Field Investigation of Mine Waters in the Northern Anthracite Field Pennsylvania

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MINING HYDROLOGY

UNITED STATES DEPARTMENT OF THE INTERIOR

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CONTENTS

ILLUSTRATIONS

TABLES

FIELD INVESTIGATION OF MINE WATERS IN THE NORTHERN ANTHRACITE FIELD, PENNSYLVANIA

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ABSTRACT

Results of a chemical study of anthracite coal mine waters under field conditions show conclusively that the mine-water compositions are controlled by mineral-water reactions. Oxygen-free (strongly reduced) samples were obtained from as little as 60 feet below the water surface in open shafts. The results of the field study may be rigorously interpreted in terms of the postulated reactions and the information available on the mineralogy of the coal measures. Dissolved-iron concentrations and redox potentials observed at different levels in three mine shafts agreed with the principles in a published theoretical discussion.
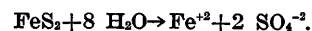
INTRODUCTION

In an earlier report (Barnes and Clarke, 1964) the compositions of coal-mine waters were considered using data from published sources. From the total iron concentrations reported and the pH data cited, there was little likelihood of the occurrence of detectable dissolved oxygen in most coal-mine waters until such water discharged onto the land surface.

The predicted absence of dissolved oxygen cast some doubt on the effectiveness of reactions involving dissolved oxygen in producing the solutions found in mines. Reactions involving oxygen, however, are commonly accepted in the literature (Hanna and others, 1963, is a recent example) as the cause of acid-bearing water. A frequently cited reaction is

$$2\ FeS_2 + 7\ O_2 + 2\ H_2O = 2\ FeSO_4 + 2\ H_2SO_4.$$
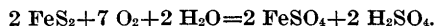
Barnes and Clarke suggested that dissolved oxygen (or air) be discarded as a major reactant in mine waters and that reactions involving only water and minerals be considered as controls of subsurface mine-water quality. The effects of subsequent oxygenation were outlined, but, as was pointed out, the oxygenation effects are superposed on the initial water-mineral reactions. Mine waters are commonly observed to contain appreciable iron and sulfate in solution, and this observation leads to the commonly accepted and quite plausible conclusion that iron-sulfur compounds or minerals are responsible for the composition of mine waters. The most commonly observed iron-sulfur minerals in the coal measures are pyrite and marcasite, both having the composition FeS_2 but differing in crystal structure. From the theoretical study based upon available chemical analyses, it was concluded that pyrite and water must be the reactants (oxygen being ruled out) and that iron and sulfate must be among the dissolved products. The theoretical study also showed that the iron in solution must be divalent (ferrous ion), leading to the partial reaction based on observation

$$FeS_2 + 8\ H_2O \rightarrow Fe^{+2} + 2\ SO_4^{-2}.$$

Recapitulating the reasoning, the iron in mine water must come from iron-sulfur minerals, which are also the major supply of the sulfate. Production of sulfate from sulfide or disulfide minerals requires oxygen, but there cannot be enough dissolved oxygen as a reactant, and the only other sources of oxygen are water and silicates. The silicates are not deoxygenated, so the major supply of oxygen must be the water itself. The reduction of water to supply the oxygen raises a further problem. The complete reaction suggested by Barnes and Clarke was

$$FeS_2 + 8\ H_2O = Fe^{+2} + 2\ SO_4^{-2} + 2\ H^{+1} + 7\ H_2,$$
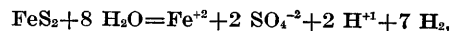
and the problem raised was the fate of the hydrogen. It was suggested that in addition to dissolved hydrogen some of the hydrogen could be used in hydrogenation of nonaromatic fractions of the coal. Some of the hydrogen might also dissolve in the coal. A less likely reaction between the coal and hydrogen might produce methane. Many other organic products containing and not containing sulfur may be postulated. In the absence of detailed analyses of gases dissolved in mine water, no test may be made of the postulates.

