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GEOCHEMISTRY OF MINE EFFLUENTS IN THE FRONT  
RANGE MINERAL BELT OF COLORADO

By

Armando Jose Ramirez Rojas

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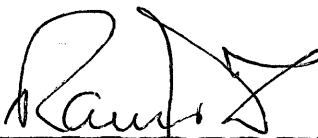
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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Geochemistry.

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ABSTRACT

The chemical analyses of water draining from 7 mine adits within five mining districts were done during the last two years and the results were compared to the ore petrology, ore mineralogy, and type of ore deposit. The water samples were collected in the Front Range Mineral Belt of Colorado in which most of the metal deposits are predominantly a complex mixture of copper, lead, zinc, and silver sulfides, gold tellurides and arsenides.

It has been found that the oxidation of pyrite which is associated with these complex ores yields acid water containing high concentrations of iron, sulfate and other trace metals contained in its structure. This acidity promotes the dissolution and oxidation of the other sulfides which release high concentrations of base metals to the water, but no additional acidity. It also has been found that the position and movement of the water table related to the ore veins and the type of ore play an important role in determining changes in the water quality from metal mine drainages. From these results, it was found that all the mine effluents studied in this paper fit the diffuse aquifer system.

The Emmett and the Clyde Mines are a good example of the type of ore versus the water quality. In the Emmett

Mine the acidity generated from the oxidation of pyrite promotes the solubility of fluorite which releases hydrofluoric acid which attacks the silicate rocks. All these reactions together are responsible for the chemistry of the water found in this adit. On the other hand, the Clyde Mine, which shows almost complete absence of sulfide minerals, has the best water quality of all the mine effluents studied.

Calculated values for redox potentials using the ferric/ferrous couple and taking into account the ionic strength activity coefficients, and ferric sulfate and fluoride complexes agree very well with the measured Eh values. Conductivity was also found to correlate really well with the total dissolved solids. These results demonstrate the utility of Eh and conductance measurements in acid mine drainages.

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Finally, the author would like to thank his wife and daughter for being so patient throughout his school work.

## INTRODUCTION

Many detailed studies on coal mine effluents have been done by Barnes and Clarke (1964), Barnes and Romberger (1968), Smith and Shumate (1970), Rivett and Oko (1971), Rubin (1974), and many others. Schmidt and Conn (1971), Boyles, et al. (1974), Moran and Wentz (1974), Wentz (1974), Wildeman, et al. (1974), Wildeman (1976) have studied the waters associated with base metal mines, especially in the mineral belt of Colorado. Most of these papers related to mine drainages are written from an environmental or engineering point of view, e.g. Galbraith, et al. (1973).

This paper investigates the geochemistry of effluents from metal mines for the following reasons:

1. To establish the correlation between the geology, mineralogy and type of ore and the chemical composition of the water.
2. To determine the mobility of a few elements related to Eh, pH, and other variables.
3. To look for possible seasonal variation in the chemistry of the water.

Weathering processes depend upon many factors such as size of rock particles, position of the water table, mineralogical composition, permeability, climate, micro-biological activity, and amount of oxygen and other gases

in the system. We hope to establish which of these parameters are important in determining the chemistry of the water as it flows from the mine in the Front Range.

Acid mine drainages result from the breakdown of pyrite and marcasite when they are exposed to oxidizing conditions, Barnes and Romberger (1968), Smith and Shumate (1970). In this process, the iron is released as ferrous ions which can be oxidized to ferric ions forming insoluble ferric hydroxide depending upon the pH of the water. Metal sulfides other than pyrite and marcasite such as galena, sphalerite and chalcopyrite will be broken down by these acid waters releasing more metals (lead, zinc, cadmium, copper, etc.) but not increasing the acidity. According to Lundgreen, Vestal and Tabita (1972) iron and sulfur oxidizing bacteria are associated with metal sulfide minerals in natural environments. These bacteria promote the oxidation of sulfur to sulfate and ferrous iron to ferric iron. The high concentrations of trace elements which these waters may contain can be harmful to aquatic organisms, humans and livestock.

#### Geological Description

The following geological outline is based upon the work done by Lovering and Goddard (1950), Sims and Tooker (1963), and Bastin and Hill (1917). The crystalline core of the Front Range is essentially Precambrian granite,

schist and gneiss. The oldest rocks are the schists and gneisses of the Idaho Springs formation which are highly metamorphosed sedimentary rocks of early Precambrian age. The porphyritic intrusive rocks of the Laramide orogeny are almost limited to a narrow belt extending southwestward from Boulder to Breckenridge, within which nearly all the productive Laramide mineral deposits of the Front Range have been formed. The northwestern side of the mineral belt is marked by a line of stocks that range in composition from diorite to quartz monzonite.

The sequence of intrusion is similar throughout the mineral belt, but the latest members of the magmatic series are found only in the northeastern part. In the area southwest of Georgetown, where complex lead-silver-zinc ores predominate, only diorite, monzonite, quartz monzonite, sodic quartz monzonites and closely related rocks are present. Northeast of Silver Plume where pyritic gold ores appear, bostonite, alkalic pyrite, and alkalic trachyte porphyry are found.

Table 1 shows the type of rocks, ore mineralogy, gangue and ore deposits in the mining districts where mine effluents were collected. A better description of the mining districts is given in Appendix 3.

#### Collection of Samples and Analytical Methods

Samples were collected in Silver Plume, Central City,

Table 1. Comparison of the type of rocks, ore mineralogy, and gangue of the mining districts where water samples were collected.

Mining Districts	Ore Deposits	Pre-cambrian Rocks	Intrusive Rocks	Ore Mineralogy	Gangue Minerals
Silver Plume	Veins	Quartz-Biotite schist Hornblende-Diopsid gneiss	Monzonite Quartz monzonite Dacite Granite	Galena Sphalerite Pyrite Chalcopyrite	Quartz Some carbonates
Central City	Veins Stock-works	Quartz-Feldspar-Biotite gneisses Calc.-Silicate Gneiss	Granodiorite Quartz monzonite Quartz Diorite	Pyrite, Sphalerite Galena Chalcopyrite Tennantite Enargite	Quartz Very little carbonate Barite Fluorite
Boulder Tungsten County	Veins	Granite Gneissic Aplite Pegmatite	Hornblende-Biotite Monzonite Diorite	Ferberite	Quartz Some sericite and clays
Gold Hill	Veins	Quartz-Biotite Gneiss	Quartz monzonite Diabase Bostonite	Petzite Sylvanite Calaverite Pyrite Chalcopyrite Galena Sphalerite	Quartz Some ankerite
Jamestown	Veins Breccia	Biotite-quartz-sillimanite schist Lime-Silicate rocks	Quartz monzonite Granodiorite Sodic Granite	Fluorite Pyrite Galena Sphalerite Chalcopyrite	Quartz Some ankerite Barite

Boulder County tungsten, Gold Hill, and Jamestown mining districts located in the Front Range Mineral Belt of Colorado. The adits chosen were those which were draining throughout all the year, making possible the collection of samples during any season in the year. The water samples were collected unfiltered at the adit entrances in one liter polyethylene bottles and acidified with 5 ml of 1:1 doubly distilled nitric acid. The reason why the water samples were acidified in the field was to prevent the precipitation of ferric hydroxide which forms an orange film on the bottle which probably adsorbs other metals depending upon the pH of the water.

Field measurements included pH, Eh, conductivity, dissolved oxygen, and temperature. The pH and potentiometric readings (Eh) were measured by a Leeds and Northrup Model 7417. Specific conductance readings were made with a YSI Model 33 S-C-T meter. Dissolved oxygen and temperature were measured with a YSI Model 57 oxygen meter.

All the elements were analyzed by atomic absorption spectrophotometry on a Perkin-Elmer Model 303. The Na, K, Mg, Fe, Mn, Cu, Zn, Co, Ni, Cd, and Pb were determined by direct aspiration using an air-acetylene flame. The Ca, Al, and Si were analyzed by direct aspiration using a nitrous oxide-acetylene flame. Arsenic (As) was previously reduced to arsine and then analyzed with a hydrogen flame and nitrogen as carrier gas. Sulfate analyses were attempted

by atomic absorption spectrophotometry using the indirect method of precipitation as barium sulfate, but was unsatisfactory. Finally, it was determined by using the gravimetric method described in Skoog and West (1976). Fluoride concentration was analyzed using an Orion specific ion electrode. A citric acid-sodium citrate buffer solution was used and the pH was adjusted to 7.5 before each reading.

#### Geochemical Behavior of Major and Minor Elements

The Si, Al, Na, K, Ca, and Mg are considered in this paper to be the major elements and Fe, Mn, Co, Ni, Cu, Zn, Cd, Pb, As, S, and F the minor elements. The primary source of these elements is the weathering of rock-forming silicate minerals and sulfide and sulfosalt minerals under oxidizing conditions.

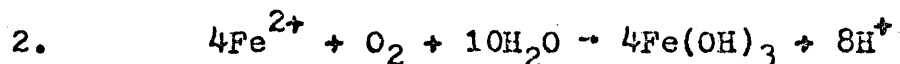
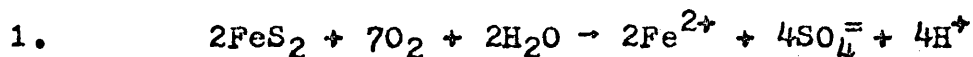
Silicon is the second most abundant element in the earth's crust and it is the principal constituent of silicate minerals whose weathering stability is better understood through the Goldich's weathering series in which olivine and anorthosite are the least stable and quartz and clays the most stable. The final weathering products are generally considered to be clays which probably control the mobility of Si, Al and K. Silicon is transported in aqueous solutions mainly as silicic acid ( $H_4SiO_4$ ) and hexafluoride complex ( $SiF_6^-$ ) which predominates at low pH and high fluoride concentration. Millot (1970) and Valetton (1972) discuss

the formation of clay minerals and the mobility of Si and Al.

Aluminum occurs as aluminum-silicate minerals and oxyhydroxides, gibbsite, bayerite, diaspore, and boehmite. In aqueous solutions Al can be transported as hydrolytic monomeric and polymeric species (Rubin, 1974) and as sulfate and fluoride complexes depending upon the concentration of those two ligands. The mobility of Al is strongly dependent on pH, being practically immobile between pH 4-7 where the oxyhydroxides are the most stable forms. Sodium is a major constituent in feldspars, feldspathoids, and many other silicate minerals. It is relatively more mobile than K which is an essential chemical component of orthoclase, microcline, sanadine, leucite and other siliceous minerals. It can readily be adsorbed by clays decreasing its mobility in natural environments. Calcium forms many important minerals such as plagioclase, wollastonite, calcite, dolomite, aragonite, ankerite, anhydrite, gypsum, apatite, fluorite, and a few others. The concentrations of sulfate and fluoride are probably the most important parameters controlling the mobility of Ca in ground waters but other cations such as Fe and Al which tend to form complexes with fluoride and sulfate ions may increase the mobility of Ca where those two ligands are present. Magnesium is a principal constituent in the mafic and ultramafic rock-forming minerals such as olivine. It also forms the carbonates dolomite and magne-

site and the hydroxide brucite. Mg has a high mobility being transported as aqueous species only.

Iron is a major constituent in many minerals, ferromagnesium silicates, oxides, oxyhydroxides, carbonates, sulfides, and sulfosalts. The most important iron sulfide minerals found in the Front Range mineral belt of Colorado are pyrite, chalcopyrite, tennantite, and tetrahedrite. The oxidation of these minerals (Sate, 1960) releases high concentrations of Fe and other trace elements into the ground water system. Pyrite is the most abundant sulfide mineral and its oxidation controls the acidity of the water. The following equations show the reaction of pyrite when exposed to air and water and the oxidation of Fe(II) forming insoluble iron hydroxide.



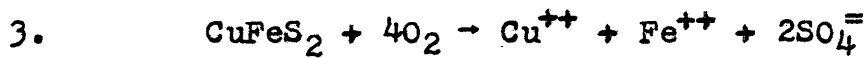
Iron exists in natural environments in two oxidation states, Fe(II) and Fe(III). The behavior of both iron forms is strongly controlled by Eh and pH. Fe(III) is less mobile than Fe(II) and it starts precipitating at very low pH adsorbing other trace elements (Boyles and others, 1974). Iron is found in waters forming many hydrolytic species, fluoride, and chloride complexes. Three Eh-pH diagrams for the iron system are shown in figures 7, 8, and 9.

Manganese is frequently present in silicates where it may occupy the same structural position as Fe. Other mineral forms for manganese are oxides, oxyhydroxides, carbonates, and sulfides. It may exist in different oxidation states but Mn(II) is the most common found for the Eh-pH range in natural environments. Mn(II) is really mobile for pH below neutral, at higher pH it starts forming oxyhydroxides. The control of trace elements by hydrous Mn and Fe oxides has been studied in detail by Jenne (1967), Loganathan and Bureau (1973) and Whittemore and Langmuir (1975).

Cobalt and Ni are found as minor constituents replacing either iron or manganese in the ferromagnesium silicates. Co is also found forming a few uncommon sulfide minerals, linnaeite, cattierite, cobaltite, cobalt rich pentlandite, and cobalt arsenides. It is always associated with iron sulfides and often copper and nickel sulfides. Nickel forms a rare large group of sulfides, vaesite, polydymite, millerite, pentlandite, and a few others. It is always associated with iron including laterites deposits. Both Co and Ni are relatively mobile at low pH ranges.

Copper is found as a major constituent in a great number of minerals, malachite, azurite, cuprite, chrysocolla, chalcocite, covellite, bornite, chalcopyrite, enargite, tennantite, tetrahedrite, and many others. The most important sulfide minerals of copper found in the Front Range mineral belt of Colorado are chalcopyrite, enargite, tennan-

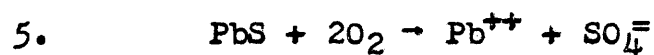
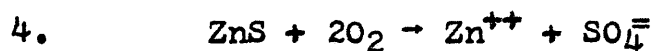
tite, and tetrahedrite which are the main source for this element and other trace elements which they are capable of incorporating in their structure. The mobility of Cu is controlled by pH and type of sediment being in contact with the water (Collins, 1973). The following equation shows the chemical reaction under oxidizing conditions for chalcopyrite:



Zinc and Cd have similar chemical characteristics but Zn is much more abundant and is slightly more mobile than Cd. The three most common Zn minerals are sphalerite, wurtzite, and smithsonite. In oxidation conditions, where Zn sulfides are very unstable, and low carbonate content Zn is primarily controlled by pH. Cadmium forms only one significant mineral, greenockite, which is very rare in occurrence. Cadmium is contained in sphalerite where it is camouflaged in the crystal structure. Hem (1972) discusses the geochemical behavior of Zn and Cd in more detail.

The most important Pb minerals are galena, anglesite, cerussite, and hydrocerussite. In metal mine environments where oxidation of sulfides takes place the main source of Pb is galena, but its concentration is controlled by the solubility of anglesite. In acid mine drainages the concentration of carbonate is very low, therefore cerussite is not expected to control mobility of Pb. The presence of

high amounts of hydrous iron oxides in the sediments may control the mobility of Pb by adsorbing it on the solid phase. An Eh-pH diagram for Pb minerals is shown in fig. 1. Equations (4) and (5) show the oxidation of sphalerite and galena respectively.



Arsenic forms a few minerals such as arsenopyrite, tennantite, enargite, Ag and Au arsenides, and Co and Ni arsenides. The oxidation of these minerals may form soluble arsenates which can enter into the surface and ground water system. The mobility of As is strongly controlled by pH and the concentration of Fe, Ca, Cu, Pb, Cd, Zn, and Ni with which it forms very insoluble arsenates.

Sulfur is the most important anion of sulfide, sulfosalt and sulfate minerals. It is very mobile under oxidizing conditions where it is mainly transported as sulfate ions. An Eh-pH diagram for the predominance of aqueous sulfur species is shown in fig. 2.

Fluorine is found as a major constituent in fluorite, cryolite, fluorapatite, and topaz. Fluorite is the most important fluorine mineral found in the area studied and it is probably the only source for F in the mine drainages. The presence of high concentrations of Al increase the

solubility of fluorite by forming very strong complexes with fluoride. High amounts of F increase the weathering of silicate rocks especially at low pH ranges. Handa (1975) found a negative correlation between calcium and fluoride concentrations for ground waters in India.

Figure 1. Stability fields of Pb solid phases as a function of Eh and pH at 25° C and 1 atm. total pressure.

