XXIV. SOME EXPERIMENTS ON THE OXIDATION OF SLUDGE AND SLUDGE- SEWAGE SYSTEMS.

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It has been shown [Wooldridge, 1933], by means of experiments with methylene blue in Thunberg vacuum tubes, that sewage sludge, especially activated sludge, is capable of effecting a number of biological oxidations, including that of sterile crude sewage. In the present paper this activity of activated sludge (hereinafter simply called "sludge") is more fully examined using the Barcroft differential manometer as described in the previous paper [Wooldridge and Standfast, 1936]. In that paper it was shown that this apparatus could be used with advantage to follow the oxidation of non-sterile sewage. In the present paper the technique is extended to the examination of sludge and mixtures of sludge and sewage.

The oxidation of sludge.

Typical examples of the autoxidation of sludge as measured in a Barcroft apparatus are given in Table I. In Table II are given the results of a comparison of the rates of oxygen absorption by a sludge and by a sewage, the two experiments being run concurrently. It will be seen that in this particular experiment both the sludge (0.5 ml. of the suspension) and the sewage (2.5 ml.) appeared to be completely oxidised in approximately the same time, *viz.* 110 hours. The sludge, however, required a very much greater quantity of oxygen than that

Table I. *Oxygen absorption by sludge as measured by the
Barcroft manometer.*

Each cup of the apparatus contained 1 ml. of phosphate buffer, p_H 7.4, and 0.3 ml. of 10% KOH solution in the small inner chamber. The right-hand cup contained 0.5 ml. of a suspension of washed sludge and 1.5 ml. of water. The left-hand cup contained 2 ml. of water. The sludge was prepared by collecting a known quantity from an experimental tank, washing it thrice by centrifuging and re-suspending in water and finally making it up to a strength of three times that used in the tank. Finally, to facilitate accurate measurement the suspension was passed through muslin to remove exceptionally large particles. After the cups had been filled the apparatus was assembled, placed in a bath at 24° and shaken for 20 min. with free access to the outside air. The stopcocks were then closed and readings of the height of the manometric fluid taken at once and subsequently at the end of every hour. The figures give the oxygen absorption in μ l. per ml. of sludge suspension.

Sludge	Hours										
	1	2	3	4	5	6	10	22	30	43	48
1	34	54	71	86	101	118	160	249	310	412	457
2	97	135	170	199	227	252	333	572	784	972	—
3	37	70	99	122	147	171	237	377	459	547	572
4	71	138	180	223	253	—	375	542	—	—	—
5	58	96	137	173	—	227	295	469	—	—	—

Table II. *The oxygen absorption by crude sewage and by sludge in the presence of phosphate buffer, p_H 8.*

The sewage or sludge was placed in right-hand cups only. The figures give the oxygen absorption in $\mu\text{l.}$ at N.T.P. per ml. of the sewage or sludge. Other conditions as in Table I.

		Hours at 24°											
		1	2	4	6	10	20	35	50	70	90	110	144
Crude sewage		10	16	23	29	35	45	60	78	94	105	115	144
Sludge		88	140	230	312	420	620	940	1240	1506	1580	1600	1600

required by the sewage. The experiments show that the Barcroft manometer may be used to follow the oxygen absorption by sludge, and that the course of the experiment may be followed to completion if suitable quantities of material are chosen. As might be expected this uptake of oxygen is directly proportional to the amount of sludge present (Table III). Hence, at least within the limits of the concentrations chosen, the effect of dilution on the oxidation of the sludge is negligible. Experimental details are given in the table headings.

Table III. *Oxygen absorption by different quantities of washed sludge.*

Experimental details were the same as for Table I except that no buffer was added to any of the cups.

Volume of sludge suspension ml.	Oxygen absorption in $\mu\text{l.}$ after							
	30 min.	60 min.	90 min.	120 min.	150 min.	180 min.	210 min.	240 min.
0.5	6.0	10.7	14.1	18.8	24.1	28	31.7	36.5
1.0	11.5	20.3	28.7	36	45.5	53.2	61.1	71.6
1.5	17.3	30.1	45.8	53	66.2	79.2	90	103.8
2.0	22.8	40.8	58.1	72.8	91.9	108	122	142
2.5	28.3	50.2	72	92.2	115	136	155	180
3.0	34.4	62.1	88.7	113	141	166	188	218

The oxidation of crude sewage in the presence of sludge.

