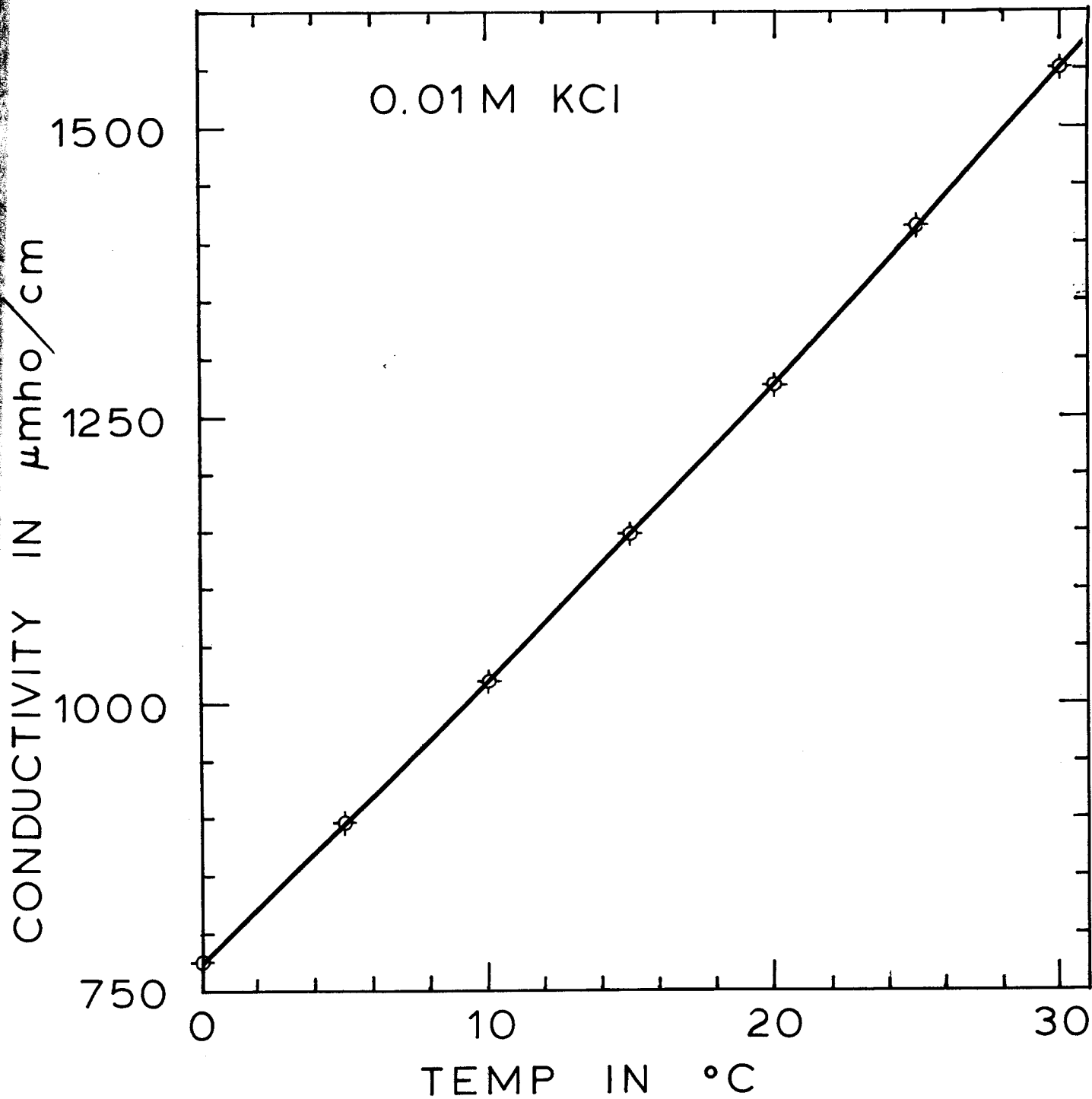


FIGURE 8. CONDUCTIVITY VERSUS TEMPERATURE OF A KCL SOLUTION.