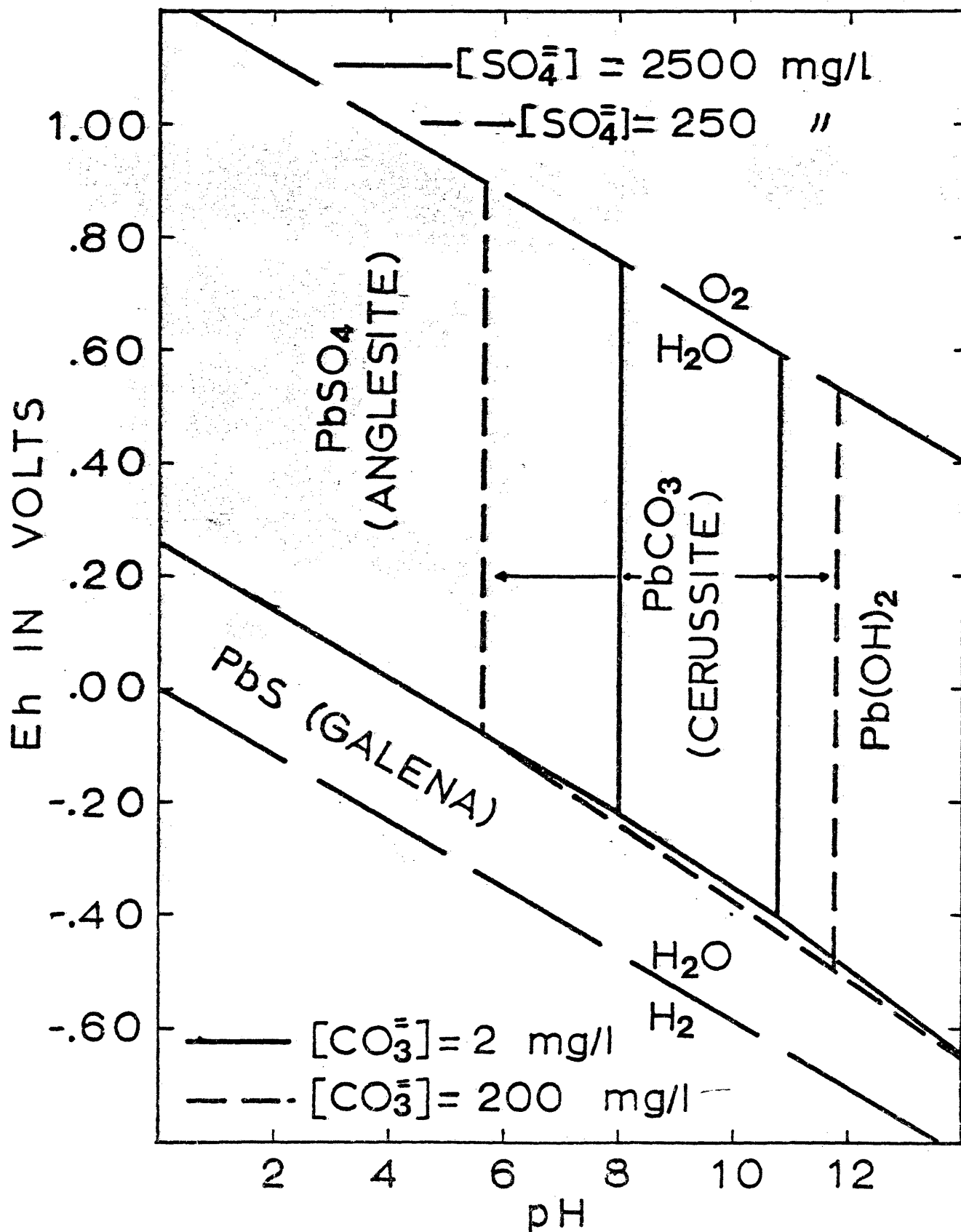
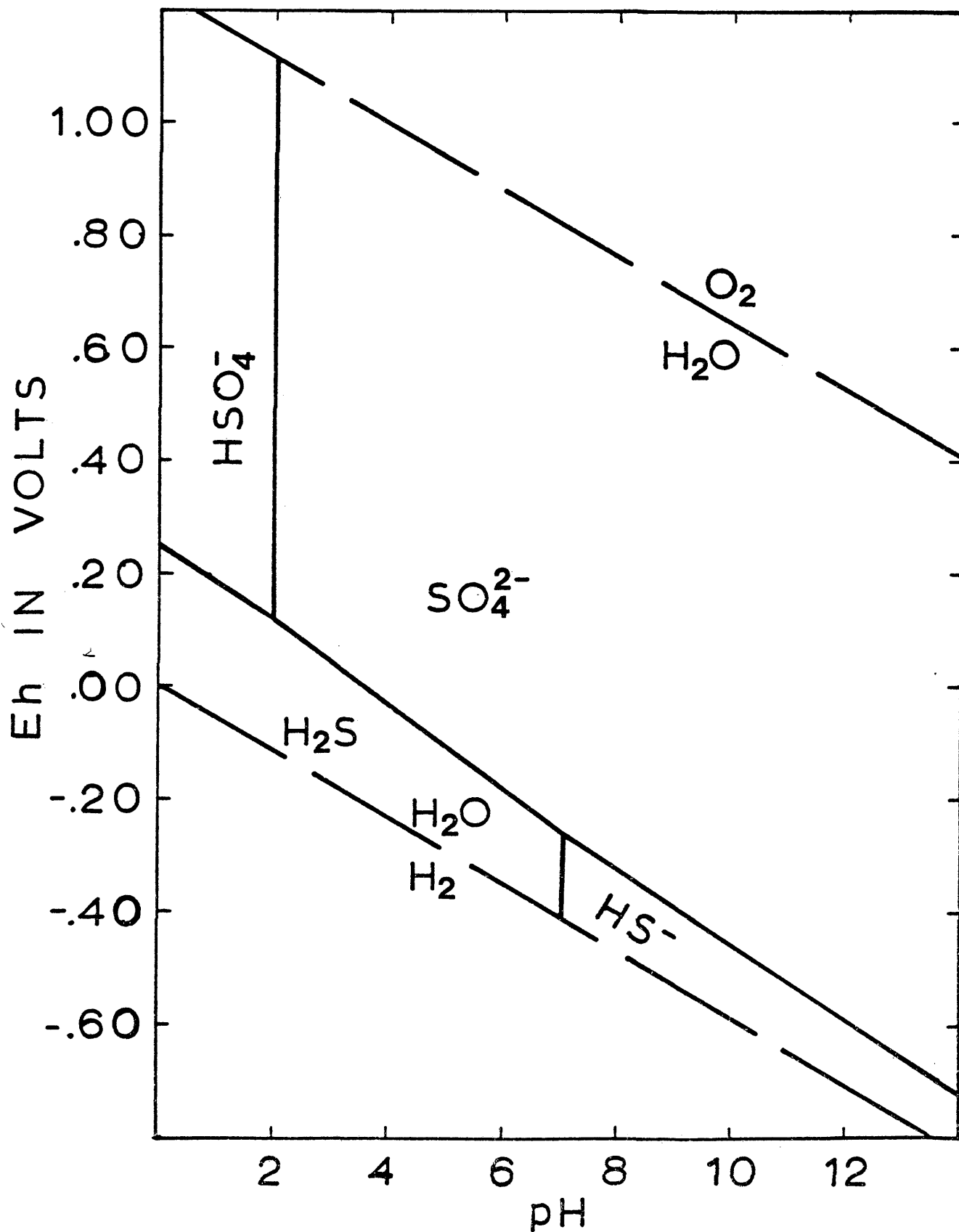


Figure 2. Equilibrium distribution of sulfur species in water at 25° C and 1 atm. total pressure.



## RESULTS

Chemical analytical data for the 7 mining adits which were analyzed for 22 variables are shown in Appendix 1. Table II shows the detection limits for most of the elements determined. Table III shows the average for the 22 variables measured during the 1974, 1975 and 1976 seasonal years. Comparison between the Argo Tunnel drainage analysis done by Wentz (personal communication, 1976) in March and April of 1976 and those presented in this paper (February and April of 1976) shows excellent agreement. Results and accuracy of the analytical methods are better discussed in Wildeman and Ramirez (1975, 1976) which are in Appendix 2.

### Seasonal Variations

Collections were made in fall, winter, spring, and summer from October of 1973 through June of 1976. The seasonal year was chosen to start on October 1 and finish on September 30. As is seen in Table III, the concentrations of all the elements detected are remarkably consistent in most of the adits studied during the three years period.

In accordance with this observance it is possible to conclude that all of the mine effluents studied fit the diffuse aquifer model (Wildeman, 1976) generated by studies made in Pennsylvania by Shuster and White (1971) and Jacobson and Langmuir (1974). In the diffuse flow-feeder system the water recharge is by infiltration through soils, faults,

Table II. Detection limits (ng/ml).

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ELEMENT	CONCENTRATION
Fe	40
Mn	20
Co	50
Ni	100
Cu	20
Zn	20
Cd	25
Pb	80
Al	1000
As	3

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Table III. Average concentrations of the elements analyzed in the 7 mining adits studied. Concentrations are in mg/l except for Cd, Pb, Co, Ni, and As which are in  $\mu\text{g/l}$ .

Adit	Argo Tunnel			Emmett Mine		
	1974	1975	1976	1975	1976	
Eh	660	670	680	460	540	
PH	2.6	2.7	2.7	3.8	3.5	
Conductivity	2800	2610	2600	2630	2820	
Diss. O <sub>2</sub>	n.a.	5.0	2.6	4.6	4.5	
Water temp.	24.5	15.8	15.5	10.3	12.1	
Na	20	21	22	300	290	
K	3.0	3.3	3.4	27	28	
Ca	340	330	320	480	460	
Mg	170	150	150	90	91	
Al	33	26	24	160	150	
SiO <sub>2</sub>	50	48	48	56	59	
Fe	240	200	190	150	170	
Mn	120	100	90	150	150	
Cu	8.4	6.2	5.9	.36	.24	
Zn	63	50	47	37	37	
Cd	240	190	170	50	48	
Pb	100	95	99	170	180	
Co	210	200	200	700	700	
Ni	380	350	350	600	600	
As	370	230	200	n.d.	n.d.	

n.a. = not analyzed; n.d. = not detected  
 Eh units are in millivolts; temp. is in C  
 Conductivity is in micromhos/cm

Table III. continued

Adit	Lucania Tunnel		Burleigh Tunnel	
	1974	1975	1976	1976
Eh	420	390	490	480
pH	6.0	6.4	6.6	6.5
Conductivity	1050	990	1000	540
Diss. O <sub>2</sub>	n.a.	8.1	7.8	8.0
Water temp.	9.2	8.9	8.8	11.9
Na	21	20	23	8.8
K	4.9	4.8	4.6	2.5
Ca	220	220	220	78
Mg	78	79	77	51
Al	n.d.	n.d.	n.d.	n.d.
SiO <sub>2</sub>	28	26	31	6.2
Fe	1.5	.77	.65	.26
Mn	4.0	3.1	2.7	1.7
Cu	n.d.	n.d.	n.d.	n.d.
Zn	2.2	1.8	1.8	40
Cd	n.d.	n.d.	n.d.	80
Pb	n.d.	n.d.	n.d.	n.d.
Co	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.
As	n.d.	n.d.	n.d.	n.d.



and intergranular spaces. The water movement is slow and it is usually clear. The chemical composition shows little response to changes in precipitation and seasons through the year. The recharge is on the order of months. This is in contrast with the conduit model where the water chemistry responds to changes in precipitation and seasons and the residence time for the water is on the order of days.

There are variations in the concentrations of some elements from year to year in the Argo, Lucania, and Burleigh effluents and further changes in concentrations from season to season in the mine drainages of Argo and Lucania Tunnels. The description and analysis of these changes will focus on what is observed in the Argo Tunnel since more data has been accumulated for this water and the changes are more pronounced in this case. In the Argo site there is a generally decreasing trend in the concentrations of all elements except Na, K, and Pb which are constant within analytical precision. Figure 3 shows this trend graphically for Fe, Al, and Na from year to year. It is also observed an increase in the concentrations of most base metals during the springtime. Figure 4 shows these variations for Cu, Al, and Na from Spetember of 1974 through August of 1975. The data for the Argo Tunnel presented by Moran and Wentz (1974) and Boyles and others (1974) also show an increase in the concentrations of base metals during the springtime.

These seasonal and year to year effects can be explained

by assuming that at certain times the water table is lower and sulfides are exposed to oxidation and dissolution, then when the water table rises, base metals ions formed from decomposition of sulfide minerals are flushed into the aquifer. On the other hand, the weathering of the silicate rocks does not require oxidation and thus does not show any change; this is observed in the consistency of the concentrations of the major elements except for Al which shows some changes in its concentration and this can be attributed to its formation of clays and oxyhydroxides.

Tables IV and V, which contain the streamflow data for Clear Creek near Lawson and Golden in Colorado respectively, were extracted from Water Resources Data for Colorado, Part 1, Surface Water Records. The monthly average discharge for Clear Creek correlates really well with the variations in concentration for the base metals in Argo Tunnel as seen in figure 4, suggesting that this may well be the case for the movement of the water table in that area.

Table VI shows the concentrations of Fe, Mn, Cu, Zn, and Cd for Argo Tunnel from January of 1973 through June of 1976. By comparing the total annual discharge for Clear Creek, which shows a very low peak in the 1972 water year, and the variations in concentration for those five elements listed in Table VI, it is possible to say that in 1972 the sulfide minerals were exposed to oxidation and decom-

position for a longer time than during the last five years. Then, the water table rose in 1973 and flushed the base metals into solution. After that year, the water table has probably been leveling out and no big changes in the concentrations of base metals have been observed in the last two years. The average concentrations for most elements analyzed in 1976 are very close to those analyzed by Moran and Wentz (1974) in January of 1973.

Figure 3. Year to year variations for Fe, Al, and Na in the Argo Tunnel and Clear Creek discharge near Lawson, Colorado.

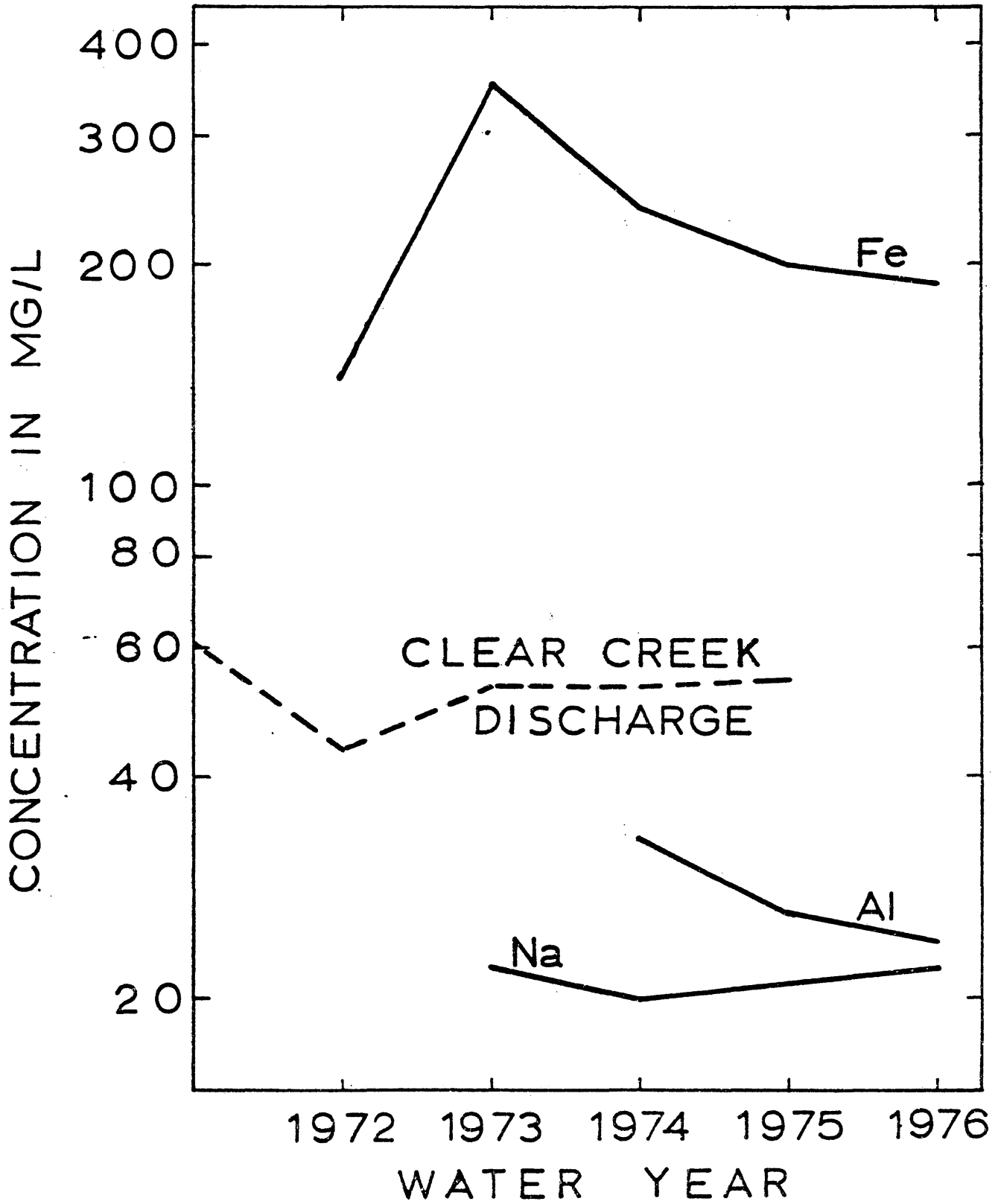


Figure 4. Seasonal changes for Al, Na, and Cu in the Argo Tunnel.