A purely inorganic consumption of hydrogen was suggested by Henry G. Jacobson of the U.S. Bureau of Mines in a personal communication. The suggested reaction was the reduction of ferric minerals such as hematite by the hydrogen produced by the reaction of pyrite and water. The reduction of hematite may be written

$$Fe_2O_3 + H_2 + 4\ H^{+1} = 2\ Fe^{+2} + 3\ H_2O.$$
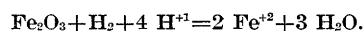
FIELD METHODS

A field study of mine waters was undertaken to test the earlier theoretical conclusions. The techniques developed by Back and Barnes (1961) were adapted to the problem of sampling water from shafts of flooded mines. As was mentioned by Barnes and Clarke (1964), reliable dissolved oxygen and redox measurements are mutually exclusive. The theoretical study showed oxygen to be essentially absent; and hence the theory was cast in terms of redox potential (Eh), pH, and compositional variables.

The problems found in the investigation of mine-water compositions were anticipated from the earlier work of Barnes and Back (1963). Essentially, the sampling was done by pumping from a predetermined level to the land surface, care being taken to avoid the ingress of air or any other contaminant into the sample. To accomplish this, a submersible plastic-coated pump was lowered into the water in the mine shafts. The water was pumped to the land surface through 1½-inch plastic pipe (high-pressure polethylene) which had nylon insert couplings. The only metals in contact with the water in the pumping system were bronze pump impellers, a brass gate valve for throttling the flow on the land surface, 6 inches of copper tubing, and the brass top of the sampling chamber. The metals in contact with the water are all nonferrous and, considering the brief contact time, could not produce an appreciable effect on the water composition. No check valve was used on the pump. The maximum residence time for water in the pumping system from the deepest sampling level was less than 6 minutes, and nearly all that time the water was in contact with the inert plastic pipe and fittings.

In the South Wilkes-Barre mine, an operating 4,000-gpm turbine pump was used for sampling. The residence time of the water in the turbine pump column was less than 1 minute, which was an insufficient time for appreciable water composition changes.

Where the submersible pump was used, it was set in the shaft at elevations corresponding to the elevations of openings from the shaft into the mine workings where possible. The pump used was operated continuously until sampling was complete. Each level was sampled as the pump was lowered to minimize contamination. The water in the South Wilkes-Barre shaft was sampled at the fixed level of the pump intake.

The water pumped from the mines was sampled for Eh using the techniques of Back and Barnes (1961) using a saturated calomel reference electrode (SCE) and a platinum thimble electrode. The operation of the electrodes was tested frequently using the solution described by ZoBell, as reported in Garrels (1960, p. 68). The observed Eh of the ZoBell solution deviated by no more than 0.012 volt from the known value; so the Eh data should be regarded as reliable within 0.012 volt.

Sampling for Eh was assumed complete when there was no detectable change in the measured electromotive force (Eh+E_{SCE}) over a 10-minute period. The meter used for Eh measurement was a Beckman model G, which yields readings reproducible to ±2 millivolt.

The meter used for pH was a Beckman model N, which has been shown accurate to ±0.02 pH under field conditions (Barnes, 1964). The pH was measured by the two-buffer technique described by Barnes to correct for departures from ideal behavior of the pH measurement system. Analyses in the field for ferrous iron concentrations were made by the permanganate method (Furman, 1962, p. 544–546), not using the Jones reductor. The permanganate method results are preferred for the high concentrations observed. Laboratory sulfate analyses were by the spectrophotometric titration method (Rainwater and Thatcher, 1960, p. 281–282). The manganese determinations were the same as described by Rainwater and Thatcher (p. 205–207) except that the excess hydrochloric acid was removed by evaporating the samples almost dry after adding nitric acid. Aluminum determinations were made by the method described by Rainwater and Thatcher (p. 97–99) after a preliminary separation as given by Furman (p. 78). The separation of magnesium and calcium was effected by the precipitation of iron, aluminum, and manganese by ammonium hydroxide at a pH of 7.5–8.0. Total hardness and calcium were determined in the filtrates by the methods of Rainwater and Thatcher (p. 174–176, 127–129), except that the pH adjustment in each sample was measured by a pH meter rather than by adding a standard volume of base to all samples. Magnesium was calculated as the difference between total hardness and the calcium concentration. Silica was determined following the procedure of Rainwater and Thatcher (p. 259–261). For sodium and potassium, samples were evaporated and the soluble material was dissolved in hot water, filtered and then analyzed on a flame photometer. For chloride determi-

nations, the samples were neutralized by adding sodium hydroxide and boiled to remove iron and aluminum. The chloride concentration in the filtrate was determined following the method described by Rainwater and Thatcher (1960, p. 141–143).

