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Introduction

Dissolved oxygen is essential for the aerobic biological treatment of waste waters containing biodegradable organic matter. It is utilized in the biochemical reactions by which organic impurities are oxidized to innocuous products and from which micro-organisms derive energy for their survival and growth. Its rate of transfer into waste water during treatment, if inadequate, may therefore limit the rate of treatment. In a system in equilibrium, the rate of transfer will depend on the deficit of



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dissolved oxygen; by using oxygen instead of air, the rate of transfer of oxygen into solution (under similar conditions of temperature and total pressure) is increased at least fivefold.

Many claims have been made for the benefits of using commercially available oxygen instead of air in the treatment of waste water [1-8]. Without such benefits, oxygen could still be economically used if its production costs were low and its wastage could be avoided. Therefore, the techniques used to dissolve oxygen are as important to the economics of the use of commercially available oxygen in treatment of waste water as the methods used to separate oxygen from air.

This paper describes the development of commercial techniques for separating oxygen from air and for dissolving oxygen in water, and the results of their application in the UK in the treatment of waste waters.

Production of oxygen

Techniques

In the early 1900's Linde successfully developed a commercial method of using the Joule-Thomson effect to liquefy air by adiabatic expansion. Liquefaction of air followed by fractional distillation to produce oxygen is still the major commercial process today; cryogenic plants are in operation capable of producing daily 1500 tonnes oxygen of 99.7 per cent purity. In 1958 dr. C. W. Skarstrom pioneered a new process for commercial production of oxygen. This involved the adsorption of nitrogen from air at a pressure of about 200-300 kPa by a zeolite and its subsequent desorption at atmospheric pressure (100 kPa) in a process normally described as 'pressure-

swing adsorption' (PSA). The PSA process produces oxygen-enriched air (containing between 70 and 90 per cent oxygen, depending on the method and conditions of operation) and is automatic in operation; commercial plants are now available to produce 1-50 tonnes oxygen daily. The development and operation of the PSA process is adequately described elsewhere [9-11].

Costs

The manufacturers [9, 10] claim that a PSA plant has a lower capital cost than a cryogenic plant for producing oxygen in quantities ranging from 1-20 tonnes/d but requires more power for operation. For an output greater than 20 tonnes/d the capital cost of a cryogenic plant is generally less than that of a PSA plant producing the same quantity of oxygen. In a recent paper [10] the capital costs of cryogenic plant have been compared with those of PSA plant, although no PSA plant with an output above 50 tonnes/d has been constructed. To the capital cost of cryogenic or PSA plant must be added the capital cost of providing an adequate emergency (standby) capability for occasions when the equipment fails to operate satisfactorily [12].

Energy requirements

Energy requirements per tonne oxygen produced are little affected by scale of production. For a cryogenic plant they are reported [9, 10] to be about 350 kWh/tonne oxygen, compared with 350-600 kWh/tonne for a PSA plant, depending on the material used to adsorb nitrogen.

Dissolving oxygen in water

Techniques

To achieve maximum utilization of available gaseous oxygen the method used to dissolve it in water must prevent its loss to the atmosphere. Several techniques have been developed to permit oxygen to be used efficiently. These include agitation of water and oxygen in an enclosed tank; release of oxygen as very fine bubbles at the bottom of an open tank of water, at a rate sufficient to achieve adequate mixing without excessive loss of oxygen at the surface; injection of oxygen under pressure into a side-stream of liquor which is returned to the main flow of water; and injection of oxygen bubbles into a down-flowing stream of water so that their upward movement is prevented.

The first of these techniques has been developed in the USA by the Union Carbide Corporation in what is termed the Unox process [2, 7]. Air Products and Chemical Corporation developed a similar system in

their process [8, 13], which also includes the use of residual gas (oxygen and carbon dioxide) to strip dissolved nitrogen from the incoming waste water. The second technique has been developed [14, 15] in the USA by the FMC Corporation and its use is proposed in studies with pilot plant in the UK. The side-stream injection technique has been developed in the UK by BOC Ltd, and has been used successfully to provide a system for increasing the oxygenation capacity of existing conventionally-aerated activated-sludge plants. A down-flow bubble oxygenation system was first described in 1970 [16] and BOC Ltd now advertise the use of such a system commercially.

Energy requirements

The energy required to dissolve oxygen in water depends largely on the technique used. In the activated-sludge process much energy is also used in achieving mixing and in maintaining the activated sludge in suspension.

Data available in the UK indicate that the electrical energy required to dissolve commercially produced oxygen varies from about 300 kWh/tonne for agitation in an enclosed tank to about 400 kWh/tonne for the side-stream technique.