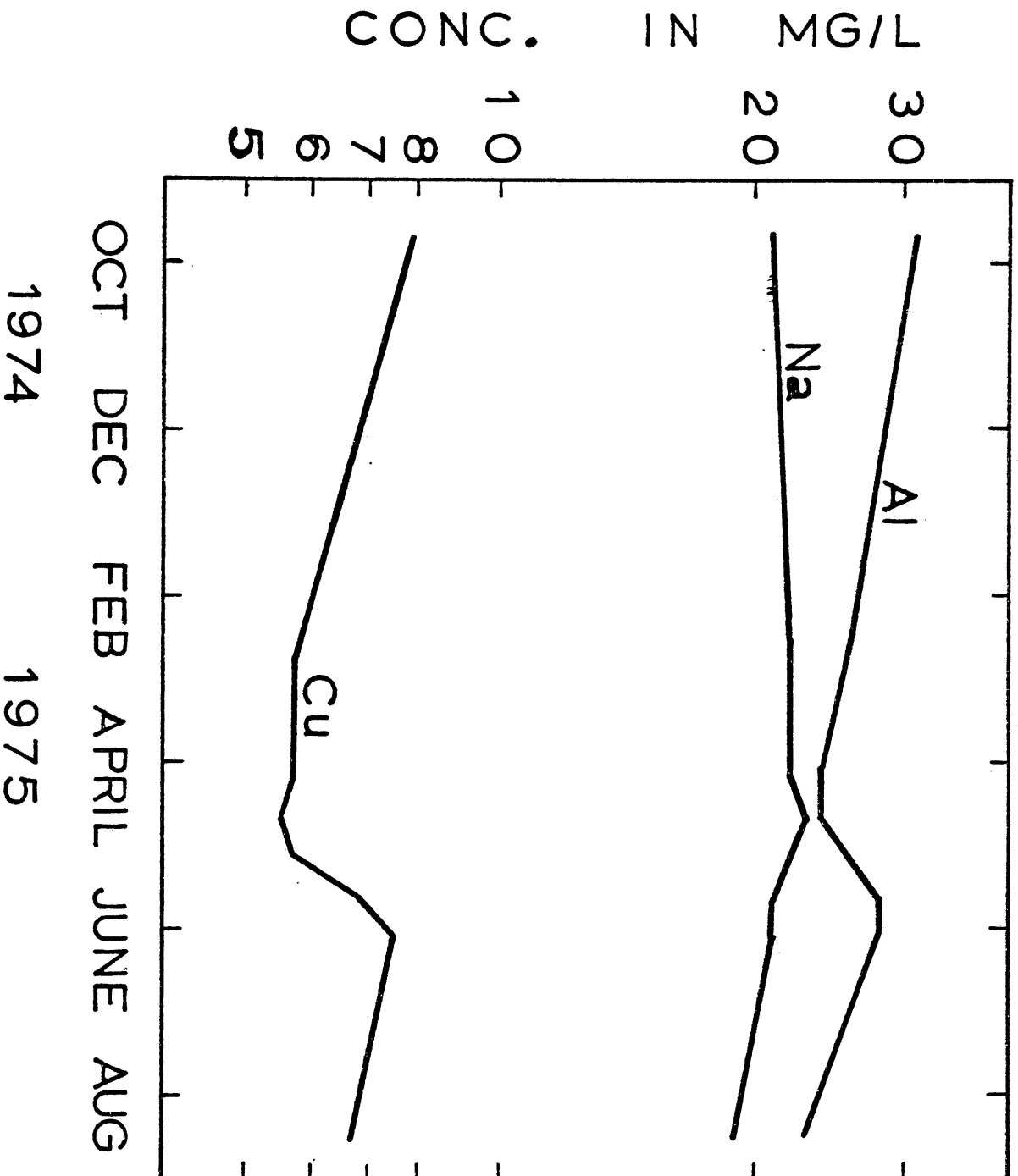


Figure 5. Seasonal changes for Cu in the Argo Tunnel compared to the Clear Creek discharge near Lawson, Colorado.

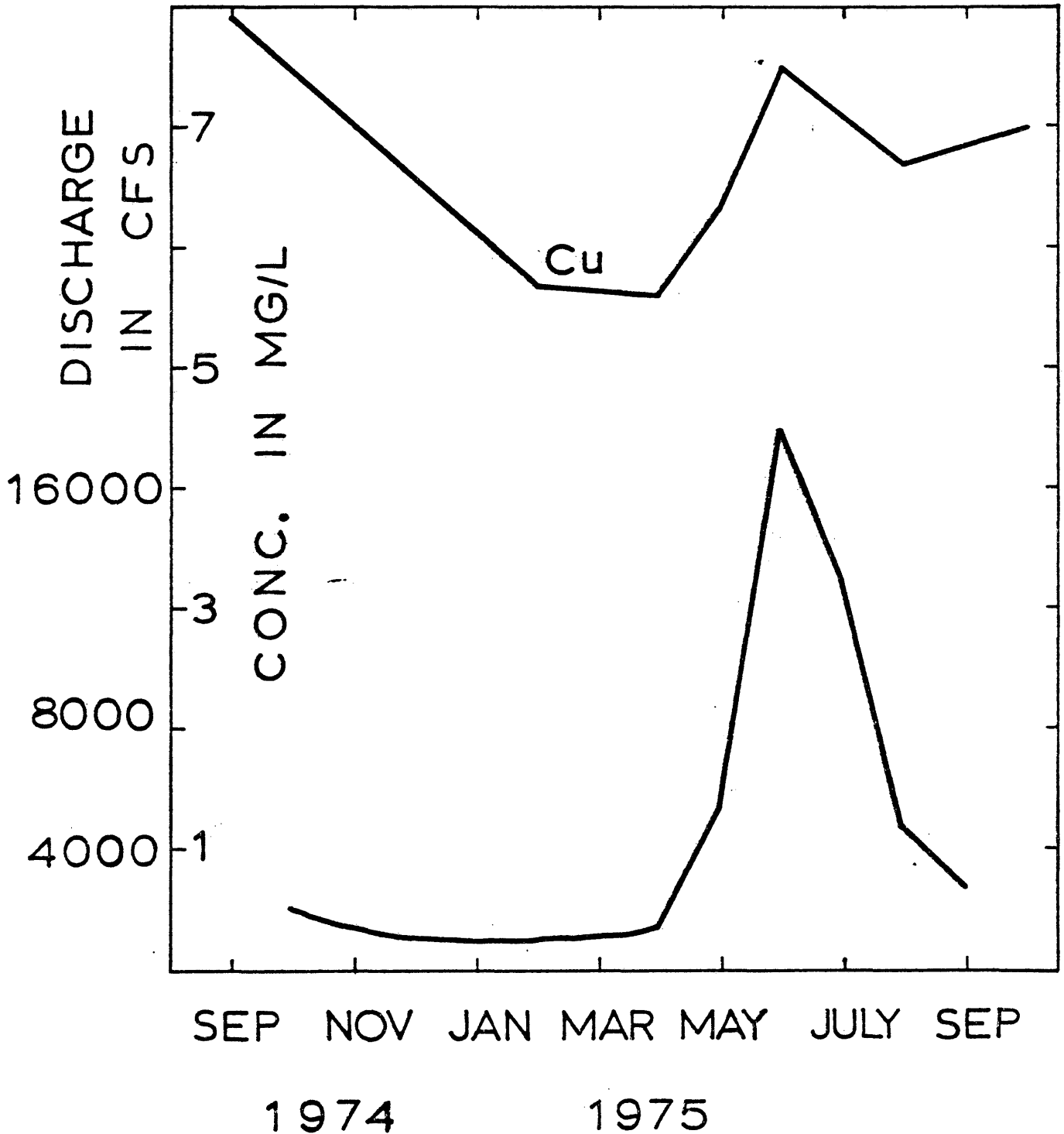


Table IV. Streamflow data (c.f.s.) for Clear Creek near Lawson, Colorado.

	Total Av. monthly Daily 1971	Total Av. monthly Daily 1972	Total Av. monthly Daily 1973	Total Av. monthly Daily 1974	Total Av. monthly Daily 1975	Average
Oct.	2667 86.0	2144 69.2	1900 61.3	1708 55.1	2020 65.2	2088
Nov.	1564 52.1	1431 47.7	1350 45.0	1303 43.4	1393 46.4	1408
Dec.	1262 41.0	1149 37.1	1044 33.7	1081 34.9	1062 34.3	1122
Jan.	1270 41.0	1086 35.0	917 29.6	1097 35.4	980 31.6	1070
Feb.	992 35.4	966 34.3	808 28.9	920 32.9	921 32.9	927
Mar.	1158 37.4	1076 34.7	862 27.8	1058 34.1	1104 35.6	1057
Apr.	2250 75.0	1346 44.9	1079 34.0	1302 43.4	1276 42.5	1439
May	5238 169	4458 144	4781 154	8404 271	4031 130	5382
Jun.	21573 719	17175 573	17581 586	18625 621	14519 484	17895
Jul.	14585 470	6590 213	14659 473	10853 350	18058 583	12949
Aug.	5244 169	3230 104	5511 178	4278 138	5634 182	4779
Sept.	3175 106	2720 90.7	2578 85.9	2374 79.1	2976 99.2	2765
TOTAL	60988	43407	53070	53003	53974	52876

Table V. Streamflow data (c.f.s.) for Clear Creek near Golden, Colorado.

	Total monthly 1971	Av. Daily	Total monthly 1972	Av. Daily	Total monthly 1973	Av. Daily	Total monthly 1974	Av. Daily	Average
Oct.	4085	132	3241	105	2051	66.2	2637	85.1	3004
Nov.	3437	115	2535	84.5	1583	52.8	2024	67.5	2395
Dec.	2489	80.3	1932	62.3	1626	52.5	1587	51.2	1909
Jan.	2043	65.9	1485	47.9	1436	46.3	1622	52.3	1647
Feb.	1853	66.2	1213	41.8	1280	45.7	1409	50.3	1439
Mar.	2152	69.4	1576	50.8	1672	53.9	2247	72.5	1912
Apr.	4318	144	2139	71.3	2683	89.4	2659	88.6	2950
May	11783	380	6720	217	20224	652	14772	477	13375
June	33551	1118	24851	828	32719	1091	26141	871	29316
July	19939	643	8587	277	20959	676	14428	465	15978
Aug.	6779	219	4115	133	7510	242	5509	178	5978
Sept.	4587	153	3354	112	3683	123	3384	113	3752
TOTAL	97016		61748		97426		78419		83655

Table VI. Average concentrations (mg/l) for Na, Fe, Mn, Cu, Zn, and Cd in the Argo Tunnel.

	(a) Jan. 1973	(b) May through Sept. 1973	Oct. 1973 through Sept. 1974	Feb. 1975 through Aug. 1975	Oct. 1975 through June 1976
Fe	140	350	240	200	190
Mn	95	160	120	100	92
Cu	4.9	13	8.4	6.2	5.9
Zn	45	78	63	50	47
Cd	.16	.34	.24	.19	.17
Na	n.a.	22	20	21	22

n.a. = not analyzed

(a): (Moran and Wentz, 1974)

(b): (Boyles and others, 1974)

### Chemistry, Mobility and Redox Equilibria

This section will try to establish the possible correlation between pH, Eh, conductivity, water chemistry, and the mobility of most of the elements studied in this paper.

First concerning mobility, Table VIII shows concentration ratios for the major and minor elements in each adit. It is seen in this Table that the  $\text{SiO}_2/\text{Al}$  ratios increase when pH increases which shows a relatively high mobility of silica over Al for pH above 4. Silica was detected in all the samples analyzed; on the contrary, Al was only detected in the samples having pH lower than 4. The reason for this is that the mobility of Al is controlled by the solubility of Al oxyhydroxides. On the other hand,  $\text{SiO}_2$  is transported mainly as silicic acid having almost constant solubility in acid solutions (Mason, 1966 and Millot, 1970). The Na/K and Ca/Mg ratios seen in Table VIII are greater than unity, but do not show big changes, consequently they show a uniform mobility for the pH ranges found in the mine drainages studied.

Inspection of base metal ratios show that Cd correlates positively with Zn which shows their similar geochemical behavior (Hem, 1972). Their ratio variations might reflect changes in the composition of their source, sphalerite. The Mn/Fe ratios shown in Table VIII are less than 1 for

pH lower than 6 even though Mn is more mobile than Fe in this environment (Ramirez, et al., 1976). This result reflects the higher geochemical abundance of Fe over Mn (Mason, 1966). For pH higher than 6 the Mn/Fe ratios are greater than 1 and probably indicate the range of pH where Mn starts separating from Fe in natural environments (Mason, 1966 and Krauskopf, 1967). The small changes for Fe(II)/(Co + Ni) ratios seen in Table VIII suggest that all of them come from the same source and have similar mobility related to pH.

Concerning conductivity, Table VII shows the determined and calculated sulfate values, fluoride concentrations, calculated bicarbonate values, total dissolved solids, and the conductance corrected at 25° C for each mine effluent. The calculated sulfate values were obtained by cation-anion balance. Hem (1971) suggests this method for checking the accuracy of a complete chemical analysis of a water. The difference between the calculated and determined values for sulfate were converted to the equivalent amount of bicarbonate in order to complete the cation-anion balance. This was done by assuming that the amount of bicarbonate present is much greater than chloride. The total dissolved solids were calculated by adding the concentrations together of all the dissolved constituents found in the water including the calculated values for bicarbonate (Hem, 1971). The conductivity corrected values at 25° C were calculated by assuming

Table VII: Concentrations (mg/l) of sulfate, fluoride, bicarbonate, and total dissolved solids. Conductivity is in micromhos/cm.

	Conduc- tivity at 25°C	Total Dissolved Solids	SO <sub>4</sub> <sup>=</sup>	*SO <sub>4</sub> <sup>=</sup>	*HCO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>
ARGO	3110	3160	2300	2310	---	3
NATIONAL	1340	1330	900	950	65	<1
LUCANIA	1370	1240	810	890	100	1
BURLEIGH	700	690	350	470	150	1
CLYDE	430	360	15	280	340	<1
CORNING	1560	1540	880	1100	280	<1
EMMETT	3650	4510	2900	2940	---	240

\* Calculated by the cation-anion balance

Table VIII: Ratios for major and minor elements.

	ARGO	LUCANIA	NATIONAL	BURLEIGH	CORNING	EMMETT
pH	2.7	6.6	5.6	6.5	6.1	3.5
Na/K	6.5	5.0	3.6	3.5	1.6	10
Ca/Mg	2.1	2.8	2.6	1.5	1.5	5.1
S <sub>102</sub> /Al	2.0	>31	>40	>6	>13	.40
Mn/Fe	.48	4.2	.45	6.5	1.2	.91
Fe(II)/(Co + Ni)	130	---	110	---	---	120
Fe(II)/Fe(III)	.60	---	20	---	---	10
Zn/Cd	280	---	---	500	---	770

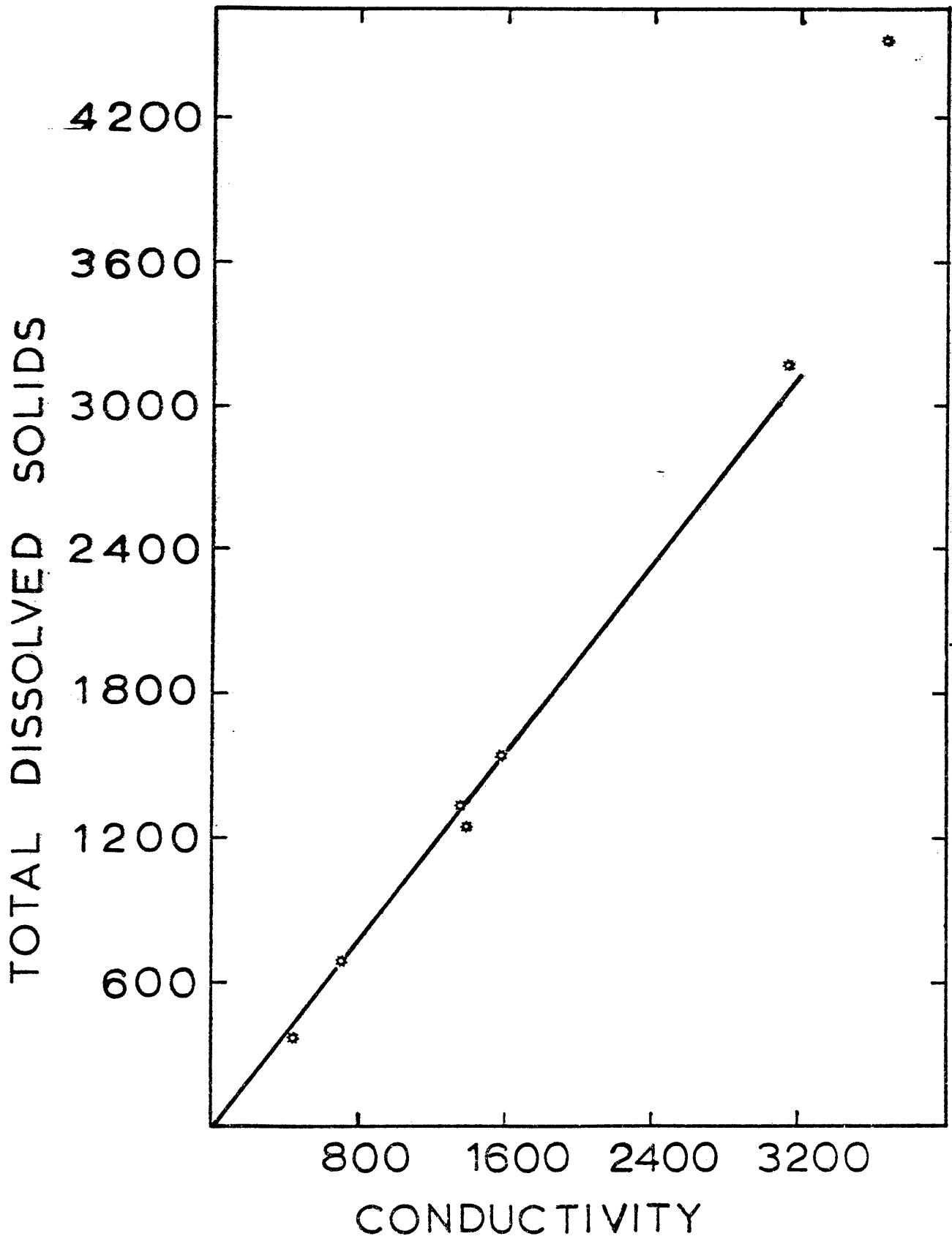
that an increase of 1° C increases the conductance by 2 percent (Hem, 1971).

It is observed in Table VII that the determined and calculated values for sulfate in the Argo Tunnel and Emmett Mine are practically the same. This excellent agreement means two things: the accuracy of the chemical analysis in the water and the very low content of carbonate species in mine drainages with low pH. The other five mine effluents show differences greater than 6 percent between the calculated and determined sulfate values and they all have pH higher than 5. These disagreements between both values mean that the content of carbonate species and possibly chloride increase when increasing pH.