The location of the mine shafts sampled is given on the index map, figure 1. The approximate stratigraphic sections are given in figure 2, which has been compiled from mine company records and by projection from other sections. Although the location of the coal is well known, the relative proportion of clastic materials is approximate. Descriptions of the detailed mineralogy

of the coal beds would not materially improve the interpretation of the water composition obtained because the detailed flow path to any sampling point is not known, even though the regional hydrology is known in general. Interconnections exist between beds as a result of mining practices. There has been collapse or failure of the rock strata by subsidence since active mining began in most of the basin, but the channels and pathways for water movement opened by such failure are not known. The lack of detailed knowledge about flow paths in no way invalidates the theoretical geochemical considerations. Iron disulfides (FeS_2) are known to be ubiquitous in the northern anthracite field, as are coal and water; hence the chief reactants are present. Subsequent side reactions which would further modify mine-water compositions are probable but speculative. The nature of some of the inorganic side reactions has been discussed briefly by Barnes and Clarke (1964).

RESULTS

The results of the field investigation and analyses of the water from Loree No. 2 shaft are summarized briefly in table 1, which gives the Eh, pH, compositions, and field description of the water as it emerged from the plastic pipe in the field.

The water in the shaft is not homogeneous; there are three chemically distinct layers of water in the mine. Stuart and Simpson's data (1961) also indicate compositional variation of coal-mine waters according to depth. The solution constituting the upper layer of water having Eh values in the range +0.31 volt to +0.32 volt is more reduced (less oxidized) than the intermediate layer (Eh +0.53 volt to +0.56 volt). The water body which is intermediate in depth is the most oxidized solu-
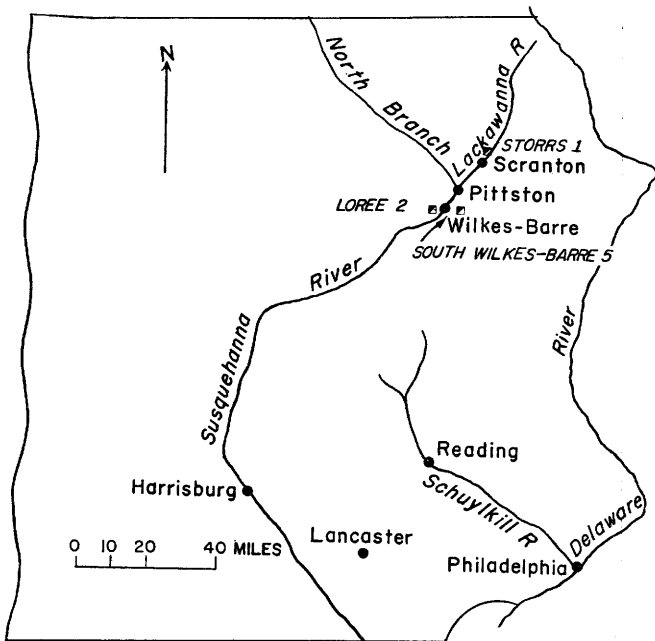

FIGURE 1.—Map showing location of mine shafts from which mine waters were sampled.

