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The α-β-γ's of wastewater treatment

High sludge age, especially when combined with powdered activated carbon, can materially improve the activated sludge process for organics removal

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The petroleum refining industry has demonstrated two approaches to improve the performance of the activated sludge process (ASP) for organics removal from wastewaters. They are operation at high sludge age and further enhancement by using high concentrations of powdered activated carbon (PAC) commingled with the activated sludge. To get the best effluent quality very cost effectively, both approaches must be used, because PAC enhancement of the ASP is most effective at very high concentrations; the higher the concentration in the mixed liquor, the lower the residual soluble organics in the treated effluent. Fortuitously, very high sludge age operation is effective with the use of PAC. Sludge ages well in excess of 100 days have been demonstrated. A 5000-mg/L equilibrium mixed-liquor PAC concentration has been maintained in a municipal plant with less than a 5-mg/L PAC makeup rate!

The key to operating the ASP in the high-sludge-age mode is to recognize the impact of influent solids on the physical properties of the activated sludge, specifically the zeta potential (*ES&T*, September 1978, p 1023) probability distribution. When the feed to the ASP is effectively pretreated by filtration or dissolved air flotation to remove colloidal and suspended matter, the activated sludge has much improved settling properties, and capture by secondary clarifiers is much more complete. Moreover, pretreatment typically reduces the contaminant concentration by about 50%; this proves to be an important response to operating results which demonstrate that the lowest residual effluent organics will be produced by the unit with the lowest feed strength.

The thrust of original research on high sludge age and PAC enhancement of the ASP centered on industrial wastewaters. To demonstrate that the principles are general and broadly applicable, Standard Oil Company (Indiana) conducted a 15-month experimental program, operating a municipal plant with dual treatment trains. One train was used as a "control" and the parallel train was modified with a granular media filter for prefiltering the influent to the activated sludge unit (ASU) for experimental high-sludge-age operation (Figure 1). The comparative performance of different activated sludge technologies was determined, including the role of powdered activated carbon for ASP enhancement. This full-scale study included ASP operation in the high-sludge-age mode and in the high-sludge-age mode enhanced with PAC.

Historically, wastewater studies

- involved wastewaters containing soluble, colloidal, and suspended matter, and the discontinuous phase matter incorporated into the activated sludge mass concealed an estimation of biomass yield
- were of low-sludge-age systems in which most of the food supply was used by the bacteria for cell yield, and the comparatively small amount used for maintenance energy could not be determined
- did not provide a sufficient data base for temperature correlation
- ignored the impact of sludge age on substrate material balance.

By contrast, high-sludge-age ASP operational data have been rare or nonexistent. Our municipal, refinery, and chemical plant results probably comprise the most extensive data base available. This unique data resource provides an insight into the biological oxidation processes operative in the ASP. In high-sludge-age ASP systems, most of the food supply is used for maintenance energy; therefore, its quantitative value is more readily determined. Also, operation is achieved by pretreatment to remove most suspended and colloidal matter; thus, the biomass yield results are not obscured with inert debris. Moreover, a wide range of temperatures and sludge ages are involved. The ubiquitous bacteria treating these widely differing wastewaters demonstrated remarkably consistent properties on a chemical oxygen demand (COD) basis:

