DEPARTMENT OF THE INTERIOR

UNITED STATES GEOLOGICAL SURVEY

CHARLES D. WALCOTT, DIRECTOR

STREAM POLLUTION BY ACID-IRON WASTES

A REPORT BASED ON INVESTIGATIONS MADE AT SHELBY, OHIO

BY

HERMAN STABLER

WASHINGTON
GOVERNMENT PRINTING OFFICE
1906

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STREAM POLLUTION BY ACID-IRON WASTES.

By Herman Stabler.

INTRODUCTION.

Stream pollution by ironworks effluents has always been an important question in countries where the iron industries are prominent. The polluting liquors, commonly known as "acid-iron" liquors, are derived from the "pickling process" common to galvanizing, tin plating, tube and sheet iron treatment, and, in fact, all work in which a clean iron surface for coating or other purpose is required. The clean surface is obtained by immersing the material in a fairly strong solution of hydrochloric or sulphuric acid, which readily removes the surface impurities and at the same time attacks the material itself, dissolving it or uniting with it to form new compounds. As a result of the process the material treated comes from the bath with a surface as clean and bright as if newly polished. By continued use the acid solution becomes gradually weaker, iron chlorides or sulphates being formed, and the whole bath becomes more or less impregnated with impurities, chief among which are practically insoluble iron oxides. Finally the solution becomes too weak for further profitable use and is discarded as waste, technically known as "waste pickle." This waste pickle, it is said, has been bottled and sold as tonics for human consumption, though not with great success. Used in small quantities, however, it is beneficial to both animal and vegetable life. It is not a desirable addition to streams (1) because it produces a reddish discoloration and turbidity, making the stream waters, bed, and banks unsightly; (2) because, by reason of its avidity for oxygen, it robs the waters of their natural supply of this essential gas and thereby, when it is present in comparatively large quantities, causes the death of fish, and (3) because it gives rise to a large quantity of iron in the stream, and thereby impairs the usefulness of the water for domestic and laundry purposes and for certain manufacturing processes.

In many cities waste pickle is discharged into the sewers. Where the quantity of pickle is relatively very small this method of disposal is not objectionable. Too frequently, however, there is enough free acid in the waste liquors to corrode the sewer joints and metal fittings, and, in case there are sewage purification plants, to interfere seriously with the working of the purification processes.

At Shelby, Ohio, acid-iron wastes have been discharged into a watercourse and also into the sewers of the town, causing conditions which have led to lawsuits and complaints directed to the Ohio State Board of Health. It was determined, therefore, to investigate at this city the factory processes which are accountable for the alleged nuisance and the conditions at the sewage-disposal farm and along the stream. The investigations were performed under a cooperative agreement between the United States Geological Survey and the State Board of Health of Ohio, each bureau participating equally in the expenses involved. All expenses for analytical work and for transportation of samples, together with the traveling expenses and subsistence of the investigators, were borne by the Ohio State Board of Health, so that joint credit should be given to the two bureaus participating in the work.

The pollution at Shelby having extended over a term of years under varying conditions, it was thought advisable to make the investigation cover (1) the history of the pollution and the attendant litigation; (2) the effect of acid-iron liquors upon sewage purification processes; (3) the conditions along the stream, and (4) the disposal of acid-iron wastes without discharge into watercourse or sewerage system.

It is desired to make acknowledgment of assistance received in the investigation from Mr. William F. Sonnanstine, superintendent of the Shelby sewerage system; Messrs. Mansfield and Long, attorneys, and Mr. A. C. Morse, superintendent of the Shelby Steel Tube Company. Mr. M. O. Leighton, chief of division of hydro-economics, U. S. Geological Survey, personally supervised and directed the course of the investigation. In addition to sharing the expense of the investigation the Ohio State Board of Health accorded active cooperation by affording the use of its laboratory to the writer and by making sanitary determinations of the eight samples of sewages listed in the table on page 18, which were made in the laboratory of the Ohio State Board of Health under the direction of Mr. E. G. Horton, bacteriologist and chemist.

HISTORY OF POLLUTION BY ACID-IRON WASTES AT SHELBY, OHIO, AND RESULTING LITIGATION.

The Shelby Steel Tube Company maintains a large plant on the bank of a brook within the city of Shelby. The tube mills were first operated in 1890, since which time the present company and its predecessors have, to a greater or less extent, discharged their liquid wastes into the adjacent brook, which, for convenience, we shall designate Red Brook, no generally recognized local name being applied to it. The flow of Red Brook varies perceptibly with the flow of waste water from the tube works, but is generally about one-fifth or one-sixth as great as that of Black Fork,[a] into which it discharges in the upper part of Shelby. Black Fork traverses the city from south to north, passing on through an agricultural district, and finally reaching Muskingum River.

Until sometime in 1902 the entire waste of the tube works was discharged into a settling basin, from which it overflowed to Red Brook, giving to it and to Black Fork a red discoloration for miles below. No very vigorous protest against this pollution seems to have been made until October 20, 1902, when petition was filed and suit for $2,500 damages was begun in the court of common pleas of Richland County, Ohio, against the Shelby Steel Tube Company by Isaac Noecker, a farmer having 50 acres of bottom land subject to overflow from Black Fork about 4 miles below the tube works. Previous to this time it was apparently the view of all parties concerned that the tube works, employing a large number of men, was an industry to be fostered; that the stream was the only available means for the disposal of its waste, and that any inconvenience resulting from stream pollution by the works should be borne on account of its general benefit to the community. This is probably the view now taken by the city in allowing the effluent from the tube works to enter its sewerage system, permission for such use of the sewers being taken advantage of by the company in 1902—a direct result, no doubt, of the growing legal complications attending the discharge of the waste liquors into the stream. At the time sewer connection for the tube works was made the overflow from the settling reservoir was conducted to a filtering bed of crushed limestone, from which tile underdrains carried it to the sewer. This arrangement supposedly stopped all pollution of Red Brook, but actually served merely to divert a moiety of the polluting liquors, for infiltration, leakage, and probably overflow from clogged filters still carried to this stream a considerable flow of acid-iron waste. However, it transferred the principal point of pollution to the sewer farm outlet, 3 miles below Shelby, and bettered conditions all along the stream very materially.

In the petition above mentioned, it was claimed that—

> Defendant [the Shelby Steel Tube Company] in operating its said factory pours into said stream great quantities of poisonous matter and offals from said factory, which poison the water in said stream and render it destructive of animal and vegetable life. And said poisonous deposits in said stream, when the water is high, overflow plaintiff's said low lands, thereby poisoning the vegetation and pasture thereon, rendering it unfit for animal food and dangerous to animal life.
>
> Said poisonous matters poured into said stream render the water unfit for domestic use and sicken and poison plaintiff's animals that pasture on said ground when they drink thereof.

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[a] Black Fork is a small stream having at this place (Shelby) a watershed of about 40 square miles, and a dry-weather flow of perhaps 1 to 3 cubic feet per second. Eighteenth Ann. Rept. Ohio State Board of Health, 1903.

In the answer of the defendant to the petition, it was claimed—

that if said stream is polluted to such an extent as to be a nuisance and of injury to this plaintiff, that the same is caused by causes other than those alleged in the petition.

The case came to trial in June, 1903. Nearly all witnesses for the plaintiff were farmers owning land along the Black Fork below Shelby. With few exceptions these men had instituted or were intending to institute similar suits against the company, concerted action having been determined upon. Each, as he testified, realized that the successful outcome of his own suit would be largely dependent upon the winning of this first suit of the series.

The testimony of witnesses for the plaintiff, in brief, was about as follows:

1. Previous to the operation of the tube works the Black Fork was satisfactory as a water supply for stock; gave no appearance of pollution; was the home of numerous healthy fish, and was used as ice and boiler supply and for domestic purposes.

2. After the installation of the tube works the stock would not readily drink the water; cows watered from the creek suffered decrease in milk; cattle pastured adjacent to the creek got sick and some died, removal to a field from the creek effecting the recovery of stock. The creek water was sometimes very red and sometimes blue, turbid, and had a black ashy sediment; overflow of the stream stunted crops, turned them red, and destroyed grass; stock refused to eat pasture which had been overflowed; dead fish were found along the stream, and few, if any, live fish could be caught, and the value of the stream as a source of ice and boiler supply was destroyed.

3. Injury to stock was believed to be due to use of creek water or pasture that had been overflowed by the creek. In some cases, however, death of stock was certainly due to other causes, as shown by autopsy.

4. Said damage occurs all along the stream from 3 to 12 miles below tube works.

Witnesses for the defense testified that:

1. No difference in pasturage was noticeable in last twenty-five years; that they had caught fish or seen others fishing all along the polluted stream, and that no damage to stock or pasture resulted on land immediately below entrance of tube works effluent.

2. Damage on stream might have resulted from bursting of an oil tank.

3. Chemical analyses in January, 1903, of samples taken from Red Brook below the tube works and from Black Fork above, 3 miles below and 4 miles below the entrance of Red Brook, showed a little free acid in Red Brook, but none in Black Fork. The stream 4 miles below showed the presence of the following amounts of solid matter, in parts per million: Silica, 11.97; iron and alumina, 8.55; lime,

127.99; sulphuric anhydride, 102.60. The expert witness who made these analyses, Prof. Albert W. Smith, of the Case School of Applied Science, Cleveland, Ohio, testified, in part, as follows:

In the process of pickling, an acid is used for the purpose of cleaning the surface of iron. The iron surface is covered with what is called rust, and the acid dissolves rust; it combines with it chemically, and both acid and the rust, as such, are destroyed—they become a new substance. When two things combine chemically a new thing is formed; that is what is meant by chemical action. When acid and iron rust come together, both the acid and rust, as such, are destroyed, and they form a new substance, green vitriol or iron sulphate. That cleans the surface of the iron, and the iron sulphate forms a clear solution with the water that the acid is dissolved in, but the acid and the iron have been destroyed as such.