TABLE 1.—*Analyses of water from Loree No. 2 shaft*

[Concentrations in parts per million; water level 162 feet below land surface]

| Depth below land surface (feet)	T (°C)	Eh(v)	pH	Color	Gas	Odor	Fe+2	SO4−2	Mn+2	Al+3	Ca+2	Mg+2	SiO2	Na+1	K+1	Cl−1
224	14	+0. 322	3. 41	Clear_____	Slightly effervescent.	None_____	34	1, 260	12	7	180	148	14	_____	_____	____
233	14	+. 312	3. 40	___do_____	___do_____	_____do_____	34	1, 260	13	9	172	152	15	_____	_____	____
292	17	+. 533	3. 55	Yellow turbidity.	Very effervescent.	_____do_____	478	3, 320	37	79	342	292	30	<25	<10	____
438	17	+. 533	3. 51	___do_____	___do_____	_____do_____	488	3, 400	39	83	343	299	31	<25	<10	____
467	17	+. 568	3. 36	Slight yellow turbidity.	No gas evolved.	_____do_____	488	3, 650	44	86	363	326	33	<25	<10	____
579	17. 5	+. 562	3. 40	___do_____	Effervescent.	_____do_____	546	3, 960	44	99	378	354	37	_____	_____	____
751	17	−. 025	4. 00	Clear_____	No gas evolved.	Pronounced "rotten egg" smell.	1, 073	5, 800	90	135	439	452	60	_____	_____	____
808	17	−. 103	3. 92	___do_____	Effervescent.	_____do_____	1, 463	6, 720	92	143	456	462	85	35	<10	11
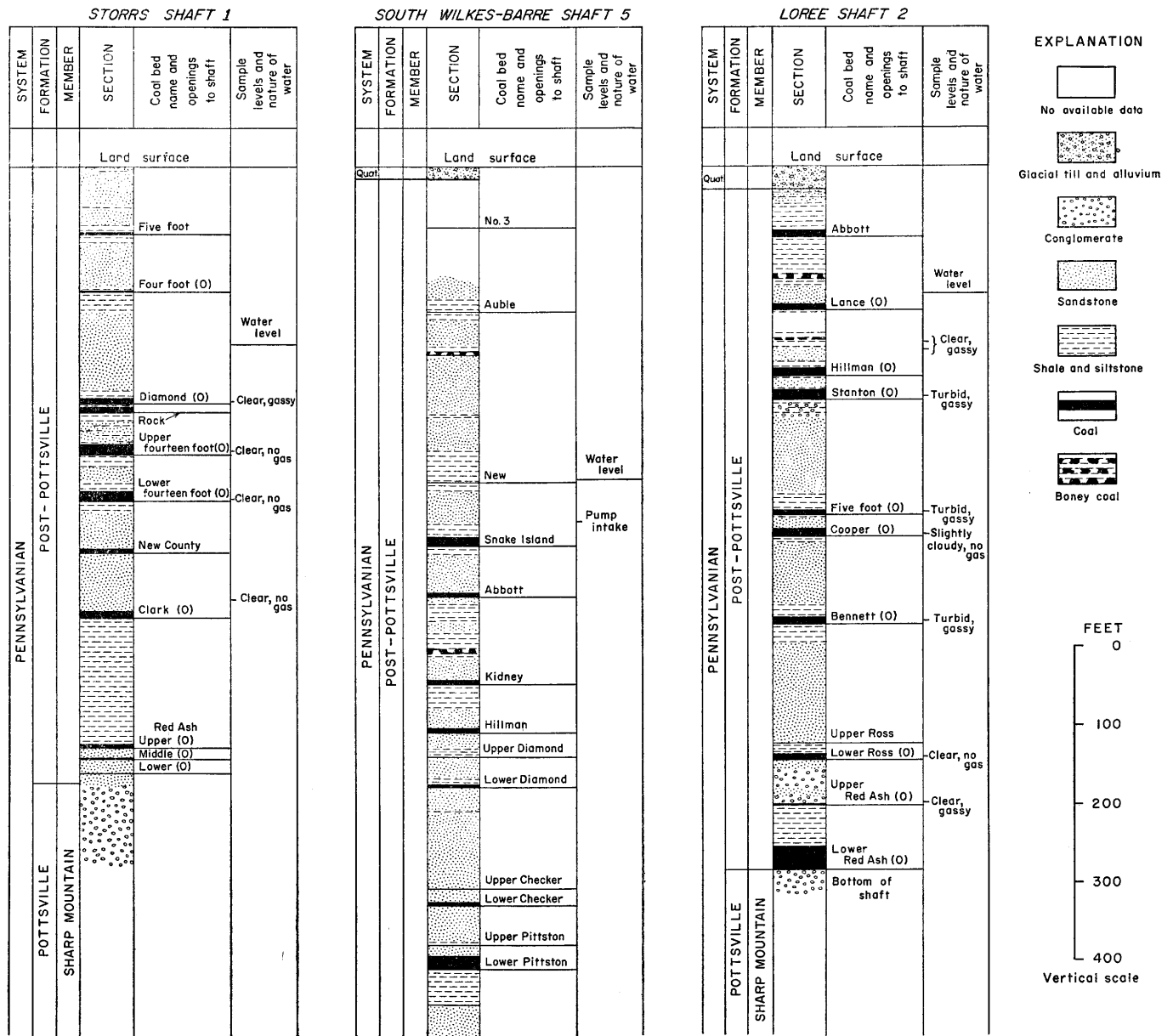
FIGURE 2.—Sections at shafts showing generalized stratigraphy.

