COMBINED CHEMICAL–BIOLOGICAL TREATMENT STUDIES

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ABSTRACT

The paper will comment upon the OECD study of chemical treatment of urban sewage. Particular attention will be given to the relation between cost and performance of alternative processes. Swedish experience in this field will be analysed. The application of combined chemical and biological treatment processes will be discussed with regard to factors which influence the stability of performance.

INTRODUCTION

When an empirical approach has been of importance for the development of a certain area of technology, the associated terminology will not always come up to the mark with regard to stringency and exactness. This holds in particular for that part of the waste water technology which includes processes for the removal of pollutants by precipitation. An illustration of this is the expressions 'third stage' and 'nutrient removal' which are still in frequent use as names for the precipitative treatment of domestic sewage with lime or salts of aluminium or iron. The term 'phosphorus removal' seems likewise to be inadequate in a general context, as it diverts attention from the fact that it stands for a type of treatment which has great advantages other than the capability to reduce phosphorus to levels below 0.5 mg/l.

It may seem inappropriate to begin a main lecture with a reference to apparently petty semantic matters. In my experience, however, this is well justified in view of the difficulties which are frequently met with when technological options are to be presented to non-expert decision-makers. These difficulties are certainly not reduced when the presentation has to rest on confusing terminology.

The above would seem to indicate that the title of this paper 'Combined chemical-biological treatment systems' is also open to question, as in its usual sense it excludes several chemicals of potential or already established applicability to effluent treatment systems. It should be stated, therefore, that the title refers only to the second and the third and to some extent also to the first of the following unit operations:

Clarification	Chemo-oxidation
Bio-oxidation	Reverse osmosis
Precipitation/flocculation	Ion exchange
Absorption/adsorption	

THE OECD STUDY

Precipitative ('chemical') treatment of waste water has hitherto been applied to domestic sewage in a majority of cases. The almost exclusive aim has been to control that form of pollution which reveals itself as an excessive growth of algae and other aquatic plants in lakes, reservoirs, slow-moving rivers and shallow coastal waters, and which is now generally referred to as 'man-made' eutrophication. The prefix 'man-made' is added to distinguish it as a true form of pollution, thus differentiating it from eutrophication as a natural and usually very slowly progressing phenomenon. A comprehensive study of the different aspects of man-made eutrophication was recently carried out under the auspices of the OECD. The project was begun in late 1970 and the reports finalized late in 1972.

One of the basic assumptions was that the plant nutrients, in particular phosphorus and/or nitrogen, contained in urban sewage are of major importance for the development of man-made eutrophication. One main subject of the study was, therefore, a thorough examination of the technical and economic aspects of available processes for the removal of these materials from sewage.

The report recognizes that the present state of domestic and industrial effluent treatment is still inadequate in many countries, either due to lack of treatment facilities, to overloading, obsolescent design or poor management of existing ones, or to a combination of these factors. In the light of the high priority now given to environmental matters it is reasonable to assume that any local, regional or national programme for environmental protection should have as one of its primary goals—with due regard to the economic and technical resources available—an efficient reduction of the detrimental effects of discharges of sewage. When one of these effects is a not negligible growth of aquatic vegetation, this can be counteracted only by extensive removal of one or more of the causative plant nutrients from the sewage.

It may be said from the outset that the OECD experts were unanimously agreed that the treatment of urban (domestic) sewage with precipitating chemicals is not only a powerful but under most conditions also an indispensable method for controlling this form of pollution. As the report provides qualitative and quantitative information which may be applicable to chemical treatment of effluents in general, a short review would seem justifiable. As an aid to its work the OECD group adopted the definitions summarized in *Figure 1*.

At the time of reporting, adequate amounts of data from full-scale installations were available only in Finland, Sweden and Switzerland. An internationally based comparison of costs and performance of alternative processes was not possible, however. One reason for this was the lack of comparable design criteria and another the national as well as local differences in important cost factors. A third was the differences in national conditions which had led the three countries to develop different technical policies: Finland and Switzerland practise largely simultaneous precipitation, while post-precipitation is the method of choice in Sweden.