When this liquid flows into this little stream [Red Brook] it makes it acid, and the little stream contains this sulphate of iron. It is a clear liquor solution, just like sugar in tea. The large brook [Black Fork] contains lime in solution, a clear, transparent liquid, but the lime is there, just the same, in solution. When the lime and the iron sulphate come together they combine chemically and form a new substance. They form sulphate of lime, or land plaster, which is soluble in water, and the same iron rust that was present in the iron; that is, the iron has gone back to the same condition it was in when it was rust on the iron, and as such is not soluble in water. It will not dissolve any more, so it spreads out, a yellowish and brownish rust. The iron rust settles to the bottom of the creek, and hence is separated from the water. There would be no iron in the water, as it settles to the bottom and stays there, just as so much clay or mud would. It settles in the water below, and there is neither acid nor iron.

The iron, after it separates and is precipitated to the bottom, is of a yellow or reddish-yellow color, just like yellow clay, and is very much the same in its chemical properties.

I think it would have the same effect upon plants or animals as so much clay would. This is inert matter, just like clay or mud.

The charge of the court (Robert M. Campbell, trial judge) is of particular interest, voicing as it does the rights of riparian owners and the views of such rights that obtain in Ohio. The prominent points in the charge are as follows:

1. All riparian owners have a right to the use of stream waters in a normal state.

2. Their right to the use of the water is limited to such use as shall not substantially decrease the value of the stream to riparian owners below them.

3. Their right to the water in a normal state is subordinate to a usual and ordinary use of the water by riparian owners above them.

4. Every party contributing to stream pollution is responsible for damage done thereby.

5. Riparian owners injured by stream pollution have a right to compensation for such injury in direct proportion to the loss sustained.

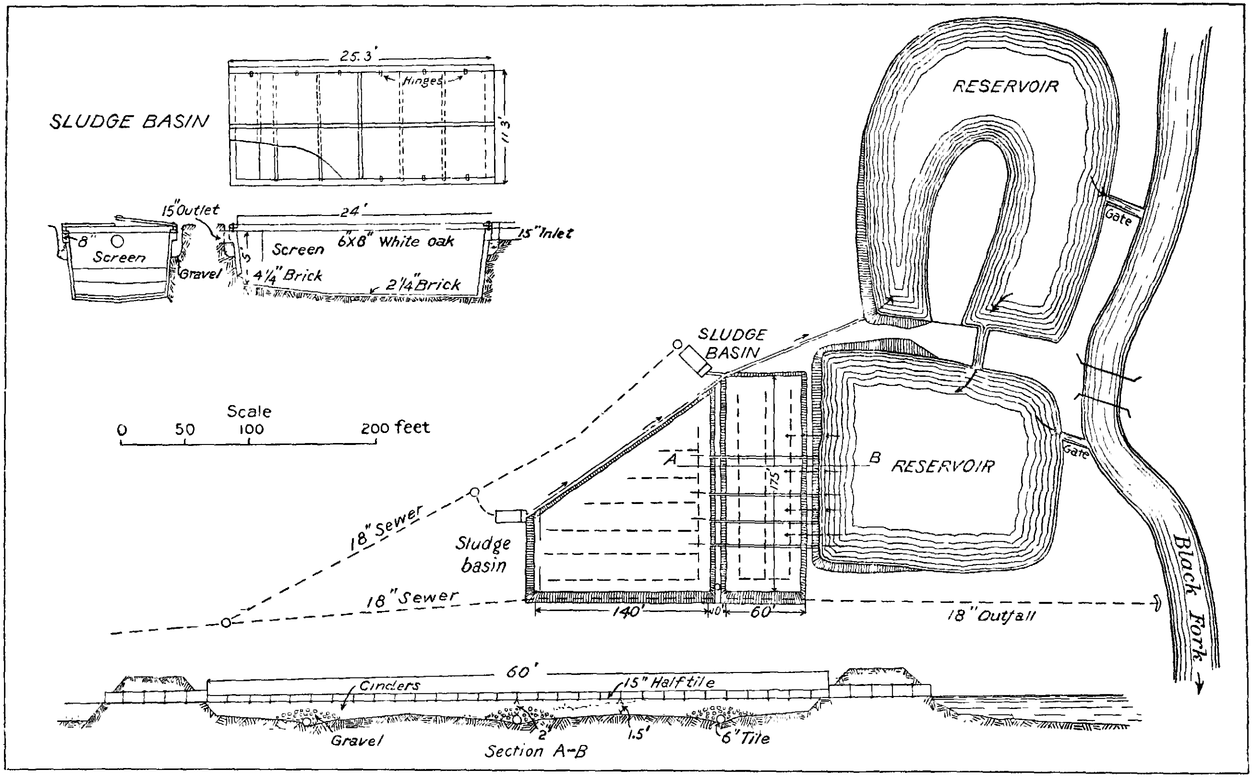
6. The injury sustained may be in the nature of a deprivation of the use of the water for any reasonable purpose or of damage done to property, but must be substantial and not mere inconvenience or occasional annoyances in order to warrant an award for damages.

Verdict for the plaintiff was returned, damages being fixed at $317. This is at the rate of $6.34 for each acre of plaintiff's bottom land for the four years to which the statute of limitations confined the consideration of pollution.

The case was appealed to the circuit court of Richland County and then to the supreme court of Ohio, the judgment of the lower court being affirmed in each case.

A careful review of the testimony given at the trial convinces one that the acid-iron pollution rendered the stream less suitable for domestic purposes as a boiler water, as an ice supply, and as a water supply for animals. The riparian rights of landowners below Shelby had been interfered with, and, in the judgment of the jury, interfered with in a substantial degree.

Injury to vegetation or stock was, to say the least, problematic. The only evidence offered indicating such injury was circumstantial and merely indicated the possibility of such injury. The claim for injury to vegetation was based on the flooding of lands. From the plaintiff's testimony it appears that the cross section of the stream at his farm is about 150 square feet, and the stream at lowest flood must carry at least 30,000 pounds of water per second. Only 6,000 pounds of 78 per cent acid are used at the tube works in a day, and nearly all of this is converted into iron sulphate before it is discharged as waste. From a scientific standpoint, therefore, it seems incredible that by any means the pollution arising from this acid, or ten times as much acid, could noticeably affect the pasture land or crops. Were the waste liquor stored for days and discharged only at time of stream flood (a practice that was not followed to any great extent), it would not pollute the water sufficiently to kill vegetation by merely washing over it. It is of course physically impossible under the conditions existing that any free acid should be in the stream after the polluting liquors have been thoroughly mixed with the stream water. The alkalinity of the Black Fork at its lowest dry-weather flow is sufficient to neutralize twice as much acid as is used at the tube works were the acid not already nearly neutralized in the pickling process before being discharged into the stream. It is to iron oxides and sulphates that we must look for injurious pollution; but with added information regarding the qualities of these substances the probability of ill effects upon vegetation grow still fainter. In Thorpe's Dictionary of Applied Chemistry, vol. 2 (1891), page 367, we find the statement that the coloring matter of clays is chiefly iron oxide, and clays, except so far as by their compactness and impermeability they prevent the percolation of water, certainly are not injurious to vegetable life. Furthermore, on page 368 of Thorpe's Dictionary we find the following statement concerning ferrous sulphate: "In weak solution it is said to promote the growth of certain plants, especially of roots."



PLAN OF SEWAGE-DISPOSAL PLANT AT SHELBY, OHIO.

Injury to stock depends upon a different set of conditions. The time of lowest stream flow in dry weather would be the time of greatest pollution. It is possible that large charges of waste pickle at such times might at certain hours of the day produce a pollution which would be injurious to animal life, for although iron sulphates and oxides are beneficial in small quantities and are largely used in tonics for human consumption, great amounts of the sulphates might do harm. The testimony was more or less conflicting upon this point, but a careful review of all statements leads to the conclusion that probably no actual injury was suffered by stock because of the condition of the stream water.

The winning of this action by the farmers was followed by a succession of suits for damage to lands farther downstream. This sort of litigation has been kept up intermittently until the present time, when three or more suits, recently filed, are awaiting trial.

The discharge of pickling wastes into the city sewers, with more or less direct pollution of the stream, was continued until August, 1904, when a plant was installed for disposing of the strong iron-sulphate liquors by converting them into crystal copperas. A full description of this plant is given later. At this point it will be sufficient to state that one-fifth of the acid used is thus recovered as a commercially marketable substance. Waste of valuable material and stream pollution are therefore obviated by this plant to a considerable extent. No further changes have been made in the disposal of the waste pickle, except that the copperas plant was enlarged somewhat in June, 1905.

At present, therefore, a part of the waste liquor from the pickling process is recovered as copperas; a part is discharged into the city sewers, passes through the sewage-purification works, and thence to Black Fork, and the remainder flows into Red Brook and thence to Black Fork.

EFFECT OF ACID-IRON LIQUORS UPON SEWAGE PURIFICATION PROCESSES.

GENERAL CONDITIONS.

To understand the discussion that follows, no detailed knowledge of the polluting liquors is necessary beyond a mere recognition of the fact that they consist chiefly of iron sulphate, with an admixture of iron oxides and free sulphuric acid in varying quantities.

A brief description of the sewage-disposal plant at Shelby (see Pl. I) is, however, essential. The plant is located about 3 miles north of Shelby on a 25-acre tract owned by the city and known as "the sewer farm." An 18-inch sewer from the city acts as a gravity conduit for the sewage, which amounts to 250,000 or 300,000 gallons a day, varying in quantity with the amount of ground water that finds entrance to the system. Rough measurement by the writer in July, 1905, indicated a flow of about 275,000 gallons. The sewage first enters a sludge basin for the removal of the larger suspended matter, a wire screen of ½-inch mesh being placed over the exit. There are two of these basins, which are used alternately. Each is of brick, 10 by 24 feet and 6 feet deep, and contains about 8,000 gallons. It is customary to use one basin about three months and then to pump out the accumulation of sludge for use as manure on the farm. The sludge is said to be an excellent fertilizer and promotes the growth of unusual crops.

From the sludge basin the sewage flows through two shallow reservoirs, together holding about five days' flow, which are arranged in series, and thence is distributed by half-tile carriers over filter beds of cinders and gravel. The filters are two in number and have a total area of 25,000 square feet. Six-inch underdrains are laid 20 feet apart in depressions and covered with a 6-inch layer of gravel 6 or 8 feet wide, the sides of the depressions sloping to the drains. The whole is then covered by 18 inches of cinders averaging one-fourth inch in diameter. The underdrains lead to an 18-inch outfall sewer, which discharges into Black Fork a few yards away. The filters are used only during the warm months and receive no attention except an occasional weeding. A by-pass provides for the discharge of raw sewage into the outfall sewer, and gates lead from each reservoir to the stream. The whole plant is subject to occasional overflow of high water from Black Fork.