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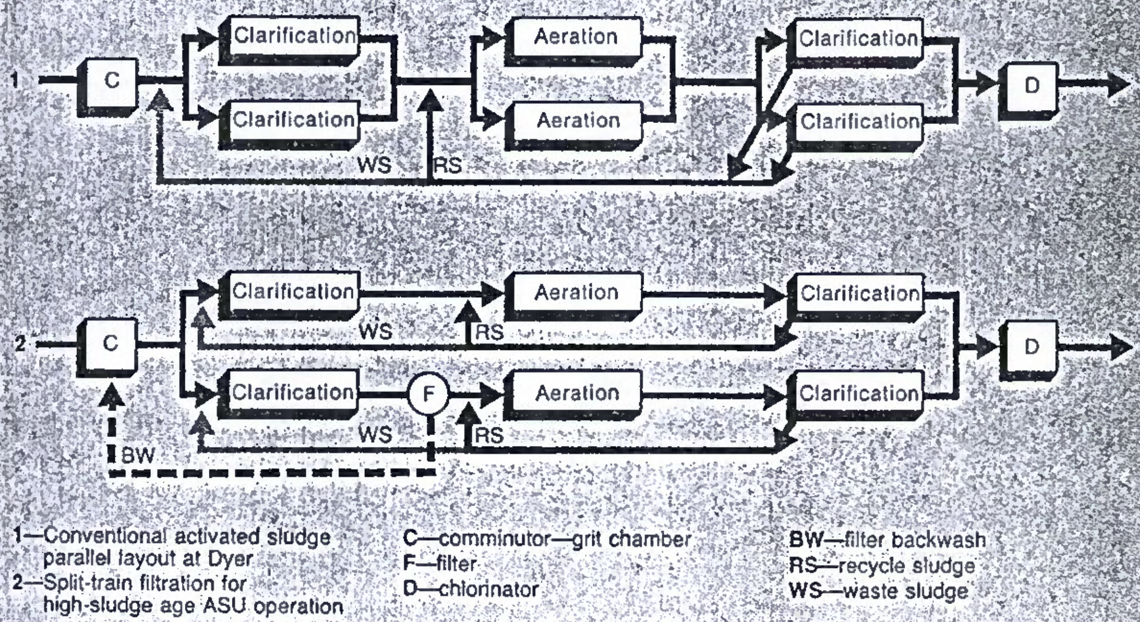
FIGURE 1
Activated sludge waste treatment process



- The cell yield coefficient (alpha) is constant, having a value of about 0.3.
- The cell maintenance energy coefficient (beta) is always constant, but varies linearly with temperature over the range of our data.
- The organic contaminants inventoried by the cells (gamma) relate to the sludge age.

Biological purification

Bacteria exist only to make copies of themselves, that is, to self-replicate. The bacteria constituting the activated sludge mass in the ASP purify wastewaters by using contaminants for energy and new cell material (Figure 2). Contaminant materials enter the bacteria; then, some are excreted as end products of the bacteria's energy metabolism. The remainder is converted by enzyme reactions into cell material. Water constitutes about 70-80% of a bacterial cell, and an elemental composition that accounts for 99% of the dry mass is $C_5H_7NO_2$. The cytoplasm is an aqueous solution of soluble proteins and small-molecular-weight metabolites. About 11.5% of the bacterium is proteinaceous; 5% ribonucleic acids; 1% each of deoxyribonucleic acid, polysaccharides, and lipids; and 0.5% small molecules. A growing bacterium chiefly consists of the macromolecules which are assembled from the intermediates, and are the constituents of the cell.

Since bacteria are self-replicating, the polysaccharides, enzymes, lipids, metabolites, nucleic acids, peptidoglycans, and so on, uniformly increase at the same rate. When a bacterium grows and doubles its cellular inventory of the thousands of different kinds of molecules present, it partitions into two daughter cells, each similar to the original cell. The maximum possible cell yield (dry weight) per unit of food material is called alpha (α).

To change contaminants in wastewaters into a copy of itself, a bacterium requires a supply of energy. Initially, the contaminants must be transported across the cell membrane against a concentration gradient, which requires energy. Creating order out of disorder in the cell also requires energy—to bring out construction of the required lipids, polysaccharides, proteins, nucleic acids, and the organizing of these macromolecules, for example. The chief energy source is from chemical oxidations, and the energy requirement is termed beta (β).

Thus, in a growing bacterium there are two metabolisms. One is biosynthetic, in which the food supply is changed to the components of the cell; the other is an energy one, in which cell energy needs are supplied.

According to molecular genetics, genetic material directs the synthesis of protein molecules, which are macromolecules assembled from amino acids. Those polyaminoacids, fated to be catalytic enzymes, fold into a three-dimensional globular protein with catalytically active site(s). The polar constituents of the enzyme are oriented primarily toward the exterior surface of the globular enzyme associating with the water solvent. The catalytic site often is a cavity below the surface of the enzyme, such that reactants can be effectively isolated from the aqueous phase and its high dielectric constant. The hydrocarbon interior of the enzyme has a low dielectric constant which permits stronger electrical forces to bear on the reactants causing the chemical change.

Enzymes are the organic solvents of the living cell. The more rapid the growth rate, that is, the lower the sludge age, the more numerous the enzymes participating in macromolecule biosynthesis, and the more in situ substrate (gamma) en route to its final end use.