The OECD experts seemed to agree that post-precipitation would be the preferable method in the long run, at least in plants of reasonable size. The

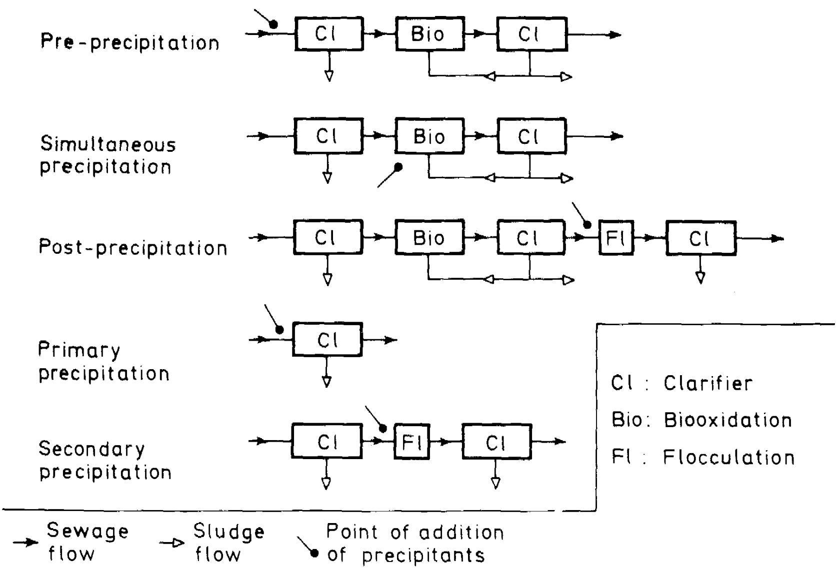

Figure 1. Nomenclature regarding treatment of urban sewage by precipitation.

installation of facilities for simultaneous and pre-precipitation, on the other hand, may offer a quick and cheap route to a provisional and sometimes, e.g. in extended aeration systems, permanent solution.

When combined with an activated sludge system, the pre- and simultaneous precipitation methods do not react to differences in sewage characteristics in a fully analogous manner. Sufficient information is not available to decide under what conditions one or the other is to be preferred. Pre-precipitation seems to offer a better overall performance in situations of incomplete control of discharges of industrial effluents to municipal sewerage. It may, on the other hand, impose fairly strict requirements with respect to the ratio between phosphorus and BOD in soluble form. The uncertainty on this point is of small importance, as a switch from one of these methods to the other and back again is a quite simple matter.

Either aluminium sulphate (alum), di- and trivalent iron salts or lime can be used as precipitant. The electrochemical dissolution of aluminium or iron from sacrificial electrodes *in situ* has been suggested but has not yet passed the experimental stage. Alum and iron(III) salts perform similarly under most conditions. The latter give slightly better results with simultaneous precipitation but may sometimes require the addition of some lime for optimum results. The choice between the two is largely a matter of cost at the plant site. Being cheap chemicals, the transportation cost is of considerable importance. Alum was previously at a disadvantage with respect to cost. Today, however, there is a cheap 'sewage grade' alum available on some markets. The cost aspect is thus losing in importance.

According to Scandinavian experience iron(II) sulphate from steel pickling, normally being the cheapest precipitant, may be used with advantage in extended aeration plants without preceding, separate oxidation. It is used in this way also in an activated sludge plant in Helsinki. The plant is designed for plug flow and the precipitant is added about midway in the aeration tank. The pre-requisites for direct application of iron(II) in activated sludge systems are not yet quite clear, however.

Finally, as regards iron(II), the crystallized material should be used if possible. To rely on a supply of liquor straight from the pickling line is not advisable. The quality varies and the deliveries may cease periodically with short notice.

Lime offers the advantage that it does not add an anion to the treated water. It adds, on the other hand, a high pH, for which reason carbonation of the final effluent may be necessary in a majority of cases.

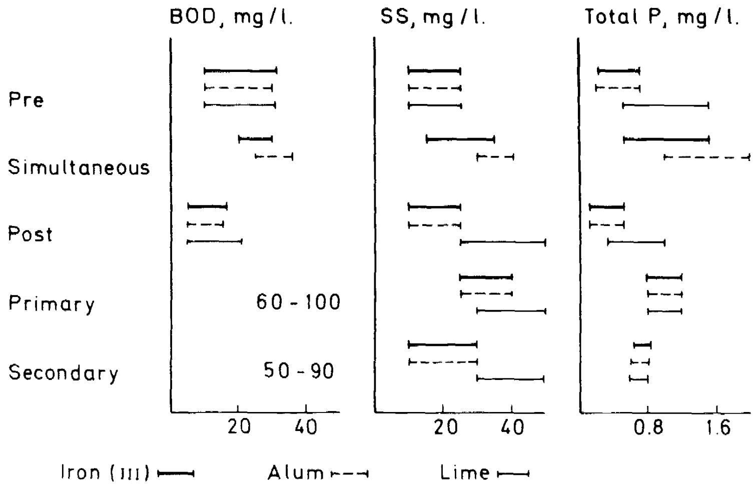

Figure 2. Data of performance for alternative precipitants used for chemical treatment of sewage.

