WATER SCIENCE AND TECHNOLOGY

Special Issue Celebrating the 80th Birthday of Dr. S. H. Jenkins

Edited by:
D. JENKINS

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University of California, Berkeley, U.S.A.

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In order to make this volume available as economically and as rapidly as possible the authors' typescripts have been reproduced in their original forms. This method unfortunately has its typographical limitations but it is hoped that they in no way distract the reader.

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FOREWORD

A couple of years ago I was in Austria attending an IAWPR Specialized Conference on Problems and Research in Large Wastewater Treatment Plants. We took two memorable field trips in conjunction with this Conference; indeed it was those field trips that gave genesis to the volume that is now before you. The first was to a Wastewater Treatment Plant close to Vienna. After an excellent treatment plant tour that commenced with a welcome from a local folk music group on the neatly trimmed lawns of the plant; continued with a well organized tour and ended in the golden afternoon sunshine with a "schnapps reception" the party headed for dinner and entertainment in a nearby village.

On the bus returning to Vienna I had the good fortune to sit with Klaus Imhoff and, considering the amount of ethanol we had collectively treated that day, it is easy to imagine that we were in a reflective mood ... and the conversation turned to fathers. He said something to me that I had known for years but never formulated into words. "You know David, there is something very special to have a famous father in the same profession as your own." How right he was. He went on to reminisce about the special years he had spent working closely together with his famous father; about the special quality of knowledge gained from your own creator; about the special relevance of experiences that are shared not only from a technical point of view, but also with knowledge that there is care and love in the words. These feelings, so ably verbalized for me by Klaus Imhoff, led me to believe that the occasion of my famous father's first 80 years should not go unnoticed in the professional world in which he has strived for so long.

The second field trip was a pleasure trip through the beautiful Austrian countryside to the south and west of Vienna. We visited Maziazell, Halstadt, Krippenstein (there was a garbage dump and sewage treatment plant at the summit) and Bad Ischel. After 2 days we headed for home. I was exhausted and sought a quiet seat, out of ear shot of our friendly, superbly organized though loquacious guide, where I could sleep off the effects of several days of "conference". And where was my father? Well, he, with Willi Von der Emde and John Andrews called a planning meeting at the front of the bus to set up the program for the next Specialized Conference on Large Scale Plants.

At this point my resolve was made; something should be done to recognize the achievements and contributions of Sam Jenkins to water pollution research and especially IAWPR; and hopefully that something should relieve him of a little work as well. What better, then, than to produce a volume of Water Science and

Technology that he did not have to edit.

This volume is a celebration, by some of his friends and colleagues, of the 80th Birthday of Samuel Harry Jenkins. To their significant contributions I wish to add a personal word of thanks to my father... thanks for providing an example of hard work, honesty, kindness and humility; thanks for the encouragement and the criticism; and last, but not least, thanks for the freedom to choose my own path in life.

> David Jenkins
> Berkeley, California,
> USA
> June 1981

SAMUEL HARRY JENKINS

Samuel Harry Jenkins was born of immigrant parents on December 25th 1901 in
Manchester, England. He was the 5th child of a family of 10. He attended the
Central High School in Manchester from 1914 to 1918. Following this he worked as
a laboratory assistant in the photographic and fur dyestuffs department of Claus
and Company, Clayton, Manchester - a company that became part of British Dyestuffs
Corporation and then ICI. Through attending evening classes at the College of
Technology in Manchester he obtained a 3 year scholarship that enabled him to
take degree courses in the Faculty of Technology at the Victoria University of
Manchester. In 1923 a B.Sc. in Technical Science with first-class honors was
conferred.

With a further scholarship and a demonstratorship Sam Jenkins conducted research
on the spontaneous combustion of powdered coal in connection with mine safety.
This was performed in the fuel research department of the Victoria University of
Manchester and in 1924 a Master of Technical Science was granted. He was all
set to start a career with the British Government in fuel research; however a
government appointment in this field was blocked because his father was not of
British birth.

At this time (1924) Sam Jenkins switched back to his earlier interests in dyestuffs
and became a chemist at the dyeworks of Robert Cawley & Co., Manchester. In 1926
he ventured abroad to Parets del Valles in Catalonia, Spain, taking a position in
a cotton and linen dyeworks.