Figure 6 shows the total dissolved solids versus the conductivity. It is seen in this figure that all the points fit a straight line with the exception of the highest in total dissolved solids which corresponds to the Emmett Mine. This deviation from the straight line shown by the Emmett Mine can be explained by the decreasing ionic mobility of the ionic species in concentrated solutions and also by the concentration of fluoride which forms strong complexes with Al decreasing the net charge of the solution. This result agrees quite well with predictions for dilute and simple solutions (Hem, 1971).

Concerning Eh, the question is how well this corresponds to the Fe(II), Fe(III), and pH of the water. Consequently

Figure 6. Dissolved solids (mg/l) as a function of the conductivity (micromhos/cm).



Fe(II) was determined directly in the field and in the laboratory by titration with  $\text{KMnO}_4$  as described in Skoog and West (1976). Samples for Fe(II) determinations in the laboratory were acidified in the field with  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  and the titrations were made on the same day as collected and again a few weeks later. This was done in order to see the stability of ferrous iron in mine drainages. Table IX shows the results of these titrations and it is seen that  $\text{H}_2\text{SO}_4$  keeps ferrous iron in solution for a longer time than  $\text{HNO}_3$  does. This is important because Fe(II) does not have to be determined in the field but can be determined in the laboratory within two weeks after collection if the samples are properly acidified with  $\text{H}_2\text{SO}_4$ . Similar results were found by Gang and Langmuir (1974) for high Fe(II) content samples acidified with  $\text{H}_2\text{SO}_4$ . Also, total Fe was determined by previous reduction with  $\text{SnCl}_2$  and then titrated with  $\text{KMnO}_4$ . These total Fe values were compared to those obtained by atomic absorption spectrophotometry analysis and they showed excellent agreement. The difference between both values was less than 3 percent. Finally the Fe(III) values were calculated by subtracting Fe(II) from total Fe. These values for Fe are presented in Table X.

As seen in Table III the concentration of total Fe correlates really well with the pH of the water. The reason for this is that the mobility of Fe is controlled by the formation of Fe oxyhydroxides which are a function of pH.

Table IX: Comparison between the stability of ferrous iron in nitric and sulfuric acids solutions.

Date Analyzed	Acid Solution	Fe(II) in mg/l		
		ARGO	EMMETT	NATIONAL
4-20-76	HNO <sub>3</sub>	65	163	39
4-20-76	H <sub>2</sub> SO <sub>4</sub>	64	161	38
5-6-76	HNO <sub>3</sub>	n.d.	117	n.a.
5-6-76	H <sub>2</sub> SO <sub>4</sub>	62	158	38
5-20-76	H <sub>2</sub> SO <sub>4</sub>	62	158	36
6-22-76	H <sub>2</sub> SO <sub>4</sub>	n.d.	152	35

Table X. Concentrations of Fe in mg/l determined by titration with  $\text{KMnO}_4$ .

Adit	Date	Fe(II)	Fe(Total)	Fe(III)
ARGO TUNNEL	10-11-75	65	200	135
	2-7-76	65	192	127
	4-20-76	61	182	121
	5-4-76	65	190	125
	5-13-76	63	184	121
	5-28-76	65	186	121
	6-11-76	63	197	134
EMMETT MINE	10-11-75	130	142	12
	2-7-76	154	164	10
	4-20-76	163	176	13
	5-4-76	164	176	12
	5-13-76	166	180	14
	5-28-76	164	178	14
	6-11-76	157	170	13
NATIONAL TUNNEL	4-20-76	39	41	2
	5-4-76	38	40	2
	5-13-76	40	41	1
	5-28-76	40	43	3
	6-11-76	33	35	2

Table XI. Calculated and measured Eh values (millivolts) and the distribution of the hydrolytic species for iron obtained from mass balance. Concentrations are in mg/l.

	ARGO TUNNEL	NATIONAL TUNNEL	EMMETT MINE
pH	2.7	5.6	3.5
Eh calc.	690	420	600
Eh meas.	680	410	540
Fe(III)	126	2	13
Fe <sup>3+</sup>	6	≈10 <sup>-5</sup>	.4
Fe(OH) <sup>2+</sup>	1	---	.6
Fe(OH) <sub>2</sub> <sup>+</sup>	.2	2	.7
FeF <sup>2+</sup>	---	---	.8
Fe(II)	64	38	160
Fe <sup>2+</sup>	64	38	160
FeSO <sub>4</sub> <sup>+</sup>	119	---	11

The Fe(II)/Fe(III) ratios shown in Table VIII increase as the pH increases and the Eh decreases. This result shows a relatively high mobility of Fe(II) over Fe(III) which is better seen in Figure 7. Figure 8 and 9 shows the Eh-pH predominance diagram for all the hydrolytic iron species and ferric sulfate complex in a solution saturated with amorphous iron hydroxide.

In three mine effluents, redox potentials were calculated from ferric/ferrous couple. The mass balance for Fe(III) and Fe(II) was done by using all the iron aqueous species shown in Figures 8 and 9 and the ionic strength calculated from the chemical composition of the water. The equilibrium constant for the ferric sulfate complex was checked by measuring the Eh, pH, Fe(II), and total Fe to a solution containing ferric-ferrous-sulfate ions. The equilibrium constant calculated value agrees with the reported value in the literature (Sillen and Martell, 1964).

Table XI shows the measured and calculated Eh values, pH, Fe(II), and Fe(III) for Argo Tunnel, National Tunnel, and Emmett Mine. As seen in this Table the measured Eh readings agree very well for the Argo and National Tunnels but not for the Emmett Mine which has a difference of 60 millivolts between the calculated and measured Eh values. This difference of about 11 percent found in the Emmett Mine between the calculated and measured Eh values can be attributed to its more complex chemistry. In general, the

Figure 7. Predominance fields of Fe aqueous and solid species at 25° C and 1 atm. total pressure containing 2300 mg/l of total sulfate.

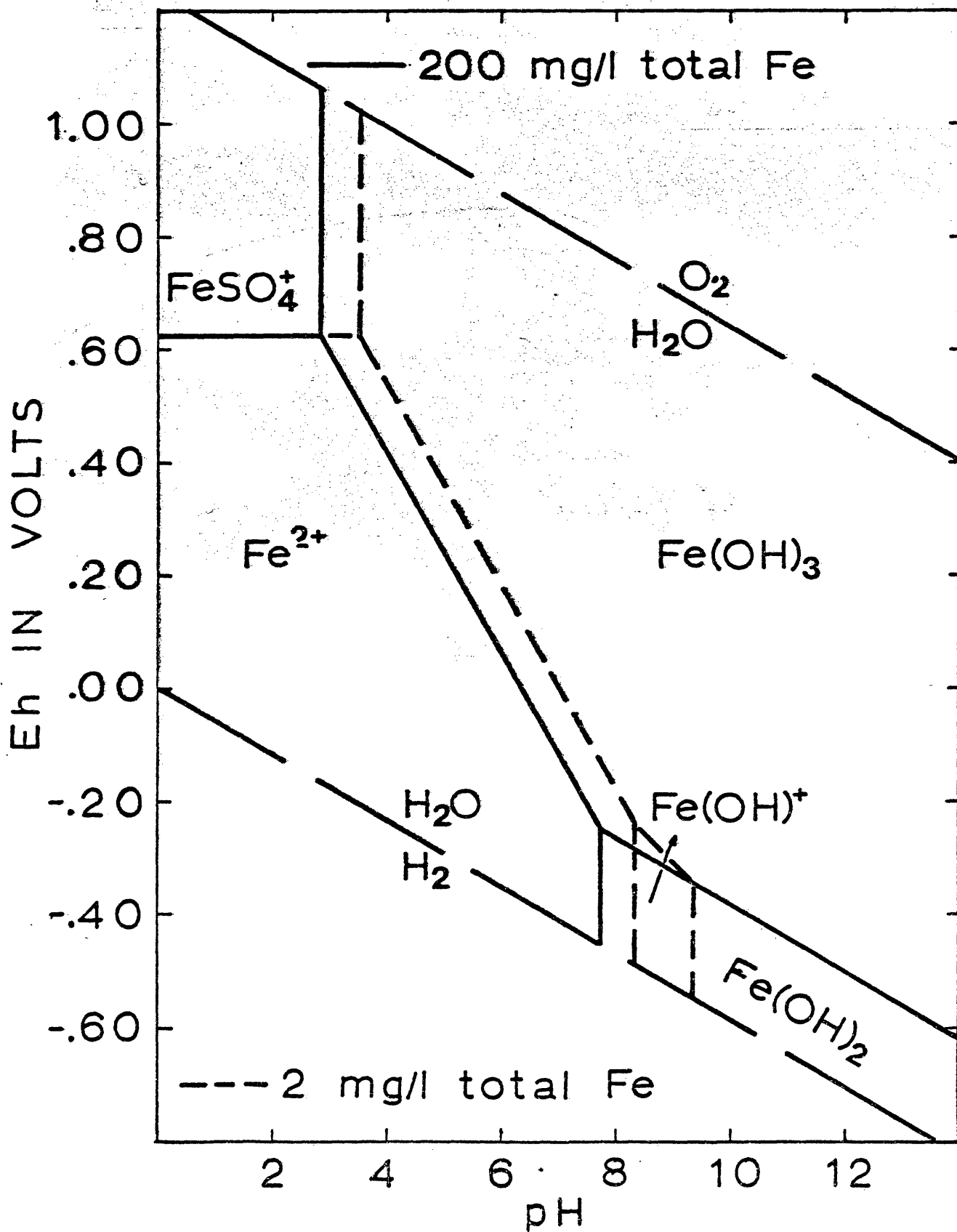


Figure 8. Predominance fields of Fe aqueous species saturated with  $\text{Fe}(\text{OH})_3$  at  $25^\circ\text{C}$  and 1 atm. total pressure.

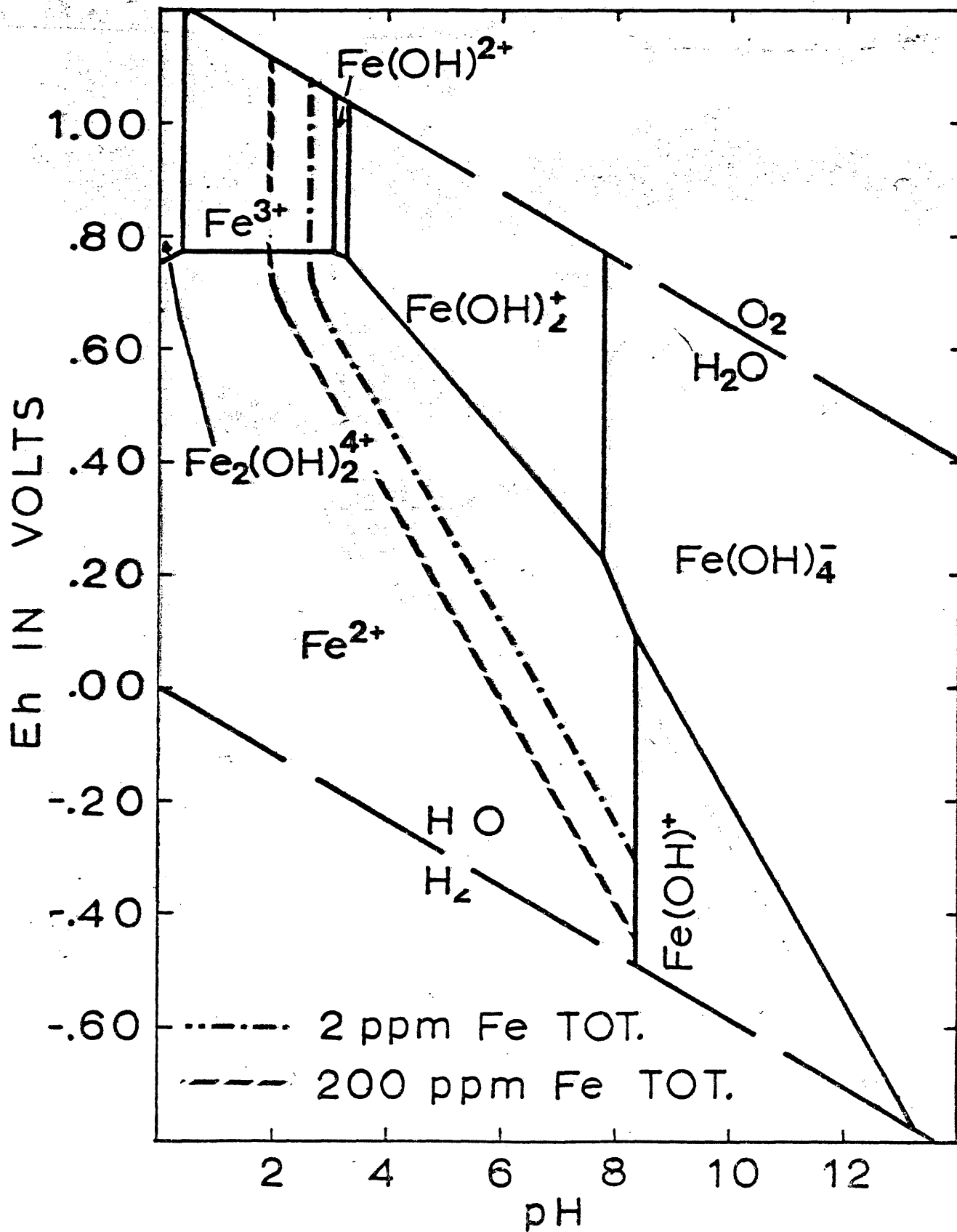
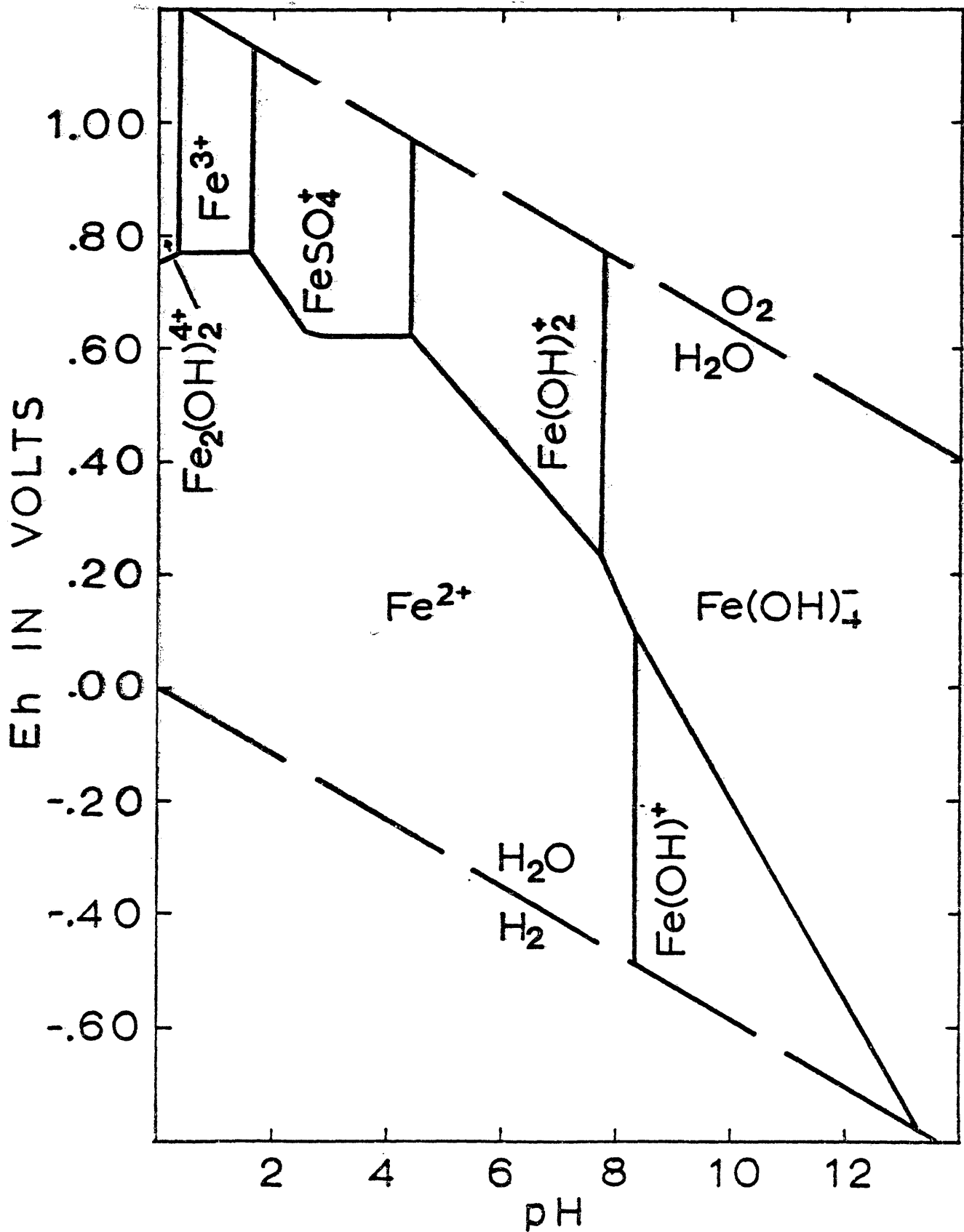


Figure 9. Predominance fields of Fe aqueous species saturated with  $\text{Fe}(\text{OH})_3$  at  $25^\circ\text{C}$  and 1 atm. total pressure. Total concentration of sulfate species is 2300 mg/l.



results obtained in this paper for the redox potentials agree quite well with the conditions established by Morris and Stumm (1966) and Nordstrom (1976) and also show the utility of Eh measurements in acid mine drainages.

Appendix 4 shows the equations used in the calculation of Eh, ionic strength, activity coefficients, mass balance and also the equations and thermodynamic data used in the construction of the Eh-pH diagrams shown in Figures 1, 2, 7, 8, and 9.

