Persistent Odour-Taste Removal: the Use of Ozone and Microcoagulation or Carbon

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Abstract

A lowland impounded water was to be treated at up to 30 M\$\ell\$/day for public supply, but intense seasonal blooms of Microcystis aeruginosa (clathrate form) and other algae produced severe treatment problems, including the generation of intense odour-taste producing metabolites, resulting in a totally unpalatable supply.

This paper describes the attempts from 1968 to overcome these problems, from laboratory investigations through to commissioning in 1974, of a treatment plant based upon ozone.

The role of carbon is also considered at length, including bi-functional filters and fluid bed applications.

The authors have made reference to the desirability of plant performance monitoring, a feature lacking in many treatment stations; and also to the benefits of ozonisation, which can result in a subsequent microcoagulation process.

Historical Background

In 1963 the then West Somerset Water Board acquired the Durleigh Reservoir and the adjacent treatment works, which were commissioned in 1930 by the Bridgwater M.B.C. The sta-

tion had a maximum throughput of 10 M ℓ /day, drawing from the lowland reservoir (situated 2 km NE of Bridgwater) with a maximum capacity of 950 M ℓ , and a maximum depth of 7 m.

This water was treated by conventional process to an industrial standard – the entire output being taken by a single local industry for non-potable usage in the production of cellulose film. The manufacturers further treated the supply by either base exchange, or lime soda softening, or ion-exchange softening according to their needs.

The existing treatment is shown schematically in Fig. 1 and the seasonal variation of taste level in the reservoir is indicated in Fig. 2.

The chief problems at the time were:

- (1) Ineffective coagulation. High doses of coagulant (30-60 mg/ℓ) were required, due in part to the high pH and high organic loading of the incoming water. The raw pH was up to 8,6; however the combined effect of alum and chlorine did reduce the coagulation pH to 7,2-7,3.
- (2) Ineffective settlement. The horizontal sedimentation tanks were poorly designed and the theoretical settlement time was by no means achieved. There were no facilities for continuous sludge-bleeding. It was not unusual to experience 75-90% carry-over of floc onto the receiving filters.

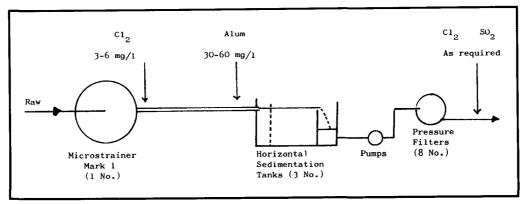


Figure 1
Existing treatment, Durleigh Works

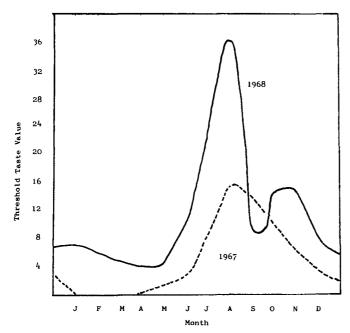


Figure 2
Seasonal variation of taste level in Durleigh Reservoir

- (3) Residual aluminium in the filtered water. It proved difficult to obtain a 0,3 mg/ ℓ standard, and not infrequently figures of 0,5 ppm were encountered.
- (4) Residual poly-uronic acids separated in the laboratory by acidification and precipitation and filtration, and detected by the acid-carbazole reaction. These poly-saccharides are a soluble metabolite of species of microcystis. Apart from well-documented industrial problems, these compounds can be in-mains precipitated and give rise to biological problems.

The whole subject of the coagulation process was given a thorough investigation. Twenty-five coagulant-aids were screened in the laboratory for possible use, and ten were subsequently assessed by plant trials, including activated silica, sodium aluminate, sodium alginate, Fullers Earth, four polyacrylamides and two liquid cationic polyectrolytes. The only success was with the cationic materials, and this supported earlier zeta-potential measurements.

The polyelectrolyte used was Superfloc® 521, a liquid polyamide. The search for an effective coagulant aid had occupied so much time that the 521 trials did not commence until 1969, by which time the odour/taste pilot work using ozone and carbon was well under way.

Increased Supply Proposals

It had been proposed in 1967 to increase the supply to the town and Rural District of Bridgwater, ultimately by 20 Me/day, and that this could be achieved by abstracting this amount from an existing 15 mile aquifer carrying water from the R. Tone at Taunton to the now disused docks at Bridgwater. The aquifer was constructed as the "Taunton-Bridgwater Canal" and formerly carried industrial goods.

The source, the River Tone, was of good quality, except in spate conditions, and the canal effectively gave 4-5 days storage on-the-move, markedly improving the clarity of the water, its bacteriological quality, and reducing, in season, the rather high nitrate and phosphate content.

It was proposed that the canal water be discharged mainly to the Durleigh Reservoir, or, diverted direct to the treatment works; or proportioned between the two, as shown schematically in Fig. 3.

The laboratory was asked to investigate the proposals and to draw up treatment possibilities and treatment design for 27-30 M ℓ /day.

Initial Laboratory Tests

The Canal and River had periodically been examined in the past, and the rate of sampling was increased. Several points were obvious:

- (1) The bacteriological improvement of the water during its five days traverse along the canal was dramatic an average of 91% reduction in coliform E. Coli (1) counts were obtained.
- (2) Spate conditions in the river resulted in very high turbidities, which were also vastly improved by the 'storage'.
- (3) The canal contained nutrients in the form of up to 1 ppm phospate (P₂O₅) and 5 ppm nitrate (N), which would contribute to the already intense algal blooms in the reservoir.
- (4) The canal water was amenable to conventional treatment, and presented no odour-taste problems, direct or upon storage.

