

## USE OF ACTIVATED CARBON FOR MINE WATER TREATMENT

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### ABSTRACT

Extremely rapid oxidation of the ferrous iron in raw acid mine water is possible without the use of costly oxidants and precipitating agents. This was achieved by catalytic oxidation in an activated carbon-air-mine water system. The ferrous iron content of an acid mine water flowing through aspirated, granular, activated carbon was reduced from about 700 to 10 ppm in less than 1 minute. Incorporating a catalytic oxidation step in the treatment of acid mine water containing ferrous iron would facilitate treatment by virtual elimination of aeration equipment and precise stoichiometric control of pH. Limestone would replace expensive alkaline reagents, thus lowering reagent costs. Finally, smaller settling ponds would result through sludge volume reduction. The process would essentially consist of oxidation, neutralization, and settling of solids.

### INTRODUCTION

Mine drainage is now classified as an industrial waste. Although mine waters vary widely in chemical composition, the most damaging constituents--acid sulfate and/or iron--are invariably present, and economical removal of these pollutants constitutes the problem of mine water treatment at the present time. From an economic standpoint, one of the most difficult technical aspects of mine water treatment is iron removal. If the iron is in the ferric state ( $Fe^{+++}$ ), removal would be relatively simple and inexpensive. Iron, aluminum, and acid could be effectively removed from mine water by raising the pH to about 6 with a cheap alkaline agent such as limestone. However, in most mine waters the iron is predominantly in the ferrous form ( $Fe^{++}$ ). Ferrous iron is more difficult and more expensive to remove, especially when present in appreciable quantity.

Conventional mine-water treatment processes consist of lime neutralization, aeration, and sludge settling. Aeration is utilized primarily to oxidize ferrous iron because less sludge results when iron is in the ferric form, and savings in reagent costs can be realized with the use of lower pH. If aeration were not applied, a high pH (about 9) would be needed to guarantee a low soluble iron content (<7 ppm) in the treated water. Larger sludge volumes would result because of a more flocculent precipitate and thus further complicate the sludge disposal problem.

An inherent disadvantage to this mode of treatment is the difficulty of process control. Neutralization of acidity is not achieved until most of the iron has been converted to the insoluble ferric state. Therefore, regulation of the alkaline reagent feed cannot be established by a set pH limit for efficient operation without continuous monitoring of acidity and ferrous iron load. Some semblance of control is possible if the raw mine water feed is equilibrated in holding ponds and aeration equipment capabilities and performance are firmly established. But sudden changes in the acid and iron load may result in excess alkalinity or acidity in the treated water. Only experience and trial and error, therefore, can provide some degree of control in such a mine water treatment process.

When acid mine water is exposed to the atmosphere the ferrous iron oxidizes to ferric iron. The oxidation rate, however, is exceedingly slow, even with the aid of aeration (1).<sup>1/</sup> To accommodate large volumes of mine water having appreciable ferrous iron, prohibitively large basins and aeration facilities would be required. Chemical oxidants can be used to accelerate the rate of oxidation, but a brief analysis of the stoichiometric requirements and the unit cost of oxidants show that such oxidation would be too costly. Certain substances (2) enhance the oxidation of ferrous iron, but none are used in practice.

The best approach to acid mine water treatment is to convert the ferrous iron to the ferric form prior to neutralization. Complete iron removal would then readily be achieved by simply increasing the pH above 4.5.

Recent developments (2) in the Bureau of Mines Pittsburgh Mining Research Center laboratory indicate that extremely rapid ferrous iron oxidation in an acid mine water is possible without the use of high-priced chemical oxidants, without expensive precipitating agents, and without extensive aeration equipment. This catalytic oxidation reaction was achieved in an activated carbon-air-mine water system. Activated carbon accelerates the rate of oxidation of ferrous iron in sulfuric solutions (4). Acid mine water effluents are dilute solutions of sulfuric acid and acid salts. Although only an exploratory effort was made with granular activated carbon as a means of catalyzing the air oxidation of ferrous iron in acid mine water, the initial results are promising. The brevity of this study did not allow defining the reaction kinetics or resolving the factors affecting the activated carbon-air-acid mine water system. Therefore, only a general description of the test and the test results can be made.

#### EXPERIMENTAL WORK

The carbon used throughout the tests was a commercial-type, coal-base, activated carbon sized 12 by 40 mesh. Mine water containing 613 to 945 ppm Fe<sup>++</sup>, 810 to 960 ppm total Fe, 2,100 to 2,400 ppm total acidity, and with a pH ranging from 2.70 to 3.15 was used for the tests. A typical analysis of the mine water is shown in table 1.