#### Ore Petrology and Mineralogy Compared to Water Quality

There is a very good correlation between the ore petrology, ore mineralogy, and the water quality of the mine effluents studied in this paper. Similar results have been found by Wildeman, et al. (1974) in the Central City mining district. In this district the zones of mineralization and the zonal distribution of the ore mineralogy have been well established by Sims and others (1963). The central zone consists mainly of pyrite and quartz and the peripheral zone is composed of quartz, sphalerite, and galena. It is observed in Table III that the pH of the water increases from the central zone to the peripheral zone with a decrease in the concentrations of the base metals. By comparing the abundance of pyrite versus the chemistry of the water in this district, a negative correlation is found between pyrite and the water quality. This result is supported by the aqueous oxidation

of pyrite which releases high concentrations of iron, sulfate, and hydrogen ions which promote the dissolution and oxidation of other sulfide minerals releasing high concentrations of base metals. This is the reason why the highest concentrations of Pb, Zn, and Cd occur in the central zone even though galena and sphalerite are most abundant in the peripheral zone.

According to Lovering and Goddard (1950) and Sims and others (1963) galena and sphalerite have almost the same abundance in the intermediate-peripheral zone and in the Silver Plume mining district but the content of Zn found in the waters draining from these areas is much higher than the Pb content. This is attributed to the fact that the oxidation of galena yields anglesite. The major elements do not show dramatic changes except Al. This constancy is supported by the similar composition of the wall rocks as seen in Table I, and this seems to be the case according to Wildeman and others (1974).

The Clyde Mine, which is located in the Boulder County Tungsten mining district, has the best water quality of those measured where only the major elements with the exception of Al and sulfate were detected. Most of the wall rocks found in this district are felsic (granite, pegmatite) and the only important ore mineral is ferberite with the very rare occurrence of sulfides. It was the only mine effluent where neither Fe nor Mn was detected and also it showed the

lowest concentrations for Na, K, Ca, Mg, and  $\text{SO}_4^{=}$ . These results may be explained by the high content of felsic rocks which are the most resistant to weathering (Mason, 1966) and the almost complete absence of sulfide minerals (Lovering and Goddard, 1950).

The Emmett Mine which is the deepest fluorspar mine in the Jamestown mining district is the adit which shows the highest concentrations for the major elements and its base metal contents are slightly higher than those found in the Argo Tunnel even though its pH is higher. It is distributed around the sodic granite porphyry stock and lime-silicate rocks are also present (Lovering and Goddard, 1950). Pyrite is disseminated throughout and small amounts of galena, chalcopyrite, and sphalerite are locally present.

The poor water quality found in this mine effluent can be explained by the following steps:

1. Oxidation and decomposition of pyrite ( $\text{FeS}_2$ ) generates high amounts of Fe, Co, Ni,  $\text{SO}_4^{=}$ , and  $\text{H}^+$ .

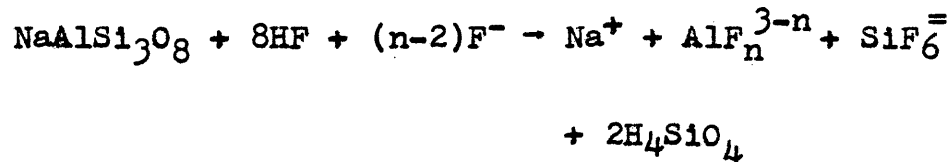


2. The  $\text{H}^+$  released in step 1 promotes the dissolution of fluorite ( $\text{CaF}_2$ ) releasing Ca and hydrofluoric acid (HF).



3. The HF formed in step 2 attacks the silicate rocks

releasing high concentrations of Na, K, Ca, Mg, SiO<sub>2</sub>, and Al.



4. Al and Si form strong complexes with fluoride (F<sup>-</sup>) which increase their mobility in the water system; therefore the rate of decomposition of the silicate minerals and the solubility of fluorite increase.
5. The high acidity generated in steps 1 and 2 mobilizes the base metals (Fe, Mn, Cu, Zn, Cd, Co, Ni, and Pb) released by the oxidation and dissolution of galena (PbS), sphalerite (ZnS), and chalcopyrite (CuFeS<sub>2</sub>).

Even with the high Ca, F, and SO<sub>4</sub><sup>=</sup> concentrations found in this adit, the water is still below saturation for fluorite and calcium sulfate minerals, gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) and anhydrite (CaSO<sub>4</sub>). It was found that only less than 1 mg/l of F was as free fluoride ions. This was determined by using the same procedure for total fluoride determination except that buffer solution and pH adjustment were not used.

### SUMMARY

There are two important factors controlling the water quality in a mine effluent: the composition of the wall rocks which supply the major elements and the sulfide minerals which input the base metals and sulfate. Pyrite is considered to be the most important sulfide mineral because its oxidation and dissolution control the acidity of the water which promotes the decomposition of other sulfides and the weathering of the silicate rocks. The pH is considered to be the master variable controlling the mobility of the base metals and Al in mine drainages except Fe which is controlled by both Eh and pH. The presence of ligands such as fluoride are also important because they increase the mobility of a few elements and the solubility of their solid species.

The position of the water table related to the ore veins, and the type of ore also play a very important role in the water quality from metal mine drainages.

All the mine effluents studied in this paper fit the diffuse aquifer system. The small seasonal variations and year to year changes found in the Central City mining district are because of the movement of the water table and the length of time the sulfide minerals are exposed to oxidation and decomposition.

The calculated values for redox potentials using the

ferric/ferrous couple and taking into account the ferric sulfate and fluoride complexes agree quite well with the Eh measured values. These results demonstrate the utility of Eh measurements in acid mine drainages. The total dissolved solids and the specific conductance have a direct correlation which indicates the usefulness of these measurements.

### RECOMMENDATIONS

It was observed in the course of this study that the following suggestions might be followed in future work:

1. Improve the analytical methods for the determination of Pb, Co, Ni, Zn, Cd, and Cu in mine drainages. The extraction method using APDC-MIBK for Ag, Pb, Cu, Cd, Co, and Ni does not work for mine drainages because the partition coefficients for these elements are probably different between the aqueous and organic phases and they do not show any correlation to each other.
2. Sulfate, chloride, fluoride, and carbonate should be determined in each sample in order to better understand the chemistry of the water.
3. The sediments should be analyzed and compared to the chemical composition of the water draining from the different mining adits. This would be helpful in studying the mobility of the major and minor elements between the water and the sediment and looking for any possible equilibrium between both aqueous and solid phases.
4. Study the role of organic activity in the oxidation and reduction of iron.

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APPENDIX ICHEMICAL ANALYTICAL DATA

n.d. = not detected

n.a. = not analyzed

Eh units are in millivolts

Water temp. is ° C

Conductivity is micromhos/cm

Concentrations are in mg/l except for Cd, Pb, Co,

Ni, and As which are in µg/l.





ARGO TUNNEL, CONTINUED

Date	10-11-75	2-7-76	4-20-76	5-4-76	5-13-76	5-28-76	6-11-76
Eh	650	650	650	670	680	680	680
pH	2.7	2.7	2.8	2.7	2.7	2.7	2.5
Cond.	2600	2600	2600	2550	2500	2650	2630
Diss. O <sub>2</sub>	4.4	5.9	2.0	1.75	1.33	1.35	1.75
Water temp.	15.0	15.0	15.5	15.5	15.5	16.0	16.0
Na	20	22	23	23	23	22	21
K	3.3	3.5	3.5	3.4	3.5	3.4	3.4
Ca	310	320	320	320	320	320	320
Mg	150	150	150	150	150	150	150
Al	27	25	22	24	22	24	24
SiO <sub>2</sub>	48	48	48	48	48	48	47
Fe	200	190	180	190	180	190	200
Mn	90	100	90	100	90	87	90
Cu	7.0	5.6	5.1	5.2	5.2	6.3	6.6
Zn	53	54	44	46	44	44	44
Cd	200	180	150	170	150	150	160
Pb	100	100	100	96	96	98	100
Co	200	200	200	200	200	200	200
Ni	350	330	350	350	340	350	350
As	270	190	180	180	180	200	200
SO <sub>4</sub> <sup>=</sup>	2310	n.a.	n.a.	2250	n.a.	n.a.	2270
F <sup>-</sup>	n.a.	n.a.	n.a.	n.a.	n.a.	3.2	n.a.





LUCANIA TUNNEL, CONTINUED

Date	4-20-76	5-4-76	5-13-76	5-28-76	6-11-76
Eh	420	490	450	530	500
pH	6.8	6.5	6.6	6.7	6.4
Cond.	980	1000	1000	1050	1000
Diss. O2	7.9	7.8	7.7	7.95	7.25
Water temp.	7.0	10.5	9.5	9.5	10.0
Na	23	23	23	23	23
K	4.5	4.5	4.5	4.4	4.4
Ca	210	210	210	220	210
Mg	77	77	77	77	77
Al	n.d.	n.d.	n.d.	n.d.	n.d.
SiO2	30	31	32	33	33
Fe	.72	.60	.67	.67	.38
Mn	2.6	2.7	2.6	2.7	2.9
Cu	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	1.5	2.0	1.6	1.9	2.5
Cd	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	n.d.	n.d.	n.d.	n.d.	n.d.
Co	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.
As	n.d.	n.d.	n.d.	n.d.	n.d.
SO4	n.a.	n.a.	n.a.	800	n.a.
F-	n.a.	n.a.	n.a.	.56	n.a.



## BURLFEIGH TUNNEL, CONTINUED

Date	10-11-75	2-7-76	4-20-76	5-4-76	5-13-76	5-28-76	6-11-76
Eh	520	420	440	480	480	490	500
pH	6.0	6.6	6.6	6.4	6.5	6.8	6.8
Cond.	550	550	520	550	550	550	540
Diss. O <sub>2</sub>	7.4	8.4	7.7	8.3	8.3	7.7	8.1
Water temp.	7.8	6.0	11.0	15.5	7.0	17.0	19.0
Na	7.5	9.0	9.0	9.1	9.2	9.0	9.0
K	2.6	2.8	2.2	2.4	2.7	2.7	2.4
Ca	75	87	77	77	77	75	75
Mg	50	52	48	57	55	54	50
Al	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SiO <sub>2</sub>	6.4	6.4	7.2	7.2	5.4	5.4	5.4
Fe	.30	.28	.26	.28	.26	.26	.18
Mn	2.0	1.9	1.8	1.7	1.5	1.4	1.4
Cu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	50	49	40	38	35	33	33
Cd	120	100	72	72	65	65	65
Pb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Co	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
AS	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SO <sub>4</sub>	n.a.	n.a.	n.a.	n.a.	n.a.	340	n.a.
F	n.a.	n.a.	n.a.	n.a.	n.a.	.80	n.a.





NATIONAL TUNNEL, CONTINUED

Date 4-20-76 5-4-76 5-13-76 5-28-76 6-11-76

Bh	370	390	480	430	430
pH	5.7	5.6	5.5	5.5	5.6
Cond.	950	950	950	980	1000
Diss. O <sub>2</sub>	7.8	8.3	7.6	7.9	8.3
Water temp.	7.0	7.5	7.5	8.5	8.8
Na	26	26	26	26	26
K	7.2	7.2	7.2	7.2	7.2
Ca	190	190	190	190	190
Mg	71	71	71	71	71
Al	n.d.	n.d.	n.d.	n.d.	n.d.
SiO <sub>2</sub>	41	42	41	41	38
Fe	40	40	40	43	34
Mn	20	20	20	20	20
Cu	.12	.11	.12	.10	n.d.
Zn	5.8	5.8	5.8	5.8	5.8
Cd	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	n.d.	n.d.	n.d.	n.d.	n.d.
Co	120	110	110	110	110
Ni	250	240	240	250	240
As	n.d.	n.d.	n.d.	n.d.	n.d.
SO <sub>4</sub>	n.a.	n.a.	n.a.	890	n.a.
F <sup>-</sup>	n.a.	n.a.	n.a.	.47	n.a.



CLYDE MINE, CONTINUED

Date	10-11-75	2-7-76	4-20-76	5-4-76	5-13-76	5-28-76	6-11-76
Eh	420	420	460	440	480	420	360
PH	6.0	6.4	6.8	6.4	6.5	6.6	7.0
Cond.	300	290	320	310	310	320	305
Diss. O <sub>2</sub>	7.0	8.4	8.6	7.8	8.0	7.1	7.8
Water temp.	5.5	4.0	9.0	9.0	9.0	9.0	7.5
Na	7.9	8.0	8.2	8.2	8.2	8.2	8.2
K	2.0	2.0	1.8	1.8	1.8	1.8	1.8
Ca	48	48	46	46	46	46	46
MG	40	38	37	37	37	37	37
Al	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SiO <sub>2</sub>	15	17	18	18	18	18	18
Fe	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cd	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Co	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
AS <sup>=</sup>	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SO <sub>4</sub> <sup>=</sup>	n.a.	n.a.	n.a.	n.a.	n.a.	15	n.a.
F <sup>-</sup>	n.a.	n.a.	n.a.	n.a.	n.a.	.50	n.a.



CORNING TUNNEL, CONTINUED

Date	2-7-76	4-20-76	5-4-76	5-13-76	5-28-76	6-11-76
Eh	370	340	310	390	380	290
PH	5.9	6.0	6.3	6.0	6.0	6.3
Cond.	1100	1100	1200	1100	1150	1170
Diss. O <sub>2</sub>	5.5	1.6	3.5	.85	.55	.60
Water temp.	8.0	8.5	9.0	8.5	9.2	8.0
Na	10	11	11	11	11	11
K	6.8	6.8	6.8	6.8	6.8	6.8
Ca	210	210	210	210	210	210
Mg	140	140	140	140	140	140
Al	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SiO <sub>2</sub>	13	13	13	13	13	13
Fe	4.4	5.5	6.0	5.5	5.3	5.2
Mn	6.2	6.2	6.1	6.1	6.1	6.0
Cu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cd	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Co	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
As =	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SO <sub>4</sub>	n.a.	n.a.	n.a.	n.a.	900	n.a.
F =	n.a.	n.a.	n.a.	n.a.	.33	n.a.

EMMETT MINE

Date	2-22-75	4-5-75	4-20-75	5-3-75	5-19-75	6-2-75	8-15-75
Eh	290	430	390	500	510	540	550
pH	3.9	4.0	3.8	3.7	4.1	3.4	3.5
Cond.	2200	2600	2650	2600	2800	2550	3000
Diss. O <sub>2</sub>	6.5	4.8	4.8	4.5	3.6	3.6	5.0
Water temp.	3.0	10.2	9.2	11.0	12.5	12.0	14.0
Na	310	300	300	300	300	260	310
K	29	28	28	28	28	25	25
Ca	480	480	480	480	480	470	470
Mg	90	90	90	90	91	86	93
Al	160	160	160	160	160	150	160
SiO <sub>2</sub>	57	56	57	56	55	55	55
Fe	160	160	160	160	160	130	150
Mn	150	150	150	150	150	140	150
Cu	.26	.28	.27	.30	.30	.41	.70
Zn	37	38	37	38	37	36	38
Cd	48	47	50	50	48	52	54
Pb	170	170	170	180	170	170	170
Co	700	700	700	700	700	700	700
Ni	600	600	600	600	600	600	580
As	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SO <sub>4</sub>	2900	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
F <sup>-</sup>	250	250	250	250	250	230	250

EMMETT MINE, CONTINUED

Date	10-11-75	2-7-76	4-20-76	5-4-76	5-13-76	5-28-76	6-11-76
Eh	550	540	520	520	550	540	540
pH	3.3	3.5	3.6	3.5	3.7	3.5	3.6
Cond.	2900	2540	2750	2800	2840	2950	2970
Diss. O <sub>2</sub>	7.5	16.2	4.0	1.25	.90	.42	1.2
Water temp.	14.0	8.0	9.0	11.5	10.0	11.2	11.0
Na	300	300	280	280	280	280	280
K	27	26	29	29	29	30	29
Ca	470	450	460	460	460	460	460
Mg	91	90	90	92	92	92	92
Al	160	150	150	150	150	150	150
SiO <sub>2</sub>	54	53	64	60	55	76	52
Fe	140	160	180	180	180	180	170
Mn	150	150	150	150	150	150	150
Cu	.50	.24	.20	.20	.20	.18	.18
Zn	37	37	37	37	37	37	37
Cd	49	49	47	47	47	47	47
Pb	170	200	180	180	180	190	190
Co	700	700	700	700	700	700	700
Ni	590	590	600	600	600	600	600
As =	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SO <sub>4</sub>	n.a.	2890	n.a.	n.a.	n.a.	2800	n.a.
F <sup>-</sup>	250	250	240	240	240	240	240

APPENDIX 2A. DESCRIPTION OF THE ANALYTICAL METHODS, RESULTS  
AND ACCURACY OBTAINED IN THE  
ANALYSIS OF MINE DRAINAGESB. COMMENTS ON THE COLLECTION AND STORAGE OF  
MINE EFFLUENT WATERS

This report is a summary of the practical development of a multielement analytical procedure for drainages from base-metal mines from different mining districts within the Front Range Mineral Belt of Colorado (1). The concentration ranges for those constituents which are routinely analyzed are listed in Table 1; and the matrix changes from a natural water of moderate hardness to an industrial effluent. The problem to overcome is not pushing detection limits to lower levels but rather is determining whether the matrix interferes in the application of the standard methods of analysis for natural waters. In this regard, the change from Mg, Ca, Na, and K being the major constituents to Fe and  $\text{SO}_4^{=}$  being the major constituents is important in determining whether the standard methods will apply.

Because of the criteria established above, procedures follow the usual schemes (2, 3) and methods described in more recent reviews (4, 5) were avoided until problems arose. This plan, of course, then means that atomic absorption spectrometry (AAS) analysis is the primary technique and essentially it is an exercise in avoiding an analysis by

the standard addition method for every element in every sample (6). As one might expect, for the most part, there were no problems; but for certain elements, the matrix effects have been particularly troublesome.