Following his return to England in 1927 he worked in the fermentation department
at Rothamsted Experimental Station in Harpenden. It was here that his first
contact with the field of water pollution occurred. The British Water Pollution
Research Board, which was formed in 1927, had no laboratory facilities so they
contracted out this type of work. Rothamsted Experimental Station conducted
laboratory and pilot-scale investigations on topics such as the treatment of beet
sugar effluents and dairy wastes; Sam Jenkins worked with Hannaford Richard, a
member of the Royal Commission on Sewage Disposal, on these topics and related
issues such as the chemical, nutritional and microbiological aspects of the
aerobic and anaerobic decomposition of sugars, fats and fatty acids. For this
work he was awarded the Doctor of Philosophy in Biochemistry from the University
of London in 1931. Major discoveries in this work were the role of nutrients
(nitrogen and phosphorus) in biological treatment, the development of alternating
double filtration, high rate filtration and activated sludge for milk waste

treatment. A novel process in which anaerobic pretreatment was followed by
activated sludge was developed. However the sponsors of this work (The Water
Pollution Research Laboratory) would not allow this work to be published because
biological filtration was the then current vogue.

Dr. Jenkins joined the Birmingham Tame & Rea District Drainage Board in 1928 as
Chief Chemist. With this Organization (later the Tame Valley Authority and now
the Severn-Trent Authority) he worked for 31 years until his retirement in 1969.
At Birmingham he worked with many collaborators on laboratory and full scale
investigations, the microbiology and chemistry of all types of waste treatment
processes, the control of industrial wastes and their effects and the ecology of
rivers (especially polluted rivers). In 1941 the Doctor of Science degree was
awarded from the University of London.

He was elected Associate Member of the Royal Institute of Chemistry in 1925 and a
Fellow in 1931. The Institute of Sewage Purification, now the Institute of Water
Pollution Control, elected him to Membership in 1938, to Fellowship in 1944 and
its Presidency in 1957.
He has served the International Association on Water Pollution Research from its
inception. Quoting from the citation that accompanied his election to Honorary
Membership of IAWPR in 1974 "Dr. Jenkins was a member of the committee which
organized the first International Conference on Water Pollution Research in London
in 1962, when he also joined the Editorial Board of the Journal "Air and Water
Pollution", becoming an Editor in 1964. When Water Research was started in 1967,
two years after the formation of The International Association on Water Pollution
Research, Dr. Jenkins became its Honorary Executive Editor, a post he still holds.

He made a brilliant contribution as the Editor of Water Research. His superb
style and critical ability have established Water Research as one of the top
journals in the field. The high place which this journal holds as a publication
medium for papers of international standing indicates the faith of the Governing
Board in the need for such a publication.

The part which Dr. Jenkins has played in the organization of biennial and
specialized conferences, and in editorial work connected with the publication of
their proceedings, is an expression of his special philosophy. He has always
believed that although the IAWPR must draw its strength from the generous support
it receives from many national, professional and technical organizations, the
IAWPR helps to repay such support by stimulating interest in the achievements of
national professional organizations in waste water technology".

Sam and Olive Jenkins, (on the rare occasions they are home), live in Birmingham,
England. They have four children, and six grandchildren.

MESSAGE FROM THE PRESIDENT OF IAWPR

In making reference to the International Association on Water Pollution Research or to its publications, Water Research and Water Science and Technology (formerly, Progress in Water Technology), the name "Dr. Jenkins" automatically comes to mind. In fact, to many the Association and its publications are synonymous with Sam Jenkins and with good reason. Few individuals have been so closely identified with the Association as Sam or have contributed so much to its activities.