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 $\text{SO}_4^{=}$. 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 almost a perfect 1:1 correlation between conductivity at 25°C expressed in $\mu\text{mho/cm}$ 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 drainage 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 $\mu\text{mho/cm}$; 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 made. Acid mine water of poor quality will have a pH below 3 and a specific conductance above 2000 $\mu\text{mho/cm}$ 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 conductance is below 1000 the water probably has not weathered

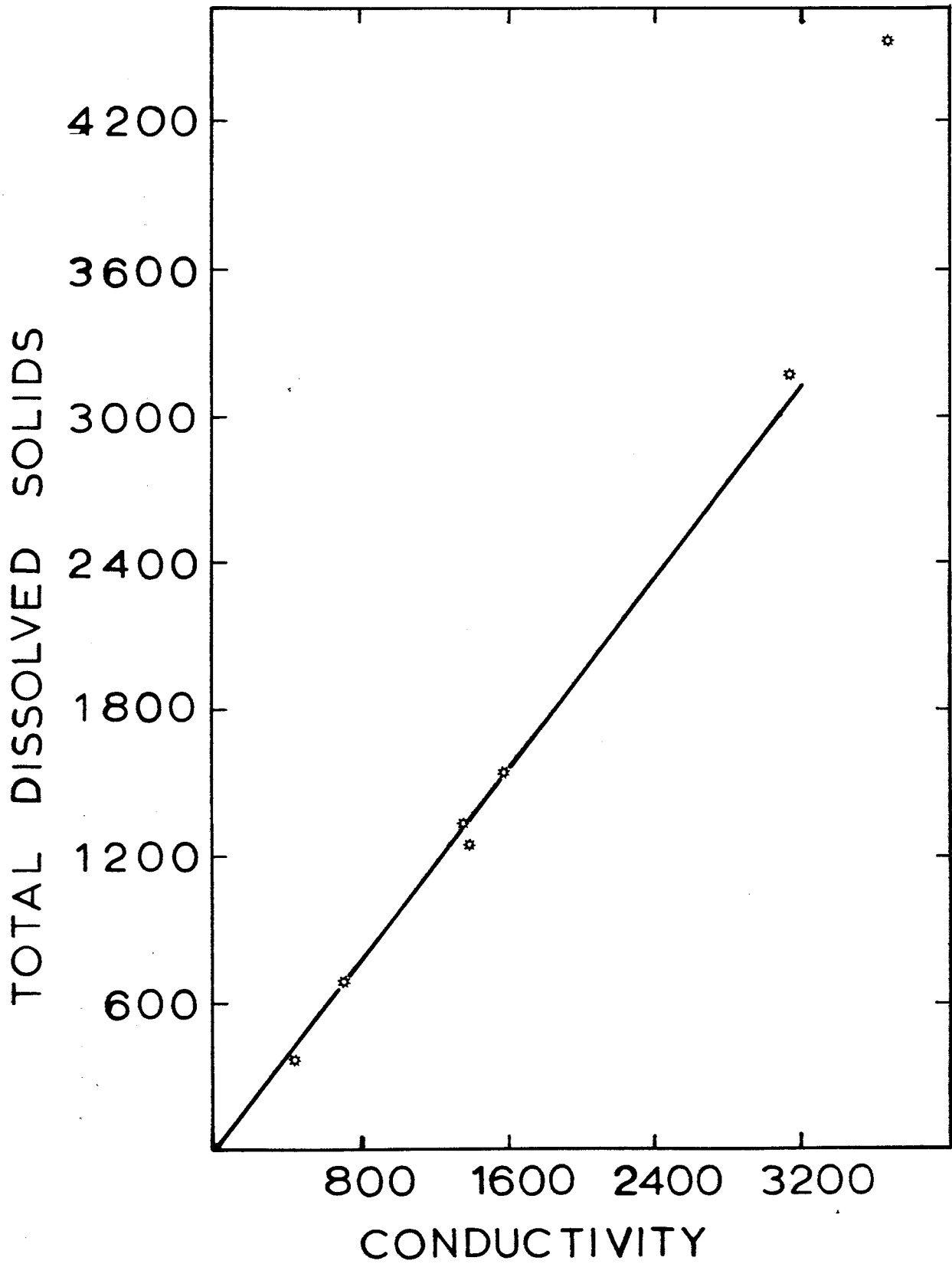


FIGURE 9. DISSOLVED SOLIDS (MG/L) AS A FUNCTION OF THE CONDUCTIVITY (MICROMHOS/CM) FOR MINE EFFLUENTS.