The following discussion will dwell on the analysis of those elements listed in Table I. It is divided into those elements which can be analyzed directly by (AAS) with no interferences, elements for which the matrix interferes in the direct determination, and problems involved in the chelation-extraction procedure. Development of techniques for Al, Si, Se, and F is now being attempted.

#### Atomic Absorption - Direct Methods

Fe, Mn, Zn, Cu, Na, K, Mg, Cd, and Pb are elements which cause no problems in direct analysis by AAS. The direct range column in Table I gives the ranges for each element over which a precision of  $\pm 10\%$  can be expected in an air-acetylene flame using no dilutions, scale expansions, ionization suppressors, or releasing agents. For these values, suitable dilutions of the SMD were used for the concentration determinations and the precision was established by analyses of five synthetic and natural water standards. In addition, pure standards of Fe, Mn, Zn, Na, K, Mg and Cd were analyzed against the SMD at various concentrations within the direct method ranges shown in Table I. In all cases, the calculated values were within  $\pm 4\%$  of the actual

values. Thus for these elements, reliable analyses of mine drainage could be achieved with single element standards using AAS. Three of these elements for which ranges are not reported in Table I are discussed below. For Mo, the concentration range in the drainages is far below the direct method detection limit, and the levels reported in Table I were estimated by colorimetric analysis (7). Attempts at analysis of Mo by the solvent extraction method will be discussed later.

#### Calcium

As has been amply demonstrated by other investigators,  $\text{SO}_4^{=}$  and possibly Fe will interfere with AAS analysis of Ca (8). Thus, it is not surprising that problems were encountered. It was anticipated that the SMD alone or the SMD used in conjunction with  $\text{LaCl}_3$  as a releasing agent would solve the problems using the air-acetylene flame (9). However, it was found that Fe and  $\text{SO}_4^{=}$  coupled in the interference of the analysis of Ca so that matrix interferences just could not be eliminated and a full study of the AAS analysis of Ca was made.

Figures 1 and 2 summarize the effects of the matrix on the analysis of Ca using standard fuel conditions and an air-acetylene flame. Note that the abscissa is given as Ca/ $\text{SO}_4$ , or Ca/Fe, or both Ca/ $\text{SO}_4$  and Ca/Fe when both constituents are present. The usual working range is 1-20 mg/l

of Ca in the usual burner configuration and 5-100 mg/l of Ca when the burner is rotated  $90^\circ$  (9). Figure 1 shows the analysis without using  $\text{LaCl}_3$  for Ca standards of 200, 100, and 20 mg/l.  $\text{SO}_4^{=}$  and Fe alone suppress the Ca peak but when together the Fe acts almost as  $\text{LaCl}_3$  should in releasing some Ca and enhancing the Ca peak. Note that at 20 mg/l, the two effects exactly cancel so that the Ca analyses are apparently reliable. Because of this coupling effect, the matrix would have to be matched exactly for a reliable analysis above 20 mg/l and analysis by comparison with the SMD alone is useless.

Addition of  $\text{LaCl}_3$ , which is often recommended, does not help the situation of concentrations of Ca that are greater than 20 mg/l. Figure 2 is a repeat of the conditions outlined above only now, 1 ml of 10,000 mg/l  $\text{LaCl}_3$  solution has been added to 10 ml of sample; thus the actual concentration of Ca is 182, 90.9, and 18.2 mg/l. If  $\text{SO}_4^{=}$  or Fe are present alone, the results are reliable at 90.9 mg/l; but when Fe and  $\text{SO}_4^{=}$  are both present the coupling effect again produces confusion. Note that at 18.2 mg/l the use of  $\text{LaCl}_3$  renders good results.

From an analysis of the above discussion, reliable operating parameters for -Ca analysis using an air-acetylene flame are as follows: Concentration should not exceed 20 mg/l, addition of  $\text{LaCl}_3$  is necessary to achieve results that are precise to within  $\pm 10\%$ ,  $\text{LaCl}_3$  also enhances the

peak height by 10%; if a precision of  $\pm 20\%$  can be tolerated,  $\text{LaCl}_3$  is not necessary.

Recently, AAS procedures for Ca have been switched from use of an air-acetylene flame to a nitrous oxide-acetylene flame, so the tests described above using, and not using  $\text{LaCl}_3$ , were repeated to test for possible interferences in this type of flame. The working range was found to be the same as for the air-acetylene flame, but at low levels of Ca, peak heights are enhanced by about 20%. The results are considerably better. Up to the maximum concentration of 100 mg/l of Ca,  $\text{SO}_4^{=}$  alone, Fe alone, of Fe and  $\text{SO}_4^{=}$  together show no interference. In all cases, calculated concentrations were within  $\pm 4\%$  of actual values. Also, adding or not adding  $\text{LaCl}_3$  makes no difference in the reliability of the results, so the releasing agent can be eliminated. Furthermore, pure Ca standards at various concentrations over the working range were compared against the SMD and again, the calculated values were within  $\pm 4\%$  of actual values. Clearly, in the case of the analysis of mine drainages, use of the nitrous oxide-acetylene flame for Ca is the superior procedure.

### Arsenic

For As, detection by direct aspiration is eliminated except at high concentration and also solvent extraction was ruled out because of general problems in the extraction

which are explained later. Thus, the procedure using arsine generation by addition of KI,  $\text{SnCl}_2$ , and Zn slurry was chosen (10). Tests of this procedure on our standard mine drainages have been contradictory and confusing. In the first series of analyses a hollow cathode arsenic lamp was used and it appeared that iron in the range of 10 to 50 mg/l interfered with the arsine generation but the lamp rapidly deteriorated before this could be confirmed. Subsequently, an electrodeless discharge lamp has been used and no Fe interference was found. We suspect that our arsine generation system is faulty and a totally revised system and procedure is now being developed.

### Sulfate

The attempt to find an accurate and rapid method for the analysis of sulfate has been particularly frustrating. The basic problem is that most standard procedures rely on the precipitation of barium sulfate and Fe and other heavy metals interfere with the precipitation (11). Figure 3 shows the results of the indirect sulfate method which uses an AAS analysis of barium remaining after a  $\text{BaSO}_4$  precipitation and the problem is clear (12). Iron in the SMD is coprecipitated with the  $\text{BaSO}_4$ , this releases some Ba resulting in a spuriously low reading for the amount of  $\text{SO}_4^{=}$  in the sample. Currently, analyses are being done by this AAS method using the mine drainage as the standard

keeping the  $\text{SO}_4^{=}$  concentration below 50 mg/l. The other possibility is removal of heavy metal ions by passing the water through a cation exchange column (11). Using x-ray fluorescence, and assuming that all sulfur in the water is the  $\text{SO}_4^{=}$  species, would eliminate a  $\text{BaSO}_4$  precipitation and so this alternative has been intensely studied. The 5.36 A  $K\alpha$  line of sulfur has been used and the operating conditions chosen were a 40 KeV excitation energy, NaCl analyzing crystal, and a gas flow proportional counter. This method also has its pitfalls; it appears that the water itself cannot be analyzed because the irradiation causes precipitation of sulfur or reaction of sulfate with the mylar covering and sample vial. Recently, a method was tried where a standard drop of the water sample was placed on filter paper using a 50  $\mu\text{l}$  syringe, the filter paper was dried, and then analyzed in the x-ray spectrometer. Preliminary tests of this procedure look promising and complete study of the procedure is now being conducted.

#### Solvent Extraction Methods

There is a necessity to be able to perform accurate analyses at levels lower than those listed on the direct range column of Table I. These limits are significantly above the U.S. Public Health Service drinking water standards for Pb and Cd which are 50 and 10  $\mu\text{g/l}$  respectively (13). Also, Cu and Zn are known to be toxic to aquatic

life at levels below those stated in Table I (14). The standard AAS procedure for increasing sensitivity is chelation of the metal by a complexing agent, usually ammonium pyrrolidine dithiocarbamate (APDC), followed by extraction of the complex into an organic solvent, usually methyl isobutyl ketone (MIBK), and then aspiration of the organic phase (2). Such a procedure will typically lower the analysis range of all four elements listed above into the 1-10  $\mu\text{g}/\text{l}$  range (2).

Unfortunately, iron interferes with this standard chelation-extraction method. Its concentration is high enough and its ability to form complexes with APDC is strong enough that some of the trace metals are lost with respect to the pure element standards usually used in this method. Figure 4 shows the effect which Fe has on the chelation extraction of Cd and Pb; by the time the concentration of Fe has reached about 25 mg/l, the organic phase is so viscous due to insoluble iron compounds, that it will not aspirate without an obnoxious filtration.

In addition, an attempt was made to try the 8-hydroxyquinoline-MICK extraction for Mo for AAS analysis (15) and Fe fouled this extraction also. Since Mo is in low concentrations in acidic waters due to the precipitation of insoluble molybdate salts (16), this effectively eliminates the use of AAS for Mo analyses of mine drainages.

Two methods are being attempted to circumvent this

problem with Fe and preliminary reports on these are contained below.

#### Iron masking method

The report of a successful chelation extract method of AAS analysis of base metals in soils with high Fe and Mn content (17) suggested that the hydroxylamine hydrochloride used in this procedure was reducing the Fe(III) to Fe(II) and complexing it to the extent that the APDC complex was not formed. Essentially, the hydroxylamine hydrochloride is working as a masking agent for Fe such as those typically used in visible-UV spectrophotometry (18). This prompted a study to discover a masking agent that retains the iron in the aqueous phase and allows the chelation extraction to function for the other base metals. Preliminary results suggest that a universal masking agent is not possible, but that use of pyrogallol as a reductant and 1,10-phenanthroline as a complexing agent for Fe results in reliable analyses of Cd and Pb by the MIBK-APDC extraction procedure up to iron concentrations of 250 mg/l.

#### Anodic stripping voltammetry (ASV) method

Recent reviews on the analysis of water have pointed out the attractiveness of ASV methods for the analysis of Cu, Zn, Cd, and Pb (18, 19). From all that has been said, it appears that the sensitivity that can be expected is at least as good as the chelation extraction methods used in

AAS. Again, the question in the application of the method in this case is whether the matrix will interfere with the stripping analysis.

The stripping cell chosen was that described by Clem and others (20, 21) which is commercially available from McKee-Pederson, Inc. The procedures described in the system instructions were closely followed and it was possible to set up an operational system with not too much difficulty. Analyses were attempted for Mn, Zn, Cd, Pb, Cu, Hg, Ag, Au, and As. Satisfactory results were not obtained for Ag, Au, and As so they were not further studied. The minimum detectable concentration for Hg is about 0.5  $\mu\text{g}/\text{l}$  and this is comparable to the flameless atomic absorption so ASV offers no real advantage for this element. Also, ASV methods for Mn appear to work well, but in mine drainages the direct method by AAS is suitable in almost all cases. For Zn, an intermetallic Cu-Zn compound is formed in the mercury amalgam when both are plated onto the electrode film (22) and thus the plating potential was set so that Cu, Pb, and Cd plated but Zn did not.

For Cu, Pb, and Cd, the samples were adjusted to pH of 2.5 to eliminate possible organic complexes and it was found that at this pH the mine drainage matrix had no effect on the analysis. Analyses were made both by the method of standard additions and by making calibration curves using the SMD and in both cases the results came

within  $\pm 10\%$  of expected values for standard samples. Furthermore, it is possible to maintain this precision down to concentrations of 1  $\mu\text{g}/\text{l}$  for Cu, Pb, and Cd.

Considering that the three elements can be analyzed simultaneously and that no extractions would have to be made, the ASV method using calibration curves would be comparable in analysis time to AAS methods. Thus, ASV is a promising alternative for the analysis of Cu, Pb, and Cd in mine drainage waters where high iron concentrations interfere with solvent extraction methods for atomic absorption spectrophotometry.

Table I. Concentration ranges in mine drainage waters and in the standard mine drainage (SMD).

Element	Conc. Units	Conc. Range	SMD Conc.	Direct Range
Fe	mg/l	<0.4-900	800	4-1000
Mn	mg/l	<0.03-150	300	0.3-50
Zn	mg/l	0.03-500	160	0.2-30
Cu	mg/l	<0.01-7-	100	0.5-50
Na	mg/l	1-80	45	0.05-15
K	mg/l	0.7-10	16	0.05-15
Mg	mg/l	30-280	300	0.05-20
Ca	mg/l	20-400	400	--
As	µg/l	<0.5-7000	2000	--
Mo	µg/l	1-90	1000	--
Cd	µg/l	<20-2500	2000	100-3000
Pb	µg/l	<50-500	1000	200-1000
SO <sub>4</sub>	mg/l	200-4000	4000	--

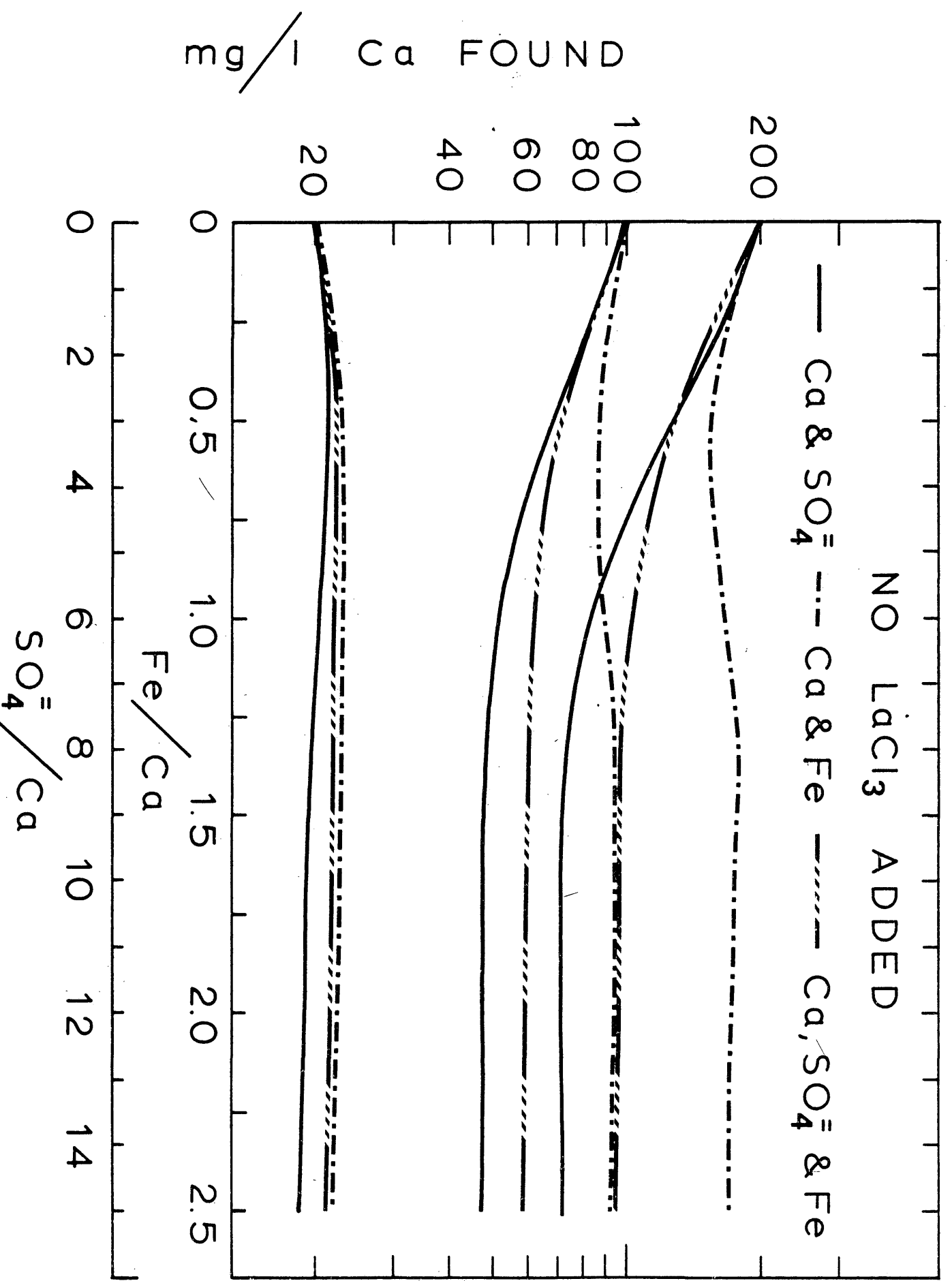
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FIGURE CAPTIONS

- Figure 1: The effect of Fe and  $\text{SO}_4^{=}$  on the AAS signal of Ca at concentrations of 200, 100, and 20 mg/l. No  $\text{LaCl}_3$  was added. Note the abscissa is in units of Fe/Ca,  $\text{SO}_4^{=}/\text{Ca}$ , or Fe/Ca and  $\text{SO}_4^{=}/\text{Ca}$  when both are present.
- Figure 2: The effect of Fe and  $\text{SO}_4^{=}$  on the AAS signal of Ca at concentrations of 182, 90.9, and 18.2 mg/l when  $\text{LaCl}_3$  has been added. The units on the abscissa are the same as in Figure 1. At 18.2 mg/l of Ca, the signal heights in all three experiments merge.
- Figure 3: The results of the analysis of  $\text{SO}_4^{=}$  in a standard mine drainage by AAS using the indirect Ba method. The SMD line shows the actual concentration; the other line shows the amount found in the SMD using the  $\text{Na}_2\text{SO}_4$  standard.
- Figure 4: The effect that Fe concentration has on the AAS analysis by solvent extraction of a 5  $\mu\text{g}/\text{l}$  solution of Cd and an 8  $\mu\text{g}/\text{l}$  solution of Pb.