The laboratory problem therefore was to design a treatment which would:

- (1) Remove the notorious odour-taste from the reservoir water,
- (2) treat the existing reservoir water, and any admixtures with the canal water – always remembering that the canal water would add to the nutrient budget of the reservoir,

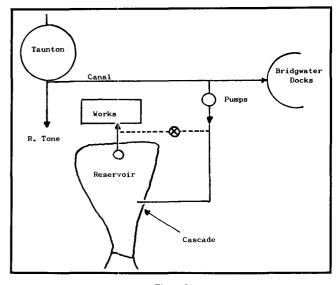


Figure 3

Durleigh augmentation proposals

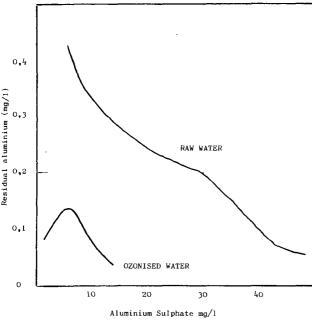


Figure 5

Jar tests (macro and micro-coagulation)

coagulation was in fact occurring, and that extremely low doses of coagulant were involved.

With micro-coagulation therefore, visual jar tests were meaningless, but if the water was then filtered, an examination of the filtrate would show whether micro-coagulation had or had not occurred. (Fig. 5).

At this stage, it had been shown that Durleigh raw water, when treated by chlorination $(4 \text{ mg/}\ell)$, and alum $(30 \text{ mg/}\ell)$ and filtered, yielded a water with $0.2 \text{ mg/}\ell$ aluminium, a strong taste, and a colour of 5 Hazen.

That same water however when pre-treated with 7-8 mg/ ℓ of ozone and dosed with 7-10 mg/ ℓ of alum and then filtered, yielded a water with 0,1 mg/ ℓ aluminium, zero taste, negligible turbidity and a colour of 1,5 Hazen.

Thus there were two, and only two, procedures worthy of further consideration, viz. active carbon and ozone.

Plant Trials and Pilot Tests

Activated carbon

Various grades of activated carbon powder were tried at different points on the Durleigh Plant. The lowest effective dose with average influent taste values was above 100 ppm, and it was felt that this approach was not viable, at least, with horizontal sedimentation.

Parallel trials at another of the Board's treatment works, however, where 8 m deep upward-flow sedimentation tanks were in operation, with intensely stable floc-blankets showed that batch-dosing of carbon powder could incorporate a high loading of carbon within the blanket, and that this acted as a fluid-bed (Weber and Morris, 1965), through which the water flowed, and organic odours could be eliminated effectively. (This method is still in use to remove undesirable tastes follow-

ing Autumnal overturn at the impounding reservoirs supplying the works in question.)

Pilot Columns

It was decided to construct and operate two pilot terminal absorption columns during the summer of 1968. These received Durleigh Final Treated Water, which had been through the conventional treatment process. These columns were therefore unifunctional in that they were performing absorption of organics only. The columns were designed to 1,7 m depth and 5 cm diameter, in perspex, and had sampling ports at 15 cm intervals. The water flow-rate was adjusted to give a 1 minute contact time between each sample port. With such a system it was possible to monitor the 'taste-front' as it travelled down the column.

One column was filled with Filtrasorb® 200, and the second for comparison, a later-developed product Filtrasorb 400, which had an 18% increased surface area, and an Iodine Number of 975. Both were 14-40 mesh. (BSS sieve numbers).

The results were interesting. The columns performed almost identically, commencing 14 Aug. 1968, and ran for 81 days continuously when taste-breakthrough occurred.

The performance of Filtrasorb 200 is tabulated (Table 1), from which a graph can be drawn, Fig. 6, showing contact time versus carbon utilisation. This shows that with an effective contact time of 5 minutes or more, the carbon consumption was 46 ppm during the period of the tests.

This was still a high dose, considering that the columns were accepting a treated water, and were operating in an efficient mode – a stationary absorption bed.

Granular active carbon filter

In 1969, with considerable advice and expertise from the manufacturers, one pressure-filter shell was emptied and structurally modified to accept activated granular carbon as the sole filter medium. The filter was to receive water direct from the sedimentation tank outlet, so that the bed was to perform a dual adsorption/filtration function.

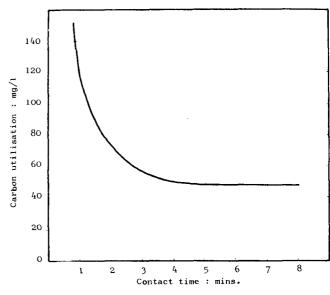


Figure 6
Effect of contact time on carbon utilisation

- (3) treat the canal water alone, when necessary, and
- (4) attempt to remove the poly-uronic metabolites.

Odour-taste problem

The taste was more obvious than the odour, and could loosely be described as earthy-nutty, reminiscent of actinomycetes – derived tastes, but not typical of those which the authors had encountered in other parts of the U.K.

Sometimes the taste was absent from the water; on one occasion the taste was detected when the water was diluted one hundred times with taste-free water.

Historically it had been quite apparent that the taste always followed in the wake of a microcystis bloom, and persisted several months thereafter. But not all such blooms produced the taste

It was therefore envisaged that there existed a relationship between microcystis aeroginosa and a species of actinomycetes resulting in odourous metabolites. (Silvey and Roach, 1956 and 1975). Reservoir control of microcystis using copper sulphate sometimes resulted in the subsequent taste levels being reduced.

It had been observed that chlorination increased the Taste Value by a factor of up to 2.

