BIOLOGICAL DENITRIFICATION OF POTABLE WATER

Final Report to the Department of the Environment

T Hall, T Zabel

November 1984

319-S

RESTRICTION: This report has the following restricted distribution:
External: DOE nominated Officer - 20 copies
Internal: Director, Appropriate Assistant Director plus 4 copies to Division Scientific Staff

DOE Contract Reference PECD 7/7/016

WRC PROCESSES
STEVENAGE LABORATORY, Elder Way,
Stevenage, Herts. SG1 1TH
BIOLOGICAL DENITRIFICATION OF POTABLE WATER

Final Report to the Department of the Environment

T Hall, T Zabel

November 1984

319-3

RESTRICTION: This report has the following restricted distribution:
External: DOE nominated Officer - 20 copies
Internal: Director, Appropriate Assistant Director plus 4 copies to Division Scientific Staff

DOE Contract Reference PECD 7/7/016
SUMMARY

The objectives of the work on biological denitrification of potable water were:

1. To test fully the process and engineering design of the prototype biological denitrification plant and to monitor its process performance.
2. To identify scale-up problems.
3. To investigate start-up techniques for biological denitrification units while monitoring critically the quality of the product water.
4. To evaluate different carbon sources.

This report summarises the main findings of the project.

The prototype biological fluidised sand bed denitrification plant was constructed at the Bucklesham treatment works of Anglian Water and commissioned on 9 June 1982. The plant had a capacity of 2.8 Ml/d and treated a quarter of the total site flow of 11.2 Ml/d. The plant was designed to remove 12.8 mg DO/l and 15 mg NO₃-N/l at a temperature of 5°C.

The denitrification plant was operated for two years using methanol as carbon source and for short periods with ethanol (11 weeks) and acetic acid (8 weeks) as carbon sources. For long periods of operation, totalling over 1 year, the denitrified water was blended into supply with no adverse effect on the final water quality.

Using methanol as carbon source the plant removed up to 14 mg NO₃-N/l at temperatures as low as 2°C confirming the validity of the design data used. No problems were experienced starting-up the biological reactor which took approximately 30 days to achieve a nitrate removal of 6 mg NO₃-N/l. Additional pilot plant work carried out on site indicated that this could probably be reduced to about 20 days.

As this was a spring-fed source the phosphate concentration in the raw water was very low, and phosphate dosing was required for optimum operation of the plant.
Elevated nitrite residuals of up to 2 mg NO₂ N/l were at times produced in the denitrified water. In most cases this could be controlled by reducing the carbon source dose. No reason for this occasionally high nitrite production has been found despite extensive pilot plant trials.

The sludge thickening and storage plant was effective in handling the sludge and reduced the sludge volume requiring disposal by at least 80%.

The reliability and accuracy of the methanol and nitrate monitors were improved significantly during the duration of the project, however, the nitrate monitor was not sufficiently accurate to be used for process control.

The direct operating costs based on the total flow of 11 Ml/d at Bucklesham has been estimated at 0.3 p/m³/mg NO₃ N/l removed. The use of ethanol and acetic acid as carbon sources would increase the direct operating costs by approximately 25% and 50% respectively.

The project was carried out jointly by Anglian Water and the Water Research Centre.
CONTENTS

SUMMARY

1. INTRODUCTION
   1.1. BACKGROUND
   1.2. NITRATE STANDARDS FOR PUBLIC WATER SUPPLIES
   1.3. OPTIONS FOR REDUCING NITRATE LEVELS IN WATER ABSTRACTED FOR PUBLIC SUPPLY
   1.4. BIOLOGICAL DENITRIFICATION

2. PROCESS DEVELOPMENT AND DESIGN
   2.1. TREATMENT STRATEGY
   2.2. DESIGN PROCEDURE

3. PLANT DESCRIPTION
   3.1. BUCKLESHAM SITE
       3.1.1. Main Works
       3.1.2. Raw water resources
   3.2. DESCRIPTION OF THE DENITRIFICATION PLANT
   3.3. PROCESS MONITORING
   3.4. SUMMARY OF OPERATING CONSTRAINTS

4. OPERATION OF THE DENITRIFICATION PLANT
   4.1. START UP
       4.1.1. Hydraulic commissioning
       4.1.2. Start-up of the biological system
   4.2. SUMMARY OF DENITRIFICATION PLANT OPERATION
   4.3. PHOSPHATE DOSING
   4.4. METHANOL REMOVAL RATES
   4.5. SAND CLEANING AND SLUDGE PRODUCTION AND HANDLING
   4.6. WATER QUALITY CHANGES DUE TO DENITRIFICATION
   4.7. TREATABILITY OF THE DENITRIFIED WATER
   4.8. OPERATIONAL FLEXIBILITY OF THE DENITRIFICATION PLANT
4.9. PROBLEMS ENCOUNTERED DURING THE OPERATION OF THE DENITRIFICATION PLANT

4.9.1. Nitrite problem
4.9.2. Periods without bed growth
4.9.3. Sludge accumulation in product tank
4.9.4. Loss of sand from the reactor
4.9.5. Pressure build-up in the distributor

4.10. OPERATION OF THE DENITRIFICATION PLANT WITH ALTERNATIVE CARBON SOURCES

4.10.1. Ethanol
4.10.2. Acetic acid

5. COST OF DENITRIFICATION

6. CONCLUSIONS

REFERENCES

APPENDIX A - PROCESS MONITORING AND ANALYSIS DETAILS
1. INTRODUCTION

1.1. BACKGROUND

Increasing nitrate levels in public water supplies obtained from borehole and surface water abstractions have been a cause for concern particularly in Eastern England, during the last fifteen years\(^1\). Since their formation in 1974 Regional Water Authorities have invested considerable money and effort in identifying long term trends in nitrate levels in public water supply resources and in determining methods for ensuring compliance with public health standards.

In the UK hydrogeochemical research in groundwater aquifers has been primarily carried out by the Institute of Geological Sciences (now renamed the British Geological Survey) and the Water Research Centre; the results of this work have been extensively reported\(^2,3\) and predict a continuing upward trend in nitrate concentrations particularly in outcrop areas of major water supply aquifers.

Trends in major surface water abstractions, particularly in lowland areas, are more readily discernible due to the availability of long term records for rivers such as the River Thames, River Stour and River Gt Ouse\(^4\). With the exception of the River Lea in the Thames basin it has been shown that sewage effluent denitrification would have little impact on reducing nitrate levels in critical UK public water supply rivers at times of peak nitrate concentrations; in the River Gt Ouse, sewage effluent accounts for less than 5% of the nitrate load during the winter run-off period. The most significant contribution comes from run-off and drainage from arable land, particularly as a result of increased use of nitrate fertilisers\(^5,6\).

High nitrate levels in drinking waters have been associated with methaemoglobinaemia in infants and, more recently, it has been suggested that nitrates may influence human cancer incidence by the formation of nitrosamines in the digestive system.

Basic research into methods of nitrate removal in the UK was carried out by the Water Research Centre\(^7,8\). Subsequently
Anglian Water has invested in full scale operational research projects on the application of ion exchange for the removal of nitrate from groundwater and surface water\(^{(9,10)}\) and on the installation of the first full scale public water supply biological denitrification plant in Europe. The prototype biological denitrification plant was commissioned in 1982 and has been operated jointly by Anglian Water and the Water Research Centre.

1.2. NITRATE STANDARDS FOR PUBLIC WATER SUPPLIES

During the last decade the UK Water Industry has operated to the guidelines specified in the World Health Organisation for Drinking Water Standards (1970)\(^{(11)}\) for the assessment of "wholesomeness" in relation to nitrate levels in public supplies. WHO guidelines on drinking water quality have been revised recently, setting a "guideline" value for nitrate of 10 mg NO\(_3\) N/l\(^{(12)}\).

The EC directive on water quality for human consumption\(^{(13)}\) was published in July 1980 for implementation in member countries by July 1985. The directive specifies a Guide Level (GL) of 5.6 mg NO\(_3\) N/l and a Maximum Admissible Concentration (MAC) of 11.3 mg NO\(_3\) N/l; the values apply at the consumers tap.

The Joint Committee on Medical Aspects of Water Quality has recently reconsidered the risk from nitrate in water supply\(^{(14)}\). The committee concluded that the concentrations of nitrate in public water supplies in the UK do not constitute a significant cancer risk. The committee advises that the concentration of nitrate in the public water supply should not exceed 22.6 mg NO\(_3\) N/l other than in exceptional and transient circumstances. Water undertakings should continue to aim to keep the concentration below 11.3 mg NO\(_3\) N/l. However, where the concentration in the water supply exceeds 11.3 mg/l but is below 22.6 mg NO\(_3\) N/l the health authorities and professions in the affected area should be informed so as to encourage monitoring for infantile methaemoglobinaemia. If the nitrate concentration exceeds 22.6 mg NO\(_3\) N/l, at any time, suitable low nitrate water should be provided for infant feeding.
The Department of the Environment is currently preparing guidelines for the UK Water Industry on the interpretation of the EC nitrate standard.

1.3. OPTIONS FOR REDUCING NITRATE LEVELS IN WATER ABSTRACTED FOR PUBLIC SUPPLY

The available options for reducing the nitrate level in a public water supply are:

(a) Blending with lower nitrate water prior to supply
(b) Treatment: ion exchange or biological denitrification
(c) Storage of raw water to allow natural denitrification to occur
(d) Closure of the source and replacement with a lower nitrate supply.

The choice of the most economic long term option for a given supply is complex and influenced by factors such as the location and availability of alternative low nitrate resources, the nature of the supply itself (i.e. surface water or groundwater) and the seasonal fluctuations in nitrate concentrations, the design of the works and its capacity for modification, the availability of land for additional plant, manpower, maintenance and operating and capital costs.

Of the two treatment options, ion exchange is generally regarded as the most economical for groundwaters receiving only safety chlorination. Ion exchange plants can be operated without breaking head, and no additional treatment steps are required. For surface water treatment biological denitrification is generally the most economical option as treatment steps for the removal of biomass carry-over from the biological reactor are already available, and the organics present in raw surface waters could lead to fouling of the ion exchange resin.