Solids balance

A critical point to recognize is that in a growing cell, the essential product is more cell. Thus, while the goal is purified water, the ASP is a unit operation in which the ubiquitous bacteria use contaminants in the wastewater to produce more bacteria. In the completely mixed system, a bacteria material balance includes:

- the increase in sludge attributable to influent solids. Influent inert suspended solids flocculate and accumulate in the activated sludge mass. For high-sludge-age systems, the key is to

FIGURE 2

The bacterial cell, its biochemical activities, and exoenzyme solubilization of insoluble substrates

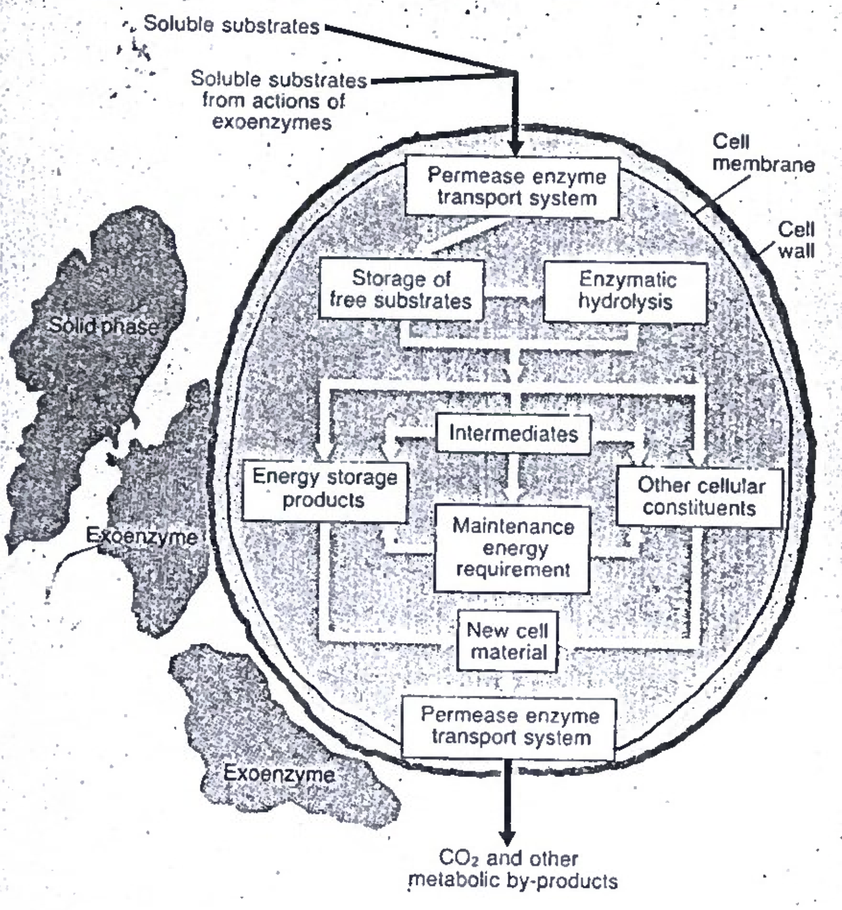
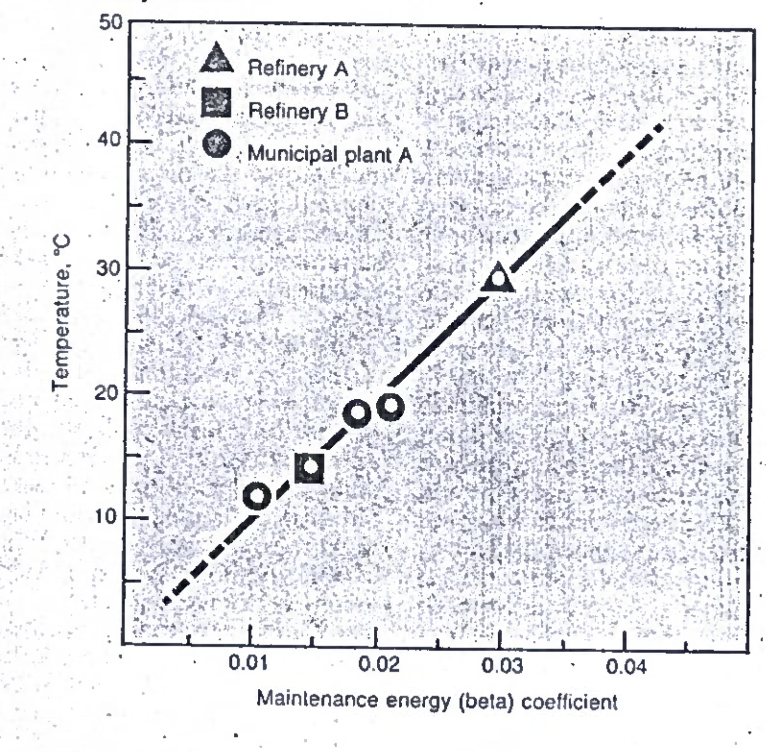