Removal of taste

The following agents were tried in the laboratory in an attempt to remove the taste:

- (1) Super-chlorination, followed by complete dechlorination, followed by marginal chlorination. The result was some marginal improvement.
- (2) Chlorine Dioxide. The raw water was treated with 8 ppm chlorine dioxide and $2.7 \text{ mg/}\ell$ of chlorine. After 3 hours the

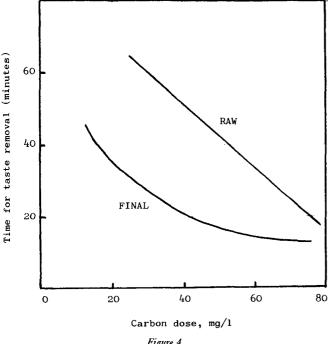


Figure 4
Carbon powder, jar tests

- residuals were 2,3 and 0,35 mg/ ℓ respectively, but the earthy taste persisted.
- (3) Potassium permanganate was tried at up to 10 ppm. No improvement was noticeable.
- (4) Hydrogen peroxide at up to 20 ppm was tried, with no success.
- (5) During May-June 1968 active carbon powder was assessed and found to be effective.

Several commercial grades were investigated, and the most promising were used in more detailed 'jar' tests.

The raw water was stirred with varying amounts of active carbon for varying times under standard conditions, and the time for taste removal recorded.

The tests were repeated in the presence of coagulant with surprisingly similar results. For comparative purposes, the tests were also conducted upon samples of the final treated water. The results are shown graphically, Fig. 4, demonstrating (a) slow absorption, (b) the competing effect of other organics further slowing the absorption and (c) the high doses of carbon required.

It is interesting to note that when this particular grade of carbon powder was used on the raw water, the time for taste removal was proportional to the applied dose of carbon; whereas, when applied to the final water (from the treatment station) it was the log-time which was proportional to the applied dose.

(6) Ozone was investigated. A micro-ozoniser was developed and fabricated in the laboratory, based upon a simple design – it having been noted that in the electrolysis of water containing a little sulphuric acid, a small proportion of ozone accompanied the production of oxygen at the anode.

During the period of these tests, the taste value of Durleigh raw water varied between 5 and 25, and the ozone demand was from 3-8 mg/ℓ , utilising a standard contact time of 8 minutes.

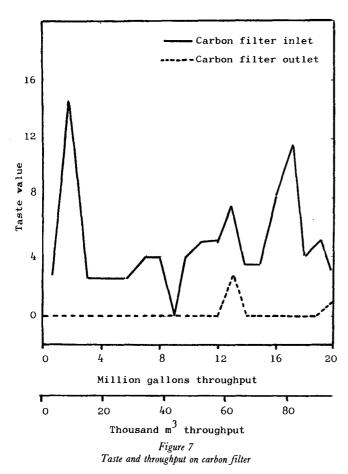
On all occasions the taste was not only removed, but the palate of the water became pleasant, and organic colour was drastically reduced. Samples of ozonised water were stored at ambient temperature, both in diffused sunlight, and in the dark for periods up to 14 days, and there was no return of colour (or taste) contrary to the findings reported elsewhere by some workers.

On the strength of these tests, a larger ozoniser was purchased for the further evaluation of ozone. This was of an aluminium-plate polythene-dielectric design, and could be fed with dry compressed air or dry oxygen. Concentrations of ozone up to 80 mg/ ℓ could be obtained.

It was now possible to treat larger volumes of sample – 5 litre volumes were eventually chosen, so that subsequent coagulation studies could be made.

Jar tests were therefore performed upon the ozonised water, and these were visually disappointing in that it did not seem that any floc was readily formed, with or without coagulant aids, and when coagulation was visually obvious, subsequent filtration (541 paper) yielded a filtrate containing an excess of residual coagulant.

But, upon further investigation it was found that micro-



The taste principal was quite volatile and was recorded in the total organic solvent fraction and could be separated by steam distillation. There was insufficient for laboratory examination with the facilities available at that time.

The early breakthrough of taste, both on the columns and on the filter, points to the taste-forming species being difficult to adsorbe.

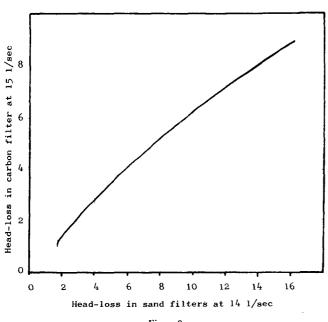


Figure 8
Head-loss comparison (Correlation coefficient, r = 0.81)

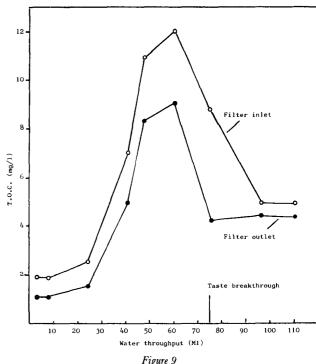
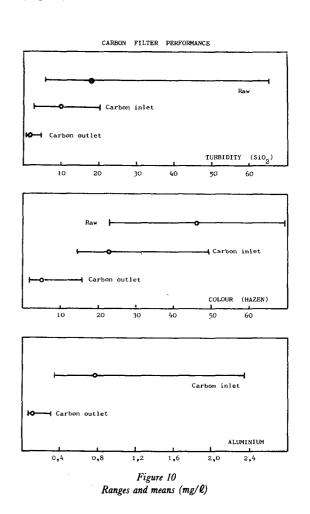


Figure 9
Total organic carbon (TOC)

Core samples were also taken for sieve analysis, and the results show that bed stratification had been obtained, even though the filter geometry was not conducive for this to happen. (Fig. 11).