Figure 2 summarizes the OECD data of achievable performance of the different processes under normal conditions of operation. The conditions are that the amount of chemical added is sufficient and that the system for solids separation is adequately designed, with regard to loading and hydrodynamic properties.

The cost estimate met with some difficulties. The problems caused by the lack of uniform design criteria and by the national and local differences in the relation between important cost factors such as labour and equipment were overcome, at least partly, by calculating and using relative costs. A more difficult problem was that there were no plants which had been designed originally for pre- or simultaneous precipitation, while the majority of the data for post-precipitation applied to new or extensively modernized systems.

Figure 3 shows the estimated total investment and running costs for secondary and post-precipitation together with those for mechanical (primary) treatment and conventional activated sludge treatment, the latter forming the basis for comparison. The costs for activated sludge treatment are given the relative number 100. The running costs cover operation, maintenance and amortization (6 per cent, 20 years), but exclude sludge handling.

		Investment costs				Running costs			
Size of plant (PE)		10^3	10^4	10^5	10^6	10^3	10^4	10^5	10^6
Type of treatment									
Mechanical		70	65	55	50	65	60	60	55
Activated sludge		100	100	100	100	100	100	100	100
Secondary	Al, Fe / Lime	90	85	70	65	110	105	100	95
Post	Al, Fe	115	115	110	110	150	145	140	135
	Lime					160	155	150	145

Figure 3. Relative total costs for secondary and post-precipitation systems.

The installation of facilities for pre- and simultaneous precipitation may in favourable cases add only a few per cent to the investment cost for conventional activated sludge treatment if no other complementary measures are called for. The running costs, on the other hand, are close to those for post-precipitation.

There follow a few comments on the conditions for process optimization. The knowledge of requirements of the pre- and simultaneous precipitation processes in terms of appropriate load data, and of the relation between soluble BOD and phosphorus in raw sewage etc. is quite scanty. Furthermore, little is known of the influence of the precipitant on the mechanism of bio-oxidation. It is not possible, therefore, to design and construct a new plant in which one or the other of these processes is combined with activated sludge. The basic dimensions must be those of a conventional, normally loaded activated sludge plant. When the construction is completed and the plant operates properly, the best way of adding a precipitant may be established. The situation is quite different for the post-precipitation process which may be introduced in the plans right from the beginning. No opportunity of process optimization will be missed in that case.

When considering the information provided by the OECD as well as others regarding costs of alternative processes, however, an important thing should be borne in mind. This is that the choice of consultant and contractor may have a much greater influence on costs than the actual choice of process. This is well established experience in Sweden.

THE SWEDISH SITUATION

It was recognized in the mid-sixties that man-made eutrophication constituted a sufficiently severe problem in Sweden to call for drastic action.

Towards the end of 1966 the responsible authorities decided on the basis of the technical information available that chemical treatment of urban sewage should be the course to follow. Accordingly a system of governmental incentives was created to support the implementation of the adopted policy. These were given the form of subsidies for construction costs. The amount of the subsidy was made dependent on the anticipated quality of the effluent. The highest subsidy, 50 per cent, normally required the installation of equipment for post-precipitation. There are some exceptions to this rule, however.

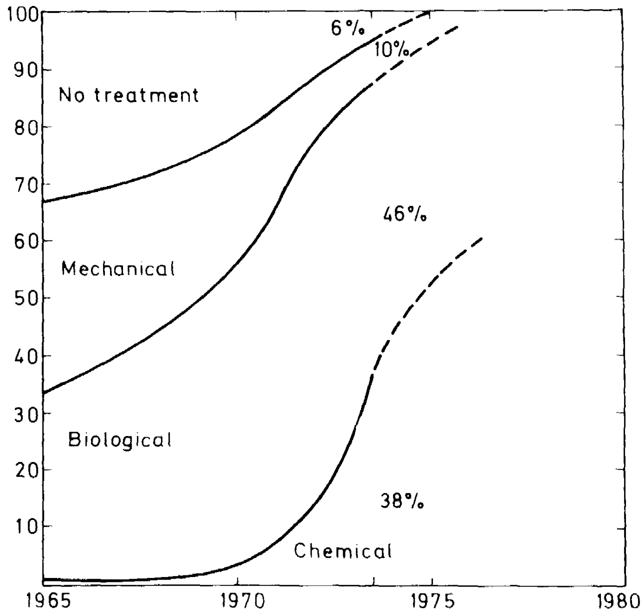

Figure 4. Treatment of urban sewage in Sweden.