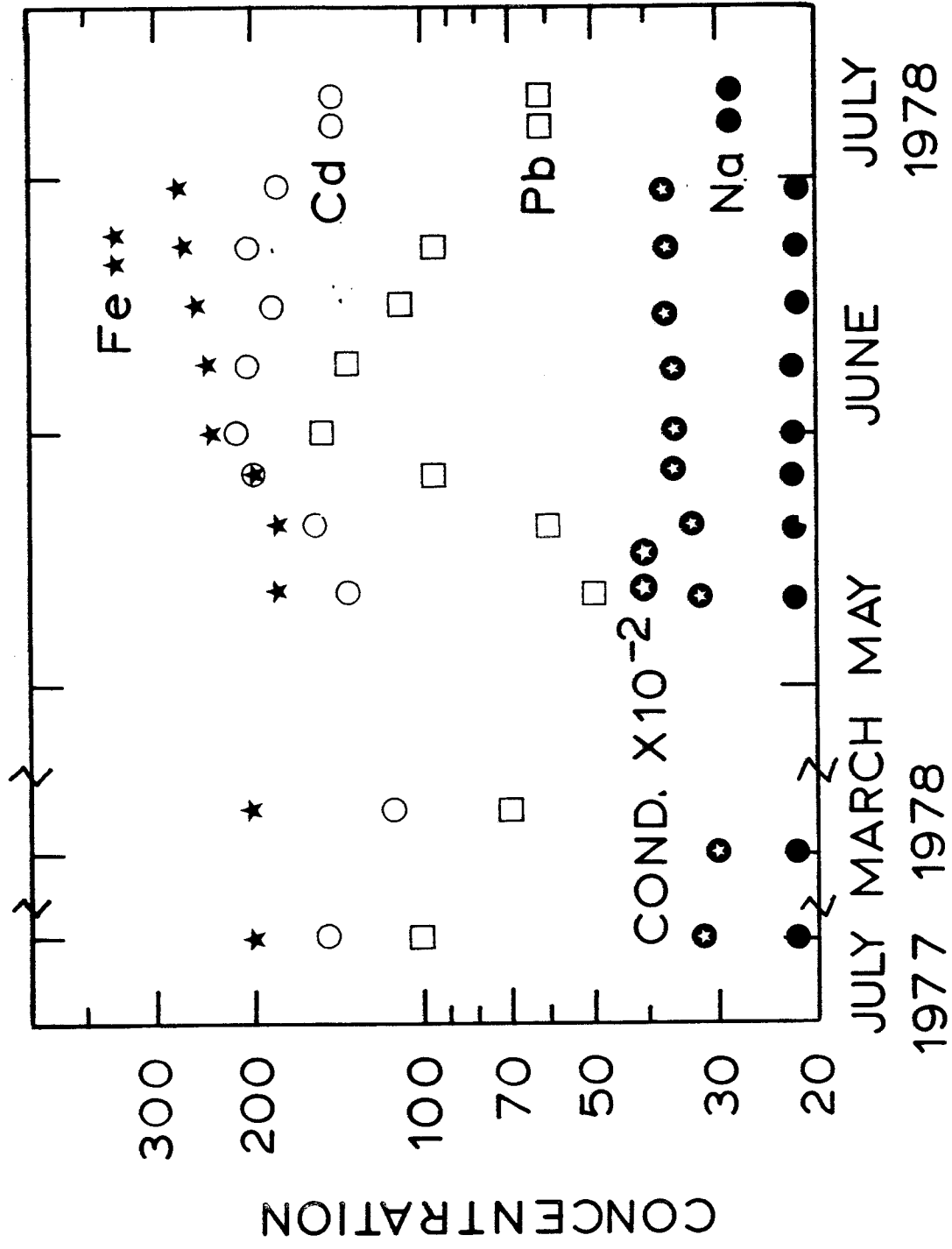


FIGURE 10. CONDUCTIVITY AND CONCENTRATIONS OF FE, CD, PB, & NA AS A FUNCTION OF TIME FOR ARGO TUNNEL WATER.