1.4. BIOLOGICAL DENITRIFICATION

Biological denitrification makes use of the ability of facultative heterotrophic bacteria to utilise nitrate, in the absence of dissolved oxygen, for respiration, reducing the
nitrate to nitrogen gas via the pathway:

\[
\text{NO}_3^- \quad \text{NO}_2^- \quad \text{NO} \quad \text{N}_2\text{O} \quad \text{N}_2
\]

This process can be applied to water treatment by encouraging the development of high concentrations of denitrifying bacteria in a biochemical reactor. This can be achieved by providing a mechanical support material (e.g. sand) with a large surface area for the adherence of bacterial growth. In the case of surface waters (normally low in biodegradable organic material) the addition of a suitable carbonaceous substrate for the bacteria is also necessary.

Pilot plant studies comparing the denitrification performance of fixed bed, suspended growth and fluidised bed reactors\(^{(8)}\) had shown that the highest denitrification rates per unit volume could be achieved with the fluidised bed system. In addition pilot studies were carried out both by Anglian Water and WRC comparing methanol and acetic acid as carbon source. Acetic acid was found to produce elevated nitrite residuals in the product water under certain operating conditions and tenacious slime formation in the inlet distributor.

Based on the pilot plant studies, the decision was taken to construct a prototype fluidised sand bed denitrification plant, using initially methanol as carbon source, at the Bucklesham treatment works, Anglian Water. This site was chosen mainly because the raw water for the plant is abstracted from streams fed by three different springs with relatively constant and high nitrate concentrations throughout the whole year. The raw water does not show the seasonal variations typical of most surface water sources. Only during periods of heavy rainfall are the nitrate concentration in the streams decreased significantly.

The report summarises the results obtained from the biological denitrification plant installed at the Bucklesham treatment works, Anglian Water.
2. PROCESS DEVELOPMENT AND DESIGN

2.1. TREATMENT STRATEGY

The Joint Committee on Medical Aspects of Water Quality set a "tentative" limit for methanol in water entering supply of 0.25 mg/l and a maximum concentration of 1 mg/l in the water leaving the reactor. In addition the maximum methanol dose was restricted to 50 mg/l. Although it was envisaged that the denitrification plant would be operated methanol limited (i.e. no methanol present in the water leaving the reactor) the limits set for methanol and the method used for its analysis placed certain constraints on the design of the plant.

1. The plant was equipped with a continuous methanol autoanalyser which monitored the reactor effluent methanol concentration and shut down the plant in case of high methanol residuals in the reactor effluent.

2. Continuous nitrate monitoring of the raw water, reactor effluent and final water entering supply was carried out.

3. An intermediate product water holding tank with a 1 hour retention time was installed after the reactor. The water from the holding tank could be diverted to waste in the event of a high methanol residual in the denitrified water. The 1 h retention was provided to allow for analysis for methanol and restandardisation of the methanol analyser which together required approximately 40 minutes.

4. The denitrified water was mixed with the non-denitrified water in the ratio 1:3 before entering supply. This ensured that the methanol concentration in the water entering supply was less than 0.25 mg/l provided the reactor effluent methanol concentration was maintained below 1 mg/l.

To evaluate the potential of the process for potable water treatment applications the following features were incorporated in the design.

1. A raw water blend tank was provided to facilitate the mixing of the different raw water sources to vary the nitrate feed concentration to the plant. The tank also enabled operation
of the reactor with partial (especially during start-up) and full (in case of high methanol concentration in the reactor effluent) recycle.

2. Separate facilities were provided for the coagulation, sedimentation and filtration of the denitrified water to investigate the effect of biological denitrification on the final water quality produced.

A simplified flow diagram of the denitrification plant and the main works is given in Figure 1. The 2.8 Ml/d fluidised sand bed biological denitrification plant was built by Dorr Oliver Ltd.

2.2. DESIGN PROCEDURE

The design of the denitrification plant was based on the Dorr Oliver Oxitron system with design input from WRC. The following design criteria were employed for the plant:

- mean design flow 2.8 Ml/d
- water temperature 5°C
- dissolved oxygen 12.8 mg/l
- maximum methanol dose 50.0 mg/l

Pilot plant studies had established methanol requirements of 2.5 mg per mg NO₃ N removed and 1 mg per mg dissolved oxygen removed. The maximum methanol dose of 50 mg/l therefore limited the nitrate removal to a maximum of 15 mg NO₃ N/l at a raw water dissolved oxygen concentration of 12.8 mg/l. The system was designed with a recycle facility. With full recycle upflow rates of 45 m/h could be achieved which were required for the start-up of the plant to initially remove fines and to fluidise the clean bed. Biomass growth on the sand particles lowered the apparent density of the particles and reduced the upflow rate required for fluidisation. Dorr Oliver experience and WRC pilot plant results had established that:

- an average biomass concentration, measured as volatile solids concentration (VS), of 15 g VS/l could be achieved
the average nitrate removal rate for biological fluidised bed plants at 20°C was 5.5 g NO₃ N/kg VS.h.

The use of kinetics at 20°C resulted in a conservative design for the specified minimum design temperature of 50°C. Using these design values and an average upflow rate of 22 m/h (the rate used in the pilot plant studies) resulted in the following reactor design:

- bed area = 5.27 m² at 2.8 Ml/d (115 m³/h) flow
- total bed height to remove 12.8 mg DO/l and 15 mg NO₃ N/l at 20°C of 4.6 m.

3. PLANT DESCRIPTION

3.1. BUCKLESHAM SITE

3.1.1. Main Works

The Bucklesham treatment works supplies an average 11.2 Ml/d of potable water to the Felixstowe area. The treatment consists of direct river abstraction through coarse screens, alum dosing, horizontal sedimentation, rapid gravity filtration and marginal terminal chlorination. A flow diagram of the Bucklesham site is given in Figure 2.

3.1.2. Raw water resources

The principal raw water source at Bucklesham is the Mill River with an average nitrate concentration of 14 mg NO₃ N/l. This can be supplemented with water pumped from the Newbourn/Cragg Springs source which has an average nitrate concentration of 25 mg NO₃ N/l. Another potential raw water source is the Wadding Duck borehole supply which has zero nitrate, is deoxygenated and can have dissolved iron concentrations of up to 0.2 mg Fe/l.

During periods of heavy rain the nitrate concentration in the nitrate containing sources can be halved by dilution. Otherwise both sources are predominantly spring fed and show negligible seasonal variations.
The Mill river exhibits a marked diurnal variation in temperature which can vary in the winter between 2°C and 6°C and in the summer between 14 and 20°C. The oxygen saturation is usually between 80 and 100%, but during summer algal activity can raise it to 140% saturation.

The temperature variation of the Newbourn/Cragg Spring water varies little during the year (6-9°C) and the dissolved oxygen saturation is generally 100%.

3.2. DESCRIPTION OF THE DENITRIFICATION PLANT

Figure 3 shows a schematic diagram of the denitrification plant. The Oxitron reactor was a rectangular column 6.4 m high with a surface area of 5.27 m². The plant was operated usually with a flow rate of 32 l/s (115 m³/h or 2.8 Ml/d) corresponding to an upflow rate of 22 m/h. The flow to the reactor was controlled by a magnetic flowmeter and an automatic flow control valve. The reactor was equipped with the Dorr Oliver flow distributor system which ensured uniform flow distribution and fluidisation of the bed. The reactor effluent was aerated over a cascade aerator before entering the product water tank and the main treatment works.

The system was provided with a recycle facility between the reactor top and the raw water tank which allowed that hydraulic loading rates could be adjusted independently of the raw water flow rate. In emergencies (e.g. should the reactor effluent methanol concentration exceed 1 mg/l) the plant could be operated at 100% recycle, maintaining fluidisation of the bed without having to discharge water to waste. The recycle system could also be used during the start-up to obtain high upflow rates without discharging large quantities of water to waste.

The two reactor feed pumps were each capable of supplying 60 l/s (41 m/h upflow) against a system head of 24 m. If both pumps were operated in parallel they could deliver 72 l/s (49 m/h upflow) against a system head of 31 m.

The raw water tank had a diameter of 5 m and was generally operated with a water depth of 2 m providing a raw water storage capacity of 39 m³. The product water tank had a diameter of 7 m

8
and was operated with a water depth of 2.8 m, giving a residence time of 56 minutes at a flow of 2.8 Ml/d. The product water tank was equipped with 4 equally spaced baffles to minimise short circuiting.

The methanol was stored in a 14 m³ capacity tank buried in a bunded area back-filled with sintered stones. The methanol was transferred to a day tank and dosed with a metering pump to the inlet pipe of the reactor. The installation for storage and handling of methanol was designed and operated in accordance with the regulations applicable to highly inflammable liquids. An in-line mixer was provided to achieve good mixing of the methanol with the raw water.

Because of the low phosphate concentration in the raw water (<0.01 mg PO₄ P/l) phosphoric acid was dosed to the reactor influent by means of a metering pump. The dose was controlled to maintain a phosphate residual in the product water of between 0.05 and 0.1 mg PO₄ P/l. Chlorine dosing (up to 1 mg/l) of the product water was provided to control an "earthy" type odour detected in the early days of operation.

To prevent sand-biomass carry-over to the product water tank a sand cleaning system was installed to maintain the bed height at less than 5 m. Biomass-coated sand could be drawn off from the top region of the fluidised bed and pumped with a centrifugal pump to a hydrocyclone. In the centrifugal pump the biomass was sheared off the sand and was subsequently separated from the sand in the hydrocyclone. The cleaned sand was returned to the reactor using a Bredel peristaltic pump.

The biomass sludge was originally lagooned, but its instability necessitated the installation of a sludge thickening and storage plant. Two 10 m³ capacity tanks were provided for the thickening and storage of the sludge. The supernatant from the sludge treatment plant was discharged to the lagoons. The thickened sludge was tankerled away for disposal.