The total power requirement (for producing oxygen and dissolving it in the mixed liquor of an activated-sludge plant) varies in the range 650-1000 kWh/tonne. In contrast, the total power required to operate conventional aeration equipment, using either fine-bubble diffused air or mechanical surface aeration (and operating at zero concentration of dissolved oxygen in the mixed liquor), is 500-700 kWh/tonne oxygen dissolved, but can be as much as 1200 kWh/tonne for a coarse-bubble aeration plant. However, to maintain a concentration of 50 per cent of the normal air-saturation concentration would increase the total power requirements by about 5 per cent for an oxygenated plant, but by as much as 100 per cent in the case of a conventionally-aerated plant.

Use of oxygen in the activated-sludge process

Experiments with pilot plants in the UK [5, 8] have shown that there is little difference in the possible rate of treatment (kg BOD removed daily/per kg activated sludge) between an oxygenated plant (OP) and an aerated plant (AP). When treating the same sewage at similar sludge loadings, there is little difference in the BOD and SS content of effluent between an OP and an AP provided that the concentration of dissolved oxygen in the mixed liquor is kept above 20 per cent of the normal air-saturation

concentration. However, since oxygen can be dissolved in the mixed liquor at a higher rate, its use can raise the rate of treatment per unit volume of mixed liquor above that obtained with conventional aeration, provided that the MLSS can be increased to keep the sludge loading at a constant rate. In the literature, benefits have been claimed [1-8] which include increased rate of treatment, increased density and rate of settlement of sludge, and reduced production of sludge. However, these benefits were not found in experiments in the UK [18, 19] in which an activated-sludge plant was operated with concentrations of dissolved oxygen in the mixed liquor of up to 7 mg/l using a conventional system of aeration, nor in other studies of aerated and oxygenated systems [20, 21, 22].

Nitrification

Difficulties have been encountered in achieving nitrification in an OP. This is attributed to the incomplete stripping of carbon dioxide from the mixed liquor by the relatively small volume of gas ultimately discharged to the atmosphere. Such an effect has been confirmed by experiments with a single complete-mixing OP operated in the UK, which showed [8] that a fully-nitrified effluent could be produced only when alkali (sodium hydroxide) was added to the mixed liquor to prevent the pH value falling below 7.5. To achieve nitrification using a Unox system, two plants have been operated in series, the first-stage plant having been designed for high-rate oxidation of carbonaceous matter using oxygenation and the second-stage plant for conventional aeration to produce a fully-nitrified effluent [5].

By contrast, an AP can consistently produce a fully-nitrified effluent in a single-stage process and has the further advantage [17] of possible denitrification, which makes oxygen from nitrate available for carbonaceous oxidation.

Sludge characteristics

Results of recent experiments with pilot plant in the UK have indicated that settleability

of activated sludge was better, and production of sludge lower, in an OP than in an AP [5, 8]. Although the data are somewhat sparse [5], the settleability of sludge from an OP was little affected by changes in sludge loading, whereas the settleability of sludge from an AP treating the same sewage deteriorated when the daily loading was increased above about 0.3 g BOD/g activated sludge solids. Production of sludge varies with the nature of the waste water being treated. When both types of plant were operated at the same sludge loading treating the same waste water, the production of sludge (Table I) from an OP was about two-thirds of that from an AP [8]. Such a difference, if achieved in practice, would have a considerable influence on the total cost of treatment.

Factors influencing the use of oxygen

Data available from the literature [4, 23] indicate that an OP has significant economic advantage over an AP for a large plant (40,000 m³/d) required to produce a non-nitrified effluent and operating in areas where unit costs of sludge disposal are high, so maximizing the advantage of a lower production of secondary sludge. The circumstances in which it is to be used in the treatment of waste water will largely determine the advantages and disadvantages of using oxygen instead of air. However, some advantages have been claimed which depend little on circumstances such as location or size of the treatment works; these include:

- (1) the possibility of dissolving oxygen at high rates into mixed liquor;
- (2) the lower production of sludge with better settling characteristics, even when operating the OP at high sludge loadings [1-8];
- (3) the reduced possibility of sludge bulking [1-5];
- (4) the possibility of treating waste waters of high BOD in plants smaller than would be required were an AP to be used [1, 3];

(5) the possibility of reducing aerial nuisance (malodours, aerosols) by the use of covered tanks from which only a small volume of gas is discharged to the atmosphere;

(6) the improved quality of effluent and stability of operation of plant resulting from the ability to control the input of oxygen to cover a wide range of diurnal variations in BOD load to the treatment plant;

(7) the possibility of lower overall costs — one paper [23] claims lower costs when treating dry-weather flows exceeding 4500 m³/d.