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TABLE 1
CARBON COLUMN RESULTS: TASTE ADSORPTION

_	Influent	, · ·							
Days Run	Taste Value	1 min	2 min	3 min	4 min	5 min	6 min	7 min	8 mir
0	35	0	0	0	0	0	0	0	0
2	35	0	0	0	0	0	0	0	0
4	35	6	0	0	0	0	0	0	0
7	35	7	0	0	0	0	0	0	0
11	20	2	0	0	0	0	0	0	0
15	10	3	2	0	0	. 0	0	0	0
18	8	4	2	0,5	0	0	0	0	0
21	8	4	1	0,5	0	0	0	0	0
24	8	3	1	0,5	0	0	0	0	. 0
31	7	4	3,5	2	1	0	0	0	0
36	17	8,5	7,5	3	1,5	0,5	0	0	0
44	16	9	6	4	2	Ö	0	0	0
56	15	5	3	3	2	1	0,5	0	0
63	14	6	5	3,5	2,5	1	1	0	0
81	26	8	6	5	3	5	4	2	1
					l				1
Brea	kthrough	3	10	16	22	35	55	70	81

^{*}Taste Value defined here and elsewhere as the volume of taste-free water to be added to unit volume of sample in order to yield a water just free of discernible taste.

The carbon can, and must, be stratified before going onstream, by backwashing causing bed expansion. Thereafter the stratification must be maintained, and this holds the masstransfer zone in place. Thus backwashing is a critical operation, and 50% bed expansion is considered to be the minimum necessary for successful stratification.

The grade of carbon chosen was that used on the columns, Filtrasorb 200, 14-40 mesh, with a uniformity coefficient of 1,7 and an Iodine No. approximately 875, and 2,3 t were used – giving a contact time of some 4 minutes when the filter was operating at its normal rate of 19 ℓ /sec.

Commissioning was on 23 June 1969, and without any set-backs the filter operated until 4 September when taste breakthrough occurred and eventually reached 'complaint' levels on 23 September. Breakthrough thus occurred after a throughput of 77 M ℓ , and the overall carbon utilisation was calculated at 33 mg/ ℓ .

This figure was lower than that obtained with the columns, and it was thought that the main reason for this was that during the column tests the time-average taste value was 20, whereas the corresponding value during the filter test was only 4.

The performance of the dual-mode filter was fully monitored and the results are shown in the following graphs and figures. (Figs. 7-10).

The filter was also monitored for pesticide removal (Table 2). The only detectable pesticide in the reservoir was y BHC (Lindane). The results showed that coagulation/sedimentation removed a greater proportion of y BHC than the carbon filter.

After breakthrough had occurred the carbon was briefly examined, and found to contain:

Total organic solvent extract	0,55% w/w
N/10 sodium hydroxide extract	4,6% w/w
Ash	5.8% w/w

TABLE 2 PESTICIDE REMOVAL

Sample	Period 1969	γ BHC ng/ℓ	Period 1969	γ BHC ng/4
Durleigh Raw	27 June to 25 July	60	26 July to 29 August	70
Sedimentation outlet	,,	20	,,	40
Carbon filter outlet	,,	20	,,	20

minutes, and at point P_2 coagulant was added. The retention in column C was 4 minutes, to allow for time for taste removal and coagulation to occur. At point P_3 , either a coagulant-aid or a boost of chlorine could be dosed. The water was gravity filtered at 450 ℓ/h , and the excess bled to waste. Samples of the water at various stages of the treatment were led to four large clarity sinks, each holding 40 ℓ .

The ozone was produced by the B.O.C. ozoniser previously described, fed with dry oxygen, and the outlet gas was mixed in the correct proportion with nitrogen to simulate ozonised air. The voltage applied to the ozoniser was regulated to maintain 15-20 mg/ ℓ in the ozone gas stream. It was possible to proportion the ozone between primary and secondary injection diffusers. Vented gas could be monitored for waste ozone.

The filter accepted conventional flow rates for rapid gravity anthracite-sand filters. A loss of head gauge was attached. Continuous monitoring of the filtrate was made possible by the construction of an automatic analyser which conducted continuous on-line analyses for aluminium and/or iron. Residuals of ozone in water were made by a specific-electrode system. All dosing was by peristaltic pumps, and the unit was constructed to function 24 hours per day with intermittent attendance.

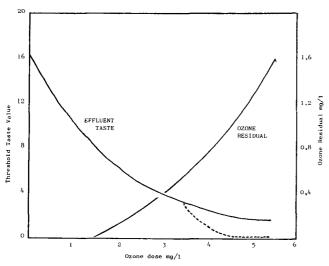
Pre-chlorination was adopted to satisfy the immediate chlorine demand of the water, and a dose of about 1 ppm was usually sufficient. This resulted in a slight lowering of the required ozone dose and reduced substantially the amount of frothing in column P. The ozone residuals aimed for immediately after the primary and secondary dosing columns were 0,2 and 0,5 mg/ ℓ respectively. This was normally achieved by proportioning the ozone 50:50 between P and S.

Instrumentation

(1) Ozone residuals by selective electrode system

An electrode was constructed from the pair of dissimilar metals: nickel anode and silver cathode. The current produced is directly proportional to the ozone concentration at constant pH and is unaffected by chlorine.

(2) Residual coagulant recorder



The dotted portion of the taste curve indicates the residual taste upon standing for 15 mins after sampling

Figure 13
Taste removal, Durleigh Water

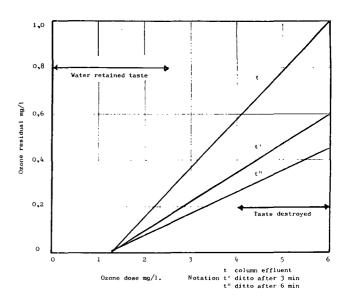


Figure 14
Ozone dose mg/litre: notation: t column effluent; t' ditto after 3 mins;
t'' ditto after 6 mins

An automatic on-line analyser was constructed in which the sample is acidified to pH 5,9 and the colour developed with Solochrome Cyanine R was measured at 530 nm and the absorption is proportional to the aluminium concentration. A similar system was used for iron, the developing reagents being hydrozone and Nitroso R Salt.