To fully appreciate Sam's deep and continuing involvement in the organization, a brief review of the Association's history is necessary. In the early 1960's, a group of scientists and engineers gathered together, drawn by a common interest in the problems and solutions related to water quality control. This group, which included Sam, together with the assistance of others in the United Kingdom, organized the very successful First International Conference on Water Pollution Research, held in London in 1962. This same core group, continuing on an ad hoc basis, without any official status, organized the Second International Conference. With the assistance of a Japanese organizing committee, this Conference took place in Tokyo in 1964 and again, was highly successful. It was at this Conference that the initial steps were taken towards formally establishing the International Association on Water Pollution Research. The ad hoc group, of which Sam was a member, finalized the formation of the Association in Harrogate, England in June 1965. As is evident from this brief account, Sam was involved in the early history of the Association and from all reports, played a leading role in its devel-opment and organization.

With the cooperation of Pergamon Press, the Association assumed the editorial responsibilities for the water-related section of the International Journal of Air and Water Pollution. As a result, a new journal was established, Water Research, and it became the official publication of the Association. The first issue appeared in January 1967 with Dr. S. H. Jenkins as Executive Editor, a position he continues to occupy today.

In reviewing Sam's many contributions to the Association, it is impossible to overlook his involvement with the biennial conferences. Sam served as editor of the proceedings of the early conferences which were published in book form. In 1972, following the biennial conference in Jerusalem, the bimonthly journal Progress in Water Technology was established for the purpose of publishing the Association's conference proceedings and, again, Sam was named Executive Editor. In

addition to this responsibility, Sam continues to be chairman of the Program Committee for the biennial conferences.

It should be obvious from the above factual information that Sam has and continues to contribute to the Association on many fronts. The scope and sheer magnitude of his involvement and his many meaningful contributions cannot be denied. His impact on the Association runs to its very core, particularly his untiring efforts to maintain and indeed enhance the quality of its publications.

Although now 80 years of age, Sam remains fully committed to the overall mission of the Association and deeply involved in its activities. He can be found in the Association's London office at least one day every week, making the trip from Birmingham armed with his customary airline flight bag bursting with edited manuscripts, correspondence, reports, publications schedules, and the like. Sam works relentlessly the entire day, donning his many "hats" in turn.

Actually, the Association's London office offers one of the better locations at which Sam is known to have worked. Sam possess the ability to "set up office" under the most difficult of conditions, creating an oasis of efficiency midst the furore of a conference registration desk, a hotel foyer, etc. As an example, during the recent remodeling of the Association's new offices in London, he managed to review manuscripts and prepare correspondence while being surrounded by workmen, sanding and painting walls.

There is no doubt about Sam's many valuable contributions to the Association. For all his hard work and resulting accomplishments, Sam has never sought any expression of thanks or appreciation. His satisfaction comes from the continuing success of the Association's conferences and its publications.

Setting aside his many professional contributions, Sam accompanied by his charming wife Olive, has provided the Association with a wealth of wit and a spirit of fellowship. Together, Sam and Olive are known and respected worldwide.

I know I speak for all his associates and many friends throughout the world when I wish Sam a very happy 80th birthday.

R. S. Engelbrecht

SINGLE SLUDGE NITROGEN REMOVAL FROM INDUSTRIAL WASTEWATER

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ABSTRACT

Nitrogen removal by the single-sludge nitrification and denitrification process offers several economic advantages over the multi-sludge systems. This paper provides a description of the processes involved, and a discussion of some chemical and kinetic aspects with emphasis on industrial applications. A relatively simple design procedure is presented using zero order kinetics for nitrogenous subtrates removal and first order kinetics for carbonaceous organics removal. The solution is obtained by a trial and error calculation procedure. Finally, two examples are presented of operating systems treating industrial wastewater. One example is a bench-scale study of an amino acid production wastewater and the other is a full-scale plant treating wastewater from a combined pharmaceutical-pesticides-herbicides processing. Both systems effectively reduce the concentration of carbonaceous organics, ammonia and nitrate to very low levels.

INTRODUCTION

Biological nitrification and denitrification are frequently the most cost effective processes available for nitrogen removal from wastewaters, both municipal and industrial. Properly designed and operated systems can reduce the concentrations of the various nitrogen forms to the low levels prescribed by existing guidelines and regulations. For municipal applications the design parameters and criteria are relatively well established since domestic wastewater have a more or less uniform composition. Industrial wastewater, on the contrary, will vary in quality from one case to the other and, therefore, require development of design parameters for each specific case. The use of design parameters which were derived from domestic plants for the design of industrial treatment systems will frequently lead to poor design and ultimate failure. An understanding of the principles and mechanisms involved in the processes is the key to successful design.