tion found in the mine. The deepest part of the pool sampled is also the most reduced. The properties of the water observed in the field may be interpreted in terms of the theoretical study by Barnes and Clarke (1964). The uppermost layer of water should not be saturated with Fe(OH)$_3$ and should be perfectly clear as it emerges from the plastic pipe. If any Fe(OH)$_3$ is in contact with the water in the upper part of the shaft, it should be dissolving. The water is also unsaturated with pyrite, which if present should also be dissolving. The water at intermediate depths is in the range predicted by Barnes and Clarke for saturation with Fe(OH)$_3$ in terms of pH, Eh, and Fe^{+2} and indeed is actually precipitating Fe(OH)$_3$ (locally known as

"yellow boy") as is indicated by the turbidity of the samples observed. The electrochemical model has the virtue of being consistent with the observations. The reactions

$$Fe^{+2} = Fe^{+3} + e^-$$

and

$$Fe^{+3} + 3H_2O = Fe(OH)_3 + 3H^{+1}$$
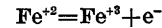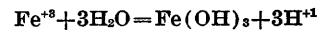
apparently do poise the Eh as was suggested by the calculation of maximum Eh values based on the reactions.

The very low Eh values for the deep waters in Loree No. 2 shaft indicate that the model of Barnes and Clarke (1964) was quite conservative. Eh data from below the Fe(OH)$_3$-pyrite boundary (and also below the pyrite-Fe$_2$O$_3$ boundary) indicate that there are

species present which are even more reduced than pyrite. The nature of the more reduced species is problematical in the absence of more detailed geochemical studies of the coal, but possibly the coal itself is the more reduced reactant.

The samples from the Loree No. 2 shaft have a narrow range of pH values in spite of the wide range in values for Eh and composition. The probability of side reactions between mine water and silicates and carbonates has been mentioned earlier (Barnes and Clark, 1964), and the pH buffering effect of such reactions has been noted. It would be unlikely that the pH data from Loree No. 2 shaft would fall between 3.4 and 3.9 if no buffer reactions took place considering the high yield of hydrogen ions from the solution of pyrite. The aluminum in solution is probably from the seat clays (underlying shale) dissolving in the acid solution.

Samples of the gas which evolved from the water pumped from a depth of 292 feet from the Loree No. 2 shaft were obtained. The gas neither burned nor supported combustion in a simple field test, but more detailed information on the composition of the gas is lacking. The gas may be nitrogen, especially if entrapped air is dissolved as the water level rises. Entrapped air might also be invoked to explain the turbidity of the water from the intermediate levels in the mine, and if so, then the pertinent reactions considered by Barnes and Clarke (1964) may be summarized as

$$4Fe^{+2} + O_2 + 10H_2O = 4Fe(OH)_3 + 8H^{+1}.$$
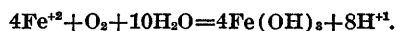
The low pH values in water near the mine-water surface and in the gas-charged water at intermediate depths relative to the higher pH values in the deepest two samples are not in conflict with a possible depletion of iron content by oxidation to $Fe(OH)_3$. The precipitation of iron from the water at the shallowest depths, if precipitation ever took place by oxidation, has now ceased. Possibly any oxygen present in this water was exhausted as the mine first flooded, and ultimately reducing conditions were established from water-mineral reactions. The existence of pH buffering reactions is indicated, because the oxidation and precipitation of the iron should produce large amounts of hydrogen ions. The low concentrations observed probably result from the hydrolysis of the silicates and seat clays present.