TABLE 1. - Typical mine water analysis

pH .....	3.10
Eh .....	6.05
Total acidity .....	ppm 2,370
Fe <sup>++</sup> .....	ppm 830
Total Fe .....	ppm 965
Ca <sup>++</sup> .....	ppm 220
Mg <sup>++</sup> .....	ppm 66
SO <sub>4</sub> .....	ppm 4,512
Dissolved solids .....	ppm 7,080

The experimental apparatus consisted of a glass cylinder with a fritted disk connected to a filtering flask. The disk supported the granular carbon and allowed passage of air and water. A side tube in the filtering flask was connected to an aspirator. The same batch of activated carbon (200 grams, 12 by 40 mesh) was used in all the tests. Two different glass cylinders were used: In one the carbon column was 6.5 cm in diameter and 12.5 cm in depth; in the other (used in later tests) the carbon column was 3.8 cm in diameter and 42 cm in depth. The longer cylinder was used to increase flow through time. A synthetic porous sponge supported the granular carbon in the cylinder and prevented the loss of

<sup>1/</sup> Underlined numbers in parenthesis refer to items in the list of references at the end of this report.

carbon particles. A sketch of the activated carbon oxidation apparatus is shown in figure 1.

Air was aspirated through the carbon column before the mine water was added and continuously throughout the test until most of the water had passed through the carbon. The mine water volumes flowing through the carbon column ranged from 175 to 1,070 cu cm per batch (test); airflow rates ranged from 0 to 3,500 cu cm per min.

Prior to testing, the batches of raw mine water were analyzed for pH, ferrous iron, and total iron. Identical analyses were made immediately after testing on the effluent from the activated carbon column. All tests were conducted at room temperature. A total of 65 separate runs, consisting of about 25 liters of raw mine water, were made in the same carbon column over a period of about 2 weeks.

#### TEST RESULTS

The pH of a suspension of the activated carbon in distilled water was about 6.6. With successive additions of the acid mine water (pH 2.70 to 3.15), the pH of the effluent decreased steadily and appeared to level off at a pH of 2.3 to 2.5 when ferrous iron oxidation was virtually complete. The raw mine water was practically colorless, but the effluent from the carbon column was a deep amber color owing to the presence of a hydroxylated ferric sulfate.

The ferrous iron content (635 to 920 ppm) of the raw mine water was reduced to about 10 ppm after flowing through the carbon column for less than 1 minute. By contrast, aeration of an acid mine water (1) in the absence of an oxidizing agent, except for bacteria which may have been present, reduced the ferrous iron concentration from 261 to about 10 ppm in 168 hours. While a direct comparison cannot be made between these results, they do indicate the enormous increase in the ferrous iron oxidation rate that can be achieved with activated carbon.

The test results are summarized in table 2. These preliminary results indicate that activated carbon catalyzed the air oxidation of ferrous iron in a ferruginous acid mine water. The initial tests also show that the activated carbon must be preconditioned to an acidic state for the catalytic reaction to take place. The low ferrous iron content in the effluent, beginning with run 26, was consistently maintained to the end of the experiment. It was likely that the activated carbon was adequately conditioned at this time. For these tests the total iron (practically all in the ferric form) in the effluent represents about 65 percent of the total iron in the feed.

After 25 liters of a ferruginous mine water had passed through the carbon column, there was no appreciable loss in catalytic efficiency and no visible sign of surface fouling or solids deposition on the surface of the carbon particles, although a portion of the iron was adsorbed by the carbon. It is possible that only an insignificant amount of iron would be held by the carbon in a continuous flow operation. If the pH of the system were maintained below 2.5, ferric hydrolysis would be negligible. The air requirements for oxidation of ferrous iron might be minimal. Run 60, conducted without aspirating air through the carbon column, produced equally effective ferrous iron removal.

TABLE 2. - Batch test results of catalytic oxidation of ferrous iron in acid mine water with activated carbon