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 intuition, 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 constant and the worry of overwhelming treatment facilities will be minimal. For conduit aquifers, the danger of overwhelming 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

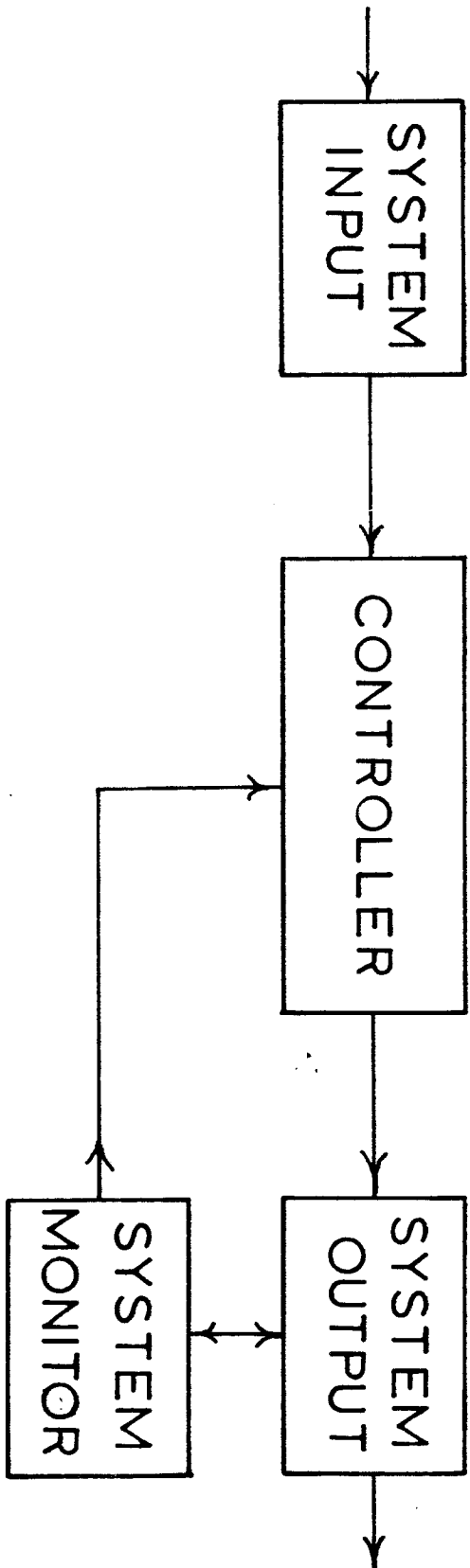


FIGURE 11. DIAGRAM OF A TYPICAL PROCESS SYSTEM
CONTAINING A FEEDBACK LOOP.

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 treatment 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 considerably 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 underground 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 Kellogg, 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

follows.

The diagrammatic reaction for adsorption shows an important 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 isoelectric 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 surface. For adsorption to be effective, the water should contain 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 appreciably 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 innovative 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 concentrations may change over time. With this knowledge the type of water can be determined and the treatment can be tailored to the water type.

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REFERENCES

1. U.S. Environ. Protect. Agency, 1975, Development document for interim final effluent limitations guidelines and new source performance standards for coal mining. EPA 440/1-75/057, 247 pp.
2. U.S. Environ. Protect. Agency, 1975, Development document for interim final and proposed effluent limitations guidelines and new source performance standards for the ore mining and dressing industry. Vol. I and II, EPA 440/1-75/061, 847 pp.
3. U.S. Environ. Protect. Agency, 1975, Inactive and abandoned underground mines. EPA 440/9-75-007, 349 pp.
4. U.S. Environ. Protect. Agency, 1975, Criteria for developing pollution abatement programs for inactive and abandoned mine sites. EPA 440/9-75-008.
5. U.S. Environ. Protect. Agency, 1976, Water pollution caused by inactive ore and mineral mines - a national assessment. EPA 600/1-76-298, 195 pp.
6. Stumm, Werner, and J.J. Morgan, 1970, Aquatic Chemistry. Wiley-Interscience, New York, 583 pp.
7. Hem, J.D., 1971, Study and interpretation of the chemical characteristics of natural water. Geol. Survey Water-Supply Paper 1473, 363 p.
8. Wentz, D.A., 1974, Effect of mine drainage on the quality of streams in Colorado, 1971-72. Colo. Water Conserv. Board, Water Resources Series, Circular No. 21, pp. 24-27.
9. Moran, R.E., and Wentz, D.A., 1974, Effects of metal-mine drainage on water quality in selected areas of Colorado, 1972-1973. Colorado Water Resources Circular No. 25, 250 p.
10. Hadley, R.F. and Snow, D.T., eds., 1974, Water Resources Problems Related to Mining. Amer. Water Resources Assn., Circ. No. 18, 236 pp.
11. Wildeman, T.R., Cain, D.L., and Ramirez, A.J., 1974, The relation between water chemistry and mineral zonation in the Central City Mining District, Colorado. Water Resources Problems Related to Mining, Amer. Water Resources Assoc. Proc. No. 18, pp. 219-229.