FIGURE 3

Maintenance energy coefficient change with temperature



Biomass balance derivation

The following biomass balance around the ASP can be derived:

$$\frac{1}{SA} = \frac{\alpha \Delta F/\Delta T - \beta}{M}$$

where SA = sludge age (days)
α = maximum possible cell yield (lb biomass/lb COD removed)
β = cell yield decrease due to substrate diversion to energy metabolism (lb biomass/lb M)
M = activated sludge mass in system (lb)
$\Delta F/\Delta T$ = substrate removed per day by the activated sludge, expressed as lb COD/d

keep the influent inert solids to essentially zero.

- the increase in sludge attributable to cell synthesis
- the decrease in sludge generation capability because the cell used the substrate for energy metabolism
- the decrease in sludge because of effluent losses.

The bacteria in activated sludge, replicating from the wide variety of materials in wastewaters at a municipal plant and several refineries, provided an extensive data base for high-sludge-age ASP operation over the temperature range of about 10–30 °C. Surprisingly, *these data indicated that the alpha was a constant having a value of about 0.3 (COD basis). Beta was a constant, linearly dependent upon temperature, as shown in Figure 3 (COD basis).*

Perhaps it should not have been too surprising to find that the ASP biomass requires a constant amount of the substrate resource. The cell formula is reasonably constant, as is, evidently, the energy requirement to construct the cell. Since a common substrate resource supplies the cell material and the energy to assemble the intermediates into macromolecules, and then directs their assemblage into the structure of the cell, a fixed amount of substrate is used per unit mass of cell material generated. The best measure of mixed substrates is the chemical oxygen demand, and this is the link to the uniformity of the alpha value.

Pools, uptake, and gamma

Cells contain pools of small molecules clearly important in growth (Figure 2). Food materials pass through the pools, and whatever regulates their entry also regulates overall cell growth. In the uptake of food, food molecules pass through a permease transport system (permease is an enzyme); the rate of uptake is a function of substrate concentration and is one factor governing pool size. The uptake rate increases with higher food concentration until the capacity of the transport system is reached.

Operation of the ASP at high sludge age and in a completely mixed mode is a demanding environment to cells, in terms of the concentration of food molecules. These conditions are a spectrum apart from the laboratory conditions of virtually unlimited food resources, from which most microbiological information is derived.

High-sludge-age ASP operation can be put into perspective by reference to Figure 4. Bacterial systems can be categorized according to the temperature range in which they operate. Also, some bacteria can multiply up to about once every 20 minutes, when not limited by the supply of carbon sources or macro and micronutrients. The dashed lines, extrapolating the bacterial systems data to the range in which biological wastewater purification plants operate, show that ASP operation at a conventional eight-day sludge age requires a bacterial growth rate about 1% of that achievable by some bacteria, and high-sludge-age systems of 80+ days, an order of magnitude lower, at 0.1%.

High-sludge-age ASP data indicate that the bacteria utilize food resources sequentially. First, the cell's energy requirements are met; then, if pool resources remain, the macromolecules are synthesized. Sequential utilization of food resources is not unexpected, because the energy resource must exist to construct and locate the macromolecules. Whereas the cell maintenance energy requirement has been determined to be very low and uninteresting by the microbiologist, in fact, the recognition of its existence results in an ASP design that provides for operation *almost entirely devoid of waste activated sludge*. In studies where a municipal plant operated at exceptionally high sludge age, the solids equilibrated and the plant operated for 3+ months with no sludge wastage, and about 4 mg/L solids were lost to the effluent. Cell growth, therefore, was controlled to equal the very small amount lost from the system.