Figure 4 shows the result of this policy. It may be mentioned that additional temporary subsidies for the construction of sewage works equipped for chemical treatment were introduced two years ago to ameliorate the labour market situation during the economic recession. This intensified the activities still further, with the result that close to forty per cent of the population are now (mid-1973) served by chemically operating sewage works.

Figure 4 illustrates not only a statistically favourable situation. An actual improvement of the quality of plant performance has taken place simultaneously. There are other explanations of this than the mere fact that the combination of biological and chemical treatment has proved to give better results in practice than was expected from the data obtained in experimental studies. Although the statistics for the period 1965–1969 may look fairly acceptable, the truth behind the data was that the performance of the corresponding installations was frequently far from satisfactory. The environmental issue has since given local authorities and their employees a better motivation to do a good job than they had earlier. This is one of the explanations. But there is an additional and quite simple one. Post-precipitation plants predominate in Sweden. When adequately operated, a very clear effluent is obtained. A simple measurement of the transparency at the end of the final clarifier will tell the operator whether or not there are problems afoot. When the transparency is 2–4 metres or more, he knows that he has done his part of the job well. If it starts to move towards 1 metre, he has reasons to worry or to be ashamed.

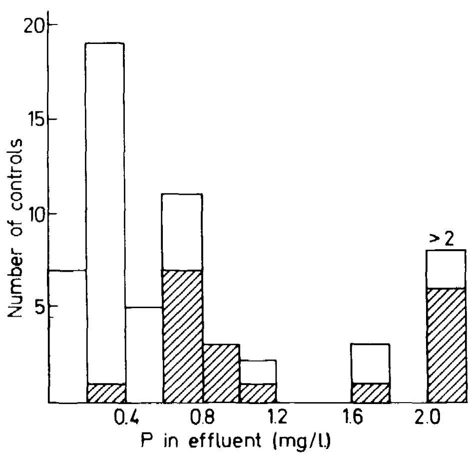

Figure 5. Performance of Swedish sewage works equipped for precipitation.

Figure 5 shows data from 58 controls of 47 treatment works as carried out and reported by the Technical Section of the National Environmental Protection Board. The shaded parts of some blocks indicate the number of controls at which it could be established that inadequate design of one or more components or inaccurate management had influenced the performance of the plant negatively. In the remaining cases of high phosphorus levels (> 0.8 mg/l) the causative factor was either not identified or was beyond the control of the operator.

The results from these controls as well as from other studies stress the importance of adequate design of the flocculator and the final clarifier. Provided that the precipitant is added in sufficient quantity, any escaping phosphorus above 0.1–0.2 mg/l will be in suspended form. This is demonstrated quite clearly by data obtained with the Electrolux microflotation system (*Figure 6*). This consists in principle of a U-shaped shaft, approximately 10 metres deep. The water is mixed with a precipitant, usually alum,

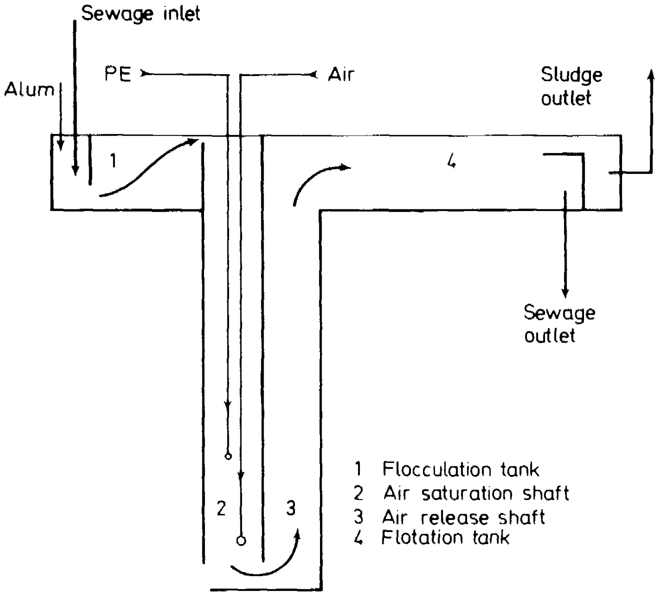

Figure 6. Electrolux flotation system.