As originally constructed the sludge basins discharged upon the filter beds. Because of rapid clogging the smaller, and later the larger, sedimentation reservoir was constructed, with beneficial effect.

When visited first by the writer in February, 1905, the filter beds were not in use, while on the second visit, in July of the same year, they were both being flooded. They showed every evidence of being badly clogged, the sewage standing over them to a depth of 18 inches. Only about half the sewage passes through the beds in any case, the remainder escaping to the stream by infiltration through the banks or by direct flow from the leaky waste gates of the reservoirs. Black Fork, which passes by the full length of both reservoirs, receives a large part of this waste flow, as is indicated in the stream by a strong discoloration of iron oxide. Indeed, a superabundance of iron oxide is apparent about the whole plant. The filtering material of the filter beds and the banks of beds and reservoirs are heavily coated with it. The sewage flow also is frequently highly discolored, especially as it nears the filter beds. The effluent from the beds is clear and free from suspended matter, but upon standing becomes turbid and receives a reddish cast from precipitation of iron. There is a lack of odor about the plant generally, which is no doubt due to the presence of a great quantity of ferrous sulphate[a] in the sewage. The odor is noticeably greater in summer, however, than in winter. During the warm months a considerable septic action or gasification is apparent in the shallow reservoirs, more especially in the first or smaller one. Much sedimentation takes place in these ponds, and a thin scum and at places a heavy crust is formed upon the surface over a considerable area.

Analyses of sewages at this plant are shown in the table on pages 14 and 15, which is adapted from the Eighteenth Annual Report of the Ohio State Board of Health (1903), pp. 550–552.

[a] "When added to excremental matters, it [ferrous sulphate] absorbs ammonia and other volatile substances and renders the matter almost odorless." Thorpe's Dictionary of Applied Chemistry, vol. 2 (1891), p. 368.

Chemical examination of sewages and effluent from Shelby, Ohio.

[Parts per million.]

BEFORE ACID-IRON WASTES HAD BEEN ADMITTED TO SEWERS. (NORMAL SEWAGE.)

No. of sample.	Description of sample.	Date and hour of collection.	Color.	Turbidity.	Sediment. a	Odor. a	Oxygen required.	Alb. ammonia.	Free ammonia.	Nitrites.	Nitrates.	Chlorine.	Alkalinity.	Incrusting constituents.	Total solids.	Suspended solids.	Loss on ignition.	Iron.
2042	Raw sewage	December 28, 1901, 8 a. m.-7 p. m.	15	73	Con.	3 sew	11.73	1.404	2.740	0.100	0.92	27.8	197	349	1,044			
2045	Raw sewage	December 28-29 1901, 8 p. m.-7 a. m.	16	135	Con.	Oily	28.51	1.608	2.560	.070	.88	22.5	187	332	1,188			
2168	Raw sewage	May 7, 1902, day	37	300	Con.	4 sew	26.11	2.780	3.800	None.	Tr.	27.6	270	210	1,042		275	
2172	Raw sewage	May 7-8, 1902, night	20	98	Con.	4 sew	11.38	1.350	3.930	.056	.35	47.6	252		914		252	
	Average		22	152	Con.	4 sew	19.43	1.786	3.258	.056	.54	31.4	226	297	1,047		264	
2043	Sludge-basin effluent.	December 28, 1901, 8 a. m.-7 p. m.	18	90	Con.	Musty, 1 oily.	13.09	.896	3.520	.076	.88	27.3	197	360	1,035			
2046	Sludge-basin effluent.	December 28-29, 1901, 8 p. m.-7 a. m.	17	73	Con.	Musty, oily.	9.62	.632	2.508	.060	.92	23.5	183	345	928			
2169	Sludge-basin effluent.	May 7, 1902, day	22	20	Dec.	4 sew	5.73	2.260	3.450	.060	.50	25.4	246	208	851		225	
2173	Sludge-basin effluent.	May 7-8, 1902, night	20	16	Dec.	3 sew	8.53	.960	3.370	.052	.50	37.0	252		860		273	
	Average		19	50	Dec.	3 sew	9.24	1.187	3.212	.062	.70	28.3	239	304	918		249	
	Per cent removed.		14	67			52	34	1.4	b 11	b 30	9.9	b 5.8	b .4	12		5.7	
2170	Effluent of small reservoir.	May 7, 1902, day	20	Sl.	Sl.	3 sew	5.41	.750	2.830	.062	.50	29.7	235	198	846		208	
2174	Effluent of small reservoir.	May 7, 1902, night	22	Sl.	Sl.	3 sew	6.22	.780	3.090	.054	.55	28.3	239		832		259	
	Average		21	Sl.	Sl.	3 sew	5.82	.765	2.960	.058	.52	29.0	237	198	839		234	
	Per cent removed.		4.5	75			70	57	9.1	b 3.6	3.7	7.7	b 4.9	33	20		11	
2044	Filter-bed effluent	December 28, 1901, 8 a. m.-7 p. m.	6	Tr.	Tr.	Musty	2.42	.260	2.580	.076	.56	23.7	197	360	960			
2047	Filter-bed effluent	December 28-29, 1901, 8 p. m.-7 a. m.	5	Tr.	Tr.	Musty	3.01	.268	3.100	.032	.64	25.7	183	350	951			

2171	Filter-bed effluent	May 7, 1902, day	19	Tr.	Tr.	1 musty.	3.78	.360	2.800	.060	.40	32.0	230	223	817	......	208	......
2175	Filter-bed effluent	May 7-8, 1902, night	18	Tr.	Tr.	1 musty.	2.90	.336	3.280	.110	.60	29.7	214	......	805	......	246	......
	Average	......	12	Tr.	Tr.	1 musty.	3.03	.308	2.940	.070	.55	27.8	296	311	883	......	227	......
	Per cent removed.	......	45	90	90	80	84	83	9.8	b25	b1.8	11	8.7	b4.7	16	......	14	......
	AFTER ACID-IRON WASTES HAD BEEN DISCHARGED INTO SEWERS FOR SEVERAL MONTHS. (ACID-IRON SEWAGE.)																	
3359	Raw sewage	December 15, 1903, 2 p. m.	......	......	......	......	307	1.890	3.560	.000	0 (?)	......	4,430	......	7,397	173	1,826	100+
3360	Sewage-basin effluent	December 15, 1903, 2 p. m.	......	......	......	......	129	1.700	3.610	Tr.	0 (?)	......	1,456	......	2,558	437	801	100+
	Per cent removed.	......	......	......	......	......	58	11	1.4	......	0	......	c 67	......	65	b 153	56	......
3361	Reservoir effluent	December 15, 1903, 2 p. m.	......	......	......	......	33	1.200	2.150	.024	0 (?)	......	990 acid	......	1,523	224	412	100+
	Per cent removed.	......	......	......	......	......	89	37	40	......	0	......	c 78	......	79	b 29	77	......
3362	Filter-bed effluent	December 15, 1903, 2 p. m.	......	......	......	......	24.8	.300	3.150	.018	0 (?)	......	13 acid	......	1,534	201	309	100+
	Per cent removed.	......	......	......	......	......	91	84	12	......	0	......	c 99.7	......	79	b 16	83	......

[a] Abbreviations: Sl., slight; tr., trace; con., considerable; dec., decided; sew., sewagic. The numbers indicate the intensity of the odor according to the following scale: 0, no odor perceptible; 1, distinct; 2, considerable; 3, decided; 4, strong.

[b] Increase.

[c] Removal of acidity.

The samples of 1901 were taken before either reservoir had been constructed, the effluent of the sludge basin being then passed directly to the filters; the samples of 1902 were taken after the first or smaller settling reservoir had been built, and the samples of 1903 were taken after both reservoirs were in use.

The first part of the table shows a rather dilute sewage, ground water doubtless having access to the long outfall sewer in considerable quantity. The presence of nitrites and nitrates indicates that a supply of oxygen is available, though we have no corroboration of this. The nitrites, nitrates, and relatively high free ammonia indicate putrefaction in the sewers in about the stage one would expect from the somewhat wide separation of city and disposal plant, about three hours being required for the sewage to pass from the city to the plant.

It is of interest to note that the sludge basin, through which the sewage passes in from one-half to three-fourths of an hour, has more effect in reducing the organic matter than any other one feature of the purification plant. By oxygen required the reduction is 52 per cent and by albuminoid ammonia 34 per cent. A reduction of 12 per cent in total solids is accomplished. The larger reduction in oxygen required and the increase in nitrites and nitrates indicate rather vigorous oxidation, presumably accomplished by oxygen dissolved in the sewage.

In the small sedimentation reservoir, which affords one day for settling, anaerobic conditions seem to have been established to some extent. The free oxygen is doubtless used up, and then the nitrites and nitrates are robbed of their oxygen to assist in breaking up the carbonaceous matter. By oxygen required a reduction of 18 per cent and by albuminoid ammonia a reduction of 23 per cent is effected by the reservoir.

The filters accomplish 14 per cent purification by oxygen required and 26 per cent by albuminoid ammonia. The entire plant shows a very good percentage of reduction. The effluent, having a slight musty odor, would seem to be somewhat putrescible, but is not chemically a poor one. It can not be regarded as a source of serious pollution of the stream into which it is discharged, even at lowest flow.

It is worth while to note that, although, owing to the construction of the sedimentation reservoir, the sewage flowing to the filters was in much better condition in 1902 than in 1901, the effluent is decidedly worse. This indicates deterioration of the filters from overwork and neglect.

The latter part of the table, giving the tests of 1903, shows a sewage in which the "acid-iron" conditions are extreme. Iron is present in large quantity and the acidity is very high, probably sufficient to prevent bacterial action. Another characteristic feature is the high value for oxygen required, the figures being practically a measure of the ferrous salts present and affording no information regarding the carbonaceous matter. The very high solids and loss on ignition are also worthy of special notice. The loss on ignition in this case bears scant relation to the organic matter present. The albuminoid and free ammonia tests show a rather small amount of organic matter and a somewhat advanced stage of putrefaction. The diminution in acidity is surprisingly rapid. No doubt some rather complicated reactions, including a circle of reduction and oxidation, take place, the results of which are largely the change from ferrous to ferric salts and the deposition or gaseous escape of sulphur compounds at the expense of the free acid. This determination is borne out by the similar diminution in total solids and oxygen required. The organic matter is reduced but little in the early processes of the disposal plant, but is removed chiefly by the filters.