Similarly, there are disadvantages which apply irrespective of the location and size of the treatment plant.

- (1) The use of oxygen implies reliance either on complex equipment requiring highly-qualified staff to operate and maintain it, or on an external manufacturer to supply oxygen without fail.
- (2) More energy may be consumed in producing and dissolving oxygen than in aeration, although this might be more than offset by lower costs (including energy costs) for disposal of sludge and construction of plant.
- (3) Nitrification cannot usually be achieved in a single-stage plant, without modification of the process, because of the effect of carbon dioxide on the pH value of the mixed liquor.
- (4) The use and storage of oxygen might be considered an unwelcome hazard at most treatment works, although strict observance of simple safety regulations should reduce the potential risks to a minimum.
- (5) There could possibly be maintenance problems arising from corrosion of equipment in sealed oxygenation tanks.

Use of oxygen in rising-main sewers

Formation of sulphide and its prevention

Sulphide is formed in sewage in the absence of dissolved oxygen. The potential for

TABLE I - Weekly average conditions of operation of pilot plants treating various waste waters showing production of activated sludge (calculated from that deliberately wasted plus that discharged as suspended solids in the effluent) per unit weight of BOD removed during treatment.

Type of treatment plant	Waste water treated	Sludge loading (g BOD/g sludge d)	MLSS (mg/l)	Production of sludge (g/g BOD removed)	Temperature of mixed liquor (°C)
Oxygenated Aerated	Mixture of domestic and industrial	0.47	5600	0.96	10—12
		0.1	6950	0.95	
Oxygenated Aerated	Domestic	0.85	3600	0.60	13—14
		0.89	3450	0.98	
Oxygenated Aerated	Domestic	0.82	6000	0.68	11—20
		0.14	4900	0.70	

* Unusually high value is attributed to the peculiarities of the sewage treated.

formation of sulphide is greatest in a rising-main sewer since the sewage normally receives no aeration within the main. Hydrogen sulphide, formed and dissolved in sewage within a rising main, does not normally result in corrosion of the main and will not affect the sewerage system unless it is liberated in the atmosphere. The use of oxygen to maintain aerobic conditions in a rising-main sewer, to prevent sulphide being formed and hence causing corrosion of concrete or steel in a subsequent length of gravity sewer or causing odour nuisance at the point of discharge, has recently been described in detail [24].

The quantity of oxygen required to maintain aerobic conditions has been shown to depend on, among other factors, the oxygen demand of the sewage and the area of internal surface of the rising main which becomes coated with a slime of micro-organisms. Typically, for sewage at 15 °C it is necessary to inject oxygen at a rate equivalent to 14 mg oxygen/l sewage h and 700 mg oxygen/m² wall surface h. The rate at which dissolved oxygen is utilized by micro-organisms both in sewage and slimes will be affected by many factors, for example pH value, temperature, and concentrations of metals and substances potentially inhibitory to biochemical oxidation. It has been shown [25] that the rate of uptake of dissolved oxygen by sewage varies widely, being low for fresh sewage (2-4 mg/l h), increasing when sewage is kept for several hours under aerobic conditions (up to rates as high as 20 mg/l h), and finally declining as the concentration of organic matter in the sewage decreases.

To prevent sewage becoming anaerobic in a rising main may require the injection of as much as 200 mg oxygen/l, depending on the size of the main and the period that sewage will be retained within it. To introduce a similar quantity of dissolved oxygen by aeration of sewage would be less satisfactory, since part of the main would be occupied by residual nitrogen, necessitating an increase in velocity of the sewage to achieve the same flow-rate and thereby producing greater frictional losses. In addition, should some sulphide still be formed in the sewage it would be partially stripped out by the nitrogen gas and still result in corrosion and odour nuisance at the head of the main. Nevertheless, aeration, or the use of hydrogen peroxide and other methods such as chlorination or the addition of bactericides, can be used to prevent formation of sulphide in sewage. Oxygen injection is only one of several methods, the choice depending on the conditions within the rising main and the potential for formation of sulphide.