The denitrified water leaving the product water tank was dosed with alum and treated by sedimentation and rapid gravity filtration prior to blending with the remainder of the works.
treated water. The mixed water was chlorinated and passed through the chlorine contact tank into supply.

3.3. PROCESS MONITORING

The following continuous and spot sampling programmes were carried out on the plant, Table 1 and Table 2.

Table 1. Continuous monitoring programme

<table>
<thead>
<tr>
<th>Sampling points</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw water:</td>
<td>Nitrate, dissolved oxygen</td>
</tr>
<tr>
<td>Reactor product water:</td>
<td>Nitrate, nitrite, dissolved oxygen, methanol, temperature</td>
</tr>
<tr>
<td>Final water to supply:</td>
<td>Nitrate</td>
</tr>
</tbody>
</table>

Table 2. Spot sampling programme

<table>
<thead>
<tr>
<th>Sampling points</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw water:</td>
<td>Nitrate, nitrite, pH, phosphate, TOC, turbidity, suspended solids</td>
</tr>
<tr>
<td>Reactor product water:</td>
<td>Nitrate, nitrite, methanol, pH, TOC, turbidity, suspended solids</td>
</tr>
<tr>
<td>Final water to supply:</td>
<td>Nitrate, methanol</td>
</tr>
<tr>
<td>Bed profiles:</td>
<td>Nitrate, nitrite, dissolved oxygen, methanol, volatile solids, total solids</td>
</tr>
</tbody>
</table>

Continuous samples of raw water, reactor product water and final water were provided for the monitoring instruments. Details of the instruments are given in Appendix A. The continuous methanol monitor was equipped with a control system which turned off the methanol dosing pump and switched the reactor to 100% recycle in the event of methanol residuals in the product water exceeding 1 mg/l.

Bed profile samples were taken weekly at 0.5 or 1 m depth intervals. Liquid samples were withdrawn using an inverted
funnel siphon arrangement and analysed for methanol, nitrate, nitrite and dissolved oxygen. A special spring loaded sampler was employed for collecting a known volume of the bed. The sample was dried at 105°C and weighed giving the total solids concentration (TS). The sample was subsequently ashed at 550°C and the weight loss was a measure of the volatile solids concentration (VS).

3.4. SUMMARY OF OPERATING CONSTRAINTS

For the majority of the operating period the water from the denitrification plant was blended into supply, and so certain restrictions were placed on the operation of the plant.

1. The methanol dose was not to exceed 50 mg/l and the methanol residual in the reactor product water had to be maintained below 1 mg/l to ensure that the methanol concentration of the water going into supply was less than 0.25 mg/l.

2. The maximum raw water flow from Newbourn was restricted to 20 l/s which limited the maximum raw water nitrate concentration to about 22 mg NO₃ N/l at a raw water flow of 32 l/s (2.8 Ml/d).

3. Because of the limited chlorination capacity available at the Bucklesham Works the nitrite concentration in the reactor effluent had to be maintained below 0.5 mg NO₂ N/l.

4. During start-up and on a number of occasions the process product water was discharged via a lagoon to the Mill River (downstream of the abstraction). During these periods a discharge consent of 3 mg/l methanol had to be complied with.

In addition discharge consent limits of 5 mg/l were set for BOD and 10 mg/l for suspended solids which required the installation of the biomass sludge thickening and holding tanks.

4. OPERATION OF THE DENITRIFICATION PLANT

4.1. START-UP

The start-up period consisted of an initial hydraulic commissioning followed by the commencement of methanol dosing.
During this period the product water was discharged to Mill River downstream of the abstraction point.

4.1.1. Hydraulic commissioning

The hydraulic commissioning was carried out by Dorr Oliver Ltd as part of their contractual obligations.

The reactor was filled with 20 tonnes of sand producing a settled bed depth of approximately 2 m. The sand was fluidised at upflow rates of up to 45 m/h. Approximately 4 tons of fines and fine sand were removed from the top of the fluidised sand bed. After the removal of the fines 97% by weight of the sand in the reactor was in the size range 0.3 to 0.5 mm with an average size of about 0.35 mm. The bed expansion of the clean sand at 65 l/s flowrate (45 m/h upflow rate) was 45%.

4.1.2. Start-up of the biological system

Different strategies can be adopted for the start-up of biological denitrification plants:

- complete recycle with high methanol doses
- partial recycle - starting with high recycle which is progressively decreased with the development of the biomass
- complete flow through with an initially low methanol dose which is progressively increased with the development of the biomass.

To limit the methanol concentration discharged to the Mill River to less than 3 mg/l the start up procedure (commencing on 9 June 1982) was as follows.

During the first 5 days of operation the plant was dosed twice with a slug dose of methanol and phosphoric acid sufficient to produce a methanol concentration of 50 mg/l and a phosphate concentration of 0.5 mg PO₄ P/l in the water. The plant was operated during this period with 100% recycle until the methanol was depleted.

After this initial start-up period the following strategy was adopted:

The fluidised bed in the reactor was maintained at approximately 40% expansion giving a bed height of about 3 m by gradually decreasing the overall upflow rate in the reactor as the biomass developed on the sand. During the same period the
portion of flow-through was steadily increased and the amount of recycle decreased.

With the development of the biomass the methanol dose was gradually increased to maintain a residual methanol concentration of <5 mg/l in the reactor effluent. The effluent itself was discharged to the lagoons which reduced the methanol concentration to <3 mg/l and the water was subsequently returned to the river.

The changes in methanol dose, residual methanol concentration and the nitrate removed during the start-up period are presented in Figures 4 and 5. Figure 6 shows the amount of recycle and flow-through passed through the reactor during this period.

Zero dissolved oxygen concentration in the reactor effluent was achieved within two days of starting some raw water flow through the reactor and denitrification commenced by the third day. Thirty six days after start-up zero methanol concentration was achieved in the reactor effluent and 10 days later the water was put into supply. At this time the plant was operated with 32 l/s raw water flow and zero recycle (22 m/h upflow rate) and a methanol dose of 26 mg/l removing 6 mg NO₃ N/l. The increase in biomass development during the start-up period measured as volatile solids (VS) concentration on the sand is given in Figure 7, which indicates that for a methanol dose of 28 mg/l the biomass concentration in the bed stabilised at about 18 g VS/l of bed.

Subsequent pilot plant trials have shown that methanol removal of 30 mg/l can be achieved within 3 weeks using 5 mg/l dose increments at 3 day intervals. This indicates that the start up time can be reduced considerably provided optimum start-up conditions are employed.

4.2. SUMMARY OF DENITRIFICATION PLANT OPERATION

During the initial 5 months operating period (July to November 1982) the plant was maintained at a raw water flow of 32 l/s (22 m/h upflow rate) with zero recycle and the methanol dose was kept constant at 26 mg/l removing 6 mg NO₃ N/l.
As the water temperature decreased in the autumn the methanol dose was progressively increased to a maximum of 45 mg/l at a 32 l/s flow rate. Under these conditions a nitrate removal of up to 14 mg NO₃ N/l was achieved at temperatures as low as 20°C.

Figures 8 and 9 show typical nitrate removal performance of the denitrification plant for two different operating periods August 82 to December 82 and October 83 to May 84. Methanol residuals were maintained during these periods at non-detectable levels (<0.2 mg/l) and the water from the plant was put into supply.

Typical bed profiles during operation of the plant at low temperature (6°C) are shown in Figure 10 for total solids (TS) and volatile solids (VS) and in Figure 11 for nitrate, nitrite, dissolved oxygen and methanol. The profiles indicate that the dissolved oxygen was removed within the bottom 0.5 m of the bed and that complete methanol removal was achieved within the bottom 2 m of the bed of a total bed height of 4.5 m. The profiles confirm that a large excess of biomass was maintained in the reactor.

Average volatile solids concentration (VS) during these operating periods (at plant flows between 30 and 32 l/s) varied between 15 and 25 g/l depending on the methanol loading applied.

The raw water temperatures during these operating periods varied between 2 and 20°C and the dissolved oxygen concentration of the raw water averaged 11 mg/l with diurnal variations during the summer months between 8 and 14 mg/l.

4.3. PHOSPHATE DOSING

The phosphate concentration in the raw water was low, less than 0.1 mg PO₄ P/l, and phosphate dosing, using phosphoric acid, was therefore required to achieve optimum biological growth.

Phosphate dosing was controlled by maintaining a phosphate residual of between 0.05 and 0.1 mg PO₄ P/l in the product water. This required doses of between 0.2 and 0.4 mg PO₄ P/l depending on the methanol dose applied. The methanol to PO₄ P removal ratio was 150:1 equivalent to a C:P ratio of 56:1.
For an 8 day period in November 1982 no phosphoric acid was
dosed because of dosing pump failure. During this time the
average biomass concentration in the bottom 1 m of the bed
decreased from 8 g VS/l to 4 g VS/l Figure 12 and the methanol
removal throughout the bed was significantly reduced, Figure 13.
Normal conditions in the bed were restored within 5 days after
resumption of phosphate dosing.

4.4. METHANOL REMOVAL RATES

Bed profile data as shown in Figures 10 and 11 were used to
calculate average methanol removal rates per unit volatile solids
(VS). Methanol dose, reactor upflow rate and the average
volatile solids concentration in that part of the bed which
reduced the methanol concentration to less than 1 mg/l were used
to calculate the methanol removal rate. For instance the
profiles shown in Figures 10 and 11 produce an average methanol
removal rate of 23.4 g methanol/kg VS.h at 60°C. For the
calculation it was assumed that the methanol was removed in the
bottom 2 m of the bed, Figure 11.

Figure 14 shows the average methanol removal rates
calculated for the whole range of operating conditions and
temperatures experienced. The scatter of the results may be
explained by the accuracy of the sampling and by the different
upflow rates and methanol loadings employed, and by the fact that
bed samples were only taken in 0.5 m intervals i.e. methanol
concentrations may have been reduced to less than 1 mg/l within
the 0.5 m interval. Because of the sampling regime adopted the
average methanol removal rates can be considered as conservative
in terms of plant design.