The effluent is a very good one from a sanitary standpoint, so far as may be judged from the analyses under consideration. The little free acid it contains can not be considered as an objectionable addition to the highly alkaline waters of Black Fork. The high oxygen-absorbing power, however, would tend to produce conditions unsuitable for fish life and the extreme amount of iron would render the stream unsightly and its waters unfit for domestic use.

In the following table will be found analyses of sewage samples taken by the writer in 1905. This set of samples differs from those of 1903 chiefly in the fact that the acid-iron waste is less in the later samples by reason of the installation of a copperas plant at the tube works. Of the determinations in the table, dissolved oxygen, acidity, sulphates, and iron, and the plating of bacteriological samples and preparation of cultures for transplanting were the work of the writer. The remaining work is all that of officials of the laboratory of the Ohio State Board of Health. The following methods of analyses were used: Organic nitrogen, Kjeldahl; free ammonia, distillation; residue in platinum, drying at 100°; chlorine, silver nitrate with potassium chromate; oxygen required, boiling five minutes; acidity, sodium carbonate tablets with methyl orange indicator; sulphates, candle turbidimeter; iron, colorimetric; putrescibility, incubation five days at 37°. Regarding the methods referred to in brief that are not in general use, it may be mentioned that those used for acidity, sulphates, and iron are the field methods of the United States Geological Survey.

This table shows a strong acid-iron sewage with a moderate content of organic matter. The acid-iron element is greater in the night than in the day sewage. Owing to the iron sulphate the sewage is only moderately putrescible by odor upon incubation. The bacterial content is very low, probably one-fourth that of a purely domestic sewage of similar concentration. The effect of the acid is shown in reduction of bacteria from day to night, and more strikingly in reduction of acid-forming bacteria, to which the acidity appears to be specially unfavorable.

Analyses of sewage from the sewage-purification plant at Shelby, Ohio. (Modified sewage.)

[Parts per million.]

Source.	Date, July, 1905.	Organic nitrogen.	Free ammonia.	Residue on evaporation. Total.	Residue on evaporation. Dissolved.	Residue on evaporation. Suspended.	Oxygen required.	Dissolved oxygen.	Acidity, as $CaCO_3$.	Sulphates, as SO_3.	Iron, as Fe.	Putrescibility.	Bacteria per cubic centimeter.	Red colonies per cubic centimeter in lactose litmus agar.	B. coli communis isolated from 1 cubic centimeter culture.
Raw sewage, day	12	2.94	3.50	3,492	3,233	259	130.8	0.0	156	1,980	500	+	(a)	600	.....
Raw sewage, day	13	2.61	3.25	3,142	3,128	14	108.8	0.0	201	....	600	+	325,000	(a)	.....
Average	12-13	.278	3.38	3,317	3,180	136	119.8	0.0	178	1,980	550	+	325,000	600	.....
Raw sewage, night	12-13	2.34	3.00	4,062	3,942	120	38.8	0.0	558	2,210	......	+	350,000	b 0	.....
Raw sewage, night	13-14	2.59	2.66	3,710	3,657	53	121.7	0.0	502	2,390	500	+	200,000	4	.....
Average	12-14	2.46	2.83	3,886	3,800	86	130.2	0.0	530	2,300	500	+	275,000	4	.....
General average	12-14	2.62	3.10	3,602	3,490	112	125.0	0.0	354	2,140	525	+	300,000	302	.....
Reservoir effluent	12-13	1.10	4.00	2,116	2,012	104	66.2	0.0	116	1,730	675	Tr.	2,000	b 0	—
Reservoir effluent	13-14	1.07	3.75	2,569	2,464	105	83.6	0.0	162	1,440	500	Tr.	2,800	40	.....
Average	12-14	1.08	3.88	2,342	2,238	104	74.9	0.0	139	1,580	585	Tr.	2,400	40	—
Per cent removed	....	59.00	c 25	35	....	......	40	......	61	26	......	.....	99.2	......	.....
Filter-bed effluent	12-13	.74	4.00	2,062	1,798	264	46.2	0.0	6	1,310	625	—	2,000	b 0	—
Filter-bed effluent	13-14	1.30	4.00	2,312	2,109	203	58.9	0.0	44	1,310	350	—	1,100	b 0	—
Average	12-14	1.02	4.00	2,187	1,954	234	52.6	0.0	25	1,310	485	—	1,550	b 0	—
Per cent removed	....	61.00	c 29	39	....	......	58	......	93	39	8	100	99.5	100	.....

a Lost, overgrown, or slipped. b In 0.05 cubic centimeter sample. c Increase.

The effluent is, organically, a fair one from a chemical standpoint and is nonputrescible. Bacteriologically it is very good, containing but a small number of bacteria, and these not of the colon family. Its content of iron sulphates, however, makes it unsuitable for addition to any but a very large stream.

It will be observed that the filters take but little part in the purification. From their physical aspect this was to be expected, although the extent of their deterioration is surprising. Their chief value at present seems to be in accomplishing a reduction in acidity and oxygen-absorbing power. The plant accomplishes an organic purification of about 60 per cent and a reduction in mineral matter between 35 and 40 per cent.

The values obtained for suspended solids are subject to variation, owing to a gradual precipitation of iron, especially from the effluent. The absence of dissolved oxygen serves to show more decidedly the avidity for oxygen possessed by ferrous sulphate. The large reduction in sulphates is not unlooked for, but the permanence of the iron is surprising. One would naturally expect the sulphates to be the more persistent.

A comparison of the three sets of analyses and their relative conditions will assist in answering the following questions, which are of general interest in their relation to sewage disposal in those cities where acid-iron liquors are encountered:

1. How does a disposal plant—consisting of sludge basin, large, shallow sedimentation reservoirs, and cinder and gravel filters—affect acid-iron sewage as compared with domestic sewage?
2. How is such a plant affected by these two classes of sewage?
3. Should large quantities of acid-iron liquors be admitted to a sewerage system?
4. Is a copperas-recovery plant of value as a means of preventing the overcharge of sewage with such liquors?

TOTAL SOLIDS.

Reduction in total solids occurs chiefly in the sludge basin and reservoirs, the filters having little or no effect on any of the sewages considered. Such effect of filters as is shown by analyses is less than the sampling error. In sludge basin and reservoirs the per cent of solids removed increases with the increase of solids in the sewage. By far the greater part is removed in the sludge basin, and the ratio of per cent removed by sludge basin to per cent removed by reservoir increases with the increase in solids in the sewage.

Effect of acid-iron wastes, and of such wastes modified by a copperas-recovery plant, upon the efficiency of sewage-purification processes at Shelby, Ohio.

[Parts per million and percentage removed.]

	Oxygen required.		Organic nitrogen.		Albuminoid ammonia.		Free ammonia.		Nitrites.		Nitrates.		Alkalinity.		Total residue.		Loss on ignition.	
	Parts per million.	Per cent.	Parts per million.	Per cent.	Parts per million.	Per cent.	Parts per million.	Per cent.	Parts per million.	Per cent.	Parts per million.	Per cent.	Parts per million.	Per cent.	Parts per million.	Per cent.	Parts per million.	Per cent.
Sludge basin:																		
(a) Normal sewage	10.19	52			0.599	34	0.046	1.4	-0.006	-11	-0.16	-30	- 13	- 6	129	12	15	6
(b) Acid-iron sewage	178.00	58			.190	11	- .050	-1.4	Tr.	- ∞	.00	0	-2,974	- 67	4,839	65	1,025	56
Difference (a-b)	-167.81	- 6			.409	23	.96	2.8	- .006	+	-.16	-30	2,961	61	-4,710	-53	1,010	-50
Sedimentation reservoir:																		
(a) Normal sewage (1 day)	3.42	18			.422	23	.252	8	.004	7	.18	33	2	1	79	8	15	6
(b) Acid-iron sewage (5 days)	96.00	31			.500	26	1.460	41	- .024	- ∞	.00	0	- 466	- 11	1,035	14	389	21
Difference (a-b)	- 92.58	-13			- .078	- 3	-1.218	-33	.028	+	.18	33	468	12	- 956	- 6	- 374	-15
Basin and reservoir combined:																		
(a) Normal sewage	13.61	70			1.021	57	.298	9	- .002	- 4	.02	4	- 11	- 5	208	20	30	11
(b) Acid-iron sewage	274.00	89			.690	37	1.410	40	- .024	- ∞	.00	0	-3.440	- 78	5,874	79	1,414	77
(c) Modified acid-iron sewage	50.10	40	1.54	59			- .780	-25			.00	0	- 215	- 61	1,260	35		
Difference (a-b)	-260.39	-19			.331	20	-1.112	-31	.022	+	.02	4	3,429	73	-5,614	-59	-1,384	-66
Difference (a-c)	- 36.49	30					1.078	34			.02	4	204	55	-1,052	-15		
Difference (b-c)	223.90	49					2.190	65			.00	0	-3,225	- 17	4,612	44		
Filter beds:																		
(a) Normal sewage	2.79	14			.457	26	.020	1	- .012	-21	.03	- 6	31	14	- 44	- 4	7	3
(b) Acid-iron sewage	8.20	3			.900	48	-1.000	-28	.006	- ∞	.00	0	- 977	- 22	- 11	0	103	6
(c) Modified acid-iron sewage	22.30	18	.06	2			- .120	- 4			.00	0	- 114	- 32	155	4		
Difference (a-b)	- 5.41	11			- .443	-22	1.020	29	- .018	-	-.03	- 6	1,008	36	- 3.3	- 4	- 96	- 3
Difference (a-c)	- 19.51	- 4					.140	5			-.03	- 6	145	46	- 199	- 8		
Difference (b-c)	- 14.10	-15					- .880	-24			.00	0	- 863	10	- 166	- 4		
Entire plant:																		
(a) Normal sewage	16.40	84			1.478	83	.318	10	- .014	-25	-.01	- 2	20	9	164	16	37	14
(b) Acid-iron sewage	282.20	92			1.590	84	.410	12	- .018	- ∞	.00	0	-4,417	-100	5,863	79	1,517	83
(c) Modified acid-iron sewage	72.40	58	1.60	61			- .900	-29			.00	0	- 329	- 93	1,415	39		
Difference (a-b)	-265.80	- 8			- .112	- 1	- .092	- 2	.004	+	-.01	- 2	4,437	109	-5,699	-63	-1,480	-69
Difference (a-c)	- 56.00	26					1.218	39			-.01	- 2	349	102	-1,251	-23		
Difference (b-c)	209.80	34					1.310	41			-.01	0	-4,088	- 7	4,448	40		

The removal of solids in the acid-iron sewage occurs probably in greatest measure as sedimentation of certain compounds after chemical change by reduction, oxidation, and substitution. Next comes the influence of water of crystallization. Total residue, as determined upon the water bath, includes water of crystallization for both ferrous and ferric sulphates. Oxidation from the ferrous to ferric sulphate is accompanied by a loss of 36 per cent of such water, which is, of course, thus lost to the total residue determination. It seems probable that about three-fourths of the reduction in solids can be attributed to sedimentation, nearly all the remainder to change from ferrous to ferric compounds, and a little residue to the escape of volatile compounds.