NO  $\text{LaCl}_3$  ADDED

—  $\text{Ca}$  &  $\text{SO}_4^-$     - - -  $\text{Ca}$  &  $\text{Fe}$     - · - · -  $\text{Ca}$ ,  $\text{SO}_4^-$  &  $\text{Fe}$

mg / l Ca FOUND

200

100

80

60

40

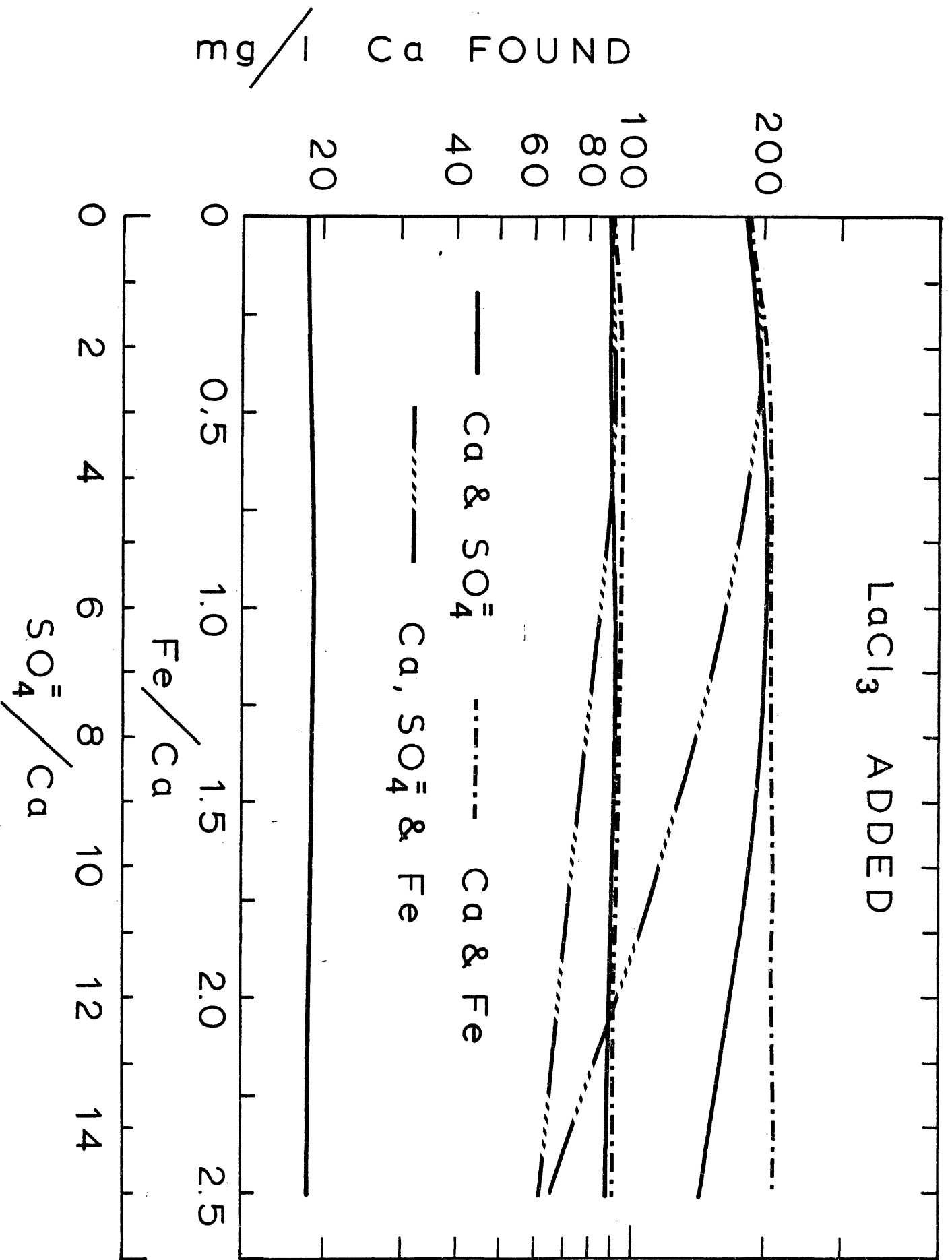
0 0.5 1.0 1.5 2.0 2.5

0 2 4 6 8 10 12 14

Fe / Ca

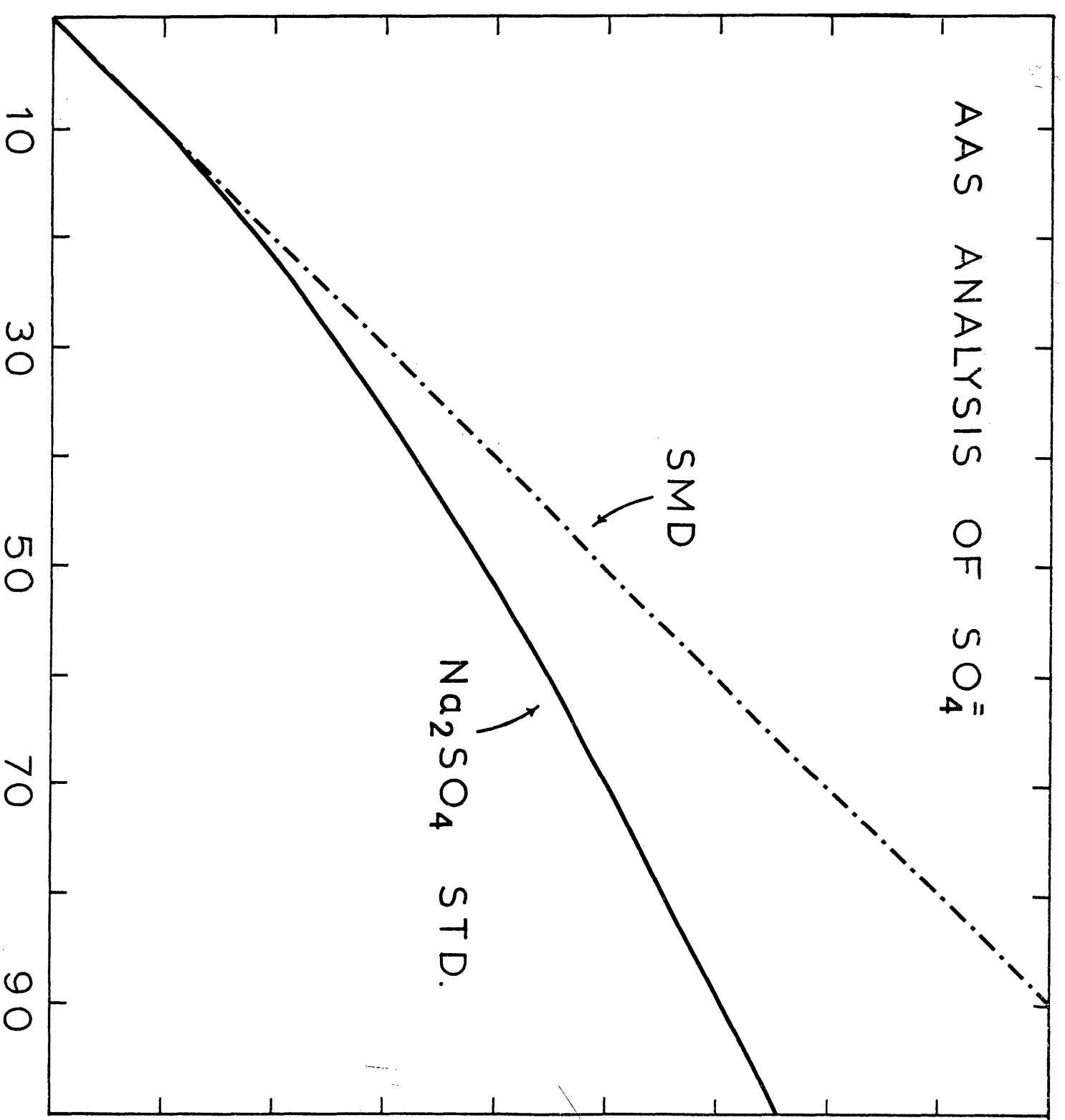
$\text{SO}_4^-$  / Ca

LaCl<sub>3</sub> ADDED

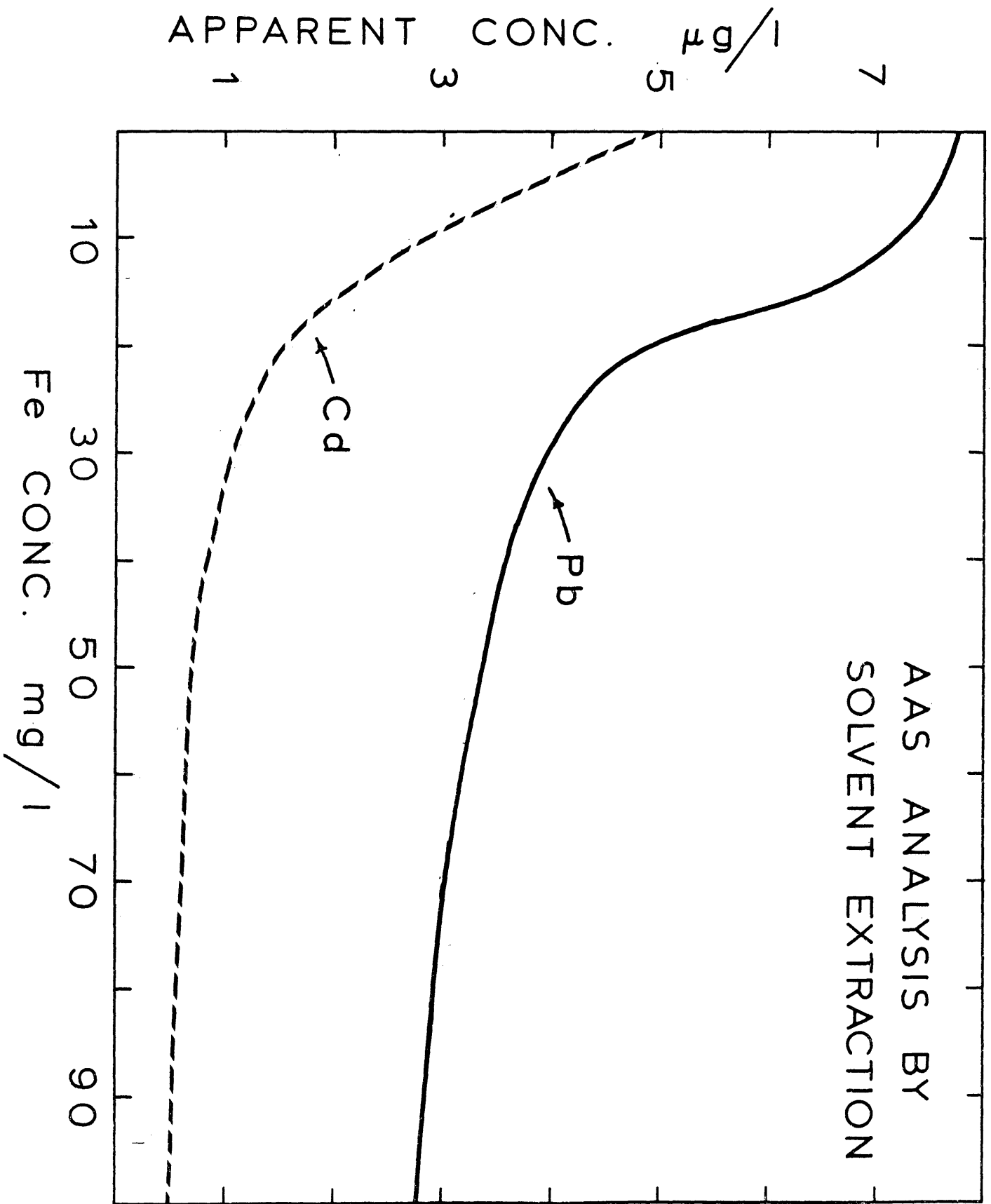


# AAS ANALYSIS OF $\text{SO}_4^{=}$

mg/l of  $\text{SO}_4^{=}$  FOUND



AAS ANALYSIS BY  
SOLVENT EXTRACTION



COMMENTS ON THE COLLECTION AND STORAGE  
OF MINE EFFLUENT WATERS

Two of the questions which must be considered when developing analytical methods on a specific material are how does sample preparation bias the analytical results and does the material change upon storage. This note describes various tests which we have made to try to pin down some of the aspects of these two questions which affect mine effluents.

Water Collection

The majority of the sample preparation decisions and some of the storage decisions concerning water samples are performed on site when the sample is collected. These decisions include whether or not to acidify the sample, whether or not to filter the sample, and what type of bottle to use. Many of these questions are addressed in the analytical methods manual which the Water Resources Division of the U.S. Geological Survey publishes (1).

Of the above decisions, the one which we have found to be most vexing is that of whether to filter or not. This collection decision obviously defines what is suspended solids as opposed to dissolved solids but it also defines what chemical species will be in the sample. Also, if the sample is not filtered but acidified, then some of the cations which are adsorbed onto the suspended material will

probably be extracted into solution. Even though the method of filtration is well defined as passage of the water through a  $0.45\ \mu\text{m}$  membrane filter using compressed gas (1), the elimination of particles down to this size implies that colloidal sized particles are split with most passing through the filter and the largest being retained. The result is that surface adsorption effects are ignored.

The mine drainages which we sample are typically in a low energy flow situation so the water is usually not carrying suspended solids which were scoured from the bottom sediments. We have always used the rule of thumb that we won't filter particulates we cannot see, so consequently we do little filtering during collection. Logistics and laziness certainly play a role in this decision. Nonetheless, this rule generated uncertainty concerning the interpretation of the results especially with regard to colloidal material. So in August of 1975 when all the mine and surface waters were in low-flow, non-turbulent configurations, we tested our collection procedure at 7 mine sites and 7 surface drainage sites. Collection was made by four methods: unfiltered, filtered with  $0.45\ \mu\text{m}$  using air, filtered to  $0.45\ \mu\text{m}$  using  $\text{N}_2$ , and filtered to  $0.10\ \mu\text{m}$  using  $\text{N}_2$ . The air and  $\text{N}_2$  collections address the question of whether air oxidizes  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  causing the precipitation of  $\text{Fe}(\text{OH})_3$  on the filter. The  $0.45\ \mu\text{m}$  and  $0.10\ \mu\text{m}$  collections address

the question of the role of colloidal material in the samples.

Except for two sites the abundances of all the elements at all the different sites, using all four of the collection methods were the same. The abundances of the elements were analyzed by atomic absorption spectrophotometry and the four samples from each site were analyzed in sequence. Hence, relative changes could be detected to better than  $\pm 5\%$ . The elements analyzed were Na, K, Mg, Ca, Al, Si, Fe, Mn, Zn, Cu, Co, Ni, Cd, and Pb.

At one mine adit, the drainage course had been recently disturbed and the water was slightly turbid. Fe dropped from 55 mg/l in the unfiltered sample to 50 mg/l in all 3 filtered samples. Al, Cd, Pb, Ni, and Co were below the detection limit. All other elements were unchanged. At the other mine adit, the sample couldn't be filtered for 15 minutes due to logistics problems. Fe changed from 3.4 mg/l in the unfiltered sample to 2.5 mg/l in the three filtered samples. Cu, Cd, Pb, Al, Co, and Ni were below detection limits. All other elements were unchanged.

The conclusions are that for these samples, colloidal material down to  $0.10\mu\text{m}$  is unimportant and if the water isn't turbid there are no suspended solids. Also, if filtering has to be performed, it should be done immediately so that Fe won't begin to precipitate. When  $\text{Fe}(\text{OH})_3$  does precipitate it doesn't necessarily adsorb other cations and

remove them from solution. It also appears that using air to pressurize the filtering apparatus, does not oxidize the  $\text{Fe}^{2+}$ .

### Storage of Samples

Our interests in mine drainage concentrate on the metals in solution. Consequently, samples are collected in 32 oz. polyethylene or polypropylene bottles and are immediately acidified with 5 ml of doubly distilled  $\text{HNO}_3$  that has been diluted by 50%. The concentration of  $\text{HNO}_3$  is about 0.25% by volume; and the pH is around 1.5.  $\text{HNO}_3$  appears to hold cations in solution better than other acids (1, 2, 3). Although teflon appears to adsorb cations from solution the least, polyethylene and polypropylene are adequate and much less expensive (1, 3). In addition, the bottles are rinsed with 25%  $\text{KNO}_3$  to eliminate previously adsorbed elements (4).

### Tests for Aging of Samples

Our analytical scheme for mine drainages was developed in 1974 and relies heavily upon atomic absorption (5). To check for matrix effects and interelement interferences a standard mine drainage (SMD) was prepared in February, 1974. For this standard,  $\text{CaCO}_3$ ,  $\text{MgO}$ ,  $\text{Mn}$ ,  $\text{Zn}$ , and  $\text{Cu}$  were dissolved in  $\text{HNO}_3$ ,  $\text{Na}$  and  $\text{K}$  were added as chlorides,  $\text{As}_2\text{O}_3$  and  $\text{MoO}_3$  were dissolved in  $\text{NaOH}$  and a correction was made for the final abundance of  $\text{Na}$ . Iron was added in the form of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and the remainder of the sulfate was

added using standardized  $\text{H}_2\text{SO}_4$ . Care was taken to see that the concentration of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{=}$  did not exceed the solubility product of gypsum. All concentrations were set to about the highest levels which have been found in Colorado mine effluents. The compositions of the 1st SMD and the most recent SMD are given in Table 1. When dilutions are made, 0.25%  $\text{HNO}_3$  is the dilutant. Three more standards have been made since 1974. In more recent standards, Fe powder as well as Al, Co, and Ni metals are dissolved in  $\text{HNO}_3$ .