12. Wildeman, T.R., 1976, Mine effluents in the Front Range Mineral Belt of Colorado. Colorado Mining Association, 1976 Mining Yearbook, pp. 54-58.
13. American Public Health Association, 1976, Standard Methods for the Examination of Water and Wastewater, 14th ed., Washington, 1193 pp.
14. Brown, E., Skougstad, M.W., and Fishman, M.J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases. U.S. Geological Survey, Techniques of Water Resources Investigation, Book 5, Ch. A1, 160 pp.
15. Wildeman, T.R., and Ramirez, A.J., 1977, Chemical analysis of mine drainage waters. In Proc. Symposium on Molybdenum in the Environment, W.R. Chappell and K.K. Peterson, Eds., Marcel-Dekker, New York, pp. 739-752.
16. Garrels, R.M. and Mackenzie, F.T., 1971, Evolution of Sedimentary Rocks. Norton and Co., New York, 397 pp.
17. Krauskopf, K.B., 1967, Introduction to Geochemistry. McGraw-Hill, New York, 721 pp.
18. Nordstrom, D.K., 1976, Kinetic and equilibrium aspects of ferrous iron oxidation in acid mine waters. G.S.A. Abstracts, v. 8, p. 1030.
19. Amer. Inst. of Mining Eng (AIME), 1973, International Symposium on Hydrometallurgy, D.J.I. Evans and R.S. Shoemaker, eds., AIME, New York, 1184 pp.
20. Amer. Inst. of Mining Engr., 1974, Solution Mining Symposium. F.F. Aplan, et al., eds., AIME, New York, 469 pp.
21. Boyles, J.M., Cain, D.L., Alley, W.M., and Klusman, R.W., 1974, Impact of Argo Tunnel acid mine drainage, Clear Creek County, Colorado. National Symposium on Water Resources Problems related to mining. Amer. Water Resources Assoc., Proc. No. 18, pp. 41-53.
22. Singer, P.C., and Stumm, W., 1970, Acid mine drainage - the rate-determining step. Science, v. 167, pp. 1121-1123.
23. Dugan, P.R., 1972, Biochemical Ecology of Water Pollution, Plenum Press, New York, 159 pp.

24. Dugan, P.R. and Apel, W.A., 1978, Microbiological desulfurization of coal. In: Metallurgical Applications of Bacterial Leaching and Related Microbiological Phenomena, Academic Press, New York, in press.
25. Apel, W.A. and Dugan, P.R., 1978, Hydrogen ion utilization by iron-grown thiobacillus ferrooxidans. In: Metallurgical Applications of Bacterial Leaching and Related Microbiological Phenomena. Academic Press, New York, in press.
26. Updegraff, D.M., 1978, Colorado School of Mines, personal communication.
27. Andrews, R.D., 1976, Technical development of NPDES permits in the mineral extraction industries. Colorado Mining Association Yearbook, 1976, pp. 61-64.
28. Shuster, E.T., and W.B. White, 1971, Seasonal fluctuations in the chemistry of limestone springs: A possible means for characterizing carbonate aquifers. J. Hydrology, v. 14, p. 93-128.
29. Jacobson, R.L., and D. Langmuir, 1974, Controls on the quality variations of some carbonate spring waters. J. Hydrology, v. 23, p. 247-265.
30. Wentz, D.A., 1977, Quantity and quality of drainage from the Argo Tunnel and other sources related to metal mining in Gilpin, Clear Creek, and Park Counties, Colorado. Report to the U.S. Army Corps of Engineers.
31. Federal Register, 1975, vol. 40, no. 248, pp. 59566-59574.
32. Wentz, D.A., 1974, Stream quality in relation to mine drainage in Colorado, Water Resources Problems Related to Mining, Amer. Water Resources Assoc. Proc. No. 18, pp. 158-173.
33. Robins, J.D., 1976, The implementation of effluent limitations guidelines. Colorado Mining Association, 1976 Mining Yearbook, pp. 65-67.
34. Thurman, M., 1977, U.S. Geological Survey, personal communication.
35. Ramirez, A.J., 1976, Geochemistry of mine effluents in the Front Range Mineral Belt of Colorado, M.S. Thesis T-1888, Colorado School of Mines, 112 pp.