Treatment of sewage

The use of oxygen rather than air to maintain aerobic conditions in the sewage is justified largely because of the high concentrations (perhaps 200 mg/l) that may be required. With such a high requirement for dissolved oxygen, the BOD of sewage will be significantly reduced during passage of the sewage through a rising main. In practice, it should be possible to construct a rising main of sufficient length to ensure that, when it has become coated internally with slime, sewage flowing through it under aerobic conditions would be substantially treated by the time it was discharged from the top of the main and would require little more than settlement to remove accumulated solids. Experiments are in progress in the UK to investigate further the possibilities of injection of oxygen to treat sewage. In one such investigation [26], oxygen is being injected into a rising main 8.16 km long and about 0.8 m diameter, at a rate between 51 and 54 kg/h, in order to maintain aerobic conditions, and its effect on the BOD and treatability of the sewage is being studied. When oxygen was injected at a constant rate, the concentration of dissolved oxygen in the sewage depended on the rate of pumping. The highest concentration of dissolved oxygen was achieved when the flow-rate of sewage was lowest and when the retention time of sewage in the rising main was longest, and conversely the lowest concentration was obtained when the flow-rate of sewage was highest and the retention time was shortest. In this way the requirement of the micro-organisms for dissolved oxygen, at a concentration which is directly related to the retention time of sewage in the main, is matched by the injection of oxygen at approximately the required concentrations.

The effect of oxygen injection on the performance of the biological filtration works to which sewage from the head of the main was discharged was also assessed. During the summer months (June-September) the performance of the primary sedimentation tanks was better than had been achieved previously at similar times of year; the average percentage reduction of BOD was 62 and of suspended solids (SS) was 76, with flow rates of sewage into the tanks such that the retention was on average 4 h and the upward-flow velocity 1.5 m/h (compared with conventional design standards in the UK the sedimentation tanks were 40 per cent hydraulically overloaded). During a period of normal operation that followed (September-December) — without injection of oxygen into the rising main — the average percentage reduction achieved, at similar hydraulic loadings, had decreased to 41 for BOD and 60 for SS.

However, subsequent injection of oxygen (December-March) did not significantly improve the performance of the sedimentation tanks, although the results obtained were possibly affected by changes of temperature in the sewage between summer (20 °C) and winter (11 °C).

As a result of keeping the sewage aerobic, the BOD and SS content of the final effluent from the biological filtration plant, treating the settled sewage, decreased from previous average values of 58 and 61 mg/l respectively to 19 and 21 mg/l although this change occurred at the same time that the average temperature of the sewage increased from 13 to 21 °C. The improvement in effluent quality was observed to last for several months after oxygen injection was stopped and the plant was again operated normally. This might be expected as the treatment system with oxygen injection is similar to double filtration with the oxygenated rising main acting as the primary filter and the normal biological filters as secondary filters. Improvement in effluent quality, achieved during the summer, did not change significantly when oxygen injection ceased and the rising main no longer acted as a primary filter. The performance of the normal filters which has been rested by loading at a low rate (0.07 kg BOD/m³) during the previous period of oxygen injection was eventually affected by the increased BOD loading resulting from discontinuation of oxygen injection — hence changing the plant to normal single filtration. The relatively poor quality of effluent (average BOD 28 mg/l and SS 29 mg/l) obtained with injection of oxygen in the rising main during the winter months (December-March) was possibly affected by a decrease in the temperature of the sewage that occurred at the same time.

The total weight of sludge (primary and humus) for disposal from the works was little affected by treatment of the sewage in the rising main, although the volume of consolidated sludge withdrawn from the primary sedimentation tanks was reduced by about 10 per cent.

Thus, summarizing the above, the use of oxygen for partial treatment of raw sewage in a rising main has been shown [26] to have significant beneficial effect on the subsequent treatment of the sewage. It has enabled a biological filtration works, known to be overloaded by about 40 per cent, to produce consistently an effluent of high quality (average values: BOD 19 mg/l, SS 21 mg/l, and 75 per cent reduction of ammoniacal nitrogen), during the summer months when flow-rates in the river for dilution of the effluent would have been low

without the need for major capital expenditure.

It has been estimated [26] that the total annual expenditure for injection of oxygen during 1976 (sufficient to maintain consistently aerobic conditions in the rising main) will be about £ 19,000. To obtain a reduction in the BOD loading applied to the existing biological-filtration plant (similar to that achieved by injection of oxygen into the rising main) by provision of an additional 14,450 m³ of medium to the biological-filtration capacity would have involved an estimated capital expenditure of over £ 500,000.

Because costs are of crucial importance in deciding on the method of treatment, the use of oxygen has to be evaluated by its effect on the economics of those processes where it may be used as an alternative to aeration. In some cases, injection of oxygen into rising-main sewers has a clear economic advantage over injection of air, particularly when a significant degree of treatment of the sewage can be achieved. In such circumstances, the value of injecting oxygen can be determined from the improvement brought about in the performance of the plant used to treat the sewage and the net cost or benefit of the oxygen injection assessed.

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