The noxious odor of the gases evolved from the water pumped from the deepest sampling levels presumably indicates the presence of sulfur compounds. More elaborate analyses than were possible in the field would be necessary to determine the exact nature of the volatile components. The occurrence of H_2S is possible, but in part the sulfur may also be found to be organically combined. Further work on the detailed composition of the gases dissolved in mine water may well elucidate what reactions might be of significance in addition to those studied. The entirely inorganic reactions which were quantitatively studied would not produce such low Eh solutions as were found deep in Loree No. 2. A semiquantitative analysis for reduced nitrogen compounds in the water gave negative results. Certainly either H_2S or organic gas components should show that the dissolved or gaseous oxygen postulated by earlier workers cannot be a factor in producing compositions such as those obtained from the deep waters sampled. Although the samples of water from the greatest depths in Loree No. 2 also have the lowest Eh and the highest iron and sulfate concentrations, to assume any depth control on water compositions might lead to error. Before any definite conclusion could be reached, it would have to be shown that the compositional differences could not be explained on the basis of different mineral assemblages or coal compositions. Perhaps much more fieldwork could show empirically that a depth-composition relation exists, but no firm theoretical basis for such a prediction has been obtained.

There is a concomitant rise in manganese concentrations with the rise in iron concentrations. The source of the manganese is not known. The ratio of Fe:Mn varies from 3:1 to about 10:1 in Loree No. 2. If the manganese could be recovered, it might augment the meager domestic reserves of manganese.

A series of samples was withdrawn from the Storrs No. 1 shaft, and the results of analyses of these samples obtained are given in table 2.

The results of the field investigation show that there are two different water masses in the Storrs No. 1 shaft. The excellent agreement of Eh, pH, Fe^{+2}, and SO_4^{-2} in the upper body indicate the reproducibility of the analytical methods. The pH values obtained from the shallow water body in the Storrs No. 1 shaft were the highest observed from pumped samples. The nature of the mineral buffers in the pH at such high levels is not known. Carbonate minerals cannot be ruled out without further study, again emphasizing the need for more detailed work than has been reported in the past.

Much of the discussion of the gases in Loree No. 2 shaft applies to the gases evolved from the shallow samples obtained from Storrs No. 1. If carbonate minerals do participate in buffering high pH mine water as compared to the pH values obtained in the other two shafts, appreciable quantities of CO_2 may be evolved; there may be a subsequent escape of the CO_2 as a component in a gas phase as the confining pressure on the water decreases.

The lower water body, as represented by the sample from a depth of 550 feet, was strikingly different from the upper water body, the lower having about twice as high a dissolved-solids concentration and having a lower pH and a higher Eh. Probably the differences could be explained in terms of different prior histories of the two water masses; however, as has been noted earlier, a detailed discussion of differences in flow paths and environmental histories of the water bodies would be entirely speculative.

In spite of the compositional differences, all samples drawn from Storrs No. 1 shaft are saturated with both pyrite and $Fe(OH)_3$ or a less hydrous ferric oxide. The mineral pair $Fe(OH)_3$-pyrite should poise the Eh of a coexisting aqueous solution, and hence it would not be surprising to find a preponderance of observational data along the pyrite-$Fe(OH)_3$ boundary. The iron-manganese ratio is again about 10:1.

The properties of the water pumped from the South Wilkes-Barre No. 5 shaft are summarized in table 3.

The water sampled from the South Wilkes-Barre mine is among the three most reduced solutions and yet it was withdrawn only 64 feet below the water surface. The Eh is well below the $Fe(OH)_3$-pyrite boundary, again showing that more reduced materials than pyrite are reacting.