Results of ozone pilot plant trials

The studies were mainly upon Durleigh micro-strained raw water, but the plant had also to be used to assess the canal source.

PRIMARY EFFECTS

(1) Taste removal. With a single ozone column in operation, the following results shown in Fig. 13 were typical.

The effluent from the column thus had a slight residual taste, but in the presence of a moderate ozone residual, about 0,8 mg/ ℓ , this excess ozone continued to react and eventually completely destroyed the taste.

Using the same dosage of ozone – split equally between the two columns, the taste removal efficiency was increased and there was less waste ozone in the vented gases.

In comparison with the *immediate* effects that ozone has on water, that is, bactericidal, virucidal, oxidation of iron and manganese, and destruction of colour, it is obvious from the previous graph that the taste here is destroyed but slowly, and it is essential to dose at such a level as to yield an effluent containing a moderate residual of ozone, so that the final destruction of the taste principal can be achieved. However this approach is made somewhat difficult owing to the fact that ozone residuals in water are not at all persistant, and even a high residual can be dissipated within 15 minutes – see Figs. 14 and 15.

Also the situation is complicated by the low solubility of ozone in water (White, 1972).

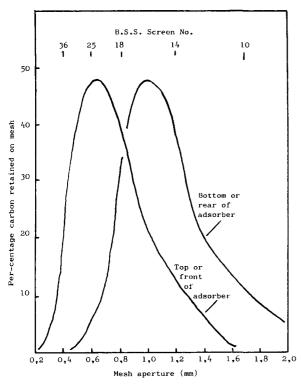


Figure 11
Carbon bed stratification

A short summary of the use of granular active carbon is therefore as follows:

(1) The filter performed in its filtration mode as well as a sand pressure filter with regard to its removal of turbidity and aluminium and final colour (Hager and Fulker, 1968).

Statistical analysis showed no significant difference between the two types of filter. There was substantial removal of chlorine by the carbon.

- (2) Taste removal was complete until breakthrough occurred.
- (3) Breakthrough occurred with a consumption of 33 mg/ℓ of carbon.
- (4) T.O.C. and pesticide removal was below expectations (Flentje and Hager, 1964; Robeck, 1965).

Ozone pilot plant

Whilst the carbon trials were under way in 1968-1969, it was decided to construct a pilot ozone plant, which was operational in early 1969. The design is outlined in Fig. 12. The plant was constructed not only to investigate the removal of stubborn taste-odour, but also the behaviour of microstrained and ozonised water towards microcoagulation, and the possibility of eliminating sedimentation as an integral part of the treatment; the behaviour of micro-coagulated water on sand/anthracite filters, and the loss of ozone in the column vents.

Description

Microstrained water from the Durleigh Treatment Plant was taken for testing; on other occasions, the canal water was used. The water was pumped to the dosing module of the pilot plant, at 700 ℓ/h , where pump P_1 applied a pre-dosing of chlorine. The water was then fed to the top of a 5 m perspex column (P), and the primary dose of ozone was applied at its base through a sand-stone diffuser. The retention time in P was 1 minute, and the water then passed to the top of column S, where a secondary dose of ozone was applied, again counter-current, in accordance with established practice. The retention in S was $2\frac{1}{2}$

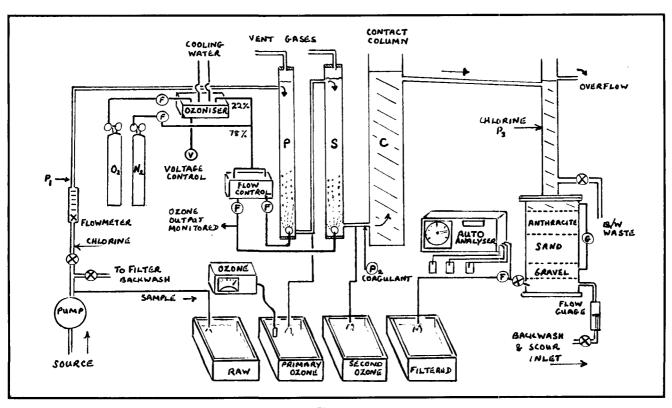


Figure 12 Ozone pilot plant

	TABLE 3	
COLOUR	RETURN	RESULTS

Ozone Dose	Colour (Hazen)			
mg/ℓ	Initially	14 days later		
Nil	22,5	18		
1	20	15		
2	12	10		
3	8	8		
4	4	4		
0.5 + 0.5	13	12		
1 + 1	6	7		
1.5 + 1.5	4	6		
2 + 2	5	5		
2.5 + 2.5	4	5		

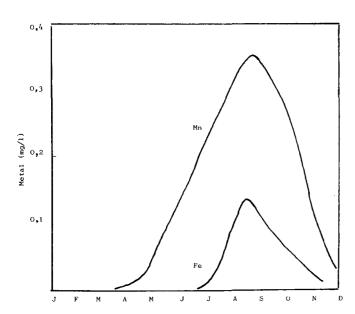


Figure 19
Seasonal variations of iron and manganese, in Durleigh Reservoir (means for 1963-1968)

upland lakes and lochs, no evidence of colour return was obtained with either Durleigh Water or the canal water here tested. Typical results upon storage are shown in Table 3.

- (4) Bacteriological results. The bactericidal effects of ozone are well documented (Kinman, 1975), but tests were nevertheless conducted on the Canal and Durleigh Water after ozone treatment, samples being withdrawn before filtration. (See Table 4).
- (5) Oxidation of organic matter by ozone. Whilst T.O.C. measurements would have been preferable, facilities were not available, so that the standard 4 h Permanganate Value was used as an indicator of organic content.