How the ASP achieves this can be illustrated. If, for instance, the observed sludge yield is to be minimized, *SA* (sludge age) must approach infinity, and $1/SA$ must approach zero.

From our municipal work where:

$\alpha = 0.3$

$\beta = 0.18$ (for a temperature of 18 °C)

$\Delta F/\Delta T = 243.65$ lb COD/d during test,

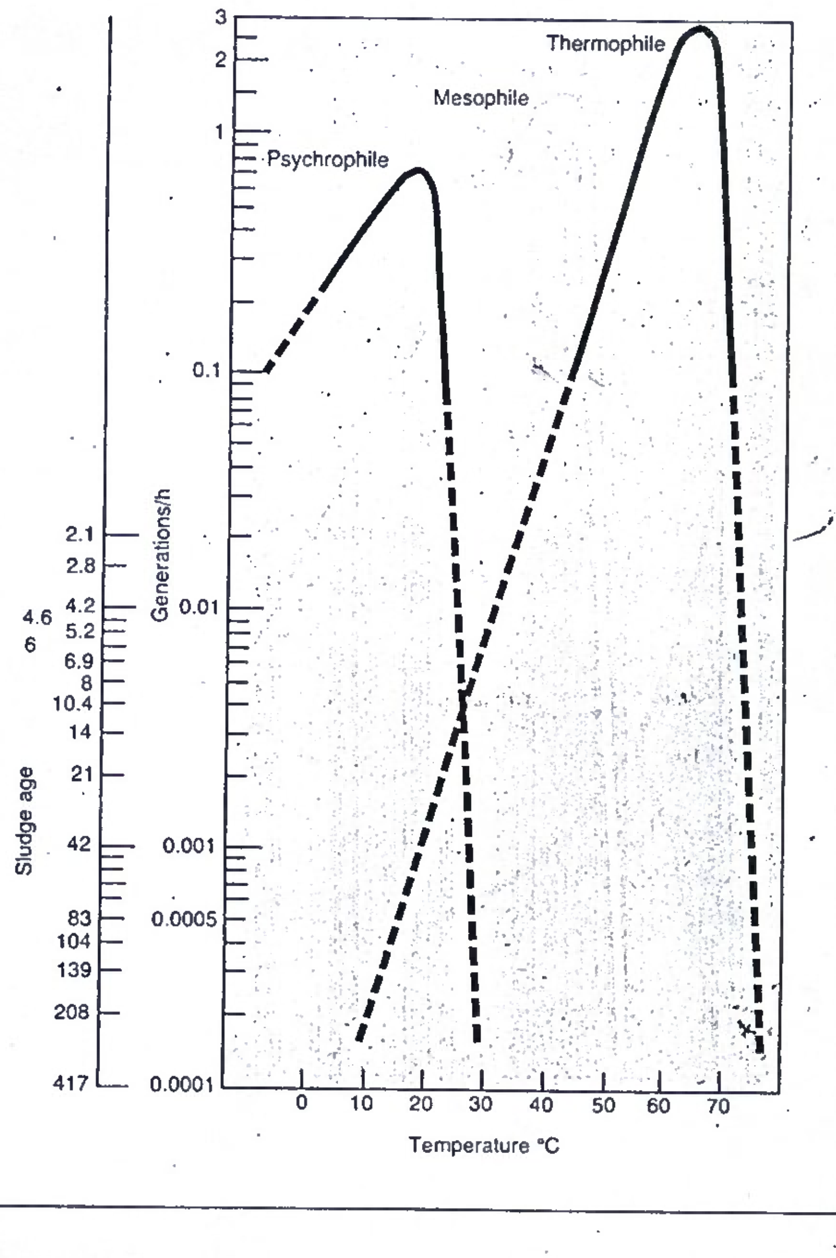
it can be calculated that about 4000 lb of biomass in inventory would use all the substrate for energy: $M = 0.3\,(243.65)/0.18 = 4060$ lb of biomass.