and allowed to flow down one of the shanks of the U, where it becomes saturated with air. A suitable polyelectrolyte is added at this point. When the water rises in the other shank, the dissolved air is gradually released. In comparison with other flotation systems, this one has a higher capacity of dissolving air and provides smaller bubbles with an apparently higher affinity for suspended matter. The principle of saturating the whole volume of water with air makes the system much less sensitive to variations in the hydraulic loading than those which operate with high pressure saturation of a part of the total flow in a separate system.

Figure 7 summarizes some of the data†. They were obtained in an experimental unit with a design capacity of 10 m^3/h. This corresponds to a detention time of 30–40 minutes. The precipitant was sewage grade alum. The data show among other things the capability of a precipitant to cope with peak loads due to operational disturbances, provided that the system contains equipment which allows high efficiency in the separation of solids.

Similar results were obtained when the equipment was used for post-precipitation. The total phosphorus and suspended solids in the effluent were below 0.2 and 4 mg/l, respectively, in eight out of ten runs. No value exceeded 0.6 and 10 mg/l., respectively.

The average cost for biological and chemical treatment exclusive of write-offs and sludge handling is approximately 50 SwCr per capita and year (*ca.* 30 DM) according to recent estimates. Thirty per cent of this is attributed to the chemical part.

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† Obtained by courtesy of Chief Engineer Å. Svanteson, Electrolux AB, Stockholm.

Detention Time, min	Alum	Total P		Suspend. solids		COD	
		IN	OUT	IN	OUT	IN	OUT
30–40	150–200	3.2–5.1	<0.1	110–130	3.2–9.4	220–270	70–190
30–40	250	125*	0.5	a 10000	25	a 3900	176
15–20	250	91*	0.25		13		152

* Operational disturbance in the sewage works

Figure 7. Secondary precipitation plus flotation

The sludge handling is certainly worth a few comments. When the programme commenced, there was some well justified worry about the technical problems associated with the handling of the resulting, mechanically highly unstable hydroxide sludge. The late 'sixties saw a very promising development in sludge dewatering techniques, however. In combination with polyelectrolytes, band presses and radically redesigned decanter centrifuges allowed anaerobically as well as aerobically stabilized sludge to be dewatered to the point where it could be carted away for final disposal with no need for particular measures. The net effect of this was that the new technology could be used by the authorities as a tool for forcing communities to abandon the still applied but obsolete and hygienically unsatisfactory procedures in favour of procedures which conform better with modern requirements.

Initially the fundamental purpose of the chemical treatment was to achieve extensive removal of phosphorus. However, accumulated experience opposes placing the stress on this single parameter. This was the conclusion of the OECD group as well, but its mandate did not allow an extended discussion on this point. The post-precipitation process in particular will significantly improve the BOD removal efficiency and make it more stable. This holds also for the removal of part of the soluble refractory organic material and of suspended and colloidal matter including parasitic worm eggs and bacteria. The remaining suspended matter will largely consist of small hydroxide flocs, which are far less obnoxious than the suspended solids escaping from conventional biological systems. Generally speaking, the process seems to offer a highly competitive route to improved sewage treatment irrespective of whether phosphorus in domestic sewage causes pollution problems or not.

COMMENTS REGARDING INDUSTRIAL APPLICATIONS

Chemical precipitation has hitherto been combined with biological processes for treatment of industrial effluents mostly for the purpose of eliminating toxic constituents in the influent to the plant or of removing specified pollutants, e.g. coloured matter, before the final discharge. An example of the former applications is the addition of lime to precipitate toxic metals etc., which is practised in the Hoechst plant near Frankfurt. The experience from the installations for treatment of urban sewage indicates, however, that the application of post-precipitation may be useful also when a particularly high removal of BOD is required or when the effluent to be treated is subject to difficult-to-control variations in volume and composition. A post-precipitation unit may in the latter case offer the only protective means for achieving a satisfactorily high and steady quality of the final effluent. This aspect finds some support in a study carried out by our Institute† in a pulp and paper mill producing bleached and unbleached kraft, unbleached sulphite as well as semichemical pulp and paper. The pilot plant design for the purpose (*Figure 8*) consisted of an activated sludge unit placed parallel