Date, 1969	Run	pH	Feed			Feed time, min	Volumic collected, cu cm	Total aspi- rating time, min	Flow, through time, min <sup>1</sup>	Air aspi- rating rate, cu cm per min <sup>2</sup>	Effluent			
			Fe <sup>++</sup> , ppm	Total Fe, ppm	Vol- ume, cu cm						pH	Fe <sup>++</sup> , ppm	Total Fe, ppm	
April 15	1	2.80	613	-	260	3.0	250	5	-	-	4.50	417	-	
	2	2.80	613	-	260	4.0	250	5	-	-	4.30	230	-	
	3	2.80	613	-	260	5.0	250	5	-	-	4.10	272	-	
April 16	4	2.80	613	-	260	3.0	250	6	-	-	3.95	175	-	
	5	2.80	613	-	260	3.0	250	7	-	-	3.75	125	-	
	6	2.80	613	-	260	3.0	260	8	-	-	3.60	130	-	
	7	2.80	613	-	260	3.5	235	8	-	-	3.45	105	-	
	8	2.80	613	-	260	3.5	220	8	-	-	3.35	75	-	
	9	2.80	613	-	260	3.0	225	9	-	-	3.50	80	-	
	10	2.80	613	-	260	3.0	230	10	-	-	3.35	85	-	
	Extracted excess water						-	125	9	-	-	3.15	190	-
	11	2.80	613	-	260	3.0	175	10	-	-	3.05	205	-	
	12	2.80	613	-	260	1.5	225	20	-	-	2.90	220	-	
13	2.80	613	-	260	1.5	210	20	-	-	2.70	165	-		
14	2.80	613	-	260	1.0	200	18	-	-	2.60	145	260		
Cleaned fritted disk														
April 17	15	2.75	745	-	260	1.5	260	5	-	-	2.55	245	-	
	16	2.75	745	-	260	2.0	260	5	-	-	2.55	270	-	
	17	2.75	745	-	260	3.5	260	9	-	-	2.50	275	575	
	18	2.75	745	-	260	3.0	260	5	-	-	2.50	90	-	
	19	2.75	745	-	260	3.0	260	6	-	-	2.45	72	-	
	20	3.15	945	-	260	3.0	260	8	-	-	2.45	70	-	
	21	2.85	920	-	260	3.0	260	10	-	-	2.45	10	215	
Cleaned fritted disk														
April 21	22	2.90	920	-	260	1.5	250	4	-	-	2.45	35	420	
	23	2.90	920	-	750	-	750	12	-	-	2.45	85	-	
	24	2.90	920	-	260	-	250	5	-	-	2.40	70	-	
	25	2.90	920	-	260	-	240	4	-	-	2.40	55	-	
	26	2.70	660	-	260	.5	240	8	-	-	2.50	5	-	
	27	2.70	660	-	260	2.0	250	10	-	-	2.45	2	250	
	28	2.70	660	-	260	.8	250	15	-	-	2.35	2	280	
Cleaned fritted disk														
April 23	29	2.70	900	-	260	1.0	260	4	-	-	2.35	5	-	
	30	2.70	900	-	260	1.0	260	6	-	-	2.30	5	550	
	31	2.70	900	-	260	2.0	250	8	-	-	2.40	5	-	
	32	2.90	800	960	260	3.0	250	11	-	-	2.40	<2	365	
	33	2.90	800	960	260	3.0	250	14	-	-	2.45	<2	430	
	Cleaned fritted disk													
	34	2.90	800	960	260	1.0	260	5	-	-	2.40	5	510	
	35	2.90	800	960	260	3.0	260	10	-	-	2.35	5	540	
	36	2.90	800	960	260	3.0	260	13	-	-	2.35	<2	490	
	37	2.90	800	960	260	4.0	260	21	-	-	2.35	<2	535	

See footnotes at end of table.

TABLE 2. - Batch test results of catalytic oxidation of ferrous iron in acid mine water with activated carbon--Continued

Date, 1969	Run	Feed				Feed time, min	Volume collected, cu cm	Total aspirating time, min	Flow through time, min <sup>1</sup>	Air aspirating rate, cu cm per min <sup>2</sup>	Effluent		
		pH	Fe <sup>++</sup> , ppm	Total Fe, ppm	Volume, cu cm						pH	Fe <sup>++</sup> , ppm	Total Fe, ppm
Cleaned fritted disk													
April 23	38	2.90	800	960	260	0.8	260	3	-	-	2.45	15	560
	39	2.90	800	960	260	1.5	260	4	-	-	2.40	12	653
	40	2.90	800	960	260	1.8	260	4	-	-	2.45	10	647
	41	2.90	800	960	260	2.0	250	5	-	-	2.45	<2	410
	42	2.90	800	960	260	2.0	260	6	-	-	2.40	<2	445
April 24	43	2.80	720	865	260	1.3	-	3	-	-	2.50	<2	420
	Installed long cylinder (3.8-cm-diam, 42-cm-long carbon column)												
April 25	44	2.80	720	865	260	2.0	250	5	-	-	2.35	<2	510
	45	2.80	720	865	260	1.8	260	5	-	2,000	2.45	<2	445
	46	2.80	720	865	260	.6	250	2	0.25	3,500	2.40	15	505
	47	2.80	720	865	245	1.3	225	3	.5	2,000	2.40	<2	520
	48	2.80	720	865	260	1.7	240	3	.6	2,000	2.40	<2	585
	49	2.80	720	865	1,000	5.0	990	8	.5	2,000	2.40	7	710
	50	2.80	720	865	720	3.5	710	6	.5	2,000	2.40	15	715
April 28	51	2.80	720	865	260	1.0	250	3	.5	2,000	2.45	15	550
	52	2.75	655	855	260	1.2	240	3	.6	2,000	2.40	<2	560
	53	2.75	655	855	1,050	5.0	1,035	8	.5	2,000	2.30	10	670
	54	2.75	655	855	1,020	5.0	1,000	8	.5	2,000	2.35	32	710
	55	2.75	655	855	1,070	5.5	1,055	8	.5	2,000	2.45	12	620
May 1	56	2.75	655	855	260	1.5	250	4	.5	2,000	2.35	5	635
	57	2.85	635	810	260	1.3	240	3	.6	2,000	2.45	10	315
	58	2.85	635	810	1,040	5.0	1,020	8	.6	2,000	2.40	10	560
May 2	59	2.85	635	810	995	5.0	980	8	.6	2,000	2.40	35	605
	60	2.85	635	810	260	1.8	250	None	.75	None	2.45	<2	320
	61	2.85	635	810	1,090	5.0	1,075	8	.6	2,000	2.40	25	620
	62	2.85	635	810	635	3.0	615	6	.6	500	2.45	7	490
	63	2.85	635	810	510	2.5	495	5	.6	500	2.50	10	470
	64	2.85	635	810	500	2.5	475	4	.6	3,500	2.45	7	490
	65	2.85	635	810	535	2.6	520	5	.6	250	2.45	15	525

