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A COMPARISON OF THE ACIDITY OF WATERS FROM SOME ACTIVE AND ABANDONED COAL MINES [1]

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INTRODUCTION

In the course of another investigation[4] during 1926 and 1927, samples of water collected from a few abandoned coal mines indicated that their drainage was usually lower in acidity than water from active mines in the same locality. In order to determine whether this condition might have a bearing on the advisability of sealing abandoned mines, a number of such mines were visited, samples of drainage were collected, and as much information as possible was obtained from officials of the mining companies and older residents of the district. The results of this work are the basis of the present report.

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COAL BEDS OF THE DISTRICT

The Lower Kittanning is the most important bed in the locality studied. A great many of the abandoned mines examined are in this bed, and nearly all of the present active ones are. The Upper Freeport bed is also mined to some extent, and a number of the abandoned mines formerly worked this bed. As only three active mines are now (1927) working the Upper Freeport, the comparison of acidities is necessarily limited. Of these three, one had been idle since 1922 until shortly before it was sampled.

1 - The Bureau of Mines will welcome reprinting of this article but requests that the following footnote acknowledgment be used: "Printed by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)"
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4 - R. D. Leitch, unpublished report.

METHODS OF COLLECTION AND TESTING OF SAMPLES

The location of most of the mines was already known from previous work, but some of them had to be located by following up streams known to contain acid waters. A sample of the outflow was collected in self-sealing bottles known as "citrate bottles" for the determination of dissolved oxygen by the Winkler method.[5] Another sample was taken for the determination of acidity according to standard methods of water analysis.[6] Ferrous iron was determined at the mine or very soon after taking the sample by titrating with a standard solution of potassium permanganate in acid solution. The hydrogen-ion value was determined by a standard double-wedge comparator.[7]

From the total acidity values in each sample, which are the most important values, the total iron was calculated on the assumption that acidity as sulphuric acid was due to dissolved ferrous sulphate. This assumption is commonly made for mine waters, but is inaccurate to the extent that free acid is already present, and some of the iron is present as ferric, rather than ferrous, sulphate. The amount of ferrous sulphate may be a rough measure of the extent to which oxygen is lacking within the mine. The permanganate titrations just mentioned showed what part of this total iron was in combination as ferrous sulphate, and the difference was assumed to be that in combination as ferric sulphate, after correcting for the amount of free acid already formed as shown by the titration values.

DISCUSSION OF RESULTS

Upper Freeport Bed

Mines 1 to 7, inclusive, Table 1, are abandoned workings in the Upper Freeport bed. The total acidity of the samples gathered from these workings, determined at boiling temperatures with phenolphthalein as an indicator, varied from 37 to 260 parts per million; with methyl orange as an indicator, it varied from 17 to 139 parts per million of free mineral acid. Three of the seven mines, Nos. 3, 4, and 5, showed alkaline water similar to natural springs. These were slightly alkaline in reaction to phenolphthalein at boiling temperatures, and were 20 to 25 parts per million alkaline when examining for free acids with methyl orange.

The dissolved oxygen values varied between 64 and 88 per cent, except for two exceeding 100 per cent. Column 10 of Tables 1 and 2 gives the percentage of oxygen saturation of the water which may indicate whether normal air is present inside the mine. Mines 4 and 5, Table 1, show percentages of 110.4 and 108.2, respectively, and similar results have previously been obtained by the writers in small rapid streams. The present results are based on the amount

5 - Scott, W. W., Standard Methods of Chemical Analysis, 2nd ed., revised, New York, 1917, p. 556.

6 - American Public Health Association, Standard Methods of Water Analysis, 4th ed., 1920.

7 - This value is a measure of the free acid (H) ions, and therefore one of the main values determining acidity characteristics.