Domestic wastewater and many industrial wastes contain nitrogen primarily in the organic or ammonium form, along with carbonaceous organics. All discussions in this work apply to wastewater of such composition. Some industrial wastes may contain substantial amounts of nitrate-nitrogen or low concentrations of carbonaceous organics. Such wastewaters are generally not amenable to the treatment schemes

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[1] On leave from Technion, Israel Institute of Technology, Haifa 32000, Israel.

discussed herein. It is further assumed that all organic nitrogen is rapidly broken down by microorganisms to form free ammonia or ammonium ion.

NITROGEN REMOVAL SYSTEMS

Complete removal of nitrogen from wastewater can be accomplished in either a multi-sludge or a single-sludge system. In the former configuration, commonly known as the "two-sludge" or "three-sludge" systems, carbonaceous organics removal, nitrification, and denitrification take place in a series of separate activated sludge units. Single-sludge systems consist of one or two reaction vessels divided into aerobic and anoxic zones, with the same sludge being recycled through both. Figure 1 depicts these two alternate systems for biological nitrogen removal.
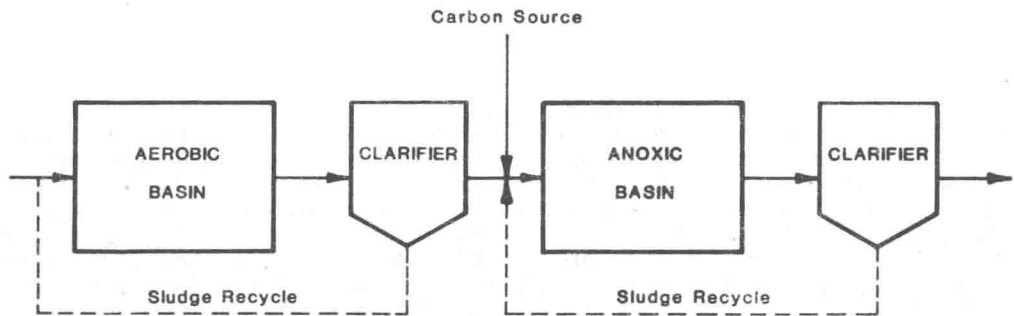
(a) Two-Sludge System
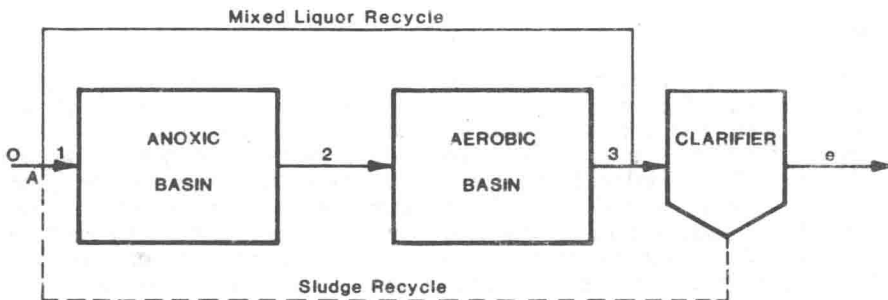
(b) Single-Sludge SYSTEM

FIGURE 1. ALTERNATE SYSTEMS FOR BIOLOGICAL NITROGEN REMOVAL

The multi-sludge system has been used rather extensively in the past, and its design and operation principles are relatively well established. The single-sludge systems have been introduced more recently and are gaining popularity because of some economic advantages they may offer. The latter system is the subject of this work.

Description of the single-sludge system and its application were reported, among others, by Barnard (1974), Matche and co-workers (1975), and Sutton and co-workers (1980). These works were directed primarily to domestic wastewaters. Sutton and co-workers (1981) described the successful operation of a single-sludge system treating industrial wastewater.

In the two-sludge system (Fig. 1a) carbonaceous organics removal and nitrification take place in the first aerobic activated sludge unit. The clarified effluent of this stage is passed to the second stage where anoxic conditions prevail and denitrification occurs. Since the organic carbon of the raw wastewater has been largely removed in the first stage, an external carbon source is required to serve as hydrogen acceptor in the denitrification basin.