<sup>1</sup>Not determined for runs 1-45.

<sup>2</sup>Approximately 2,000 cu cm per min of air drawn through carbon column for runs 1-44.

## DISCUSSION

The exploratory tests conducted with activated carbon and a ferruginous acid mine water indicate that ferrous iron oxidation takes place catalytically at an extremely rapid rate. Further investigation is necessary to determine the factors that may limit the effectiveness of the carbon, to determine the efficiency and effective life of the carbon in a continuous flow system, and to determine whether acid regeneration will restore the carbon to its original efficiency when the surfaces become fouled with solids. Cost and performance standards need to be established also.

Rapid oxidation in a carbon-air-acid mine water system to convert ferrous iron to ferric iron prior to neutralization would greatly facilitate the mine water treatment process and reduce costs to a minimum. Catalytic oxidation would provide distinct advantages:

1. Limestone, the least costly alkaline agent, would supplant the more expensive alkaline agents in common use for neutralization.
2. Stoichiometric relations could be precisely controlled at a pH level which would ensure optimum use of alkaline agent.
3. Aeration after neutralization would be eliminated.
4. The dense, small volume of sludge produced at near neutral pH conditions would significantly reduce the cost of sludge separation and sludge handling.

Other potential advantages include production of practically pure iron oxide by fractional precipitation; maintenance of optimum ferrous-ferric ratios, by means of controlled oxidation, to form dense, low-volume sludges; and the use of more reactive alkaline agents, which can be justified if significant reductions in sludge volume can be attained.

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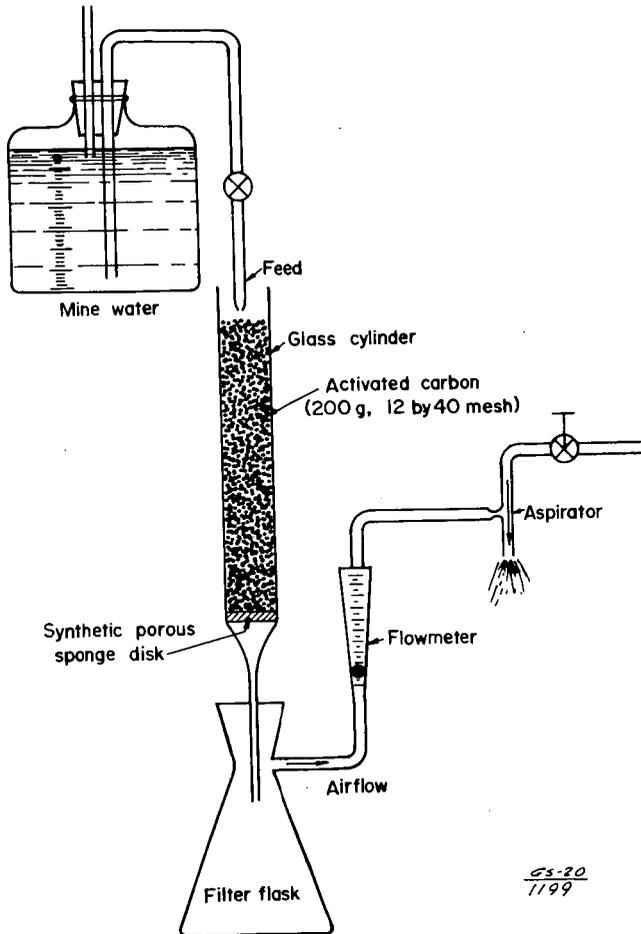


FIGURE 1. - Activated Carbon Oxidation Apparatus.