SUMMARY AND CONCLUSIONS

The electrochemical data are summarized in figure 3. Points 2 and 3 on the diagram represent samples that were turbid, and they lie in the area predicted for waters saturated with $Fe(OH)_3$, which apparently is ac-tually precipitating. The samples are the most oxidized found, and they show that the predicted upper limit of Eh is reliable. The reaction producing the turbidity from air trapped during mine flooding may be regarded as

$$4\ Fe^{+2}+O_2+10\ H_2O=4\ Fe(OH)_3+8\ H^{+1}.$$
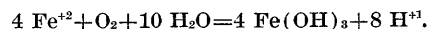
From the field data the reaction poises the Eh along the band predicted until the Fe^{+2} or the O_2 is exhausted. The fact that the pH remains in the range 3.4 to 4.0 in the Loree shaft in spite of the wide variation in iron concentrations and in spite of the large production of H^{+1} from the oxidation and precipitation of iron bears out the earlier suggestion that side reactions with clay minerals should buffer the pH. Indeed, the source of the Al^{+3} reported in the analyses could only be the clays present. Carbonates, if present, would be expected to buffer the pH at higher levels (pH 5–8).

Points 6 and 7 on figure 3 are data from Storrs No. 1 shaft. All four samples represented are in simultaneous equilibrium with iron oxyhydroxides and pyrite, and their properties are as predicted from the theoretical work. These samples have Eh values near the minimum to be expected in systems poised by pyrite and ferric hydroxide. A less stable sulfide (marcasite) or a more stable oxide (hematite) would have only a slight effect on the oxide (or hydroxide)–sulfide boundary and would have only a slight effect on predicted Eh values even if large changes in the composition of the mine water are considered. The high pH (5.5) of the shallower water at Storrs probably indicates at least a partly effective buffering of pH by carbonate minerals.

TABLE 2.—*Analyses of water from Storrs No. 1 shaft*

[Concentrations in parts per million; water level, 227 feet below land surface]

Depth below land surface (feet)	T (° C)	Eh(v)	pH	Color	Gas	Odor	Fe^{+2}	SO$_4^{-2}$	Mn^{+2}	Al^{+3}	Ca^{+2}	Mg^{+2}	SiO$_2$	Na^{+1}	K^{+1}	Cl^{-1}
300	16	−0.030	5.41	Clear	Very efferves-cent.	Noxious_____	107	1,340	11	0	247	145	16	_____	_____	____
363	16	−.028	5.41	___do___	Not efferves-cent.	Slightly noxious.	107	1,330	12	0	250	142	16	_____	_____	____
423	15.5	−.038	5.38	___do___	_____do_____	_____do_____	107	1,350	12	0	237	151	16	_____	_____	____
550	16	+.078	3.95	___do___	_____do_____	None_____	249	2,090	20	24	301	193	25	<25	<10	____

TABLE 3.—*Analyses of water from South Wilkes-Barre No. 5 shaft*

[Concentration in parts per million; water level, 398 feet below land surface]

Depth below land surface (feet)	T°C	Eh(v)	pH	Color	Gas	Odor	Fe^{+2}	SO$_4^{-2}$	Mn^{+2}	Al^{+3}	Ca^{+2}	Mg^{+2}	SiO$_2$	Na^{+1}	K^{+1}	Cl^{-1}
452	19	−0.012	4.20	Clear	No gas evolved_____	None____	839	4,530	38	20	386	278	49	305	____	10

The possibility of such buffering was anticipated in the earlier examination of the controls on mine-water compositions (Barnes and Clarke, 1964).

The low Eh values represented by points 4, 5, and 8 in figure 3 would seem to require equilibria different from those so far mentioned. The mineral species that could be involved might include components of the coal, or other material left in the mine.