TABLE 1.- Analyses of water from mines in the Upper Freeport bed

1	2	3	4	5	6	7	8	9	10	11
			Acidity, parts per million							
Mine	Year opened	Year abandoned	Total	Free [1]	pH[2]	Total iron, mg./c.c.	$FeSO_4$, mg./c.c.	$Fe_2(SO_4)_3$, mg./c.c.	Oxygen percentage of saturation	Remarks
1	1912	1923	37	15A	5.8	0.040	0.006	0.121	88.3	Opening caved.
2	1917	1922	260	139	<3.2	.139	.066	.411	64.0	Do.
3	1904	1916	A	20A	6.0	.000	.000	.000	84.0	Do.
4	1898	1906	A	20A	6.2	.000	.000	.000	110.4	Do.
5	1916	1923	A	25A	6.4	.000	.000	.000	108.2	Do.
6	1898	1920	145	68	<3.2	.149	.049	.468	74.3	Partly caved.
7	1916	1923	43	17	<3.2	.029	.068	.014	88.3	Do.
8	1907	Active	537	147	<3.2	.446	.044	1.535	Lost	Idle since 1922 until 1927. Open.
9	1917	Do.	580	151	<3.2	.491	--	--	94.7	Open.
10	1917	Do.	394	55	<3.2	.388	--	--	97.6	Do.

1 A = alkalinity.
2 < = is less than

of oxygen held by water at the temperature at which the samples were collected, rather than that at which they were analyzed. The breaking of a thermometer prevented the obtaining of these two temperatures at the time, and as others were uniformly about 57 or 58° F., a temperature of 58° was assumed in the calculations. This, however, may have been too high, and a temperature of 50°F. instead of 58° F. for the water would have shown practically 100 per cent saturation. From the fact that the samples from mines 3, 4, and 5 have no iron salts in solution and also have such relatively high percentages of oxygen saturation, they appear to be surface waters entering the mine near the original opening rather than true mine waters. Since rapidly flowing water can have an oxygen supersaturation and the character of these streams can not be determined exactly, mines 4 and 5 may be such as to produce supersaturated waters.

Mine 8 had been idle five years until opened about one month before the sample was taken. The operator said that the water first coming from the mine when it was reopened was much higher in acidity than under normal operating conditions, and this old drainage was not entirely out of the mine at the time the writers were there. If this is true, the average of the three active mines, Nos. 8, 9, and 10, in Table 1 may be somewhat higher than it should be. Samples in the last two mines in Table 1 were taken during the course of other work and no figures are shown for ferrous and ferric iron, but the total iron has been calculated from the acidity as in the other cases.

To sum up, therefore, seven abandoned mines in the Upper Freeport bed that have been inactive for periods of 4 to 11 years and openings caved for a somewhat shorter period show a total acidity varying from 0 to 260 parts per million, and the average is 69 parts. Mines 3, 4, and 5 in Table 1 may have surface water issuing from them. The free acidity varies from 25 parts per million alkalinity to 139 parts per million acid, and the average is 21 parts per million. To compare with this it is seen that the three active mines vary between 394 and 580 parts per million and average 504 parts per million total and 118 parts per million free acidity. That these differences between active and inactive mines are not due to the difference in ages is shown by the fact that the inactive mines are older generally than the active mines and yet the water from them is less acid or not acid at all. The highest acidity from any of the abandoned mines is only about half that of the average of the active mines and only two-thirds that of the lowest active mine. There is nothing especially remarkable about the various forms of iron present in solution, although it is to be noted that iron in water from the abandoned mines is much lower in every case than in water from active mines.

The values for dissolved oxygen indicate that the water has been wholly or in part in contact at some point with atmospheres containing a considerable amount of oxygen. Whether this contact is in the remote mine workings or in a zone just before the water issues from the mine is difficult to ascertain. Such a zone might be expected from "breathing" due to changes in barometric pressure or temperature, or both. The Upper Freeport bed in this district has light cover, and the superstrata is said to be badly cracked after caving, which might admit air as stated. If the water is true mine drainage -- that is, if the water has travelled considerable distances through the mine before its exit -- this explanation of a zone relatively high in oxygen just within the outlet appears to be the more logical, since, according to reports, the mines are badly caved. If the reports are true, an atmosphere void of oxygen or at least containing much less than that indicated by the samples, would be expected in the workings. On the other hand, surface cracks and "breathing" may also admit some air to the mine at a great many points and thus maintain an atmosphere more or less approaching a normal oxygen content.