In general terms, ozone, when applied by double injection will reduce the P.V. by about 50%. This has been found to be so for instance with Loch Turrett Water, and similar results were obtained with tests upon the canal water. For raw water the analysis was P.V. 2,9 mg/ ℓ , colour 30 Hazen, and turbidity 7,5 mg/ ℓ (SiO₂ scale), while the results for treated water are indicated in Table 5.

(6) Iron and manganese removal. Trace iron presents no problems, as might be expected. However manganese removal is a potential problem at many works, and as manganese is a seasonal contaminant of Durleigh Reservoir every year, see Fig. 19, manganese removal by ozone was the subject of special investigation.

TABLE 5
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OXIDATION OF ORGANIC MATTER BY
OZONE

	Column Effluent			
Ozone Dose mg /ℓ	P.V. mg /ℓ	% remova		
0.5 + 0.5	2,1	28		
1 + 1	1,9	34		
1,5 + 1,5	1,8	38		
2 + 2	1,7	41		
2.5 + 2.5	1,65	43		

TABLE 4
BACTERIOLOGICAL RESULTS

	Plate Count 37°C 24 h/mℓ	Coliforms/ 100 m ℓ	E.Coli (1)/ 100 m <i>l</i>
Durleigh Raw Water	Uncountable	450	16
4 ppm ozone single dose	24	0	0
7 ppm ozone single dose	10	0	0
Canal Raw Water	Uncountable	45 000	3 100
7 ppm ozone single dose	A few merging colonies	0	0

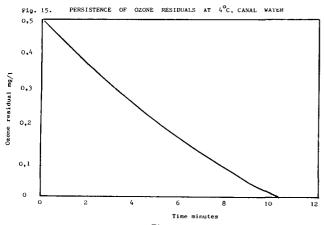


Figure 15
Persistence of ozone residuals at 4°C, Canal water

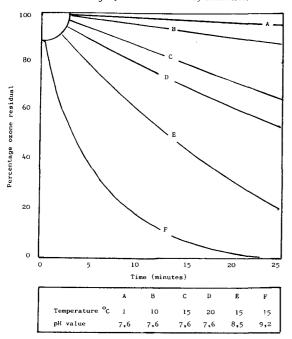


Figure 16
Persistence of ozone residuals in pure water under various conditions of pH
and temperature

A more detailed investigation into ozone decomposition in pure water is given in Fig. 16 where the dependence upon temperature and pH is shown; pH is obviously a dominant factor.

(2) Colour removal. Here colour is defined as soluble colour, passing a 0.45μ membrane filter, measured in Hazen Units. Figure 17 shows the effect of ozone upon colour of the canal water. The 'raw' colour was 36 Hazen, and samples were withdrawn immediately after the columns, that is prior to filtration. Plots of single and double injection techniques are given, and it is seen that double injection is again more efficient.

Thus to reduce the canal colour to 6 Hazen, a single dose of 3,8 ppm was required. However to achieve the same result with double injection, the required colour is obtained with only 2,4 ppm.

Although it might be argued that a residual colour of 6 Hazen is not indicative of complete colour removal, further work, quoted later, shows that this residual is readily removed by micro-coagulation and filtration.

For comparison, the results obtained by Messrs. Trailigaz of Paris on a pilot installation at Lough Gill, Sligo, Republic of Ireland in July 1968 are also plotted in Fig. 17. These latter are using a single injection technique upon microstrained Lough water.

Ozone demand can often be related to colour, although of course other organics exert an ozone demand. See Fig. 18. It may thus be argued that with a percentage of waters, the organic colour is the dominant oxidisable entity.

(3) Colour return. Whilst other workers have found some colour return (Campbell, 1963) can be a feature of some ozone treated

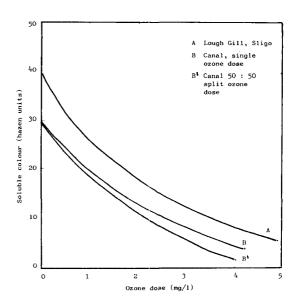


Figure 17
Effect of ozone dosage upon soluble colour (Oct '68)

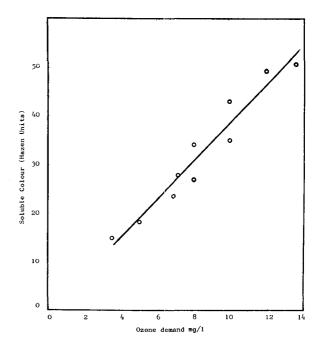


Figure 18
Ozone demand and soluble colour of canal water (July through Sept 1970)

45-75 days, and a typical carbon loss by cyclic regeneration per annum could vary between 25 to 40%.

On-site regeneration would have been necessary, involving hydraulic transfer of carbon by slurry pumps to drain tanks, and conveyor to a multi-hearth furnace, and further slurry tanks and pumps for transfer of reactivated carbon to the filters.

As for operation of the filters, the operators would have to decide, by tasting each filter each day, when regeneration was needed, as there would be no fore-warning that breakthrough was imminent. It was felt that with 15 filters in operation that the final water may at times have had some slight discernible taste.

Carbon would of course destroy the pre-chlorination residual, and terminal chlorination would have to be added.

Ozone however, in the trials had always produced a very palatable water, providing an adequate dose could be maintained. High doses are difficult to achieve in a single injection and multiple injection was a necessity.

Vent losses had to be considered, owing to their toxic nature, and the high cost of producing wasted ozone. (Fig. 20).