In March, 1976, the first SMD as well as the original dilutions of this standard were checked to see if any change occurred during two years of storage. All analyses were performed by atomic absorption using direct aspirations down to the concentration level at which a precision of  $\pm 5\%$  could be maintained. Comparisons were made with dilutions of the most recent SMD and also pure element standards of the appropriate concentration.

In all the tests, there were no concentration changes to within  $\pm 5\%$ . The elements analyzed and the lowest concentrations to which analyses were performed are given in Table II. In the case of As, Mo, and  $\text{SO}_4^{=}$ , our analytical procedures are not developed to the extent that the results are reliable to within  $\pm 10\%$ . Consequently, we cannot accurately determine whether deterioration has occurred.

In addition to the tests made on the original SMD, repeat analyses were made on 8 mine drainages which were

collected in December, 1973 to check for deterioration. In all cases, the original results were duplicated to  $\pm 5\%$  down to the levels shown in Table II. Next, repeat analyses were made for Zn, Cu, Fe, and Mn on 10 groundwater samples which were 2 years old. In this case, the first analyses were made using completely different standards. There was a scatter of the results which averaged 16% for Fe, 4% for Mn, 8% for Zn, and 5% for Cu. No trend towards lower concentrations could be established.

The conclusion is that for the elements listed in Table II and down to the concentration levels listed in Table II there appears to be no deterioration of samples or standards of mine effluents so long as the specimens are collected and stored according to the procedures described.

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Table I. Chemical Compositions of the Original Standard Mine Drainage (SMD - 1974) and the Most Recent SMD. All concentrations are in mg/l.

Element	SMD - 1974	SMD - 1976
Na	30	46
K	10	16
Mg	300	300
Ca	350	400
Fe	800	800
Mn	300	300
Cu	100	100
Zn	150	160
Cd	1.0	2.0
Pb	0.50	1.0
As	1.0	2.0
Mo	1.0	--
SO <sub>4</sub> <sup>=</sup>	4000	4000
Al	--	260
Co	--	1.0
Ni	--	1.0

Table II. Concentration Levels to Which Dilutions of the 1974 SMD Were Checked for Aging.

Element	Dilution	$\mu\text{g}/\text{l}$
Fe	1000	0.80
Mn	1000	0.30
Ca	100	4.0
Mg	2000	0.15
Na	50	1.0
K	50	0.40
Cu	1000	0.10
Zn	1000	0.16
Cd	10	0.20
Pb	5	0.20

APPENDIX 3Geological Outline of the 5 Mining Districts  
Where Water Samples Were Collected1. Silver Plume District

It is located in the west-central part of Clear Creek County surrounding the town of Silver Plume. Precious metals were first discovered in 1859. The rich surface ores were worked chiefly for gold although most of the veins in depth have since produced more silver than gold.

The most abundant rocks are the Idaho Springs formation and the Silver Plume granite, being quartz-biotite schist, the most abundant and widespread type of schist. The principal metals produced in this district are silver, lead, zinc and gold. The ore deposits are classified in two groups: silver-lead and pyritic gold deposits. The principal metallic sulfides of the lead-silver ores are sphalerite and galena with locally considerable pyrite. The silver minerals found are polybasite, argentiferous galena and tetrahedrite, argentite, pyrargyrite, and proustite. The most abundant gangue mineral in the lead-silver veins is quartz, but there are also considerable amounts of carbonate such as siderite, ankerite, rhodochrosite, magnesite, calcite, and dolomite; sericite, barite, cherty silica and locally kaolinite are also common. The sequence of mineral deposition in the veins is as follows:

1. Quartz and some pyrite
2. Massive galena, sphalerite and pyrite with some quartz
3. Carbonates and quartz
4. Other gangue minerals

The chief minerals in the pyritic gold deposits are pyrite, chalcopyrite, gold, small amounts of silver, and quartz. Galena and sphalerite are generally present in small amounts. The gangue minerals include quartz, brown carbonates, and sericite. The valuable metals in the ores are gold, silver and copper. The Burleigh Tunnel is in the galena-sphalerite ores with some polybasite, tetrahedrite and a little pyrite.

## 2. Central City-Idaho Springs District

This district is historically the most important of the several mining districts that form the mineral belt of Colorado. It is in a terrain of Precambrian crystalline rocks intruded by many small dikes and irregular bodies of porphyritic igneous rocks of early Tertiary age and are cut by abundant faults which contain the ore deposits. The most abundant rocks are schist and granite gneiss. Schist predominates in the Idaho Springs region but includes numerous lenses of granite gneiss and pegmatites. Intrusives of the Laramide revolution are abundant in the mineralized area. The porphyries occur in numerous dikes and

small irregular stocks.

The ores that occur in this district are gold, silver, copper, lead, zinc, and uranium but the most important valuable metals have been gold and silver. The ore deposits are veins and stockworks formed during the Laramide revolution and are genetically related to porphyritic intrusive rocks. The ores are of two main types: one consisting mainly of pyrite, chalcopyrite and quartz and the other of galena, sphalerite, chalcopyrite and subordinate pyrite.

The central zone is formed by the pyritic ores which are predominantly pyrite and gangue with subordinate amounts of chalcopyrite, tennantite, gold, enargite, and other metallic minerals. Gold predominates in value over the other metals. Gold and silver are chiefly associated with chalcopyrite and tennantite. The gangue minerals are quartz, siderite, fluorite and sericite.

The peripheral zone is formed by the galena-sphalerite ores composed of galena, sphalerite, and pyrite with subordinate amounts of chalcopyrite, tennantite, and bornite. The common gangue minerals are quartz, calcite and siderite. The Lucania Tunnel cuts mines that are of this type with little disseminated pyrite.

The intermediate zone is integrated by the composite ores which are those transitional in character between the pyritic and galena-sphalerite ores. The National Tunnel is located in this zone.

### 3. Boulder County Tungsten District

Most of this district lies within the batholith of Boulder Creek granite and a small but very productive part lies within the area of metamorphic rock bordering the batholith on the west. Tertiary dikes of hornblende monzonite porphyry and hornblende diorite porphyry are common in the western part. In the eastern part, dikes of biotite monzonite porphyry and the associated intrusion breccias of biotite latite have been found.

The mineral composition of most of the veins is very simple. Although many minerals have been found, only a few are common. The gangue is microgranular quartz locally known as "horn" and the only ore mineral is ferberite. Sericite and some clay minerals are common throughout the district, barite in small quantity is widely distributed, and in certain veins iron sulfides are sufficiently abundant to lower the grade of the ore. Hematite and magnetite occur with some of the ferberite ore at scattered localities. Pyrite, marcasite, galena, and sphalerite are rare but are locally associated with the ferberite as late minerals. Calcite and ankerite occur as early minerals in some of the veins and andularia is present locally in the veins and wall rocks.

Nearly all the tungsten ore mined contains so little manganese that it is classed as ferberite instead of wolframite. The primary tungsten ore is found in veins, most of

which are vertical or dip steeply. The ore is almost entirely a fissure filling and shows little or no replacement of the country rock. The Clyde Mine is one of the more productive mines of this district.

#### 4. Gold Hill District

It is located northwest of Boulder and is known for its rich gold-telluride ores. It is mostly within the northern part of a batholith of Boulder Creek granite, but schist is present in the western parts of the district. Pegmatite dikes are abundant, and in places there are dikes of gneissic aplite, hornblende diorite, and Silver Plume granite.

The ore deposits are closely related structurally to the early Laramide faults called breccia reefs. Most of the vein fissures strike northeast and dip steeply southeast. They are filled chiefly with gold-telluride ores, but some contain valuable pyritic gold ore and a few contain silver-lead ore.

The principal ore minerals of the tellurides are petzite and sylvanite, and free gold is common in places. Pyrite and chalcopyrite are the characteristic minerals of the pyritic gold veins, being the gold largely associated with the chalcopyrite. In the silver-lead veins, argentiferous gray copper and argentiferous galena are the principal minerals, but sphalerite is common in places.

The Corning tunnel intersects the slide vein which contains high grade telluride ore and very finely disseminated pyrite. It also intersects the Klondike and twin veins which are of low-grade pyritic ore.

#### 5. Jamestown District

It lies in the central part of Boulder County, northwest of Boulder. In 1875 the first telluride ore was discovered and in 1903 the presence of commercial deposits of fluorspar was known. This district is entirely located within the Precambrian complex of the Front Range. The type of rocks are Precambrian metamorphic rocks, Precambrian granites, and intrusives of the Laramide revolution, including a variety of porphyry stocks and dikes.

This mineral district has been primarily producing gold but has also been supplying considerable amounts of fluorspar, lead, silver, and small amounts of copper. The deposits are generally divided in four types based on age and characteristic minerals:

- (1) Lead-silver deposits
- (2) Fluorspar veins and breccia zones
- (3) Pyritic gold veins
- (4) Telluride veins

These four types of deposits are irregularly distributed around the sodic granite porphyry stock in a rough zonal arrangement and appear to be genetically related to that

stock.

The lead-silver deposits include both veins and irregular and pipelike bodies in or bordering fluorspar breccia zones. Abundant argentiferous galena and gray copper and variable amounts of chalcopyrite, sphalerite, and pyrite are mixed with a gangue of glassy to milky quartz and some fluorspar.

The fluorspar deposits consist of breccia zones and veins that form a northwestward trending belt in granite and granodiorite. The veins and breccia zones are filled with purple to deep violet fluorspar, both granular and coarsely crystalline, and contain some quartz, clay minerals, disseminated pyrite, and small amounts of galena, gray copper, sphalerite and chalcopyrite.

The pyritic gold veins fill the later faults fissures consisting chiefly of glassy, milky quartz and coarse-grained pyrite and chalcopyrite. Galena and sphalerite are present in some veins and are locally abundant. The gold occurs free or is closely associated with chalcopyrite.

The Emmett mine is the deepest fluorspar mine in the district. The vein is filled with abundant coarse-grained fluorspar fragments cemented by fine-grained fluorspar, clay minerals, and quartz. Pyrite is disseminated throughout, and small amounts of galena, chalcopyrite, sphalerite, and gray copper are locally present.

APPENDIX 4

The equations and thermodynamic data used in the construction of the Eh-pH diagrams and in the calculation of redox potentials are presented in this section. The thermodynamic data were extracted from Sillen and Martell (1964), Stumm and Morgan (1970), and Rubin (1974).

<u>Equation</u>		<u>-Log. K</u>
(1) H <sub>2</sub> O	----- H <sup>+</sup> + OH <sup>-</sup>	14.00
(2) HSO <sub>4</sub> <sup>-</sup>	----- H <sup>+</sup> + SO <sub>4</sub> <sup>=</sup>	1.96
(3) H <sub>2</sub> S	----- H <sup>+</sup> + HS <sup>-</sup>	7.04
(4) PbS (galena)	----- Pb <sup>++</sup> + S <sup>=</sup>	28.20
(5) PbCO <sub>3</sub> (cerussite)	----- Pb <sup>++</sup> + CO <sub>3</sub> <sup>=</sup>	13.00
(6) PbSO <sub>4</sub> (anglesite)	----- Pb <sup>++</sup> + SO <sub>4</sub> <sup>=</sup>	7.89
(7) Pb(OH) <sub>2</sub> (s)	----- Pb <sup>++</sup> + 2OH <sup>-</sup>	14.93
(8) 2Fe <sup>3+</sup> + 2H <sub>2</sub> O	----- Fe <sub>2</sub> (OH) <sub>2</sub> <sup>4-</sup> + 2H <sup>+</sup>	2.91
(9) Fe <sup>3+</sup> + H <sub>2</sub> O	----- Fe(OH) <sub>2</sub> <sup>2+</sup> + H <sup>+</sup>	3.05
(10) Fe(OH) <sub>2</sub> <sup>2+</sup> + H <sub>2</sub> O	----- Fe(OH) <sub>2</sub> <sup>+</sup> + H <sup>+</sup>	3.26
(11) Fe(OH) <sub>2</sub> <sup>+</sup> + 2H <sub>2</sub> O	----- Fe(OH) <sub>4</sub> <sup>-</sup> + 2H <sup>+</sup>	15.49
(12) Fe <sup>3+</sup> + 3H <sub>2</sub> O	----- Fe(OH) <sub>3</sub> (s) + 3H <sup>+</sup>	3.30
(13) Fe <sup>2+</sup> + H <sub>2</sub> O	----- Fe(OH) <sup>+</sup> + H <sup>+</sup>	8.30
(14) Fe <sup>2+</sup> + 2H <sub>2</sub> O	----- Fe(OH) <sub>2</sub> (s) + 2H <sup>+</sup>	12.90
(15) Fe <sup>3+</sup> + F <sup>-</sup>	----- FeF <sup>2+</sup>	-5.20
(16) Fe <sup>3+</sup> + 2F <sup>-</sup>	----- FeF <sub>2</sub> <sup>+</sup>	-9.13
(17) Fe <sup>3+</sup> + 3F <sup>-</sup>	----- FeF <sub>3</sub>	-11.97

(18)	HF	-----	$H^+ + F^-$	2.94
(19)	$Fe^{3+} + SO_4^{=}$	-----	$FeSO_4^+$	-4.16
(20)	$FeSO_4^+ + 3H_2O$	-----	$Fe(OH)_3(s) + SO_4^{=} +$ $3H^+$	7.46
(21)	$FeSO_4^+ + 2H_2O$	-----	$Fe(OH)_2^+ + SO_4^{=} +$ $2H^+$	10.47

<u>Equation</u>	<u>E° (volts)</u>
(1) $O_2 + 4H^+ + 4e^-$ ---- $2H_2O$	1.23
(2) $2H^+ + 2e^-$ ---- $H_2$	.00
(3) $Fe^{3+} + e^-$ ---- $Fe^{2+}$	.77
(4) $HSO_4^- + 9H^+ + 8e^-$ ---- $H_2S + 4H_2O$	.25
(5) $SO_4^{2-} + 10H^+ + 8e^-$ ---- $H_2S + 4H_2O$	.26
(6) $SO_4^{2-} + 9H^+ + 8e^-$ ---- $HS^- + 4H_2O$	.21
(7) $FeSO_4^+ + e^-$ ---- $Fe^{++} + SO_4^{2-}$	.53
(8) $Fe(OH)_3(s) + e^- + eH^+$ ---- $Fe^{++} + 3H_2O$	.97
(9) $Fe(OH)_3(s) + e^- + H^+$ ---- $Fe(OH)_2(s) + H_2O$	.20
(10) $Fe(OH)_3(s) + e^- + 2H^+$ ---- $Fe(OH)^+ + 2H_2O$	.48
(11) $Fe_2(OH)_2^{4+} + 2H^+ + 2e^-$ ---- $2Fe^{++} + 2H_2O$	.86
(12) $Fe(OH)_2^+ + 2H^+ + e^-$ ---- $Fe^{++} + 2H_2O$	1.14
(13) $Fe(OH)_4^- + 4H^+ + e^-$ ---- $Fe^{++} + 4H_2O$	2.06
(14) $Fe(OH)_4^- + 3H^+ + e^-$ ---- $Fe(OH)_2^+ + 3H_2O$	1.57
(15) $PbSO_4(s) + 8H^+ + 8e^-$ ---- $PbS(s) + 4H_2O$	.25
(16) $PbCO_3(s) + SO_4^{2-} + 9H^+ + 8e^-$ ---- $PbS(s) + 4H_2O +$ $HCO_3^-$	.29
(17) $Pb(OH)_2(s) + SO_4^{2-} + 10H^+ + 8e^-$ ---- $Pb(s) + 6H_2O$	.41

Mass Balance of Fe

$$[\text{Fe(TOTAL)}] = [\text{Fe(II)}] + [\text{Fe(III)}]$$

$$[\text{Fe(III)}] = [\text{Fe}^{3+}] + [\text{FeSO}_4^+] + [\text{FeF}^{2+}] + [\text{Fe(OH)}^{2+}] + \\ 2[\text{Fe}_2(\text{OH})_2^{4+}] + [\text{Fe(OH)}_2^+]$$

$$[\text{Fe(II)}] = [\text{Fe}^{2+}] + [\text{Fe(OH)}^+]$$

NERST EQUATION:  $E_h = E^\circ + \frac{.0591}{n} \log \frac{(\text{ox.})}{(\text{Red.})}$

Other equations used were the following:

$$1. \quad I = \frac{1}{2} \sum m_i Z_i^2$$

$$2. \quad \log f_i = - \frac{AZ_i^2 I^{\frac{1}{2}}}{1 + a_i^{\circ} B I^{\frac{1}{2}}} + B^{\circ} I$$

$$3. \quad a_i = f_i m_i$$

where I = ionic strength

$m_i$  = molar concentration of specie i

$Z_i$  = charge for ionic specie i

$a_i$  = activity of specie i

$f_i$  = activity coefficient of specie i

$a_i^{\circ}$  = aqueous ion size of specie i

A, B, and  $B^{\circ}$  are constants and at  $25^{\circ}\text{C}$  for aqueous solutions have the following values:

$$A = .501$$

$$B = .328$$

$$B^{\circ} = .041$$

Ion Sizes, Activity Coefficients, and Ionic Strength Are  
Tabulated

Ionic Species	Ion Size	Argo Tunnel I = .10	National Tunnel I = .04	Emmett Mine I = .15
$\text{Fe}^{3+}$	9	.18	.27	.15
$\text{Fe}_2(\text{OH})_2^{4+}$	10	.06	.11	.04
$\text{Fe}(\text{OH})^{2+}$	5	.38	.50	.34
$\text{Fe}(\text{OH})_2^+$	5	.79	.85	.76
$\text{FeF}^{2+}$	5	.38	.50	.34
$\text{Fe}^{2+}$	6	.41	.52	.37
$\text{SO}_4^{=}$	4	.36	.48	.31
$\text{F}^-$	4	.78	.83	.75
$\text{Ca}^{++}$	6	.41	.52	.37
$\text{FeSO}_4^+$	5	.79	.85	.76