Another explanation that may apply to some samples is that the water issuing from the mine may be wholly or in part surface water which enters the mine immediately back of the seal, and therefore retains most or all of its original dissolved oxygen. Values for the two active mines (Nos. 9 and 10) show approximately complete saturation.

Lower Kittanning Bed

Table 2 gives data covering mines in the Lower Kittanning bed. The acidity of drainage water from this bed is uniformly higher than of that from the Upper Freeport in the locality investigated. Mine 11, Table 2, was the first opened in this locality and was 49 years old in 1927. For many years after the mine was abandoned in 1883 or 1885 it was intermittently worked by different people taking out domestic coal, and it was reopened and worked regularly in 1918 for some time. The entry seemed to be open in 1926, but was caved in 1927. It is doubtful, therefore, whether water coming from it should be considered representative of a mine abandoned for more than a year. Mines 12 to 18, inclusive, are all of approximately the same age. As these mines were opened they were numbered consecutively from 1 to 36 by the operators. Mine 14, Table 2, was No. 21 in this series, and as pillars were being drawn in that mine as early as 1883, it seems likely that all mines reported in Table 2, except No. 18, which was No. 36 in the series, must have been opened between 1878 and 1883. There are no written records, but company officials and old residents agree on these points and also furnish the information that methods of coal mining in that day did not permit the economical working of mines past a rather limited development. New openings into fresh coal were frequent, and the district was soon honeycombed with entries, but parts of some old mines were kept open as haulageways for new mines, airways, and manways. The exact year when they were really abandoned is therefore indeterminate; but with two exceptions, Nos. 11 and 18, Table 2, it is generally agreed that they were all abandoned and caved by 1898, at least. Number 18 is still open along the main entry, but butt entries have been caved for some years. The dissolved oxygen value of 37.0 per cent saturation for this mine is low, and seems to indicate that a considerable amount of drainage is coming from areas void of oxygen. As the main entry has been driven entirely through a long hill, air can circulate through; and if water travelled a considerable distance along the entry, it would rapidly absorb oxygen and be more nearly saturated.

TABLE 2.- Analysis of water from mines sampled in the Lower Kittanning bed

Mine	Year opened	Year abandoned	Acidity, parts per million Total[1]	Free[1]	pH[2]	Total iron, mg./c.c.	$FeSO_4$, mg./c.c.	$Fe_2(SO_4)_3$, mg./c.c.	Oxygen percentage of saturation	Remarks
11	No. 11 opened in 1878 and remainder in succeeding four years.	From about 1893 to 1898.	935	52	<3.2	1.018	0.0437	3.626	0.0	Reopened for short time in 1918.
12			1030	338	<3.2	.790	.470	2.760	0.0	Caved tight.
13			712	96	<3.2	.705	.497	2.452	0.0	Do.
14			503	9	<3.2	.574	.431	1.992	0.0	Do.
15			225	61	<3.2	.187	.086	.657	41.4	Do.
16			320	9	<3.2	.356	.333	1.230	0.0	Do.
17			199	78	<3.2	.139	.147	.478	4.4	Do.
18			199	17	<3.2	.208	.038	.740	37.0	Main haulage still open.
19	1918	1924	A	25A	<3.2	.000	.000	.000	Lost	Caved tight.
20	1918	1924	181	70	<3.2	.128	.063	.439	71.7	Abandoned but still open.
21	1900	Active	2475	230	<3.2	2.195	--	--	98.5	
22	1906	Do.	2384	194	<3.2	2.041	--	--	96.9	
23	1914	Do.	380	150	<3.2	.223	--	--	78.5	
24	1917	1927	4519	343	<3.2	4.097	--	--	85.4	