Micro-coagulation

The pilot ozone trials had revealed the benefits of microcoagulation using very low doses of coagulants. These low doses conferred two main advantages:

- Sedimentation could be avoided indeed no visible floc was formed.
- (2) Sludge volumes would be reduced by a factor of 6, making sludge disposal a small-scale exercise.

Ferric salts appeared to be the preferred coagulant.

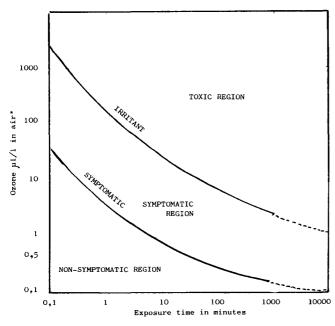


Figure 20
Human tolerance for ozone
Symptomatic region – first sensations – irritation of throat
Irritant area – coughing – running of eyes – headache
Toxic symptoms – prolonged coughing – pain in chest – laborious breathing

Microstraining

Microstraining would be essential to both processes – carbon or ozone. The existing mesh was 35μ , and it was considered that 23μ mesh would be very much preferable, as this would effectively remove most particles above 10μ in size. With ozone, efficient microstraining would reduce the ozone demand and enhance the micro-coagulation stage.

Cost factors

Rough estimates of the overall requirements for both processes were made, and the ozone treatment plant came out 23% cheaper than carbon treatment and regeneration plant. The major factor was that carbon treatment required sedimentation facilities whilst ozone did not.

At 1970 prices, carbon replacement costs were estimated at £0.55-£0.85 per M ℓ , with regeneration costs at £0.5 to £0.9 per M ℓ , giving an overall granular carbon cost of £1 to £1.7 per M ℓ .

Ozone generation costs, including air preparation were estimated at £0.7 per $M\ell$.

Of course today's figures would look quite different, but those quoted were the ones influencing the decision. Present ozone costs can be based upon a power consumption of 21 Whr/g of ozone produced and this includes air preparation.

Thus based upon economy of plant design and efficiency of performance it was decided to design the works around the ozone pilot plant findings and experiences. It was felt that with ozone there was an opportunity to exploit the unique properties of the treatment, which go far beyond the conventional present applications of disinfection, phenol removal, colour removal or final polishing.

Works Design for Ozone Treatment

The designed treatment works consisted of:

Microstraining: Two microstrainers were installed, 3 m x 3 m, equipped with 23 μ stainless steel mesh, having a peripheral drum speed of 45 m/min. They will thus accept 22,5 M ℓ /d, with a filtrability index of up to 8,0.

Pre-chlorination: Up to 5 mg/ ℓ can be applied.

Ozonisation: The ozone is injected in two consecutive countercurrent chambers (which are 6 m deep) through sintered stainless steel diffusers. The chambers are sized such that retention in the primary is 2,5 minutes and 5 minutes in the secondary. The vent gases which can carry up to 10% of waste ozone (i.e. $1,5 \, \mathrm{Mg/\ell}$) are then reinjected by a split-ring compressor into the microstrained water in a pre-ozone dosing chamber. The ozone in these vent gases is readily absorbed by the microstrained water, and the spent gases are discharged, after passing through a carbon filter, to atmosphere.

Coagulant: The coagulant dosing is flexible. Ferric or Aluminium salts can be added just before a 15 minute contact chamber, and a coagulant aid or polyelectrolyte can be added in the pump sump. Further, pH correction has been added and is achieved by dosing prior to the main coagulant.

When ozone is injected into a raw water containing manganese, the latter if complexed with organic matter is generally liberated as the free ion. This is rapidly oxidised (cf. slow oxidation with chlorine), either to hydrated oxides, or, if ozone is in excess, traces of permanganate are formed. In the former case there is an increase in the Hazen colour after ozone injection; in the latter permanganate obviously yields a ping tinge to the water.

Hydrated oxides can subsequently be removed by two mechanisms:

- (1) The manganese can be coagulated out using AL^{3+} or Fe^{3+} , at the appropriate pH value.
- (2) A conditioned filter (where the medium sand or anthracite is coated with manganese dioxide) where manganese is removed catalytically and builds on the existing coating.

For example a river water at pH 7,8 was dosed with 3,5 mg/ ℓ of manganese as the sulphate, and then treated with a double injection of ozone $(4+4 \text{ mg}/\ell)$. The water was filtered through a conditioned bed and the residual manganese was only 0.03 mg/ ℓ . In a second run 5 mg/ ℓ of ferric sulphate was added as a coagulant, and after filtration, the filtered water contained below 0,005 mg/ ℓ of manganese.

When only traces of manganese are present, that is from $0{,}005$ to $0{,}1$ mg/ ℓ , it is likely that ozone will oxidise the manganese completely to permanganate, which is subsequently removed by filtration. Two processes for the removal of permanganate seem possible:

- (1) Permanganate is reduced to dioxide by organic matter on the filter, or
- (2) Permanganate is reduced by dioxide already coating the filter. This last statement may sound suspect, but to test the hypothesis a pyrolusite column was prepared and it was found that this substantially removed permanganate from water flowing through it.

SECONDARY EFFECTS

The secondary effects concern the subsequent coagulant and filtration stages after preliminary ozonisation.

The pilot plant confirmed that a microfloc was formed with coagulants after ozonisation. The microfloc could be removed by conventional filtration, yielding a water, with a slight blue tinge, clear and bright and free from sediment upon storage.

Aluminium sulphate was used in the early trials, and the doses required were in the range 5-15 mg/ ℓ , but aluminium residuals were high. Residuals could be reduced to below 0,05 mg/ ℓ , using a suitable polyelectrolyte, but this was not always possible.

When ferric salts were tried as coagulants, more promising results were obtained. The coagulant dose was maintained fairly constant during the trials at 5 ppm Fe Cl₃, and produced water of good quality as above, but with much less tendency for residual coagulant in the filtered water.