If the oxidation of a mixture of sludge with crude sewage is followed in a Barcroft manometer concurrently with similar experiments in which the same quantities of sludge or of crude sewage are allowed to oxidise separately, then it is found that the oxygen absorption recorded by the mixture is greater than the sum of the absorptions of the two constituents taken separately. Hence in the presence of each other the rate of oxidation would appear to be increased (Table IV). In Table IV the figures represent the differences in the quantities of oxygen absorbed in the two cups of each respirometer after the experiments had been in progress for different periods of time. After the respirometer had been shaken at 22° for 6 hours, the quantity of oxygen absorbed in the right-hand cup exceeded that in the left by an amount equivalent to 60 $\mu\text{l.}$ at 0° and 760 mm. In this particular experiment the difference represents the quantity of oxygen absorbed by the sewage as the left-hand cup contained only water. Experiment B was similar to experiment A but 1 ml. of sludge and 2 ml. of water were placed in the right-hand cup. The quantity of oxygen absorbed by this amount of sludge in 6 hours was 227 $\mu\text{l.}$ If a mixture of sewage and sludge absorbed the same quantity of oxygen as the sum of the amounts absorbed by the same volumes of sewage and sludge examined separately, the result for experiment C after 6 hours should have been 287 $\mu\text{l.}$ Actually the uptake of oxygen in 6 hours by a mixture of these quantities of sewage and sludge was much greater, viz. 605 $\mu\text{l.}$ This shows

Table IV. *Absorption of oxygen from air at 22° by crude sewage, activated sludge and mixture of sewage and sludge.*

Nett absorption of O_2 in μ l. at N.T.P. The contents of the cups of each manometer are indicated below; the abbreviations CS., Sl. and W. signify respectively 2 ml. crude sewage, 1 ml. sludge and water *ad* 3 ml. CO_2 was absorbed in all cups by the usual method of adding 10% KOH to the inner cup.

Exp.	Contents of Barcroft cups		Period in hours					
	Left	Right	1	2	3	4	5	6
A	W.	CS. + W.	16	32	46	49	55	60
B	W.	Sl. + W.	51	97	137	175	204	227
C	W.	Sl. + CS.	116	229	336	446	532	605
D	Sl. + W.	Sl. + CS.	81	148	210	279	325	391
E	CS. + W.	CS. + Sl.	102	211	305	408	484	555
	(A + B)		67	129	183	224	259	287
	C - (A + B)		49	100	153	222	273	318
	E - B		51	114	168	233	280	328
	D - A		65	116	164	230	270	331

that by mixing crude sewage and activated sludge the rates of oxidation by air of the sewage or sludge or of both are greatly accelerated. Without this acceleration the figures for experiment E should be the same as those for B, and the results for D (where the sludge oxidation is balanced) should equal those for A. In the lower part of Table IV the sum of the results for experiments A and B is given and then the increased oxygen absorption due to mixing the sewage and sludge is calculated from the experimental results in three ways, *viz.* C - (A + B), E - B and D - A. The good agreement between these figures lends considerable support to the deductions made. A comparison of these figures with the totals for A and B shows that during the first 6 hours and with the particular samples employed the rate of oxidation of a mixture of sewage and sludge by air was about twice the sum of the rates for the constituents agitated with air separately.

That this increased oxygen absorption is mainly an acceleration of the normal oxygen uptake is brought out by the experimental results given in Table V. Here are compared the rates of oxygen absorption by a crude sewage alone and

Table V. *The acceleration of sewage oxidation in the presence of sludge.*

In these experiments 0.5 ml. of phosphate buffer, p_H 7.0, was present in each cup and 2 ml. and 0.5 ml. of sewage or sludge suspension respectively in the cups indicated. The total volume of the liquid contents of each cup was made up to 3 ml. with water. CO_2 was absorbed in each cup by 10% KOH. The temperature of the bath was 24°. In the Table below W., B., CS. and Sl. signify water, buffer, crude sewage and sludge respectively. The figures indicate the oxygen absorption in μ l. at N.T.P.

Contents of left cup	Contents of right cup	Hours										
		1	2	3	4	6	8	9	21	28	33	40
B. + W.	CS. + B. + W.	5	12	17	22	40	70	85	125	135	140	155
Sl. + B. + W.	Sl. + CS. + B.	41	62	80	94	112	125	130	160	162	162	162
B. + W.	Sl. + B. + W.	50	69	87	100	124	143	155	271	361	420	455
CS. + B. + W.	CS. + Sl. + B.	70	115	140	160	181	186	188	304	375	430	465

by a crude sewage-sludge mixture with an equal amount of the sludge alone in the other cup. Thus after 4 hours' agitation at 22° the experiment with sewage alone shows an oxygen utilisation of 22 μ l. whilst in the other experiment the difference between the oxygen absorption of the sewage in the presence of sludge and that due to the sludge alone is 94 μ l. After 40 hours however, the figures are in

comparatively close agreement, *viz.* 155 μ l. and 162 μ l. respectively. A similar result can be demonstrated by a second pair of experiments in which are compared the oxygen absorption values for sludge alone and a for system sludge *plus* crude sewage with crude sewage alone in the opposite cup. In these experiments the 4-hour figures were 100 μ l. and 160 μ l. and the 40-hour figures 455 and 465 μ l. Thus it is shown that although the final total amount of oxygen absorbed by a sewage and a sludge oxidising separately will together equal the amount absorbed by the constituents mixed together yet the rate of oxidation is greatly accelerated by admixture. The rate of the acceleration is, as expected, dependent to some extent on the amount of sludge present in the mixture. The rate of oxidation however, is not necessarily directly proportional to the concentration of sludge as will be seen from the results given in Table VI, although the increased oxidation