For the municipal ASP in which high-sludge-age research, operating at about 120% of hydraulic design, was conducted, the material balance around the unit for sludge age operation up to 300 days is shown in Figure 5. The sludge age is the abscissa, the right-hand ordinate indicates the pounds of biomass in inventory, and the left-hand ordinate shows the mass of waste biomass generated each day. The alpha is the *maximum theoretical cell yield predicted by high-sludge-age ASP systems which are reducing the COD levels to levels approaching irreducible minimums.*

Solids-handling operations

The dual train municipal units operated at 120% of hydraulic design, and the limiting operational condition was the amount of solids that could be retained. The "control" unit consistently averaged only 1000 mg/L suspended solids in the aeration tank before excessive effluent losses were a threat. The high-sludge-age experimental unit could achieve 2400 mg/L

FIGURE 4
Growth rates of psychrophiles, mesophiles, and thermophiles relative to temperature



total suspended solids(TSS) in the aeration tank before excessive effluent losses were a threat. At these operating conditions, the volatile suspended solids (VSS), or "biomass" level, was 2050 mg/L.

Figure 5 indicates a sludge age of about 45 days, which requires a wastage of 40.5 lb/d VSS, or about 47.4 lb/d TSS. If the TSS in the effluent is at the EPA advanced-waste-treatment level of 10 mg/L, this loss accounts for wastage of 29.7 lb/d TSS. Thus, 17.7 lb/d TSS (47.4 − 29.7) has to be intentionally wasted to maintain equilibrium at 45-day sludge age. This miniscule amount is 0.6 gpm from the aeration tank.

In practice, the high-age activated sludge flocculated superbly, and only about 2.5 mg/L TSS was lost to the effluent (0.2–0.3 Jackson Turbidity Units), amounting to 7.43 lb/d. The additional 40-lb/d TSS wastage (47.4 − 7.4 = 40 lb/d TSS) required for process control was achieved by siphoning 1.4 gpm from the aeration tank to the inlet wet well by means of a garden hose. It is obvious that if an average of 16-mg/L TSS loss to the effluent is acceptable, the system would also be in solids equilibrium at 45-day sludge age and no additional intentional wastage is needed.

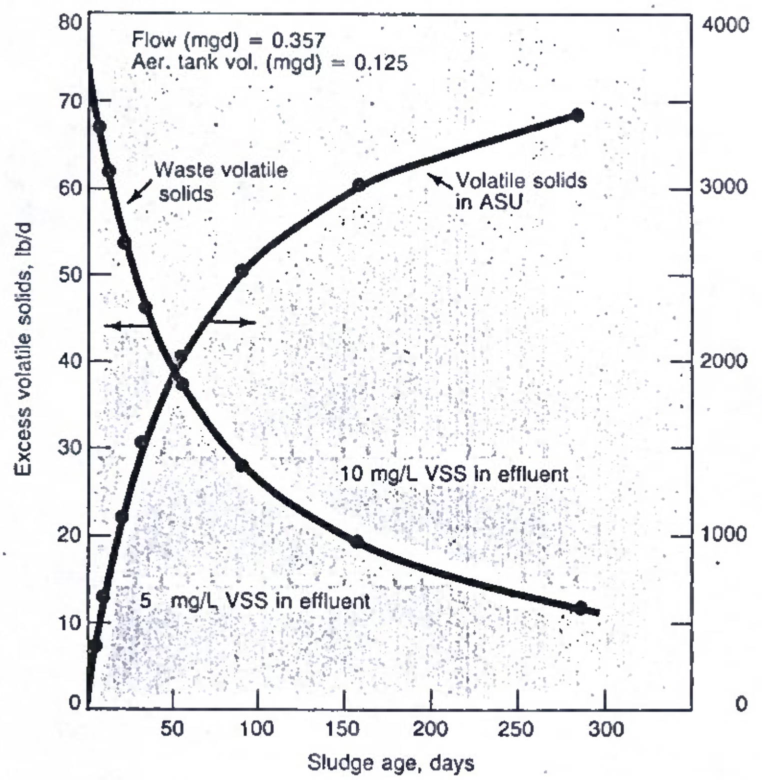
The previous discussion described the first solids-handling operating limitation encountered at the Dyer, Ind., municipal plant. The ASU clarifier could only handle 20.88 lb TSS/d-ft^2, and this limited aeration tank solids levels to 2400 mg/L. The effect of more clarifier capacity can be determined from Figure 5. Thus, if the clarifier solids-handling capacity were increased only 25% to an aeration tank TSS of 2975 mg/L (VSS = 2625 mg/L), a 100-day sludge age could be attained. At that age, total required wastage would be 26 lb TSS/d; that is, only 8.75 mg/L solids loss in the effluent would account for all necessary wastage.