Thus the general effect of high ozone doses was to yield a water which responded to micro-coagulation. The only periods when this beneficial aspect was not fully operative was with siliceous turbidity following heavy rainfall (flood conditions) resulting in raw water turbidities of 30-50 mg/ ℓ (Durleigh) and 100 mg/ ℓ (Canal). These conditions were rare, and when encountered, increased coagulant doses were beneficial.

It should be emphasised again that during these trials no visible floc was formed.

Finally, during periods of (natural) high turbidity, due to growths of diatoms and algae, these were removed by microstraining, and there were no pilot treatment problems.

To summarize, with micro-straining, chlorination, double ozone dosing (counter current) and micro-coagulation the following peak conditions of poor raw water quality were successfully treated during the pilot trials.

- Peak colour of 80 Hazen treated to a residual colour of 3 Hazen using 6 mg/ℓ of ozone.
- (2) Peak manganese of 0,18 mg/\ell\$ reduced to zero by 2,5 mg/\ell\$ of ozone. A 'spiked' water containing 3,5 mg/\ell\$ of manganese was also reduced to zero without altering the treatment.
- (3) Peak turbidity of 33 mg/ ℓ due to microcystis was reduced to 0,5 mg/ ℓ using 6 mg/ ℓ of ozone.
- (4) Peak filtrability index (Boucher, 1947) value of 4,2, due to aphanizomenon, treated successfully with 7 mg/ℓ of ozone to a residual turbidity of 2 mg/ℓ.
- (5) The Peak value of the taste removed during the trials was 16, treated with 4,8 mg/ ℓ of ozone, and at no time whilst the pilot plant was in use did the final water contain the offensive taste-odour which was to be removed. In fact the palate was excellent. The only stipulation was that relatively high doses of ozone had to be applied, such that a moderate residual of ozone was produced. Therefore in the final contact column, C, the excess of ozone had reaction time to destroy the taste principal.

The Choice between Carbon and Ozone

It was clear from the evidence that the organic loading in Durleigh Reservoir was high – a $10 \text{ mg/}\ell$ P.V. had been recorded; a peak T.O.C. of $12 \text{ mg/}\ell$ after microstraining and sedimentation had been found. These high values were not considered agricultural pollutants, but the result of a high bio-mass in the reservoir, and particularly to the polyuronic metabolites of microcystis. It was equally clear that the taste principal was a difficult entity to remove, being adsorbed with difficulty onto carbon, and destroyed but slowly by ozone.

Taste removal

Granular carbon beds had been shown to be feasible, acting in a dual role as filters and organic adsorbers. The problem was the limited bed life, and filter design would have had to incorporate vertical cylindrical geometry, with capacity for 50% bed expansion on back-washing. A loading of 4 t per filter would be necessary for a filter flow-rate of 20 ℓ /sec. A bank of some 17 filters would be necessary, with 2 on stand-by.

Calculation shows that at a consumption rate of between 30 and 50 ppm of carbon, each filter would need regeneration each

Secondary chlorination: A chlorine boost is applied before the eight pressure filters, each rated at 50 1/m²/h, and finally post-chlorination is applied before the filtered water passes into the distribution system.

Ozone Production: Ozone is of course unstable and has to be prepared on site from intensely dry air.

The air is compressed, to 0,8 kgf/cm² (70 KN/m²), refridgerated to 5°C, and dried by silica gel desicator, to a water content of less than 30 $\mu\ell$ per litre (a dew point of below –52,5°C) and then subjected to a high tension discharge of up to 20 KV 50 hertz A C in two Trailigoz tubular ozonisers, each with banks of 144 tubes, capable of producing 3-8 kg of ozone per hour, normally at a concentration of 15-20 mg/ ℓ in the effluent air-stream. The ozone dose applied to the water is varied by altering the air flow and the power supply to the ozonisers.

Instrumentation: The degree of monitoring supplied by the manufacturers was limited, and was supplemented by an electrolytic hygrometer (Walker and Campion, 1965) for determining water in the dried air-stream. The ozone output is determined by an instrument developed which measured the absorption of U V light (2537 nm). The spent gases are similarly monitored, using an instrument with a larger gas-cell. Residual coagulant is determined by an auto-analyser and residual turbidity-colour by an automatic recorder.

Conclusions and Further Work

Sufficient work has now been done to present this case history of Durleigh Treatment Works, and the early experiences of ozone treatment, and for suggestions to be made for further study.

Firstly taste, odour and colour removal had presented no problems. Manganese removal was a little anomalous requiring increased pre-chlorination, but was thereafter successful. Turbidity removal, by the treatment as a whole has presented no problems. The microstrainers have performed exceptionally well. The ozonisers, once the air supply was satisfactory, have performed well, and to specification.

Micro-coagulation has worked, but not always with the success achieved on the pilot plant, and here is a subject for further study. The answer may be obvious. On the pilot plant chlorination was by hypochlorite. On the new works, chlorination has been heavy at times, and of course gaseous chlorine is

employed. This has depressed the pH value of coagulation (compared with the pilot plant) from an average of 8,2 to 7,3. It is felt that the addition of lime to achieve a coagulation pH value of 7,8-8,0 with ferric sulphate would be well worth a trial.

The ozone dose should be regulated by monitoring the vent gas so that 97-98% adsorption can be achieved. The appearance in the vent gas of above 0,4 mg/ ℓ of ozone should be taken as evidence of overdosing. With 20-fold dilution of the waste gas, the maximum at the stack outlet would then be 0,02 mg/ ℓ . From experience 100-fold dilution can be expected in the surrounding air, and the grounds in the immediate vicinity of the works would not then have ozone in excess of the Factory Act limit of 0,1 volumes per million.

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