At the design methanol dose (50 mg/l), about 25% of the
methanol dose is used for dissolved oxygen removal and the
remainder for nitrate removal. Using the design nitrate and
dissolved oxygen removal rates derived from the pilot plant
studies (5.5 g NO₃ N/kg VS.h and 17.9 g DO/kg VS.h respectively
at 20°C) a methanol removal rate of 14.8 g methanol/kg VS.h can be
calculated by taking into account that 2.5 mg methanol is
required to remove 1 mg NO₃ N and 1 mg methanol to remove 1 mg
DO. The corresponding average methanol removal rate at 20°C shown in Figure 14 is 9 g methanol/kg VS.h. The difference between the experimental value and the design value is relatively small considering the scatter of the data and the conservative estimation of the methanol removal rates (e.g. Figure 14 gives a removal rate of 18 g methanol/kg VS.h at 60°C compared with a calculated figure of 23.4 g methanol/kg VS.h).

At lower methanol loadings a higher average methanol removal rate must be expected because of the proportionately higher methanol dose required for the dissolved oxygen removal.

4.5. SAND CLEANING AND SLUDGE PRODUCTION AND HANDLING

Sand cleaning was carried out on a regular basis to maintain the bed height within the desired limits. For the first 5 months of operation, at relatively low methanol loadings (26 mg/l), the bed height was maintained between 3.5 and 4.0 m. Subsequently the bed height was allowed to increase to between 4.5 and 5.0 m to accommodate higher methanol doses. Depending on the methanol loadings applied sand cleaning was required on average once or twice a week for 1 hour. Each sand cleaning produced on average 10 m³ of sludge with a dry solids concentration of approximately 3.9 g/l and a volatile solids concentration of 3 g/l. 80% of the biomass recovered during sand cleaning was collected as the waste sludge whereas about 20% was returned to the reactor with the cleaned sand and was carried forward to the product water tank.

In addition to the biomass removed from the reactor by the sand cleaning approximately 50% of the biomass was lost from the reactor with the product water by natural wastage as indicated by the increase in suspended solids concentration between reactor inlet and outlet of on average 2 mg/l. The total sludge production was 0.2 kg dry solids/kg methanol removed.

However, on two occasions long periods without any increase in bed height were experienced which will be discussed in more detail in Section 4.9. During these times the total sludge production was carried forward with the product water to the subsequent treatment stages resulting in an increase in suspended solids concentration between reactor inlet and outlet of 5 mg/l.
The waste sludge was initially transferred to a lagoon for thickening prior to disposal. However, it soon became apparent that the waste sludge deteriorated rapidly in the lagoon resulting in high BOD (>100 mg/l) and suspended solids (>100 mg/l) concentrations in the supernatant. The supernatant could not be discharged to the river and the whole content of the lagoon had to be tankered away to a nearby sewage works. A sludge thickening and storage plant was therefore installed consisting of two 10 m³ capacity hopper bottom tanks. The sludge was passed initially to the sludge thickening tank in which the sludge concentration increased from 3.5 to 20 g/l after 2 hours settling reducing the sludge volume by a factor of about 5. The supernatant was returned to the river via the lagoon and the sludge was transferred to the holding tank for storage prior to tankering to a nearby sewage works.

4.6. WATER QUALITY CHANGES DUE TO DENITRIFICATION

Table 3 shows the changes in water quality observed due to the denitrification process for the periods during which the product water entered supply. The results indicate that little change in water quality occurred across the denitrification process. There was a slight increase in suspended solids concentration between the raw water and the product water which was due to biomass loss from the reactor as discussed in Section 4.5. The small increase in phosphate in the product water resulted from the phosphate dosing and the phosphate control strategy to maintain a phosphate residual of between 0.05 and 0.1 mg PO₄ P/l in the product water. During the periods when the denitrified water was put into supply the nitrite concentration was maintained below 0.2 mg NO₂ N/l which did not result in a significant increase in chlorine demand of the final water. Changes in nitrate concentration were presented in Section 4.2.

The product water dissolved oxygen concentration was always zero, but increased to approximately 100% after the cascade aeration. The raw water pH was consistently around 7.9 which was reduced by the denitrification process by about 0.1 units. Bacterial respiration resulted in an increase in alkalinity corresponding to 0.9 mg CaCO₃/l for each mg/l methanol consumed.
Table 3. Changes in chemical quality across the denitrification process during periods of operation into supply

<table>
<thead>
<tr>
<th>Period</th>
<th>Determinand</th>
<th>Raw water</th>
<th>Product water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>mean SD</td>
<td>n</td>
</tr>
<tr>
<td>August 1982</td>
<td>TOC (mg C/l)</td>
<td>2.5 0.9</td>
<td>(22)</td>
</tr>
<tr>
<td>to April 1983</td>
<td>Turbidity (FTU)</td>
<td>4.3 8.3</td>
<td>(116)</td>
</tr>
<tr>
<td></td>
<td>PO4 P (mg/l)</td>
<td>0.03 0.02</td>
<td>(148)</td>
</tr>
<tr>
<td></td>
<td>NO2 N (mg/l)</td>
<td>0.02 0.01</td>
<td>(148)</td>
</tr>
<tr>
<td></td>
<td>SS (mg/l)</td>
<td>3.7 3.5</td>
<td>(47)</td>
</tr>
<tr>
<td>November 1983</td>
<td>TOC (mg C/l)</td>
<td>1.4 0.2</td>
<td>(6)</td>
</tr>
<tr>
<td>to May 1984</td>
<td>Turbidity (FTU)</td>
<td>3.1 3.0</td>
<td>(56)</td>
</tr>
<tr>
<td></td>
<td>PO4 P (mg/l)</td>
<td>0.04 0.05</td>
<td>(66)</td>
</tr>
<tr>
<td></td>
<td>NO2 N (mg/l)</td>
<td>0.02 0.01</td>
<td>(113)</td>
</tr>
<tr>
<td></td>
<td>SS (mg/l)</td>
<td>3.9 2.8</td>
<td>(42)</td>
</tr>
</tbody>
</table>

(a) Includes higher values which occurred during strike period when the plant was operated with changing methanol loadings (Section 4.9)

(b) Includes higher values which occurred during period when the bed height stayed constant, Feb-May 1984 (Section 4.10)

A slight "earthy" type odour, detectable in the product water during hot weather, could be controlled by chlorination of the product water after the aerator at a dose of up to 1 mg Cl₂/l.

Samples were taken for analysis by gas chromatography which showed that denitrification produced one additional large peak which was, however, removed by the subsequent treatment stages, Figures 15, 16 and 17.

Spot samples were also analysed for bacterial quality which indicate no significant changes in coliform, faecal streptococci and clostridium spore counts due to the denitrification process (Table 4).

Table 4. Changes in bacteriological quality across denitrification process

<table>
<thead>
<tr>
<th></th>
<th>Colony counts per 100 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coliforms (44°C)</td>
</tr>
<tr>
<td></td>
<td>Thermotolerant coliforms</td>
</tr>
<tr>
<td>Raw water</td>
<td>610</td>
</tr>
<tr>
<td>Product water</td>
<td>920</td>
</tr>
</tbody>
</table>
A few samples were also analysed for total THM concentration, Table 5. The results show no significant difference in THM concentration between the final water chlorinated with 1 mg Cl₂/l and stored for 1 hour, the reactor product water chlorinated with 1 mg Cl₂/l and stored for 40 min and the reactor product water chlorinated with 1 mg Cl₂/l and subsequently treated by sedimentation and filtration (filters 5 and 6) with a total residence time of approximately 4 hours.

Table 5. Total haloform concentrations (µg/l)

<table>
<thead>
<tr>
<th>Period</th>
<th>Sample point</th>
<th>Mean</th>
<th>n</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aug-Dec 1982</td>
<td>Final water</td>
<td>30.4</td>
<td>11</td>
<td>14.5-63.0</td>
</tr>
<tr>
<td></td>
<td>Product tank</td>
<td>33.7</td>
<td>3</td>
<td>15.0-48.0</td>
</tr>
<tr>
<td></td>
<td>Filters 5 and 6</td>
<td>22.5</td>
<td>3</td>
<td>8.5-44.0</td>
</tr>
<tr>
<td>March 1983</td>
<td>Final water</td>
<td>42.5</td>
<td>12</td>
<td>11.5-115.0</td>
</tr>
<tr>
<td>Jan-July 1983</td>
<td>Filters 5 and 6</td>
<td>43.7</td>
<td>2</td>
<td>29.5-58.0</td>
</tr>
</tbody>
</table>

4.7. TREATABILITY OF THE DENITRIFIED WATER

Jar test results indicated that an aluminium dose of 2 mg Al/l was required to achieve minimum settled water turbidity. This dose was initially adopted for the treatment of the denitrified water. However, breakthrough of particulate and dissolved aluminium was experienced and the dose was reduced to an average dose of 1 mg Al³⁺/l, the same dose applied on the main works for the non-denitrified water.

Washing of the rapid gravity filters at Bucklesham was carried out on a 16 hour cycle. Headloss build-up on the filters treating the denitrified water, Filters 5 and 6, tended to be higher at 1 to 2 m after 16 hours compared with only 0.5 m on the remaining filters. The higher headloss build-up was probably due to the higher suspended solids load of the product water compared with the raw water. Core samples taken from Filter 5 and Filter 1 indicated higher proportions of volatile solids (0.75% compared
with 0.62%) and aluminium (0.29% compared with 0.18%) on Filter 5. On occasions more frequent backwashing of Filters 5 and 6 was required.

Comparisons of filtrate quality of samples taken from Filters 5 and 6 and from the other filters are shown in Table 6. TOC samples were only taken from Filters 5 and 6 and from the final water. During the period July to September 1982 no alum was dosed on the main works, as the raw water quality was very good, which explains the low residual aluminium concentrations of the filters treating the non-denitrified water. Generally it can be stated that the filtered denitrified water quality is very similar to the non-denitrified filtrate quality. Only the average residual aluminium concentrations was higher in filters 5 and 6 compared with the other filters which was due to a few unexplained high values as indicated by the much lower median values.