Table VI. *Oxidation of sterile crude sewage in the presence of different quantities of sludge.*

In these experiments, which were carried out in triplicate, the sludge suspension was placed in both cups and the volume of the liquid made up to 2.5 ml. with water. 0.5 ml. of crude sewage, sterilised by passage through a Seitz filter, was placed in the side arm of the right-hand cup and 0.5 ml. of water in the side arm of the left-hand cup. After the preliminary 20 min. shaking the contents of the side arms were tipped into the cups, and oxidation of the sewage began. CO₂ was absorbed by KOH in all cups. The figures below represent the absorption of oxygen in μ l. at N.T.P. in the times at the head of the columns.

Amount of sludge ml.	Hours						
	1	2	3	4½	8½	9½	18½
0.5	8	10.5	14.5	19.5	40	43.5	99.5
1.0	11.7	17.3	22.3	33	68	75	111
1.5	17.7	28	39	57	102	105	119
2.0	21.3	35	52	73	116	119	128
2.5	27.3	43	63	91	127	128	141

for each additional 0.5 ml. quantity of sludge suspension is approximately constant in the early stages of the experiment. Clearly many other factors, such as concentration of substrate *etc.*, have some effect upon the rate of oxidation.

The oxidation of sewage effluents in the presence of sludge.

When sewage effluent is allowed to oxidise in a Barcroft apparatus, either alone or in the presence of sludge, results are obtained similar to those given in Table IV with crude sewage. Thus in parallel series of experiments the oxygen absorption by a mixture of an effluent and sludge exceeds the sum of the values obtained by allowing the effluent and the sludge to oxidise separately. The actual values are less with effluent than with crude sewage but the increased oxidation is nevertheless definite. Furthermore, the increase may be calculated in three different ways from the five experiments and, as will be seen from the last three lines of Table VII, the three results are approximately the same.

If the oxidation of an effluent in the presence of sludge is allowed to continue for a few days it will not necessarily reach a final maximum value but generally continues to increase slowly so that the oxygen absorption value of the effluent alone remains very much below the value reached in the presence of the sludge even when this oxidation is continued for long periods. This result differs from that obtained with a crude sewage, the values for which in the absence and in the presence of sludge generally tended to approach each other after two or more days of oxidation. In the presence of sludge, however, the oxygen absorption value

Table VII. *Absorption of oxygen from air at 22° by sewage effluent, activated sludge and mixtures of effluent and sludge.*

Experimental details as in Table IV. The abbreviations Eff., Sl. and W. signify 2 ml. effluent, 1 ml. sludge and water *ad* 3 ml. respectively.

Exp.	Contents of Barcroft cups		Period in hours					
	Left	Right	1	2	3	4	5	6
A	W.	Eff. + W.	11	17	17	19	19	19
B	W.	Sl. + W.	26	47	65	80	94	103
C	W.	Sl. + Eff.	55	86	107	125	140	151
D	Sl. + W.	Sl. + Eff.	31	44	49	50	52	53
E	Eff. + W.	Eff. + Sl.	47	76	94	112	127	137
	A + B		37	64	82	99	113	122
	C - (A + B)		18	22	25	26	27	29
	E - B		21	29	29	32	33	34
	D - A		20	27	32	31	33	34

for effluents still remains considerably lower than the value obtained within the same time by most crude sewages. Whether this oxygen uptake is entirely due to the more rapid oxidation of the constituents of the effluent by the sludge or is due to changes in the bacterial flora or to some other cause cannot at present be stated. It is noticeable with some effluents that the rate of oxidation may become practically stationary for a period of hours and subsequently increase at a greater rate again. This will be seen from an examination of the results given in Table VIII where the rates of oxygen absorption of four effluents collected from four sewage works are given over a period of 94 hours both in the presence and in the absence of sludge.

Table VIII. *The oxygen absorption values of various sewage effluents as ascertained in the presence or in the absence of sludge.*

The figures at the head of the columns represent hours and the figures in the body of the table the oxygen absorption in μ l. per ml. of effluent at N.T.P.; 2 ml. of effluent were present in all right-hand cups. Where sludge was added 1 ml. was present in both cups of the manometer. The total volume of fluid in each cup was made up to 3 ml. with water. CO_2 was absorbed by 10% KOH in the usual way. The effluents used were the final effluents obtained from four different sewage disposal works in the London area.