The final phase of the experimental program involved enhancing the high-sludge-age experimental ASU with PAC at a level of 4770 mg/L in the aeration tank. The system equilibrated at 9000 mg/L TSS; thus, the activated sludge component is 4230 mg/L (an estimated 4900 lb in the system).

Earlier, it was estimated that 4060 lb of biomass would yield minimal sludge generation. If about 80% of the 4900 lb activated sludge is VSS (biomass), the system would be close to the conditions for minimal sludge generation. Those were the conditions that the PAC-enhanced high-sludge-age ASP achieved; for three months (the experimental program was terminated), the system operated with no intentional sludge wastage, and with effluent solids averaging 4.2 mg/L (12.7 lb/d), of which 53% was PAC.

FIGURE 5

Solids balance with sludge age[a]
OC = 0.3; β = 0.018; $\Delta F/\Delta T$ = 243.65 lb/d



[a]Across Dyer activated sludge unit

Impact of hydraulic design

In growing bacterial cells, the proteins are not broken down once formed. By contrast, in some cells of higher organisms, protein is constantly recycled by being degraded and resynthesized. When bacterial cells are deprived of a carbon source, however, they break down their protein slowly and "turn it over" by remaking the same kinds of proteins with a small fraction of the amino acids being used to synthesize new protein, if an inducer is present. With wastewater treatment plants using the ASP, this protein irreversibility plays an important role in process design. For example, simple changes in hydraulic flow patterns in the aeration tank can demonstrate the phenomena of protein irreversibility, sequential use of substrate resources for energy metabolism followed by biosynthetic metabolism, and the validity of the concept of a fundamental bioengineering relationship.

The hydraulic design of the ASP has a striking impact on which metabolic route the substrate is used—the biosynthetic fate (alpha) or maintenance energy (beta). For example, consider the comparative data from hydraulic systems in Table 1, wherein the total aeration tank volumes were equal, except that one unit is a single completely mixed reactor, and the second unit is three completely mixed reactors in series. The wastewater treated was a moderately strong but highly biodegradable chemical plant wastewater. The target operating conditions for each unit was 800 g COD/m^3 aeration tank volume, 6000 mg/L mixed liquor suspended solids, and about two days' retention time.

The three reactors in series produced about 60% more biomass per mass of COD removed than did the single state unit. This is because the F/M (food to microorganism) ratio in the lead reactor is much higher than that of the single-stage unit; the maintenance energy requirement of the cell is readily satisfied; and the cell's control system for determining the metabolic route of the substrate increases the fraction going to biosynthesis. This control mechanism may be triggered simply by the concentration of adenosine triphosphate

(ATP, the chemical that stores and makes available the energy required to drive the energy-consuming biosynthetic metabolic system) and the monomer pool concentration which, in turn, is controlled by the substrate concentration in the reactor. Evidence of this latter point lies in the observation that biomass from high-sludge-age systems is extremely stable and requires no further stabilization.

By contrast, biomass from low-sludge-age systems is very actively respiring, and waste biomass must be stabilized before further processing. Thus, the mass of substrate captured by the cell must be very low in high-sludge-age systems and high in low-sludge-age systems.

The 60% increase in cell yield attributable to the hydraulic designs of the series reactors was particularly striking because both units were operating at very high sludge age. Other work has shown that the difference in cell yield between these hydraulic flow patterns can differ by *many hundreds of percent,* depending on the overall organic loading.

The high-sludge-age data base, limited as it is, also suggests that single-stage reactors and reactors-in-series units utilize the available substrate energy at different efficiencies. For example, the reactors in series satisfy the maintenance energy of more organisms per day, *in addition to* using the substrate to generate more biomass with the same fixed amount of COD. The biomass in the single-stage design, then, must satisfy their energy requirements, and dispose of the excess available energy (substrate) as waste heat. (Many examples exist of highly exothermic industrial fermentation reactions.) Once the substrate concentration increases by, for example, increasing the operating F/M ratio or changing the hydraulic flow pattern to reactors in series, the cell's monomer pool increases and the cell speeds up the biosynthetic metabolic system.