Table 7 gives average bacteriological qualities for the filtrates and final water over 2 operating periods for filters 5 and 6 treating the chlorinated denitrified water and for the remaining filters treating the non-denitrified water. The coliform and E. coli counts of the filtrate from 5 and 6 were lower than those of the other filters as the denitrified water was chlorinated prior to filtration. Otherwise there was little difference in bacteriological quality produced by the different filters. The bacteriological quality of the final water was independent of whether or not the denitrified water entered supply, and it can be concluded that denitrification had no adverse effect on the bacteriological quality of the final water.

A limited number of samples were tested for odour, using a panel size of 4 and a temperature of 40°C which showed that the Threshold Odour Number (TON) was 3.7 for filters 5 and 6 compared with 1.7 from the other filters which indicated that denitrification increased the odour of the water. However, samples taken for odour tests of the final water at times when the denitrified water entered supply, gave TON values less than 1 at 60°C which was well within the Anglian Water target value of <5.
Table 6. Average filtrate and final water quality

<table>
<thead>
<tr>
<th>Filter</th>
<th>Period</th>
<th>Colour (°H)</th>
<th>Turbidity (FTU)</th>
<th>pH</th>
<th>PV (mg/l)</th>
<th>Al$^{3+}$ (mg/l)</th>
<th>TOC (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>July–Sept 1982</td>
<td>5.8</td>
<td>0.6</td>
<td>7.8</td>
<td>0.5</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oct–Dec 1982</td>
<td>3.5</td>
<td>0.8</td>
<td>7.5</td>
<td>0.6</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oct–Dec 1983</td>
<td>5.0</td>
<td>0.7</td>
<td>7.4</td>
<td>0.7</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Jan–March 1984</td>
<td>4.5</td>
<td>0.6</td>
<td>7.3</td>
<td>–</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>July–Sept 1982</td>
<td>3.5</td>
<td>0.5</td>
<td>7.7</td>
<td>0.4</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oct–Dec 1982</td>
<td>9.3</td>
<td>0.5</td>
<td>7.5</td>
<td>0.7</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oct–Dec 1983</td>
<td>4.9</td>
<td>0.4</td>
<td>7.5</td>
<td>–</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Jan–March 1984</td>
<td>3.3</td>
<td>0.6</td>
<td>7.4</td>
<td>0.9</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>July–Sept 1982</td>
<td>6.6</td>
<td>0.4</td>
<td>7.8</td>
<td>0.3</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oct–Dec 1982</td>
<td>7.5</td>
<td>0.4</td>
<td>7.3</td>
<td>0.5</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oct–Dec 1983</td>
<td>2.7</td>
<td>0.5</td>
<td>7.4</td>
<td>0.8</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Jan–March 1984</td>
<td>3.5</td>
<td>0.4</td>
<td>7.4</td>
<td>–</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>July–Sept 1982</td>
<td>2.0</td>
<td>0.4</td>
<td>7.7</td>
<td>0.4</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oct–Dec 1982</td>
<td>11.5</td>
<td>0.4</td>
<td>7.5</td>
<td>0.8</td>
<td>0.008</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oct–Dec 1983</td>
<td>3.5</td>
<td>0.4</td>
<td>7.5</td>
<td>0.4</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Jan–March 1984</td>
<td>3.7</td>
<td>0.5</td>
<td>7.4</td>
<td>1.2</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>5*</td>
<td>July–Sept 1982</td>
<td>2.3</td>
<td>0.4</td>
<td>7.6</td>
<td>0.4</td>
<td>0.05</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>Oct–Dec 1982</td>
<td>9.1</td>
<td>0.6</td>
<td>7.5</td>
<td>0.8</td>
<td>0.47(1)</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>Oct–Dec 1983</td>
<td>4.0</td>
<td>0.9</td>
<td>7.6</td>
<td>1.3</td>
<td>0.23(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Jan–March 1984</td>
<td>6.9</td>
<td>0.8</td>
<td>7.6</td>
<td>–</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>6*</td>
<td>July–Sept 1982</td>
<td>5.4</td>
<td>0.5</td>
<td>7.6</td>
<td>0.4</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oct–Dec 1982</td>
<td>10.9</td>
<td>0.7</td>
<td>7.4</td>
<td>1.0</td>
<td>0.14</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>Oct–Dec 1983</td>
<td>10.0</td>
<td>0.6</td>
<td>7.5</td>
<td>0.9</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Jan–March 1984</td>
<td>6.0</td>
<td>0.9</td>
<td>7.6</td>
<td>0.6</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>July–Sept 1982</td>
<td>3.3</td>
<td>0.4</td>
<td>7.7</td>
<td>0.3</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oct–Dec 1982</td>
<td>12.4</td>
<td>0.8</td>
<td>7.6</td>
<td>0.8</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oct–Dec 1983</td>
<td>4.5</td>
<td>0.5</td>
<td>7.4</td>
<td>–</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Jan–March 1984</td>
<td>3.9</td>
<td>0.7</td>
<td>7.4</td>
<td>–</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>July–Sept 1982</td>
<td>4.0</td>
<td>0.4</td>
<td>7.8</td>
<td>0.4</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oct–Dec 1982</td>
<td>11.9</td>
<td>0.4</td>
<td>7.3</td>
<td>0.9</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oct–Dec 1983</td>
<td>5.0</td>
<td>0.5</td>
<td>7.3</td>
<td>0.9</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Jan–March 1984</td>
<td>2.2</td>
<td>0.5</td>
<td>7.3</td>
<td>1.1</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Final</td>
<td>July–Sept 1982</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.4</td>
</tr>
<tr>
<td>water</td>
<td>Oct–Dec 1982</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>Oct–Dec 1983</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>Jan–March 1984</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>3.0</td>
</tr>
</tbody>
</table>

PV = Permanganate value
(1) Median value = 0.07
(2) Median value = 0.10

* Filters 5 and 6 treated the denitrified water
<table>
<thead>
<tr>
<th>Period</th>
<th>Sampling</th>
<th>No of samples</th>
<th>Coliforms (no/100 ml)</th>
<th>E. coli (no/100 ml)</th>
<th>37°C Plate count (no/ml)</th>
<th>22°C Plate count (no/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mean (SD)</td>
<td>Range</td>
<td>Mean (SD)</td>
<td>Range</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>24 hr</td>
<td>48 hr</td>
<td>3 day</td>
<td>7 day</td>
</tr>
<tr>
<td>Aug 1982 to Dec 1982</td>
<td>5/6 Filtrate*</td>
<td>14</td>
<td>0 (0)</td>
<td>0-1</td>
<td>0 (0)</td>
<td>2.4 (2.5)</td>
</tr>
<tr>
<td>(chlorinated denitrified</td>
<td>1/2/3/4/7/8</td>
<td>24</td>
<td>85 (100)</td>
<td>2-318</td>
<td>67 (86)</td>
<td>0-316</td>
</tr>
<tr>
<td>water into supply)</td>
<td>Filtrate</td>
<td></td>
<td>Final water</td>
<td>14</td>
<td>0 (0)</td>
<td>0</td>
</tr>
<tr>
<td>Nov 1983 to April 1984</td>
<td>5/6 Filtrate*</td>
<td>21</td>
<td>0.2 (0.6)</td>
<td>0-2</td>
<td>0.1 (0.2)</td>
<td>0-1</td>
</tr>
<tr>
<td>(chlorinated denitrified</td>
<td>1/2/3/4/7/8</td>
<td>36</td>
<td>16 (626)</td>
<td>0-105</td>
<td>5 (9)</td>
<td>0-54</td>
</tr>
<tr>
<td>water into supply)</td>
<td>Filtrate</td>
<td></td>
<td>Final water</td>
<td>22</td>
<td>0 (0)</td>
<td>0</td>
</tr>
<tr>
<td>June 1983 to October 1983</td>
<td>Final water</td>
<td>21</td>
<td>0 (0)</td>
<td>0</td>
<td>0 (0)</td>
<td>0</td>
</tr>
</tbody>
</table>

* Filters 5 and 6 treated the denitrified water
It can be concluded, that no serious adverse problems were experienced treating the denitrified water by horizontal sedimentation, rapid gravity filtration and final chlorination and that no deterioration in final water quality was found.

4.8. OPERATIONAL FLEXIBILITY OF THE DENITRIFICATION PLANT

To establish the operation of the plant on a standby basis in case of emergencies three modes of operation were investigated. During these studies the product water was discharged to waste.

1. Operation of the plant with 25% flowthrough and 75% recycle without methanol or phosphate dosing. This mode was used during holiday periods when no emergency cover was available.

2. Operation of the plant with 25% flow through and 75% recycle with a 30 mg/l methanol dose (based on the flow through portion of the total flow) to maintain denitrification but to avoid the need for sand cleaning. This mode was employed during periods of limited emergency cover.

3. Operation of the plant during the day under normal design denitrification conditions and at night at the same conditions outlined in 2. This mode was adopted for the period when no emergency cover for the plant was available during the night.

The first mode of operation was investigated during 2 holiday periods for 10 days each, Christmas 1982 and Easter 1983.

Bed profiles taken at the beginning and end of the stand-by period indicated that the mean volatile solids concentration decreased from 15.1 to 12.7 g VS/l with a corresponding drop in bed height from 4.6 to 3.9 m. Most of the volatile solids were lost from the bottom 2 m of the bed. The plant was restarted with a methanol dose reduced by 15%, from the dose applied before the stand-by period equivalent to the proportional drop in bed height. Complete methanol removal was observed immediately after re-commencement of dosing, although the residual nitrite concentration increased for 1 to 2 days after the restart to values of up to 0.5 mg NO₂ N/l.
The second mode of operation was adopted for 25 days during the initial period of the water industry industrial action, January and February 1983. For this mode of operation the methanol dose based on the raw water flow was reduced from 35 to 30 mg/l, the raw water flow from 25 to 7 l/s and the recycle was increased from 5 l/s to 23 l/s. This resulted in a 77% decrease of the methanol load applied to the reactor. During the 25 days operation under these conditions the bed height increased by only 0.3 m. Returning the plant to the original conditions of 25 l/s raw water flow, 5 l/s recycle and 35 mg/l methanol dose resulted in total methanol removal immediately after the change-over.