		Hours								
Effluent	Sludge	3	19	25	43	51	67	75	91	94
C.	-	2.4	5.3	5.4	7.1	8.2	9.9	11.3	14.5	15
C	+	14.5	48.7	59	62	63.5	71	79	95	98
Ed.	-	0.7	4.1	4.9	6.3	7.1	8.1	8.9	10	10.7
Ed.	+	8.8	44	54	66	70.5	82	91	106	109
En.	-	1.6	4.8	4.8	5.1	5.3	6.9	9.8	10.8	11.5
En.	+	19	62	73	76	76	80	85	102	105
F.B.	-	1.9	5.9	7	7.5	9.4	12	14.2	19.6	19.7
F.B.	+	23	69.5	86	104	108	118	122	138	140

Nevertheless there would appear to be certain advantages to be gained from allowing the oxidation of a sewage or effluent to proceed in the presence of sludge, advantages which are of value in research and possibly in tests at a works. By this means a measure of the difference between a crude sewage and a sewage effluent can be shown in a few hours, *e.g.* a comparison of the oxygen absorption values in Table IV for crude sewage alone and in Table VII for effluent alone

shows that within the first 6 hours the difference between the two although evident was not very great. When however the sewage and effluent were allowed to oxidise in the presence of sludge their rates of oxidation were greatly increased and within 6 hours the increased oxygen absorption values (the autoxidation of the sludge being allowed for by its presence in the other cup of the Barcroft apparatus) showed a marked difference.

In order that the method may distinguish between the oxidisabilities of two or more effluents, however, it is preferable that there should be sufficient replicates, and that differences should only be regarded as real if the results are statistically significant. With slow rates of oxygen absorption some variation in individual results may be obtained; *e.g.* two effluents from the experimental activated sludge tank were collected, one after the sewage had been aerated for $4\frac{1}{2}$ hours, and the other after 7 hours' aeration; these effluents, in 2 ml. quantities, were put up in the right-hand cups of Barcroft manometers in the presence of washed activated sludge, the left-hand cups containing a similar quantity of sludge without the effluent. After 5 hours the oxygen absorption values of the six manometers containing the $4\frac{1}{2}$ -hour effluent were 61, 92, 68, 83, 50 and $66\mu\text{l.}$, giving a mean of $70 \pm 6.20\mu\text{l.}$ The corresponding values for the 7-hour effluent were 30, 20, 41, 51, 49, $41\mu\text{l.}$, giving a mean of $39 \pm 4.81\mu\text{l.}$ From these results [v. Corbet and Wooldridge, 1936] the value for Fisher's *t* is found to be 3.955, and hence *P* is less than 0.01. The difference between the two series of results is therefore highly significant, showing that a definite further purification of the sewage took place even after the preliminary period of $4\frac{1}{2}$ hours' aeration with sludge. For this examination less than 20 ml. of the effluent were required, whilst for a 5-day B.O.D. test a much larger quantity is required even to do a single test. The results of such a single test will probably be unreliable for weak effluents; thus the following results, which suggest that the 7-hour effluent was less pure than the $4\frac{1}{2}$ -hour effluent, were obtained. For the $4\frac{1}{2}$ -hour effluent the 5-day B.O.D. value = 1.15 parts per 10^5 and for the 7-hour effluent = 1.55. These results might vary considerably with higher replication but they suggest that the B.O.D. test is probably insufficiently sensitive to measure accurately differences between the oxidisability of good effluents.

If the method were developed as a routine procedure it would be an advantage to use a standard sludge, say one that alone would bring about an absorption of oxygen of $100\mu\text{l.}$ per hour per unit quantity. Work along these lines might make it possible to utilise this as a standard method for the rapid examination of sewage and effluents and so enable a table to be drawn up which would prove of value in assessing the quality of the sewage or effluent. There would be no difficulty in carrying out a short preliminary test with any particular sludge suspension to ascertain the quantity required to give the standard rate of autoxidation; but variations in the nature and so in the enzymic activity of the sludge from day to day might prove a difficulty in practice unless a sludge powder could be prepared in a dry stable form. Such ideas however, before general application in the field, require further careful investigation. For purposes of research into the mechanism of the activated sludge process of sewage purification however it will be seen that the method described in this paper allows continuous observation, under controlled conditions, of the process on a very small scale, with measurements of the rates of oxygen absorption.

SUMMARY.

1. It is shown that the rate of absorption of oxygen by an activated sewage sludge may be followed in a Barcroft differential manometer.

2. The initial rate of oxidation of a crude sewage or of a sewage effluent is greatly increased by the presence of sludge although the ultimate oxygen absorption value is scarcely influenced by this factor.

3. Using this method of following the oxidation of a sewage or effluent in the presence of sludge it is shown that marked differences in the oxygen demands of various sewages are demonstrated within a few hours.

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