The effect upon the plant of the increased deposition of solid matter after the acid-iron waste has been introduced will be rapid loss of efficiency of sludge basin, which can be prevented only by frequent cleaning. The same effect will appear in the sedimentation reservoirs to a lesser extent, particularly with "modified" sewage. Furthermore, the fact that reduction by filters is so much greater for "modified" sewage indicates a less complete purification in the preceding processes, and consequent crowding of filters, to their detriment.

The copperas plant appears to effect about 60 per cent reduction in the solids in the raw sewage, due to the acid-iron liquors.

LOSS ON IGNITION.

For this determination we have comparison only on normal and acid-iron sewages. The ratio of loss on ignition to total residue is nearly the same in both cases, being slightly less for the acid-iron sewage. Loss on ignition for the acid-iron sewage would appear to be due largely to breaking up of water of crystallization. The variation of the ratio of loss on ignition to solids and its decrease by oxidation of ferrous salts therefore affords a means of rough comparison of oxidation and sedimentation in the purification processes. Sedimentation seems to be the greater force in the sludge basin, but is unable to keep pace with oxidation in reservoirs and filters. In other words, the combined forces tending to a reduction of solids act more vigorously in the sludge basin and less vigorously in the reservoirs and filters than does the single force of oxidation. The variation is not, however, extensive.

OXYGEN REQUIRED.

This determination means two different things with the different classes of sewage. With normal sewage it may be taken as an approximate proportional measure of the carbonaceous material. With acid-iron and modified sewages it measures the ferrous salts also, and these are so abundant, the carbonaceous matter being comparatively insignificant, that its value as a measure of organic matter is nil. For the latter classes of sewage therefore the oxygen required may be assumed with but little error to be a measure of ferrous salts present in the sewage. Loss in oxygen required will therefore be proportional to decrease of ferrous salts. Decrease of ferrous salts probably occurs in this case in two ways—(1) by reduction of ferrous sulphate to iron sulphide and sedimentation of the iron sulphide, and (2) by oxidation of ferrous to ferric sulphate. Just what changes take place we have not sufficient data to determine, but it seems probable that at Shelby the former is the more prominent reaction in the sludge basin and the latter predominates in reservoirs and filters. This conclusion is borne out by the fact that the ratio of loss on ignition and of oxygen required to total solids increases from raw sewage to sludge basin effluent and decreases thereafter.

The ratio of loss on ignition to oxygen required for acid-iron sewage is practically constant in sludge basin and filters, but undergoes a slight increase in the reservoirs. This is in marked contrast to the variation in the similar ratio for normal sewage, which undergoes rapid increase as the sewage passes through the works. This ratio offers the most distinctive difference in the action of the purification processes upon the two sewages.

ALBUMINOID AMMONIA AND ORGANIC NITROGEN.

Albuminoid ammonia for normal and acid-iron sewages and organic nitrogen for modified sewage are the only determinations from which may be gathered the comparison of effect of plant upon the organic matter of the sewages considered. The sludge basin appears to cause three times as much reduction in organic matter for normal as for acid-iron sewage; the reservoirs seem to have about the same effect upon the two, while the filters offset the effect of the sludge basin, making the effluents of about equal purity. Although the organic nitrogen of modified sewage should not be directly compared with the albuminoid ammonia of normal and acid-iron sewage, a general consideration of these determinations would seem to indicate equally as good reduction for modified as for normal sewage in sludge basin and reservoirs, but practically no reduction is secured by the filters on modified sewage. From the condition of the filters this last result was to be expected.

It may safely be said that the introduction of acid-iron wastes interferes with the reduction of organic matter in sludge basin and reservoirs, and thus tends to crowd work upon the filters. The effect upon the plant will be a more rapid decrease of efficiency than would otherwise be the case. The copperas plant is beneficial in alleviating these conditions, apparently to a very great extent.

FREE AMMONIA.

This determination shows wide variation under the different conditions. With normal sewage there is a slight but persistent decrease in free ammonia in all the purification processes, the greatest decrease being found in the reservoirs. With the strong acid-iron sewage there is a slight increase in the sludge basin, a very great decrease in the sedimentation reservoirs, and, finally, a great increase in the filters. It appears as though the saline nitrogen in sludge basin and filters is held in the sewage, while the reservoirs allow a very considerable escape of nitrogen gases. With the modified sewage there is a steady increase in free ammonia throughout the plant. Evidently the absorbing power of iron sulphate and the combining power of the free acid in acid-iron sewages tend to hold in the sewage the nitrogen or nitrogenous compounds, but under favorable conditions these volatile substances may escape to a greater or less extent.

NITRITES AND NITRATES.

The addition of acid-iron waste to the sewage very largely diminishes the nitrites and causes the nitrates to disappear entirely in all the sewages examined. This action is doubtless due to the reducing qualities of the iron sulphate and bears no relation to organic purification.

ALKALINITY.

The alkalinity of normal sewage is affected but little by the purification processes. The acid-iron sewage, on the other hand, with its high acidity, undergoes great change and is practically neutralized by the action of the disposal plant. Most interesting is the reduction of acidity by the filters. Apparently they provide conditions specially favorable for change from ferrous to ferric sulphate, and the free acid is thus used up. The effect of the acid upon the plant is to interfere seriously with bacterial action and in so doing to destroy in great measure the pathogenic quality of the sewage.

SUMMARY.

1. Introduction of acid-iron waste into domestic sewage (*a*) largely increases its total solids, loss on ignition, iron, sulphates, and oxygen required, causes the disappearance of nitrites and nitrates, and changes it to a highly acid liquid; (*b*) reduces the effect of the sludge basin upon organic matter, and tends toward a rapid deterioration of every part of the sewage-disposal plant; (*c*) interferes with bacterial action, but in so doing lessens the harmful quality of sewage; (*d*) reduces obnoxious odors from the sewage and reduces its putrescibility by absorption of gases; (*e*) renders the effluent of the sewage-

purification works unfit to enter any but a very large stream because of its content of iron sulphates.

2. A sewage-disposal plant consisting of sludge basin, five-day sedimentation reservoirs, and cinder and gravel filter beds (*a*) removes organic matter from highly acid-iron sewage as completely as from domestic sewage; (*b*) affords less freedom from free or saline ammonia when treating acid-iron sewage; (*c*) accomplishes greater reduction but affords a worse effluent as regards oxygen required when treating acid-iron sewage; (*d*) renders extremely acid sewage nearly neutral but affects the alkalinity of domestic sewage very little; (*e*) affords an effluent with one-fourth the quantity of nitrites in acid-iron as in domestic sewage, but with no nitrates or dissolved oxygen in acid-iron sewage; (*f*) may reduce total solids as much as 79 per cent in acid-iron sewage, while domestic sewage is reduced not more than 20 per cent; (*g*) reduces sulphates in same proportion as total solids but affords only slight decrease in iron content of acid-iron sewage; (*h*) lessens the number of bacteria in acid-iron sewage by 99.5 per cent and frees it from *B. coli communis* and other acid-producing bacteria.

3. The installation of a copperas plant recovering 20 to 25 per cent of the acid used in pickling, such plant treating the wastes before they enter the sewers, reduces the harmful effects of acid-iron sewage upon such a disposal plant by about 60 per cent, and in consequence reduces in like proportion the attention requisite for proper maintenance of the plant. The copperas plant, however, will not take the place of attention to the sewage processes; a better effluent may be obtained with an extremely concentrated acid-iron sewage and careful attention than with a 60 per cent better sewage without the attention.

In connection with these conclusions, based upon meager and fragmentary data, it will be of especial interest to review the conclusions of Kinnicutt and Eddy, based upon two years' constant work upon Worcester sewage. This sewage is about 4⅓ times as strong, organically, as the sewage here considered, but contains only 10 per cent as much solid matter and 4 per cent as much free acid as what is here designated "acid-iron" sewage, and 22 per cent as much solid matter, 24 per cent as much iron, and 50 per cent as much free acid as what is here termed "modified" sewage. The results of Kinnicutt and Eddy's work, quoted below, from pages 44 and 45 of the Fourth Report of the Connecticut Sewerage Commission, 1902, are based upon observations of the slow passage of such sewage through a closed septic tank. From this summary of results it appears—

That about one-fourth of the total solid matter contained in the sewage will be removed.

That the effluent from the tank will contain about 20 per cent less soluble matter than the crude sewage, owing to the soluble matter in the sewage being decomposed or changed into insoluble substances.

That the amount of suspended matter removed from the sewage will not greatly exceed 30 per cent unless special precautions are taken to retain in the tank the finely divided iron sulphide formed by the reduction of the soluble iron sulphate in the sewage.

That the amount of organic matter removed from the sewage as determined from the albuminoid ammonia will average from 20 to 25 per cent.

That of the suspended organic matter the amount removed will average a little under 50 per cent, and that the amount of soluble organic matter removed will not average much more than 10 per cent of the soluble organic matter in the sewage.