The third mode of operation was evaluated for 17 days during the latter part of the water industry industrial action, February 1983.

During this period the plant was operated during the day (9.00 am to 4.00 pm) with a methanol dose of 35 mg/l at a raw water flow of 25 l/s and a recycle of 5 l/s. At night the methanol dose was reduced to 30 mg/l at a raw water flow of 7 l/s and a recycle of 23 l/s. Throughout this period the methanol residual was maintained below 1 mg/l and the nitrite concentration below 0.2 mg NO₂ N/l. Denitrification was not affected and was proportional to the methanol dose applied.

The tests have confirmed that the process is very flexible in terms of changes in methanol loadings and raw water throughput.

4.9. PROBLEMS ENCOUNTERED DURING THE OPERATION OF THE DENITRIFICATION PLANT

4.9.1. Nitrite problem

For most of the time the nitrite residual concentration in the product water was below 0.1 mg NO₂ N/l. However, at times nitrite concentration as high as 2 mg NO₂ N/l were experienced. Nitrite is easily removed by chlorination, but high chlorine doses are required - 5 mg Cl₂ are needed to oxidise 1 mg NO₂ N. At sites with limited chlorination capacity such as Bucklesham high nitrite concentrations are therefore unacceptable because
they could endanger effective disinfection. For this reason a continuous nitrite monitor was installed and, at times when the denitrified water was blended into supply, nitrite concentrations were limited to 0.5 mg NO₂ N/l.

Elevated nitrite concentrations up to 0.5 mg NO₂ N/l were experienced during the start-up period, but these decreased to less than 0.1 mg NO₂ N/l once denitrification had been established and a constant methanol dose was applied.

Higher nitrite levels of up to 0.5 mg NO₂ N/l were found for short periods (1 to 2 days) following recommencement of methanol dosing after the periods of stand-by operation employed during the holiday seasons described in Section 4.8. Small increases in nitrite concentration of up to 0.2 mg NO₂ N/l were also observed during the operation with variable methanol dose levels between day and night used during the water industry strike period (Section 4.8).

The first indication of high nitrite formation during routine operation was experienced 8 months after start-up. At that time the methanol dose was increased in one step from 42 to 55 mg/l and the raw water nitrate concentration was raised by supplementing the Mill River abstraction with Newbourn/Cragg springs water. These operating conditions were adopted to determine the maximum denitrification capacity of the process by utilising a greater depth of the bed. During this test the plant was taken out of supply. Following this sudden increase in methanol dose and nitrate concentration, elevated nitrite concentrations of between 1 and 2 mg NO₂ N/l were found in the product water, Figure 18. Profile samples indicated that the nitrite concentration increased up to the 1 m bed height and remained constant at this concentration, (Figure 19) in contrast to previous profiles which showed a rise to a peak value at the same bed height but a subsequent decline to very low nitrite concentrations at the top of the bed (Figure 11). Contrary to subsequent experiences, reductions in methanol dose did not result in a decrease in the nitrite concentration (Figure 18). Only when the methanol dose was lowered to 12 mg/l did nitrite
concentrations fall significantly. At this dose level the process was removing less than 1 mg NO₃ N/l on average. It was thought that the bed had developed a bacterial population predisposed towards nitrite production. Intensive bed washing was therefore carried out to reduce the volatile solids concentration from 18 to 5 g VS/l. To maintain fluidisation of the bed at these low volatile solids concentrations the upflow rate had to be increased to 44 m/h using recycle. These measures appeared initially to alleviate the nitrite problem, allowing the methanol dose of the raw water to be increased to 39 mg/l whilst maintaining nitrite residuals generally below 0.2 mg NO₂ N/l (Figure 18). However, about one week after increasing the dose to 39 mg/l, nitrite concentrations suddenly rose again to above 1 mg NO₂ N/l despite maintaining the volatile solids concentrations at low levels.

Attempts were then made to control the nitrite residual concentration by operating nitrate-limited (zero nitrate concentration in the reactor effluent) rather than methanol-limited whilst still maintaining a methanol residual in the reactor effluent of less than 1 mg/l. This strategy was selected because the denitrifying bacteria use preferentially nitrate rather than nitrite. Once nitrate concentrations have fallen to low levels any remaining methanol will be used by the bacteria to remove residual nitrite. Nitrate-limited operation was only partly successful as a result of diurnal variations in dissolved oxygen in the raw water, the inability to measure nitrate concentrations of less than 1 mg/l, and because of the tight restriction of less than 1 mg/l residual methanol in the reactor effluent. The results of the period with nitrate limitation are illustrated in Figure 20. Increases in dissolved oxygen in the raw water due to diurnal variations without corresponding increases in methanol dose resulted in increased nitrite concentrations in the reactor effluent. Because of the slow response of the methanol analyser (analysis time 40 minutes) it was difficult to follow closely the changes in dissolved oxygen concentration. An increase in raw water nitrate concentration
without raising the methanol dose resulted also in corresponding increases in nitrate and nitrite residuals in the reactor effluent which again could be reduced by increasing the methanol dose.

Attempts to operate the plant nitrate-limited were abandoned after two weeks and the methanol dose was progressively reduced to 22 mg/l based on a raw water flow of 25 l/s with 5 l/s recycle (the volatile solids concentration had increased sufficiently to allow operation at this lower upflow rate). Nitrite residuals were initially about 1 mg NO₂ N/l, but gradually fell to 0.1 mg/l or less over the subsequent two week period up to early August 1983. Attempts to raise the methanol dose in August and September 1983 resulted in increased nitrite concentrations, and it was not until October 1983 that the dose could be raised without a corresponding increase in nitrite concentrations.

In February 1984 a rising trend in nitrite residuals was again observed, with concentrations increasing from 0.03 to 0.3 mg NO₂ N/l over a three day period. The plant had been operated at a steady 41 mg/l methanol dose on a raw water flow of 32 l/s (no recycle) for the previous 6 weeks. To reduce nitrite residuals to below 0.1 mg/l it was necessary to decrease the methanol dose to 33 mg/l, and to maintain this dose level for the following 5 weeks. After this period, however, it was possible to return the methanol dose to 41 mg/l whilst maintaining low nitrite residuals.

A pilot scale experimental plant (constructed from 15 cm ID, 4 m high perspex columns) was installed on-site to investigate possible causes of high nitrite production, in particular:

(i) sudden changes in methanol loading,
(ii) temperature changes,
(iii) presence of possible inhibitory agents (NH₃, NO₂ and biocides).

Only the addition of relatively high concentrations of biocide resulted in a significant increase in nitrite residuals in the reactor effluent with a correspondingly higher increase in methanol residual concentrations and decrease in denitrification.
On the main plant the occurrence of nitrite was not associated with an increase in methanol residual or a decrease in denitrification performance.

As the raw water sources are in an area of intensive farming activity it was thought that some agricultural chemical could have been responsible for the nitrite residuals in the product water. GCMS analysis was carried out on raw water samples during periods of nitrite production, but no individual compound was identified which could have been responsible for the nitrite production. However, it must be pointed out that only approximately 10% of organics present in surface waters are amenable to GCMS analysis.

Another possible reason for the elevated nitrite concentrations could be that the raw water was deficient in one or more of the trace elements required for the biological process, such as molybdenum. Within the time scale of this project it has not been possible to follow up this line of investigation.

Generally, operating experience has shown that to minimise the risk of excessive nitrite production any increases in dose of the carbon source should be made progressively rather than in single large steps. High nitrite concentrations can be controlled in most cases by reducing the methanol dose applied. High nitrite residuals can be avoided by operation under nitrate-limited conditions. However, this mode of operation is at present difficult to achieve because of varying surface water dissolved oxygen and nitrate concentrations, the limitations of the nitrate and methanol monitors and the requirement to maintain a methanol residual of less than 1 mg/l.

4.9.2. Periods without bed growth

Under normal operating conditions sand cleaning was required once or twice a week depending on the loading applied to the plant. However, during two periods, 13 July to 9 October 1983 and 20 February to 14 May 1984, no bed growth took place. On the contrary the bed heights decreased from 3.9 m to 3.2 m and 4.3 m to 3.6 m respectively for the two periods. Average methanol
loadings were 33 mg/l at a raw water flow of 24 l/s and 6 l/s recycle for the first period and 38 mg/l at a flow of 32 l/s and no recycle for the second period.

During the periods without bed growth a greater increase in suspended solids concentration across the reactor was experienced compared with periods of normal bed growth, Table 8. No explanation was found for this greater loss of biomass from the reactor.

Table 8. Increase in suspended solids concentration across the reactor for periods with and without bed growth

<table>
<thead>
<tr>
<th></th>
<th>Product water suspended solids concentration (mg/l)</th>
<th>Increase across reactor (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>No bed growth</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13 July to 9 Sept 83</td>
<td>5.0</td>
<td>2.9</td>
</tr>
<tr>
<td>20 Feb to 15 May 84</td>
<td>11.6</td>
<td>6.6</td>
</tr>
<tr>
<td><strong>Normal bed growth</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aug 82 to April 83</td>
<td>5.5</td>
<td>1.8</td>
</tr>
<tr>
<td>Oct 83 to Feb 84</td>
<td>4.8</td>
<td>1.2</td>
</tr>
</tbody>
</table>

4.9.3. Sludge accumulation in product tank

The product water tank was drained for cleaning in May 1984. A significant accumulation of settled biomass sludge to a depth of 0.5 m was found in the tank; some of it was anaerobic with a strong odour. However, as discussed in Section 4.7 no odour problems were experienced with the final water. Settlement of solids in the product tank reduced the suspended solids loading of the filters treating the denitrified water. This could explain why the backwashing frequency of the filters treating the denitrified water was similar to that of the filters treating raw water.