Successful predictions were made of the properties of the water in the mines studied based on the reactions of the natural materials present. There is little doubt about the validity of the earlier proposed theoretical model. Because equilibrium conditions are frequently obtained, the compositions of mine waters will follow the model until deletion of the reactants considered, and hence mine drainage pollution will continue for an extended period of time.
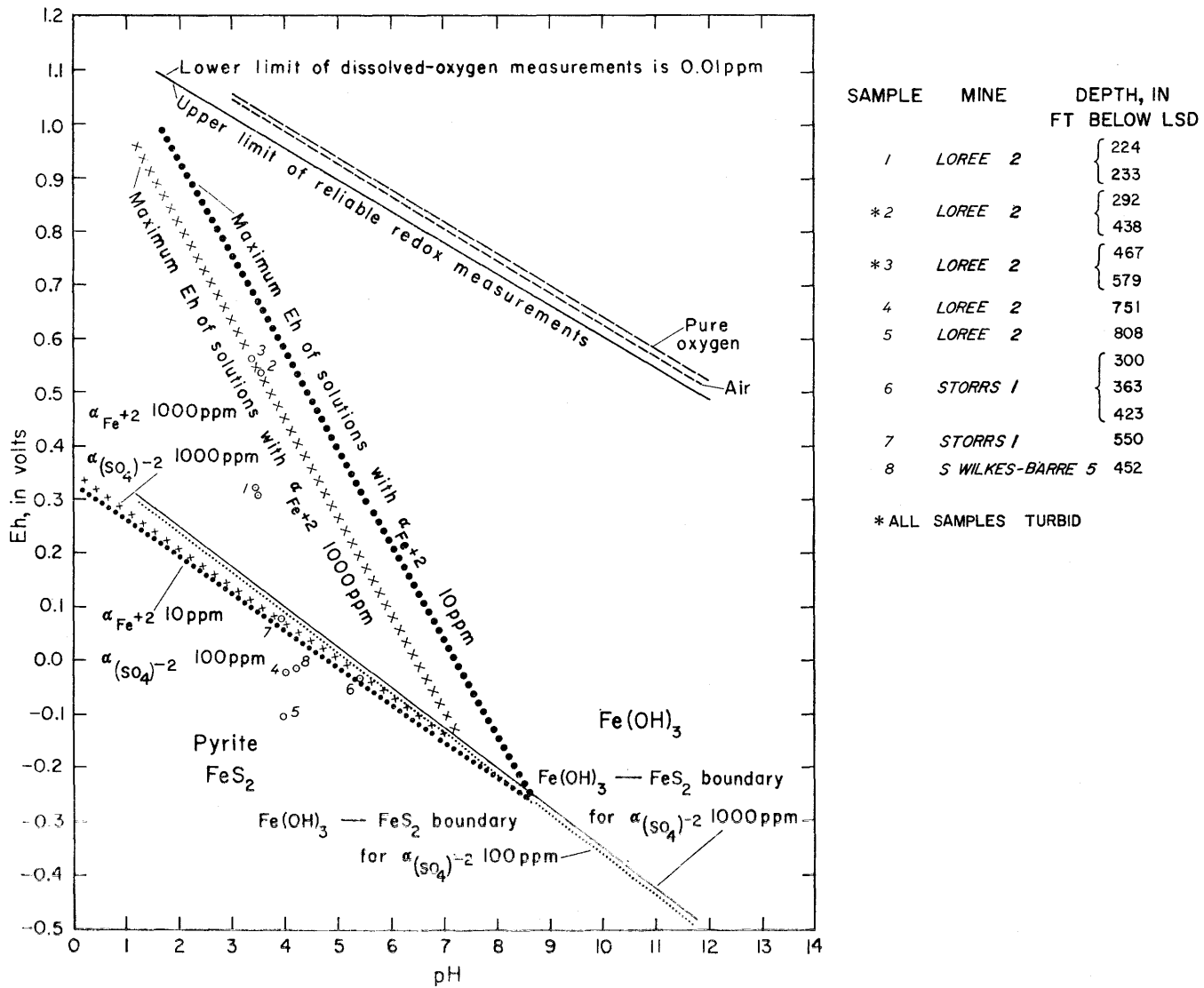

SAMPLE	MINE	DEPTH, IN FT BELOW LSD	
1	LOREE 2	224	233
*2	LOREE 2	292	438
*3	LOREE 2	467	579
4	LOREE 2	751	
5	LOREE 2	808	
6	STORRS 1	300	363 / 423
7	STORRS 1	550	
8	S WILKES-BARRE 5	452	

*ALL SAMPLES TURBID

FIGURE 3.—Eh and pH data plotted on diagram from earlier theoretical considerations.

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