That of the suspended matter taken out of the sewage in its passage through the tank, from 60 to 70 per cent will remain in the tank and have to be removed; only from 30 to 40 per cent of the arrested suspended matter being changed by the action of the bacteria into soluble or gaseous substances

That the amount of sludge that will have to be handled when it is necessary to clean out the tank will not, however, equal 60 or 70 per cent of the weight of the sludge that would be formed from the removal of the same amount of suspended matter in a sedimentation tank, but will not be more than 50 per cent of this amount, owing to the fact that the sludge in a septic tank contains less water than the sludge in a sedimentation tank.

That with an acid-iron sewage containing street washings the amount of mineral matter in the sludge will be about 50 per cent of the total solid matter in the sludge, and of this mineral matter over one-third will be found to be iron sulphide

That decomposition of the sludge, as shown by the evolution of gas, will take place in winter as well as in summer if the temperature of the sewage in the tank does not fall below 45° Fahrenheit, but the rate of decomposition will be much slower, one-half of what it is in summer.

That the amount of gas evolved from the septic tank with a sewage similar to Worcester sewage and having about the same range temperature as Worcester sewage, will average a little over one-half a cubic foot for every 100 gallons of sewage passed through the tank, the rate of flow of the sewage through the tank being eighteen hours. In the warmest months the amount evolved will, however, be about 1 cubic foot; in the coldest months about one-fourth of a cubic foot.

That the gas given off from a septic tank with acid-iron sewage does not contain hydrogen or sulphide of hydrogen, but a mixture of marsh gas, carbon dioxide, and nitrogen, in about the following proportions: Marsh gas, 75 per cent; carbon dioxide, 6 per cent; nitrogen, 19 per cent.

PRESENT CONDITIONS ALONG THE STREAM.

In July, 1905, an investigation was made of conditions along Black Fork for 7 miles below Shelby. Pollution by acid-iron wastes was easily apparent at two points. The first is at the mouth of the small stream (Red Brook) which passes by the tube works. This stream obviously receives acid-iron liquors, presumably the wastes from the pickling tubs and the copperas plant hereinafter described. The waters are highly colored with iron, and numbers of small dead minnows were found below the tube works. Lack of oxygen in the water was the apparent cause of their death, the fish coming to the surface gasping for breath and finally giving up the struggle, floating downstream belly upward. A short distance below the tube works this stream empties into Black Fork and gives its waters a high iron discoloration. For a few hundred yards below this point Black Fork is shallow and its current rapid. Then follow a succession of deep pools of slowly moving water. These conditions are ideal for the oxidation and sedimentation of the iron. Consequently, more than three-quarters of a mile below the tube works no discoloration is noticeable.

The extent of the pollution is shown roughly by the following table:

Effect of tube works effluent upon Red Brook.

[Observations made July 13, 1905; in parts per million.]

Location.	Iron as Fe.	Sulphuric acid as SO_3.	Alkalinity as $CaCO_3$.	Dissolved oxygen.	Period.
One-half mile above tube works	3.0	120	180	5.6	
One-fourth mile below tube works, one-fourth hourly composite	32.5	285	190	0.0	64.5 a. m. to 8.30 a. m.
Do	40.0	285	190	0.0	8.45 a. m. to 10.30 a. m.
Do	180.0	640	74	0.0	10.45 a. m. to 12.30 p. m.
Do	20.0	355	47	0.0	12.45 p. m. to 2.30 p. m.
Do	10.0	355	78	0.0	2.45 p. m. to 4.30 p. m.
Do	25.0	355	89	0.0	4.45 p. m. to 6.30 p. m.
Average below tube works	51.2	380	111	0.0	6.45 a. m. to 6.30 p. m.

The samples analyzed were made up of equal quantities taken from the stream every fifteen minutes during the two-hour periods shown by the table. The absence of dissolved oxygen in the stream is a point worthy of special notice and indicates the cause of the death of fish. The other determinations show that the polluting liquor contains large quantities of iron sulphates, but little, if any, free acid. At no time during the day was any free acid found in the stream waters, though their alkalinity was considerably decreased. This decrease could be accounted for by the reaction of the iron sulphates with the alkaline carbonates of the stream waters, though it is probable that a little free acid in the waste discharged is the chief contributing factor. A discharge of an increased amount of waste liquor evidently took place just before noon. Barring accidental cause, this circumstance would indicate that the pollution is to a considerable extent under control and not wholly due to uncontrolled leakage. It is estimated that the stream has a flow of about 40,000 gallons per hour. During the working day, therefore, apparently about 1,000 pounds of SO_3 are discharged into the stream at the tube works. Assuming a normal condition at the plant, this amount could come only from liquors wasted at the pickling tubs.

The second point of pollution by iron liquors is at the city sewage farm, 3 miles below Shelby. Beginning on the morning of July 12, a forty-eight-hour test of the efficiency of the sewage-disposal plant was made, samples being taken every hour during that time. The average content of the effluent, in parts per million, for this period is as follows:

Content of effluent of sewage-disposal plant 3 miles below Shelby, Ohio.

Iron as Fe	485
Sulphuric acid as SO_3	1,310
Acidity as $CaCO_3$	25
Dissolved oxygen	0

Rough measurements of the sewage flow show that it was approximately 275,000 gallons a day. Apparently about half of this amount passes out through the effluent pipe, the remainder leaking to the stream from the sedimentation basins. Both effluent and leakage turn the stream waters red, from precipitated iron.

To determine the persistency of the effects of the polluting effluents samples from Black Fork were analyzed at suitable distances below Shelby. The results of these analyses and also of analyses of the polluting liquors are shown in the accompanying table:

Analyses of water of Black Fork and Red Brook near Shelby, Ohio.

[Parts per million.]

	Iron as Fe.	Sulphuric acid as SO_3.	Alkalinity as $CaCO_3$.	Dissolved oxygen.	Date (July, 1905).	Remarks.
Red Brook ¼ mile below tube works.	51.2	380	111	0.0	13	Average of samples taken every 15 minutes from 6.30 a. m. to 6.30 p. m.
Black Fork above mouth of Red Brook.	3.0	70	190	6.4	13	
Black Fork ½ mile below Red Brook; Smiley street.	3.5	140	190	6.4	13	
Black Fork 1¼ miles below mouth of Red Brook; State street.	3.0	120	170	6.4	13	
Effluent of sewage farm	485.0	1,310	*a* 25	0.0	12-13	
Black Fork opposite sewage farm, 3 miles below mouth of Red Brook.	4.0	120	160	6.2	12	100 yards above entrance of effluent.
Black Fork 4 miles below mouth of Red Brook; ½ mile northwest of London.	14.0	320	100	2.6	14	1 mile below sewage farm.
Black Fork 5¾ miles below mouth of Red Brook; Isaac Adams farm.	2.8	185	130	6.3	14	2¾ miles below sewage farm.
Black Fork 7 miles below mouth of Red Brook.	2.0	145	150	6.6	14	4 miles below sewage farm.

a Acidity as $CaCO_3$.

It will be noticed that the iron precipitates out very rapidly. One-half mile below the entrance of the small stream it has decreased to within one-half part per million of the iron content of the Black Fork above the point of pollution. At the next sampling point, three-fourths of a mile farther down, it is normal, or, in other words, no pollution by iron can be detected. Opposite the sewage farm the leakage from the sedimentation basins causes a slight increase in iron content, while a mile below the farm an abnormal amount of iron was found. At this point the stream was highly colored by iron sesquioxide. Again, however, the iron quickly precipitates and becomes less 2¾ miles below the sewage farm than it is above Shelby.

This decrease in iron content continues, so that 4 miles below the farm the stream contains one-third less iron than above Shelby.

The influence upon the dissolved oxygen, as would be expected, is in inverse ratio to the influence upon iron content, and the result of this determination corroborates the results previously discussed. In a word, the polluting iron liquor rapidly takes up the oxygen in the stream and is itself precipitated thereby. Judging from the low content of oxygen a mile below the sewage farm, it is evident that the conditions for this distance are adverse to fish life and may cause the death of small fish.

Another effect we would expect would be decreased alkalinity and an increased sulphate content. Reaction of the iron sulphates with the carbonates of the alkaline earths would eventually result in the production of iron oxide, carbonic acid gas, calcium sulphate, and magnesium sulphate. The iron oxide and excess of alkaline earth sulphates would precipitate and the gas would escape. The effect upon the stream, therefore, would be to give it, compared with other streams of this locality, an abnormally high content of incrusting sulphates, or permanent hardness, and a comparatively low alkalinity, or temporary hardness. That such reaction actually occurs is shown by the analyses made.

The effects of pollution by acid-iron wastes at Shelby may therefore be summed up as follows:

1. From the points of pollution to a point varying from one-half mile to $1\frac{1}{2}$ miles below, the natural condition of the stream waters is seriously impaired for general use and detrimental to fish life.

2. Beyond this point no effect can be noticed aside from an increase in permanent hardness and a decrease in temporary hardness of the waters. Such effect is not prejudicial to animal or vegetable life, but damages the value of the water for use in boilers and to a less extent for domestic purposes.

RECOVERY OF COPPERAS FROM ACID-IRON WASTES.

Before entering upon a discussion of the merits of a copperas-recovery plant as a means of disposing of acid-iron wastes, it will be advisable to describe the process which produces such liquors and to show in some detail their characteristic mineral content.

THE PICKLING PROCESS.

To clean iron and steel from rust and scale it is immersed in a solution of acid in tubs or vats of shape and dimensions suitable to accommodate the material to be pickled. In tube works the pickling tubs are naturally long and narrow to accommodate the sections of tubing. In such works the material is pickled before annealing, in order that this process may have most uniform and perfect results. Moreover, one of the last steps in manufacture is the passage of finished tubing through the pickling baths, after which it is rinsed and oiled, so that it may be shipped in perfect condition. Much of such material is used in boilers and in other places where it is of the utmost importance that rust should be prevented; hence the special precautions. In tin-plate, galvanizing, and other work where iron is coated with another substance, it is necessary that the iron should be clean and free from rust in order that the coating may properly adhere. It is therefore pickled and rinsed before coating. In such works it is frequently customary to pass the material through more than one bath to produce the desired perfection of surface.