4.9.4. Loss of sand from the reactor

A small amount of sand (less than 1 tonne) was lost from the reactor during the 3 year operation of the plant.
The main loss of sand occurred during a malfunctioning of the raw water flow controller which increased the flow to the plant. This expanded the bed to such a point that sand was discharged into the recycle line and, after opening of the recycle valve, into the raw water tank.

A further, but less significant loss, occurred during operation of the plant for a few days at high loadings and high raw water temperatures in the summer of 1983. Gas bubbles, probably nitrogen produced by the denitrification reaction, became attached to sand/biomass particles resulting in sand carry-over to the cascade aerator and product water tank. The loss of sand had no significant influence on the denitrification process as the process was always operated with a large excess of biomass.

4.9.5. Pressure build-up in the distributor

Initially up to December 1982 the distributor pressure was 9 m H₂O. The pressure increased steadily and reached 14 m H₂O by early 1984. Inspection of the distributor inlet pipework showed little biological growth. However, it was not possible to inspect the individual nozzles, and partial blockage of these nozzles could have been responsible for the increased pressure drop.

4.10. OPERATION OF THE DENITRIFICATION PLANT WITH ALTERNATIVE CARBON SOURCES

4.10.1. Ethanol

Ethanol was used as carbon source on the denitrification plant from May 1984 for a period of about 11 weeks. Ethanol dosing commenced with an initial dose of 20 mg/l removing about 7 mg NO₃ N/l from a raw water flow of 32 l/s (no recycle). Product water nitrite concentrations rose steadily from 0.03 to a peak of 0.8 mg NO₂ N/l. The ethanol dose was therefore decreased to 4 mg/l which reduced the nitrite residual to 0.1 mg NO₂ N/l. The ethanol dose was subsequently raised in 5 mg/l steps at 3 day intervals, to a maximum of 33 mg/l. During this period the nitrite residuals varied between 0.1 and 0.2 mg NO₂ N/l and
decreased subsequently to less than 0.1 mg/l for the remainder of the period of ethanol dosing.

Operation of the plant with an ethanol dose of 33 mg/l produced a removal of 12 mg DO/l and 13 mg NO₃ N/l equivalent to an ethanol requirement of 0.5 mg ethanol/mg DO and 2 mg ethanol/mg NO₃ N removed.

Customs and Excise required denaturing of the ethanol in the storage tank. Permission was obtained to use phosphoric acid at a concentration of 5% w/w for this purpose. This concentration was selected to provide a ratio of ethanol:P of 62:1. No additional phosphate was dosed, and over the period of operation with ethanol the mean phosphate residual in the product water was 0.13 mg PO₄ P/l. Raw water temperatures during operation with ethanol were in the range 9 to 19°C.

Bed profiles taken during operation with an ethanol dose of 33 mg/l and at a temperature of 11°C showed that similar bed profiles to the operation with methanol were obtained, Figures 21 and 22. Complete ethanol removal occurred in the bottom 2 m of the bed.

The average ethanol removal rate for an ethanol dose range of between 25 to 33 mg/l and a temperature range from 11 to 17°C was calculated at 31 g ethanol/kg V3 h. The sludge production was 0.23 kg dry solids/kg ethanol consumed of which about 40% was removed by sand cleaning and the remainder by the water leaving the reactor as indicated by the increase in suspended solids concentration of 3.6 mg/l. These values were similar to those obtained with methanol as carbon source.

The denitrified water was blended into supply for the last five weeks of operation with ethanol. No significant deterioration in quality was observed across the denitrification unit and no problems were experienced with the subsequent treatment of the denitrified water.

4.10.2. Acetic acid

Acetic acid dosing commenced in July 1984 with a dose of 7.5 mg/l. The dose was subsequently increased in 5 mg/l steps at 3 day intervals. Nitrite concentrations in the product water
remained low (0.03 mg NO₂ N/l) until a dose of 43 mg/l was reached. At this dose the nitrite residuals suddenly rose to between 1 and 2 mg NO₂ N/l. In order to maintain the nitrite residuals at 0.1 to 0.2 mg NO₂ N/l it was necessary to reduce the acetic acid dose to 10 mg/l. However, high nitrite concentrations were also experienced at the same time on a pilot plant operated in parallel with the full-scale plant using methanol as carbon source, indicating that the occurrence of nitrite was probably due to the raw water quality rather than the type of carbon source used.

During the final two weeks operation with acetic acid doses of up to 57 mg/l removing 12 mg DO/l and 12 mg NO₃ N/l were applied with nitrite residual remaining below 0.1 mg NO₂ N/l.

The acetic acid requirements were calculated as 1.2 mg acetic acid/mg DO and 3.5 mg acetic acid/mg NO₃ N removed. Bed profiles taken during operation with acetic acid are shown in Figures 23 and 24 which are similar to the bed profiles obtained during operation with methanol and ethanol as carbon source. Only the volatile solids concentration for acetic acid operation was lower at 10 to 11 g VS/l compared to 14 to 15 g VS/l for methanol and ethanol, which was probably due to operation of the plant over an extended period with a low acetic acid dose prior to sampling. Again the acetic acid was completely utilised in the bottom 2 m of the bed.

The limited data available indicate that the average acetic acid removal rate was 44 g acetic acid/kg VS.h at a temperature of 18°C with a sludge production of 0.18 kg dry solids/kg acetic acid consumed of which again 40% was removed by sand cleaning and the remainder with the product water. The sludge produced exhibited poorer thickening properties with a maximum dry solids concentration of only 12 g/l compared with 20 g/l during operation with methanol and ethanol.

No significant changes in water quality were observed across the denitrification unit, except that the pH of the water was reduced due to the acid dosing by up to 1 unit at the maximum acetic acid dose (57 mg/l) used. The raw water pH was on average
7.6. The denitrified water was discharged to waste during the operation with acetic acid as carbon source.

5. COST OF DENITRIFICATION

Based on operating experience, direct operating cost estimates have been prepared for the 2.8 Ml/d biological denitrification plant at Bucklesham to remove 12.8 mg DO/l and 15 mg NO₃ N/l, Table 9. The direct operating costs were estimated at 4.45 p/m³ which corresponds to a cost of 0.3 p/m³ for each mg/l of nitrate removed from the total flow of 11.2 Ml/d. Therefore to reduce the nitrate concentration in the total flow at Bucklesham by 3 mg NO₃ N/l would result in an increase in direct operating costs of 1 p/m³.

Table 9. Revenue costs for operation of a 2.8 Ml/d plant removing 12.8 mg DO/l and 15 mg NO₃ N/l using methanol as a carbon source (1984 prices)

<table>
<thead>
<tr>
<th></th>
<th>£ pa</th>
<th>p/m³</th>
<th>% of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLANT</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electricity</td>
<td>3372</td>
<td>0.33</td>
<td>7.4</td>
</tr>
<tr>
<td>Chemicals</td>
<td>10818</td>
<td>1.06</td>
<td>23.8</td>
</tr>
<tr>
<td>Maintenance</td>
<td>5750</td>
<td>0.56</td>
<td>12.6</td>
</tr>
<tr>
<td>Sludge handling</td>
<td>3819</td>
<td>0.38</td>
<td>8.6</td>
</tr>
<tr>
<td>Man power</td>
<td>7950</td>
<td>0.78</td>
<td>17.5</td>
</tr>
<tr>
<td><strong>SUB TOTAL</strong></td>
<td><strong>31709</strong></td>
<td><strong>3.11</strong></td>
<td><strong>69.9</strong></td>
</tr>
<tr>
<td>LABORATORY</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2) Methanol monitors</td>
<td>2940</td>
<td>0.29</td>
<td>6.5</td>
</tr>
<tr>
<td>(3) Nitrate monitors</td>
<td>1680</td>
<td>0.17</td>
<td>3.8</td>
</tr>
<tr>
<td>(1) Nitrite monitor</td>
<td>200</td>
<td>0.02</td>
<td>0.5</td>
</tr>
<tr>
<td>Spares and maintenance</td>
<td>2300</td>
<td>0.23</td>
<td>5.2</td>
</tr>
<tr>
<td>Analyst/Technician</td>
<td>6500</td>
<td>0.63</td>
<td>14.1</td>
</tr>
<tr>
<td><strong>SUB TOTAL</strong></td>
<td><strong>13620</strong></td>
<td><strong>1.34</strong></td>
<td><strong>30.1</strong></td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>45329</strong></td>
<td><strong>4.45</strong></td>
<td></td>
</tr>
</tbody>
</table>
The operating costs presented are site specific to Bucklesham. The cost of operating denitrification plants is influenced by factors such as the dissolved oxygen concentration in the raw water, the proportion of total site flow treated in the denitrification plant and the size of the denitrification plant.

The chemical costs are directly related to the dissolved oxygen concentration in the raw water. Therefore the higher the proportion of total flow treated in the denitrification plant, the greater will be the chemical costs for the same total site flow nitrate mass removal because of the increased costs for dissolved oxygen removal. It is therefore more economical to remove a high nitrate concentration from a small stream than a low concentration from a large stream.

Large denitrification plants offer economic advantages by reducing the cost per m³ water treated, as a large portion of the operating costs are independent of flow. For example a doubling in size of the Bucklesham denitrification plant to 5.6 Ml/d would, for a 12.8 mg DO/l and a 15 mg NO₃ N/l removal, reduce the direct operating costs from 4.4 to 3.1 p/m³ equivalent to 0.21 p/m³ per mg NO₃ N/l removed from a total flow of 22.4 Ml/d.

The total capital cost of the plant and ancillary equipment (excluding interest charges) was £510,000 in 1981. This cost can be broken down as follows:

- Mechanical/electrical engineering: 60%
- Civil engineering and pipework: 25%
- Laboratory equipment: 10%
- Consultancy fee: 5%

The cost for laboratory equipment included £10,000 for the cost of the continuous methanol monitor which was bought second hand and would have cost new approximately £50,000. As the plant at Bucklesham was an experimental prototype, considerable capital and operating expenditures were associated with providing a flexible plant and with monitoring and laboratory facilities. Some cost savings should therefore be possible in an operational plant.
The use of ethanol would double and acetic acid treble the chemical costs, increasing the total direct operating costs of the Bucklesham plant by 25% and 50% respectively (at 1984 prices).