36. McWhorter, D.B., Skogerboe, R.K., and Skogerboe, G.V., 1974, Potential of mine and mill spoils for water quality degradation. Water Resources Problems Related to Mining, Amer. Water Resources Assoc. Proc. No. 18, pp. 123-137.
37. Coughanowr, D.R., and Koppel, L.B., 1965, Process Systems Analysis and Control, McGraw-Hill, New York, 491 pp.
38. Hyatt, D.E., 1976, Effluent Guidelines Compliance Technology and Cost Elements. Colorado Mining Association, 1976 Mining Yearbook, pp. 68-77.
39. Trexler, B.D., Ralston, D.R., Renison, W., and Williams, R.E., 1974, The hydrology of an acid mine drainage problem. Water Resources Related to Mining, Amer. Water Resources Assoc. Proc. No. 18, pp. 32-40.
40. Herricks, E.E., Cairns, T., and Stanholtz, V.O., 1974, Preplanning mining operations to reduce the environmental impact of mine drainage on streams. Water Resources Related to Mining, Amer. Water Resources Proc. No. 18, pp. 1-11.
41. Holcombe, L.A., 1977, Adsorption and desorption in mine drainages. Colo. Sch. of Mines Thesis No. 1944, 101 pp.
42. Jenne, E.A., 1977, Trace element sorption by sediments and soils - sites and processes. In: Proc. Symposium on Molybdenum in the Environment, W.R. Chappell and K.K. Peterson, eds., Marcel-Dekker, New York, pp. 425-551.
43. Suarez, D.L., and Langmuir, D., 1976, Heavy metal relationships in a Pennsylvania soil. Geochim. Cosmochim. Acta, vol. 40, pp. 589-598.
44. Jenne, E.A., 1968, Controls on Mn, Fe, Co, Ni, Cu and Zn Concentrations in soils and waters: the significant role of hydrous Mn and Fe oxides. Trace Inorganics in Water, Advances in Chem. Series No. 73, pp. 337-387.
45. Shaw, D.J., 1970, Introduction to Colloid and Surface Chemistry. Butterworth Inc., Boston, 236 pp.
46. Accuracy in Trace Analysis: Sampling, Sample Handling, Analysis, 1977, P.D. LeFleur, ed., Nat. Bur. Standards Spec. Pub. 422, 1304 p.
47. Bauer, H.H., Christian, G.D., and O'Reilly, T.E., 1978, Instrumental Analyses, Allyn and Bacon, Boston, 832 pp.

48. EPA, 1975, National Interim Primary Drinking Water Regulations. Federal Register, vol. 40, no. 248, pp. 59566-59574.
49. EPA, 1977, Proposed national secondary drinking water regulations. Federal Register, vol. 42, no. 62, pp. 17143-17147.
50. Colorado Dept. of Health, 1978, Water Quality Standards for Colorado, July 20, 1978.

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 procedures described below are sometimes changed from the authorized 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 N₂ 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 subject 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 turbid, 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 HNO₃ 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 temperamental 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 $\mu\text{mho/cm}$ to 50,000 $\mu\text{mho/cm}$. 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 $\pm 2^{\circ}\text{C}$ 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 $\mu\text{mho/cm}$ vs. temperature in $^{\circ}\text{C}$.

Temp $^{\circ}\text{C}$	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 measurements, 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 μ m 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 suspended 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 $\text{Fe}(\text{OH})_3$ 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.