The acids used for pickling are commercial grades of hydrochloric and sulphuric acid. Until sulphuric acid was cheaply produced hydrochloric was used almost exclusively, but, except for special classes of work in which hydrochloric acid gives better results, it has now largely been superseded by sulphuric acid, a 60° grade (about 78 per cent pure) being in most general use. The strength of solution varies somewhat with the work to be done. The best solvent for the sesquioxide of iron is a solution consisting of 8 parts of sulphuric acid and 3 parts of water. A much weaker liquor is used in pickling, however, a 10 per cent solution of the 60° acid being a common strength for making up the fresh pickling bath.

Circulation is a primary requisite of good pickling. Were the material allowed to lie in a heap in the acid, some parts would be more thoroughly cleaned than others, the surface would become pitted, and the material would be seriously damaged in value. To avoid such results a rapid circulation of the liquid or a movement of the material pickled is necessary. This is customarily accomplished by machinery which automatically alternately thrusts the material into and draws it from the bath or which forces the liquid around the material by a plunger. The pickling solution is kept at a temperature ranging from 140° F. to a little more than 212° F. in order to increase the activity of the acid. This is usually done by forcing steam into the bath from open pipes.

At the Shelby Steel Tube Works circulation and heating are accomplished by closed steam pipes of acid-proof material laid in the bottom of each tub. The liquor is thus heated to a state of violent ebullition and an eminently satisfactory circulation obtained and very rapid and thorough pickling made possible.

As previously stated, the fresh pickling bath contains about 10 per cent of acid. As the process of pickling continues, the per cent of acid becomes less and less because of the combination of acid with iron to form iron sulphates. More acid is therefore added in a continuous stream or by charges in order to keep the bath working actively. Finally, when the liquor contains about 15 per cent of iron sulphates and 2 per cent of acid it is discarded as useless and is generally discharged into the most convenient stream.

This forms waste 1, the first waste from the process. It is to be noted that the waste liquor or "spent pickle" from any one plant will be of fairly uniform consistency and is disposed of in charges, usually once or twice a day.

After pickling, the iron or steel material is passed through a rinse tub in order to free it from an excess of acid. Were it not rinsed the acid would continue to eat the material and would soon coat it with rust. The rinse tubs are usually similar to the pickling tubs in size and shape. A continuous stream of water passes through them, the discharge pipe leading to sewer or stream. This rinse water, of course, takes up a considerable quantity of iron and acid from the material pickled. It forms waste 2, the second waste from the process.

After it is rinsed the material to be coated is passed directly through the galvanizing, tinning, or other coating process, or it may first be subjected to a bath in very dilute hydrochloric acid to give a still better surface for coating. The waste from this last bath is usually inconsiderable in comparison with the others and passes out with the rinse water, waste 2. In the tube works, after pickling, the tubing is oiled in "dope" tubs similar to the pickling tubs. This process gives a little waste oil, which passes out with waste 2, but is not sufficient in quantity to merit special notice.

CHARACTER OF LIQUORS AT SHELBY.

In March, 1905, the writer visited the pickling plant at the Shelby Steel Tube Company and had samples of the various liquors collected. These samples were taken, and quantities of liquors, etc., were estimated or taken from the records of the company, by its employees. They can not, therefore, be vouched for by the writer. This is especially to be regretted, since later investigations upon stream and sewage show the presence of very much more acid-iron waste than the figures on wastes obtained from the company would lead one to expect. The officials of the company, however, appeared to be acting in good faith. Because of a disagreement between figures given for acid used and compounds of acid in wastes 1 and 2, corroborated by the writer's personal investigations in another pickling plant, it is believed that there is a large amount of drainage from pickled material and leakage from tubs, vats, etc., which passes out with these wastes, but is not taken into account in the measurements and does not influence the character of the samples taken. The writer therefore accepts without question all the figures furnished by the company. It is obvious, however, that in any plan to prevent stream pollution, such drainage and leakage should be carefully collected and treated with waste 1 instead of being allowed to combine with waste 2, as it undoubtedly does in most plants. Being an unknown quantity, except from inference, it is not further considered in this report.

The following table shows the results of analyses made of samples collected March 29, 1905:

Results of analyses of pickling-process liquors.

[Parts per million.]

	Shelby city water influent to rinse tubs.	Effluent of rinse tubs.	Pickling liquor at end of first day.	Pickling liquor at end of second day.
Sample number	28	29	30	31
Acidity (H_2SO_4)	[a] 226	260	110,600	26,700
Sulphuric acid as SO_3	302	2,184	158,700	100,400
Iron as Fe	036	1,388	50,400	57,300
Gallons per day	9,550	9,550	1,230	1,230

[a] Alkalinity in terms of H_2SO_4.

Samples 28 and 29, being from continuous flows, are hourly composite samples, showing average composition for the working day. It is the custom to begin each day with three tubs of fresh pickling solution. At the end of the day these still contain active acid. They are retained, therefore, and used the following day for pickling the rougher material. At the end of the second day they are emptied. Each day, therefore, three tubs are filled and three emptied, six tubs being used in all.

Sample 30 is composed of equal parts from tubs filled on the morning of March 29, and sample 31 of equal parts from tubs filled the previous day. Both samples were taken after the pickling for March 29 had been completed. Sample 31, therefore, is "spent pickle," to be emptied from the tubs, and may be taken as the residual liquor from one day's pickling, really representing the heavy work of March 28 and the light work of March 29 combined.

Sample 30 is the residual liquor from the heavy work of March 29 and was used for the light work on March 30 for further neutralization of the acid.

On March 28, 6,300 pounds of 60° sulphuric acid were used in pickling, and on March 29 the amount required was 6,400 pounds. We may take, therefore, 6,350 pounds of acid as the quantity affecting the analyses shown in the table. This amount of 60° acid contains an equivalent of 4,030 pounds of SO_3.

From the report of the sulphuric acid industry appearing in the Twelfth United States Census, the average value of 60° acid is $14.47 per ton, or $22.75 per ton of SO_3 content.

RINSE WATER.

At Shelby the rinse water is now discharged into the sewers. A comparison of results on samples 28 and 29 shows that the 9,550 gallons of rinse water received from the material rinsed 150 pounds SO_3.

Of the SO_3 thus lost little is in the free state, that which has not already combined with the iron or has not been neutralized by the alkaline water being only a small portion of the whole. This loss represents 5.7 per cent of the acid used, or $1.34 a day. The solution is made too dilute to admit of economical recovery of any compound it contains. Its effect upon the sewage is of interest. Let us assume that the sewage would have, normally, the same iron content and alkalinity as the city water (sample No. 28 in table). The flow of sewage during the working day is about 150,000 gallons, say 15 times the amount of rinse water. The alkalinity would therefore be decreased by about one-sixteenth the acidity of the rinse water, or 16 parts per million, leaving it with an alkalinity of 210 parts per million, approximately. This effect is inconsiderable. The iron content would be increased by one-sixteenth the iron content of the rinse water, or 87 parts per million. There is no reason to suppose that this amount would affect injuriously the operation of the sewage-disposal works.

It appears, therefore, that the rinse water might safely be added to the city sewage without fear of nuisance. While it is far too dilute for the economical recovery of iron or acid in any form, the iron might readily be reduced to an insignificant amount by precipitation before it is allowed to enter the city sewers. This could best be done, theoretically, by the use, daily, of 100 pounds of NH_3 in the form of ammonia water, a small basin being provided for sedimentation. Satisfactory results could also be obtained by the use of 165 pounds CaO in the form of lime water. The cost would approximate 65 cents a day for precipitant. The precipitated lime and iron would be of some value to paint manufacturers.

SPENT PICKLING LIQUOR.

In the 1,230 gallons of pickling liquor discarded at the close of the day, 1,230 pounds of SO_3 are found, representing a value of $14 in acid used. This exists chiefly as ferrous sulphate, some ferric sulphate and about 2.5 per cent of free sulphuric acid being also present.

About 2,650 pounds of SO_3, or nearly two-thirds (more exactly, 65.8 per cent) of the active principle in the acid used, is lost in the pickling tubs. Although a part of this passes off as fumes, it is presumed that nearly all this loss is due to splashing and leakage from the tubs and drainage from the pickled material, and that most of the lost pickling liquor passes to the sewer together with the effluent of the rinse tubs. The spent pickling liquor discarded at the close of each working day is at the present time passed through a copperas-recovery plant.

COPPERAS PLANT AT SHELBY.

With the twofold idea of preventing the discharge of the liquor into the stream and, if possible, of adding to the economy of pickling operations, a plant for the recovery of copperas from spent pickle was installed during August, 1904, at the works of the Shelby Steel Tube Company.

This plant is exceedingly simple in construction and operation. The spent pickle is drained by gravity into a lead-lined wooden receiving or storage tank of rectangular cross section, having a capacity of about 6,000 gallons—sufficient to accommodate the spent pickle from four days' work. From the storage tank the liquor is drawn by charges into an evaporator for concentration. The evaporator is a wooden tub of rectangular plan and trapezoidal elevation having a capacity of a little more than 2,000 gallons. The tub is lined with one-eighth inch lead and heated by a steam coil. It is provided with a wooden hood and a draft for carrying off the vapor. A much more economical evaporator, though more expensive in first cost, could be used.

Iron or steel turnings are introduced into the evaporator to neutralize the free acid and to reduce ferric to ferrous sulphate. The liquor is concentrated to about 45° Baumé (sp. gr. 1.453; Twaddell, 90.6°) and then drawn off into wooden crystallization tubs. These tubs are rectangular in cross section and have a capacity of about 675 gallons each. To assist in the crystallization and to provide a support for the crystals, wooden strips are hung in the tubs. The dependent crystals are gathered, drained, and barreled for shipping. The mother liquor, together with the more impure crystalline copperas from the sides and bottom of the tubs, is pumped back by hand to the storage tank or the evaporator. Occasionally such matter is discharged into the stream with wash water from the tubs to dispose of accumulated impurities.

In the original plant three crystallization tubs were used, but three more were added in the summer of 1905, making six in all.

Analysis of the crystals produced gave the following results in per cent: Acidity as H_2SO_4, 0.2; sulphuric acid as SO_3, 27.5; iron as Fe, 18.9. This approximates the formula $FeSO_4.7H_2O$ for ferrous sulphate crystals, but indicates the presence of small amounts of ferric sulphate and free acid.