The sludge in the first activated sludge system consists of a mixture of heterotrophic and autotrophic microorganisms. The former group is responsible for the aerobic degradation of organic carbon while the latter consists of the nitrifiers which convert ammonium nitrogen to nitrate. In the second system, the biomass consists of facultative anaerobes which degrade carbonaceous organics utilizing nitrate in lieu of oxygen as the ultimate hydrogen acceptor. Nitrate is converted primarily to nitrogen gas which is released to the atmosphere.

In the single-sludge system (Fig. 1b) the biomass consists of a mixture of autotrophic and heterotrophic species. The heterotrophs grow and oxidize ¬bonaceous organics in both the aerobic and anoxic basins; they utilize molecular ox¸ ¸en as the hydrogen acceptor in the former basin and nitrate in the latter. The autotrophs grow in the aerobic zone only, using molecular oxygen and inorganic carbon while nitrifying ammonia.

The influent ammonium passes through the anoxic basin to the aerobic basin where it is converted to nitrate. The effluent from the aerobic basin is recycled to the anoxic basin where the nitrate is denitrified. Thus, the key feature of the single-sludge system is the high rate of mixed liquor recycle from the aerobic to the anoxic basin.

The single-sludge system offers several economical advantages over the two-sludge system. First, the former system contains only one clarifier as opposed to two in the latter. But the main economical benefits are derived from chemical savings. The single-sludge system utilizes the carbonaceous organics originally present in the raw wastewater as a carbon source for denitrification, thus, eliminating the need for an external carbon source. Moreover, since part of the original carbonaceous organics are removed in the anoxic basin, less oxygen is required in the single-sludge system. As will be shown later, alkalinity is being consumed in the nitrification reaction and formed in denitrification. Hence, there is a partial internal neutralization in the single-sludge system which may result in the saving of neutralizing chemicals. A schematic illustration of these differences in chemical requirements is presented in Fig. 2. In both schemes, ammonia present in the raw wastewater is converted to nitrate, utilizing the same amount of oxygen. A small portion of the ammonia is assimilated in cellular material. The original organic carbon in Fig. 2a is completely oxidized aerobically utilizing its equivalent amount of oxygen. In Fig. 2b, only a fraction of the carbonaceous organics is oxidized aerobically, the remaining being oxidized in the anoxic zone. This eliminates the need for an external carbon source in Fig. 2b. The possible savings
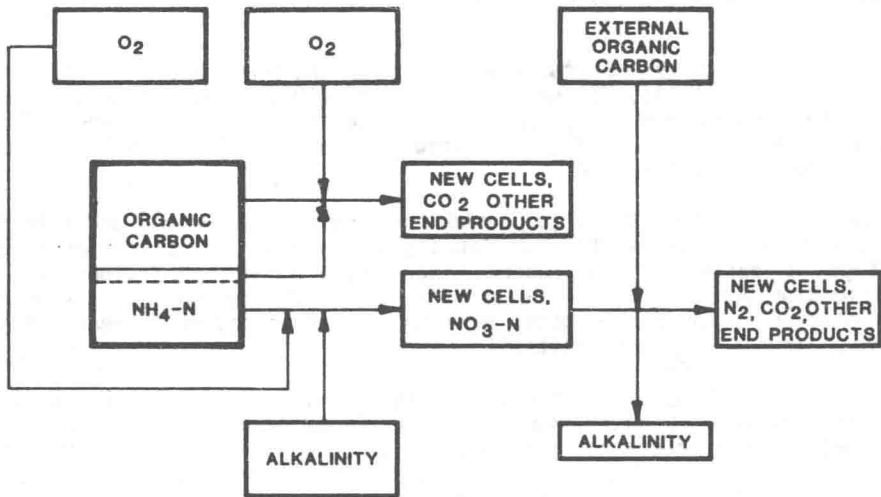
a. Two-Sludge System
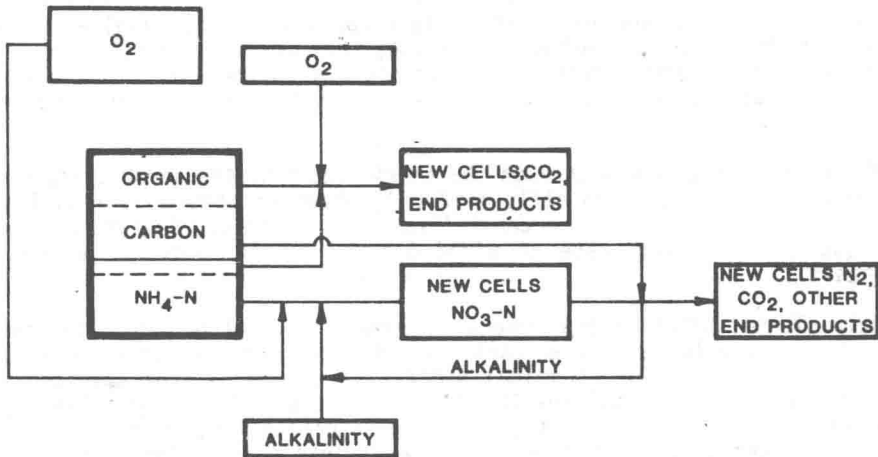
b. Single-Sludge (Recycle) System