6. CONCLUSIONS

1. The denitrification plant was operated under carbon source-limited conditions for two years using methanol as carbon source. Nitrate removal of up to 14 mg NO₃ N/l was achieved at temperatures as low as 20°C using a methanol dose of 45 mg/l. For long periods of operation, totalling over 1 year, the denitrified water was blended into supply. Except during the start-up period no methanol residuals were found in the treated water. No adverse problems with treatment of the denitrified water were experienced.

2. For short periods the plant was operated with ethanol (11 weeks) and acetic acid (8 weeks) as carbon sources. Using an ethanol dose of 33 mg/l resulted in a nitrate removal of 13 mg NO₃ N/l. When acetic acid was used as carbon source up to 12 mg NO₃ N/l removal was attained, at an acetic acid dose of 51 mg/l.

3. The operation of the plant with methanol as carbon source has confirmed the validity of the design data used.

4. During the operation of the plant with methanol as carbon source elevated nitrite residuals of up to 2 mg NO₂ N/l were at times produced in the denitrified water. No reason for this occasionally high nitrite production has been found, despite extensive pilot plant experimentation. Nitrite concentrations could in most cases be controlled by reducing the methanol dose applied.

5. High nitrite residuals were also obtained during part of the operational period with acetic acid. However, a pilot plant operated with methanol as carbon source in parallel also produced high nitrite residual indicating that the occurrence of high nitrite was probably due to the raw water quality rather than the type of carbon source used.
6. Operation of the plant under nitrate-limited conditions was effective in controlling nitrite residuals. However, this mode of operation was difficult to achieve because of the varying dissolved oxygen and nitrate concentrations in the raw water, the limitations of the nitrate and methanol monitors and the requirement to maintain a methanol residual of less than 1 mg/l.

7. The process exhibited a very high degree of flexibility of operation during stand-by periods. Despite daily approximately five fold changes in methanol dose and raw water flow rates, methanol concentrations in the reactor effluent were consistently maintained below the detection limit of 0.2 mg/l.

8. The sludge produced by the process was very unstable and storage of the sludge in lagoons was therefore not practical, because of the development of high supernatant BOD and suspended solids concentrations. The installation of the sludge thickening and storage plant reduced the sludge volume requiring disposal by at least 80% and avoided the problems experienced with the lagoons.

9. The nitrate and methanol monitors were initially very unreliable. However, increased maintenance and the installation of ultra-filtration devices at the inlet of the nitrate monitors improved their reliability. The nitrate monitors are not sufficiently accurate to be used for process control. The nitrite monitor proved reliable and was found to be essential as an early warning of increasing nitrite residuals in the denitrified water.

10. The presence of phosphate was essential for optimum operation of the process. The methanol to phosphate (PO₄ P) ratio required was 150:1 and the ethanol to phosphate ratio 60:1.

11. The direct operating costs for the removal of 15 mg NO₃ N/l from a flow of 2.8 Ml/d has been estimated at 4.45 p/m³ which corresponds to a cost of 0.3 p/m³ per mg NO₃ N/l removed from a total flow of 11.2 Ml/d. Increasing plant
size would decrease the cost of denitrification. The capital cost of the plant was £510,000. However, because of the experimental nature of the plant some cost reduction can be expected.

12. The use of ethanol as carbon source doubles the chemical costs and increases the total operating costs by approximately 25%. If acetic acid is applied the chemical costs treble increasing the total operating costs by approximately 50%.

REFERENCES


6. ROYAL SOCIETY. The Nitrogen Cycle of the United Kingdom, 1983.


APPENDIX A
PROCESS MONITORING AND ANALYSIS DETAILS

1. NITRATE MONITORING

Kent Industrial Measurement Ltd continuous nitrate monitors (Model 8006) were used for continuous nitrate monitoring. The instruments are based on the use of ion specific electrodes. The nitrate concentrations were recorded on Kent Clearspan recorders. The monitors were provided with automatic recalibration at regular pre-set intervals to correct for electrode drift. To improve the reliability of the monitors the feed lines were equipped with ultra-filtration devices to remove suspended solids and the sample streams were dosed with an ionic buffer to maintain similar ionic strengths between samples and standard solutions.

2. METHANOL MONITORING

A Technicon IV autoanalyser was used for the continuous monitoring of the reactor product water methanol concentration\(^{15}\). The sample stream was acidified and any methanol present in the water was oxidised to formaldehyde by the addition of potassium permanganate. Excess permanganate was removed by reduction with sodium arsenite. The formaldehyde produced passed through a dialysis membrane into a recipient water stream which was dosed with acetylacetone. Formaldehyde reacts with acetylacetone producing a yellow colour. The light intensity at 430 nm was a measure of the methanol concentration present in the sample.

3. NITRITE MONITORING

Another autoanalyser system was employed for continuous monitoring of nitrite. The sample stream was diluted by a factor of 10:1 with water and dosed with sulphanilamide which reacted with the nitrite producing a red colour. The light intensity at 525 nm was a measure of the nitrite concentration present in the sample.
4. DISSOLVED OXYGEN AND TEMPERATURE

Kent Industrial Measurement continuous monitoring systems were used for the determination of dissolved oxygen concentration and temperature, which were recorded on Kent Clearspan recorders.

5. METHANOL - SPOT SAMPLES

A similar autoanalyser system to the Technicon IV continuous methanol monitor was employed for determining the methanol concentration of spot samples.

6. NITRATE - SPOT SAMPLES

An ion specific electrode was used for measuring the nitrate concentration of spot samples.

7. ALL OTHER ANALYSIS were carried out using standard methods for water analysis. Gas chromatography was used for the analysis of ethanol and acetic acid giving detection limits of about 0.8 mg/l for both.

8. MONITOR PERFORMANCE AND RELIABILITY

Initially, nitrate and methanol monitor performance was unreliable, largely as a result of biological growth in the product water sample lines. The nitrite monitor had not been installed at that time. The problems were alleviated by the installation of ultra-filters in the nitrate monitor sample lines and by more regular maintenance (replacement of tubing and dialysis membranes) for the methanol monitor. Despite the installation of ultra-filters the nitrate monitors were found to be only 70% reliable (i.e. giving a steady output or varying output relative to changes in concentration) in the period June 1983 to February 1984. The major sources of unreliability were electrode drift and excessive noise. The average monitor electrode life was found to be 62 days, compared with the manufacturers recommended 90 days. A comparison of the nitrate monitor output with spot sample results showed that agreement to within ±2 mg NO₃ N/l was achieved in only 58% of all comparisons for concentrations up to 20 mg NO₃ N/l. Generally, the nitrate
monitors at Bucklesham were judged to be too unreliable and inaccurate to be used for process control.

The methanol and nitrite monitors were found to be much more reliable and accurate, although routine maintenance requirements were higher. The limits of detection for the methanol monitor and nitrite monitor were 0.2 mg/l and 0.05 mg NO\textsubscript{2} N/l respectively. Both instruments occasionally suffered from excessive noise and baseline drift, but were generally reliable for over 90\% of the time. The problems of noise and baseline drift could be controlled by regular maintenance. However, on occasions pump tube or dialysis membrane failure on the methanol monitor caused false methanol alarms resulting in the shut-down of the denitrification plant.
Figure 1. Schematic layout of the Bucklesham main works and denitrification plant.
METHANOL RESIDUAL CONTROL SYSTEM

Figure 3. Schematic diagram of the denitrification plant.
Figure 4. Methanol dose and residual during start-up period.
Figure 5. Nitrate removal during start-up period.

Figure 6. Flows during start-up period.
Figure 7. Biomass development during start-up.
Figure 8. Raw water and product water nitrate concentration, August to December 1982.
Figure 9. Raw water and product water nitrate concentration, October 1983 to May 1984.
Figure 10. Bed profiles (solids samples) using methanol as carbon source (6°C).

Figure 11. Bed profiles (liquid samples) using methanol as carbon source (6°C).
Figure 12. Effect of phosphate deficiency on the volatile suspended solids concentration in the bed.

Figure 13. Effect of phosphate deficiency on the methanol removal in the bed.
Figure 14. Mean methanol removal rate vs. temperature.
Figure 16. Gas chromatograph of denitrified water.
Figure 17. Gas chromatograph of final water.
Figure 18. Period of high nitrite production.
Figure 19. Profile during period of high nitrite production.
Figure 20. The effects of nitrate-limited operation on nitrite production.
Figure 21. Bed profile (solids samples) using ethanol as carbon source (14°C).

Figure 22. Bed profile (liquid samples) using ethanol as carbon source (14°C).
Figure 23. Bed profile (solids samples) using acetic acid as carbon source (17°C).
Figure 24. Bed profile (liquid samples) using acetic acid as carbon source (17°C).
WRC ENGINEERING
PO Box 85
Frankland Road
Blagrove
Swindon
Wilts SN5 8YR
Tel: Swindon (0793) 488301
Telex: 449541

WRC ENVIRONMENT
Medmenham Laboratory
Henley Road
Medmenham
PO Box 16
Marlow
Bucks SL7 2HD
Tel: Hambleden (Bucks) (049-166) 531
Telex: 848632

WRC PROCESSES
Stevenage Laboratory
Elder Way
Stevenage
Herts SG1 1TH
Tel: Stevenage (0438) 312444
Telex: 826168

WRC SCOTTISH OFFICE
1 Snowdon Place
Stirling FK8 2HN
Tel: Stirling (0786) 71580

WRC INTERNATIONAL OFFICE
9 Dartmouth Street
London SW1H 9BL
Tel: 01 222 0494
Telex: 848632

WRC REGISTERED OFFICE
Henley Road
Medmenham
PO Box 16
Marlow
Bucks SL7 2HD
Tel: Hambleden (Bucks) (049 166) 531
Telex: 848632

WRC CONTRACTS LTD
Henley Road
Medmenham
PO Box 16
Marlow
Bucks SL7 2HD
Tel: Hambleden (Bucks) (049 166) 531
Telex: 848632