Average figures for several months show that the copperas produced is, by weight, 50 per cent of the acid used in pickling. For the 6,350 pounds of acid used (average of March 28 and 29), therefore, a product of 3,175 pounds of copperas would be obtained, having a content of 875 pounds SO_3. This is 21.7 per cent of the SO_3 in the acid used for pickling, or 71.1 per cent of the SO_3 in the spent pickle.

There is therefore a loss—presumably taking place by leakage in the evaporator, storage tank, and crystallization tubs—of 8.8 per cent of the active principle of the acid used for pickling, or 28.9 per cent of the amount of such principle present in the spent pickle.

The estimated disposal of the SO_3, assuming an average daily use of 5,000 pounds of acid, may be summed up as follows:

Losses and recovery of sulphuric acid at Shelby Steel Tube Company.

	Per cent.	Pounds per day.		Value as 60° acid.
		Acid.	SO_3.	
Loss in rinse water	3.7	185	144	$1.34
Loss in pickling tubs	65.8	3,290	2,566	23.80
Loss in copperas plant	8.8	440	343	3.18
Recovered in copperas	21.7	1,085	847	7.85
Total	100.0	5,000	3,900	36.17

Original estimates on cost of recovery per ton of product were as follows:

Coal, at $2.25 per ton	$1.08
Iron turnings, at $13 per ton	.89
Barrels, etc., for shipping	1.90
Total	3.87

It is thought that $2 will more nearly approximate the actual cost of fuel for evaporation with the evaporator used, although, owing to the complication of heating arrangements, no exact figures are obtainable.

Accepting the other items as correct and adding $1 per ton for labor and $0.50 per ton as a 10 per cent annual depreciation upon a plant valued at $2,000, we have, for the production of one ton of copperas, the following figures:

Average value of copperas (Twelfth U. S. Census)		$9.64
Fuel, at $2.25 per ton	$2.00	
Iron turnings, at $13 per ton	.89	
Miscellaneous supplies	1.90	
Depreciation	.50	
Labor	1.00	
		6.29
Profit		3.35

This is a very liberal estimate of costs, and will, without doubt, be sufficient to more than cover the actual conditions at Shelby. Were the plant arranged to save the liquor now lost and a better evaporator used, a much better showing could be made. It must be considered that the advantageous arrangement of the plant for gravity flow contributes in some measure to the low cost of the product. Were pumping required, the cost would not in any case be more than $6.64 per ton, leaving $3 per ton as a low estimate of profit under extremely adverse conditions.

With a capital of $2,500 and a yearly product of 400 tons of copperas, the foregoing figures would show an annual profit of $1,340, or 53.6 per cent upon the capital invested. The margin of profit, with the present price of copperas, is large enough to permit the application of the method to any plant of size sufficient to create a nuisance by stream pollution.

OTHER PROCESSES FOR DISPOSAL OF PICKLING LIQUOR.

Several other processes for the disposal of sulphuric-acid pickle have been tried experimentally and a few have been applied on a commercial scale. The most prominent of these and their results are tabulated below:

Process.	Result.
Electrolytic regeneration of acid	Expensive.
Recovery of basic ferric sulphate and acid by aeration	Expensive.
Recovery of "sugar copperas"	Practicable.
Chemical precipitation	Expensive.

So far as known, recovery of copperas in large crystals and as "sugar copperas" are the only processes that will pay for the cost of disposal of the spent pickle from sulphuric acid.

For spent pickle from hydrochloric acid containing iron chlorides a cycle of regeneration has been perfected in England by Thomas Turner. The method is described at some length by Naylor in Trades Waste, pages 262–263. In brief, the pickle is fed into a reverberating furnace; iron oxide is retained and hydrochloric acid passes over with the fire products and is condensed in ordinary muriatic towers. The cost of 75 per cent acid recovered is stated at about $2. In this country it would doubtless be somewhat higher.

SUMMARY.

The investigations at Shelby, Ohio, have brought out the following points:

1. Stream pollution by acid-iron wastes has been taking place at Shelby for about fifteen years, to the annoyance of riparian residents below the city for a distance of 12 miles. Complaints against this pollution (which may be defined as the entire waste of pickling liquors in which one pound of 60° sulphuric acid is used to each 175 gallons per second of dry-weather flow in the stream) culminated in 1901 in a series of suits against the corporation responsible for the pollution, resulting in awards of damages in favor of residents along the stream living from 3 to 7 miles below the point of pollution.

2. Conditions along the stream were greatly bettered by the passage of the waste through the city sewage-purification works (consisting of a sludge basin, shallow five-day sedimentation reservoirs, and shallow cinder and gravel filters), diluted by from 10 to 20 times its volume of a weak domestic sewage.

3. The effect of the acid-iron sewage upon the sewage purification plant was to fill basin and reservoirs rapidly and thus decrease their efficiency, to destroy the working value of the filter beds in a comparatively short time, and to increase great y the care requisite for the proper maintenance of the plant. Bacterial action was seriously interfered with, the action of the early processes of the plant upon organic matter was diminished, and the effluent was rendered obnoxious by reason of a high content of iron sulphate. Odors about the plant and danger. from pathogenic bacteria in the effluent were decreased by the acid-iron character of the sewage.

4. The treatment of pickling waste in a plant for the production of crystal copperas, one-fifth of the acid used being so recovered, reduces the objectionable features of the sewage by about 60 per cent, and is therefore of great value as a means of preventing stream pollution by such wastes.

The copperas-recovery process is the best method known for treatment of sulphuric-acid pickling liquors, is attended with a large per cent of profit, and is applicable to pickling plants of all sizes. Such a plant, properly arranged, will entirely obviate stream pollution by "waste pickle."

5. Rinse water from the pickling process, not including leakage and splashage from the pickling tubs, can, in general, be discharged into the sewerage system of a town or into a stream without detrimental consequences, but it will produce a discoloration of the water unless the dilution is very great. Although such waste does not seriously affect the uses of a stream, it may be rendered entirely unobjectionable at a trifling cost by precipitation with lime or ammonia, and such treatment is advised.

6. Of the acid used in pickling at Shelby, only 21.7 per cent is recovered in the copperas product. Of the remaining 78.3 per cent, 8.8 per cent is lost in the copperas plant, 65.8 per cent is lost in the pickling process, and 3.7 per cent passes into the city sewerage system as rinse water. Of the 74.6 per cent not definitely accounted for by the officials of the company, a part passes off as fumes from the pickling tubs; some is known to be discharged directly into the streams as washings from tubs, and the remainder apparently enters the stream direct or by way of the sewers, presumably as leakage.

This "lost" acid is the cause of the present pollution at Shelby. By designing the plant so that this waste may be recovered as copperas, stream pollution can be practically obviated and the economic value of the plant greatly enhanced.

7. The present pollution at Shelby makes the stream waters red and turbid, seriously damages them for general use, and renders them deleterious to fish life for a total of not more than 2 miles. No other damaging effects were found except an increase in the permanent hardness of the water, by which it becomes less suitable for boiler and for domestic use.

CLASSIFICATION OF THE PUBLICATIONS OF THE UNITED STATES GEOLOGICAL SURVEY.

[Water-Supply Paper No. 186.]

The serial publications of the United States Geological Survey consist of (1) Annual Reports, (2) Monographs, (3) Professional Papers, (4) Bulletins, (5) Mineral Resources, (6) Water-Supply and Irrigation Papers, (7) Topographic Atlas of United States—folios and separate sheets thereof, (8) Geologic Atlas of United States—folios thereof. The classes numbered 2, 7, and 8 are sold at cost of publication; the others are distributed free. A circular giving complete lists can be had on application.

Most of the above publications can be obtained or consulted in the following ways:

1. A limited number are delivered to the Director of the Survey, from whom they can be obtained, free of charge (except classes 2, 7, and 8), on application.
2. A certain number are delivered to Senators and Representatives in Congress, for distribution.
3. Other copies are deposited with the Superintendent of Documents, Washington, D. C., from whom they can be had at practically cost.
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SERIES L, QUALITY OF WATER.

WS 3. Sewage irrigation, by G. W. Rafter. 1897. 100 pp., 4 pls. (Out of stock.)
WS 22. Sewage irrigation, Pt. II, by G. W. Rafter. 1899. 100 pp., 7 pls. (Out of stock.)
WS 72. Sewage pollution near New York City, by M. O. Leighton. 1902. 75 pp., 8 pls.
WS 76. Flow of rivers near New York City, by H. A. Pressey. 1903. 108 pp., 13 pls.
WS 79. Normal and polluted waters in northeastern United States, by M. O. Leighton. 1903. 192 pp., 15 pls.
WS 103. Review of the laws forbidding pollution of inland waters in the United States, by E. B. Goodell. 1904. 120 pp.
WS 108. Quality of water in the Susquehanna River drainage basin, by M. O. Leighton, with an introductory chapter on physiographic features, by G. B. Hollister. 1904. 76 pp., 4 pls.
WS 113. Strawboard and oil wastes, by R. L. Sackett and Isaiah Bowman. 1905. 52 pp., 4 pls.
WS 121. Preliminary report on the pollution of Lake Champlain, by M. O. Leighton. 1905. 119 pp., 13 pls.
WS 144. The normal distribution of chlorine in the natural waters of New York and New England, by D. D. Jackson. 1905. 31 pp., 5 pls.
WS 151. Field assay of water, by M. O. Leighton. 1905. 77 pp., 4 pls.
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WS 161. Quality of water in upper Ohio River basin and at Erie, Pa., by S. J. Lewis. 1906. 114 pp., 6 pls.
WS 179. Prevention of stream pollution by distillery refuse, based on investigations at Lynchburg, Ohio, by Herman Stabler. 1906. 34 pp., 1 pl.
WS 185. Investigations on the purification of Boston sewage, by C.-E. A. Winslow and Earle B. Phelps, 1906. — pp.
WS 186. Stream pollution by acid-iron wastes, a report based on investigations made at Shelby, Ohio, by Herman Stabler. 1906. 36 pp., 1 pl.

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WASHINGTON, D. C.

OCTOBER, 1906.

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