FIGURE 2. SCHEMATIC MATERIALS FLOW DIAGRAM FOR NITROGEN REMOVAL SYSTEMS

in neutralizing chemicals associated with the single-sludge system is also illustrated in Fig. 2b where part of the alkalinity consumed in the nitrification stage is obtained from the denitrification section. Saving in energy may be realized in the single-sludge system due to the lower amount of oxygen required.

However, this will be off-set by the extra pumping required for mixed liquor recycle. Hence, the net energy requirement in the single-sludge system may be smaller, equal, or larger than in the two-sludge system depending on the specific composition of the raw wastewater and the required effluent characteristics.

CHEMICAL CONSIDERATIONS

There are several factors related to the chemistry of the nitrogen removal process which need to be considered, particularly when industrial wastewaters are concerned.

First, the acid-base equilibria in a combined nitrification-denitrification system is discussed. This equilibria is affected by the consumption or release of alkalinity in the various reactions involved. The overall oxidation and synthesis associated with nitrification may be expressed by the following stoichiometric equation:

$$NH_4^+ + 1.83\ O_2 + 1.98\ HCO_3^- = 0.98\ NO_3^- + 0.021\ C_5H_7NO_2 + \quad (1)$$
$$1.88\ H_2CO_3 + 1.04\ H_2O$$
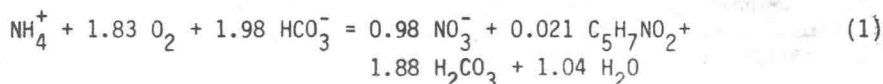
This equation indicates that 7.14 mass units of alkalinity, expressed as $CaCO_3$, are consumed for each mass unit of ammonium nitrogen nitrified. For most domestic wastes, and some industrial wastes, the alkalinity present in the wastewater is sufficient to provide the required alkalinity without a significant drop in pH. However, in some industrial wastewaters with either low alkalinity or high ammonium levels, the loss of alkalinity may result in a pH drop which will adversely affect the process. Addition of neutralizing chemicals is needed in order to restore process effectiveness. As mentioned before, one of the advantages of a single-sludge system is the partial neutralization achieved internally. This is due to the release of alkalinity associated with anoxic denitrification as expressed by the following empirical equation:

$$NO_3^- + 1.08\ CH_3OH + 0.24\ H_2CO_3 = 0.056\ C_5H_7NO_2 + 0.47\ N_2 + \quad (2)$$
$$1.68\ H_2O + HCO_3^-$$
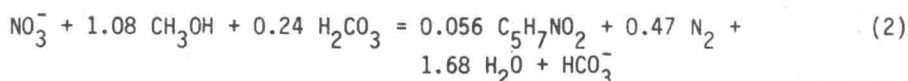
This equation, showing denitrification with methanol as a carbon source, indicates that 3.57 mass units of alkalinity are formed for each mass unit of nitrate-nitrogen that is denitrified. Thus, in the combined nitrification-denitrification system, only 3.57 mass units of alkalinity are destroyed for one mass unit of nitrogen removal.