1 A = alkalinity.
2 < = is less than.

The dissolved oxygen values in Table 2, with one exception, No. 15, show in five of the six remaining mines a condition which might be expected to result if mines were efficiently sealed after being abandoned -- that is, 0 oxygen. The sixth of these, No. 17, is also very low in oxygen, having only 4.4 per cent saturation. As the sample could not conveniently be taken just at the fall which sealed the entry, it is thought that this low percentage of oxygen could well be absorbed in the distance of about 100 feet between the seal and sampling point. All of these mine waters therefore can be said to be free from oxygen.

The separation of total iron into ferrous and ferric sulphate shows no definite relation between them. For example, drainage from mine 11 contains 1.018 mg. of total iron, of which amount 0.0161 mg. is in combination to give 0.0437 mg. of ferrous sulphate per cubic centimeter. The next mine, No. 12, has 0.790 mg. of iron of which 0.1730 mg. is ferrous sulphate -- nearly 11 times as much as mine 11, although they are only a few hundred yards apart in the same bed, are of the same age, and have no oxygen in solution. Other mines in Table 2 show similar results. It will be noted, however, that the samples of water having the highest dissolved oxygen content -- namely, those from mines 15, 18, and 20, with 41.4, 37.0, and 71.7 per cent saturation, respectively - have much less iron in combination in the ferrous state than those others where oxygen is low or at zero. Mine 15 has 16.2 per cent, mine 18 has 6.7 per cent, and mine 20 has 18.1 per cent of the total iron as ferrous sulphate. The mines having low oxygen saturation (0 to 4.4 per cent) range from 22 to 35 per cent and average nearly 28 per cent of the total iron as ferrous sulphate. The only exception to this is mine 11 which, as previously stated, has only recently been caved beyond doubt.

The active mines in the same bed, Nos. 20, 21, 22, 23, 24, in this district show greatly increased total acidity, with the exception of Nos. 20 and 23. Mine 20 is said to be caved inside, but to what extent is not known. Two drifts about 100 yards apart were open so far as could be seen, and a third opening driven to the outside, as a drainage and air passage was partly closed by an earth slide; but air was coming out of it, as indicated by condensation of moisture vapor when the mine air encountered the colder air outside. This mine can hardly be said to be open, and yet it is not entirely sealed. The other exception, mine 23, has been repeatedly sampled and always shows a lower acidity than others in the same locality, but the reason for this is not evident. Oxygen saturation values are relatively high as compared to abandoned mines, varying between 78.5 and 98.5 per cent.

The average total acidity of seven caved and abandoned mines in the Lower Kittanning bed is 427 parts per million and 81 parts per million free acidity. The same values for four active mines in the same locality and same bed is 2,440 total acidity and 229 parts free acidity per million. The total acidity is thus shown to be nearly six times as large and the free acidity nearly three times as large in drainage from active mines as in drainage from the abandoned mines which were sampled. Dissolved oxygen values for the four active mines show these to be much higher than in the abandoned mines.

CONCLUSIONS

1. The acidity of waters from abandoned and sealed mines is lower than that from active mines which may in all other respects be similar, so far as can be ascertained.

2. The water from such mines will not infrequently be found alkaline and therefore similar to natural springs or streams.

3. The dissolved oxygen content of these waters is usually low and often is 0 within the limits of accuracy of ordinary analysis.

4. It seems likely that the sealing of abandoned mines would result in decreasing the acidity of drainage from them sooner than if they were allowed to remain open.

5. There is no direct relation between the percentage of total iron in these waters and the relative proportion of ferrous and ferric salts held in solution.

6. With lower percentages of dissolved oxygen, the amount of ferrous sulphate in waters from abandoned mines has been found to be correspondingly high.

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