TABLE 1

Comparative performance of single-stage and three reactors-in-series activated sludge units

	Aeration tank reactors	
	Single stage	Three in-series
Design		
Reactor volume, total	9	9 (3 each)
Operation		
Organic loading, g COD/m^3	737	864
Field rate, mL/min	3.29	3.82
Mixed liquor suspended solids, target, mg/L	6000	6000
Suspended solids in system, g	56	56
F/M[a], g COD/d·g suspended solids	0.118	0.139
Reactor temperature, °C	24	24
Results		
Cell yield, g/d	0.49	0.92
Cell yield, g/g COD removed	0.074	0.118
Cell yield, g/g suspended solids	0.00875	0.0165
Sludge age, days	114	61
COD, g/d, influent	7.11	8.24
COD, g/d, effluent	0.48	0.46
COD, g/d, removed	6.63	7.78
Alpha, calc. using beta = 0.0245	0.28	0.29

[a] F/M = food-to-microorganism ratio

The gamma connection

Biomass from very high- and low-sludge-age units have contrasting properties. The high-sludge-age biomass is stable, has a minimal respiration rate, and requires no stabilization of waste sludge. By contrast, biomass from low-sludge-age units has a substantial respiration rate and rapidly goes anaerobic in the absence of dissolved oxygen. Thus, the high-sludge-age cells are essentially barren of substrate monomers in their resource pool, and the low-sludge-age cells are rich in substrate resources. The gamma connection, then, is defined as the substrate that has been captured by the cell, but has not yet reached its end use in either of the metabolic pathways; that is, the constituents of the cell's monomer pool increase in quantity with decreasing sludge age.

Since the historic thrust of biological wastewater treatment essentially has been in low-sludge-age systems, the gamma connection has contributed to concealing the nature of alpha and beta. For example, in the single-stage data, the sludge age was so high that the gamma function was essentially nil, and allowed alpha and beta to be estimated. When the more typical sludge age of five days is used as an operational guideline, the equilibrium mass of cells in the system is only 8.5 g, but the cell yield is increased to 1.7 g/d. As pool monomers, the captured substrate can constitute up to about 25% by weight of the dry cell mass. The COD equivalent of the monomer is two to three times its mass, and the pool monomers essentially are not measured by the TSS test, so about 15% of the influent COD in a low-sludge-age system escapes a material balance. Another important experimental problem historically concealing the accurate estimation and role of alpha and beta has been the error contributed to substrate balance caused by substrate volatility.

Additional reading

Grutsch, J. F., "Wastewater Treatment: The Electrical Connection," *ES&T,* 712, No. 79, p 1022.

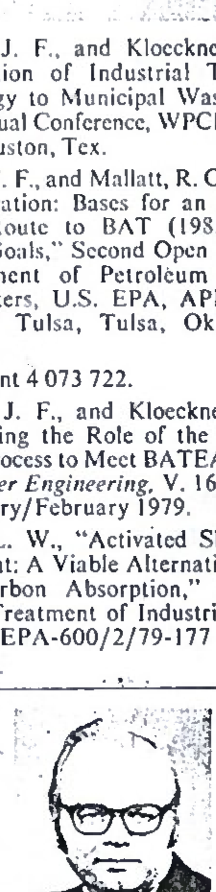
Grutsch, J. F., and Kloeckner, D. C., "Application of Industrial Treatment Technology to Municipal Wastewater," 52nd Annual Conference, WPCF, Oct. 11, 1979, Houston, Tex.

Grutsch, J. F., and Mallatt, R. C., "Design and Operation: Bases for an Activated Sludge Route to BAT (1983) Water Quality Goals," Second Open Forum on Management of Petroleum Refinery Wastewaters, U.S. EPA, API, NPRA, Univ. of Tulsa, Tulsa, Okla. (June 1977).

U.S. Patent 4 073 722.

Grutsch, J. F., and Kloeckner, D. C., "Optimizing the Role of the Activated Sludge Process to Meet BATEA," *Industrial Water Engineering,* V. 16, No. 1, p. 10, January/February 1979.

Crame, L. W., "Activated Sludge Enhancement: A Viable Alternative to Tertiary Carbon Absorption," Activated Carbon Treatment of Industrial Wastewaters, EPA-600/2/79-177 (August 1977).



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