It should be pointed out that acid-base equilibria may also be affected by the conversion of organic nitrogen to ammonium. The breakdown of amino acids through reductive deamination is an example of such a process in which acidity is consumed, resulting in rising pH.

From Equation 1, it is evident that approximately 0.08 mass units of inorganic carbon are consumed per mass unit of ammonium nitrogen nitrified. This is the inorganic carbon required by the autotrophic microorganisms for cell synthesis. In most cases inorganic carbon is available in the raw wastewater in sufficient quantities to satisfy this demand. Carbon dioxide formed in the oxidation of carbonaceous organics provides an additional source of inorganic carbon. However, in industrial wastewater of unusual composition, nitrification may be inhibited by the lack of inorganic carbon. Availability of inorganic carbon to the autotrophic organisms is also pH dependent. This is also evident from the following carbonate equilibria:

$$CO_{2(g)} \rightleftharpoons CO_{2(aq)} \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^= \qquad (3)$$
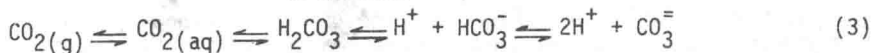
These equilibrium equations show that as the pH drops the reactions proceed to the left, and most carbonates are in the carbonic acid form. Since carbonic acid is in equilibrim with aqueous carbon dioxide, which is only slightly soluble in water, low pH conditions will result in the escape of CO_2 from solution. Hence, systems with high ammonia concentrations, if operated at low pH, may fail because of lack in inorganic carbon.

Elevated pH levels are also detrimental to the nitrification process. Anthonisen and co-workers (1976) and Ford and co-workers (1980) showed the inhibitory effects of free ammonia to the nitrification process. The level of free ammonia in a nitrification system depends on pH as can be seen from the equation:

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O \qquad (4)$$

Thus, as the total concentration of ammonia and the pH are increased, the level of free ammonia and subsequently nitrifier inhibition are increased. Nitrifiers inhibition was also reported at lower pH due to the formation of free nitrous acid. The latter is formed at low pH as can be seen from:

$$H^+ + NO_2^- \rightleftharpoons HNO_2 \qquad (5)$$

Hence, successful operation of a single-sludge nitrogen system, particularly for industrial waste treatment, requires close control of pH. In some cases, chemical addition will be required for this purpose.

KINETICS

The dimensions of nitrogen removal systems and subsequently their economics are affected by process kinetics. Three major processes are involved in the present system, namely nitrification, denitrification, and carbonaceous organic removal. The kinetics of each of these processes are discussed subsequently.

Nitrification

Three major substrates are involved in the nitrification process i.e. ammonium, dissolved oxyyen, and inorganic carbon. Thus, the Monod kinetic expression for the rate of nitrification is given by:

$$R_N = R_{NM} \left(\frac{A}{K_A + A} \right) \left(\frac{C}{K_C + C} \right) \left(\frac{D}{K_D + D} \right) \qquad (6)$$

Where R_N is the specific rate of nitrification (g NH_4^+-N/g nitrifiers-day), R_{NM} is the maximum specific rate of nitrification (g NH_4-N/g nitrifiers-day), A, C, and D are the concentrations of ammonia nitrogen, inorganic carbon, and dissolved oxygen, respectively (mg/l), and K_A, K_C, and K_D are the half saturation values for ammonium, carbon and dissolved oxygen, respectively (mg/l). The reported value of K_D is approximately 1.0 mg/l and that of K_A is in the range of 0.2 to 1.0 mg/l. Hence, when both the D.O. and ammonia nitrogen concentrations are considerably higher than 1.0 mg/l, nitrification approaches a zero order reaction low. Values of K_C have not been reported. From reported experience it appears that inorganic carbon is normally present in sufficient concentrations and has no effect on process kinetics. However in industrial applications, lack of inorganic carbon can cause process inhibition. The zero-order nature of the nitrification reaction was demonstrated by Huang and Hobson (1976) and by Wong-Chong and Loehr (1975).