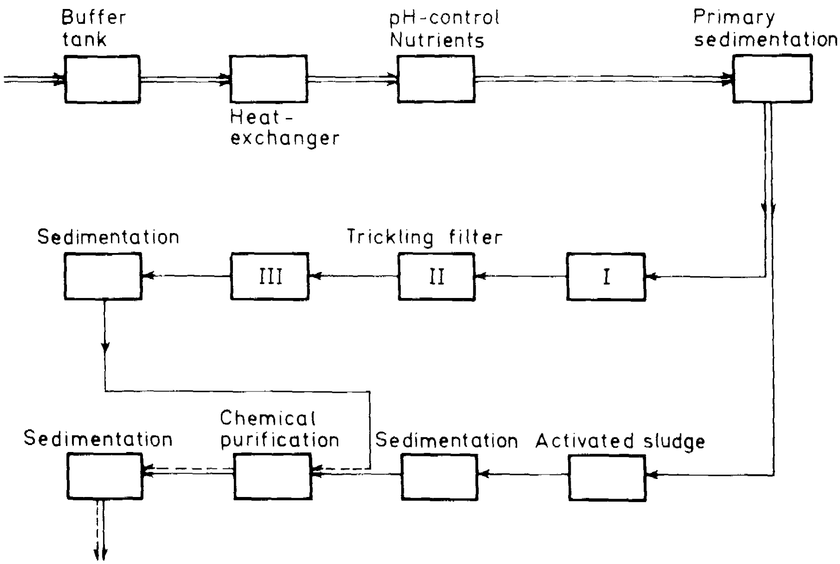

Figure 8. Flow sheet for experimental plant for biological–chemical treatment of pulp and paper mill effluent (pilot plant scale).

to three 3.1 metres deep plastic-filled trickling filters in series. A flocculating unit including clarifier could be connected to either of two biological systems. The equipment for influent control included a heat exchanger, a moderately sized buffer tank, a clarifier and a pH control system. This 'safety' system was not designed in order to make it easier for the project leader to show his ability to attain top results, but to simulate the conditions with respect to stability of effluent flow and composition which characterize an authentic situation. It was of particular interest to compare the reactions of the two biological systems to those variations in operational parameters which are routine rather than exceptional in some complex process systems.

Figure 9 presents data from a series of runs using a substrate consisting of wash water and partly stripped condensate from the plant for production

† Project leader: B. Boman, M. Eng. Sc.

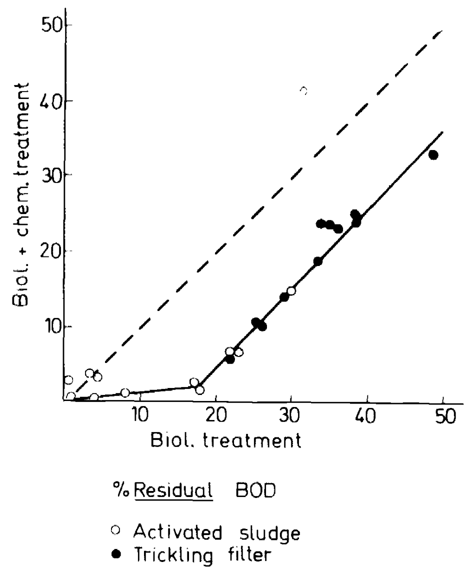

Figure 9. Biological versus combined biological–chemical treatment of pulp mill effluent.

of unbleached kraft. The BOD remaining after the biological systems has been plotted against the BOD remaining after the subsequent precipitation with alum. Use of the remaining BOD as basis for comparison instead of the BOD removal was not only more logical in this particular case but conforms better with environmental aspects.

In this series the loadings of the activated sludge unit and the trickling filters (9.3 m bed depth) were within the ranges 0.4–1.2 and 0.7–1.5 $m^3/m^3 \cdot h$, respectively. 150–250 mg/l. of alum was used for the precipitation.

The substrate was supplied in this case from a well-defined process system characterized by fairly steady operation. The treatment therefore gave rise to no problems of importance. The activated sludge unit produced the better results that would have been expected. The vertical distance between the generalized curve and the dashed line gives a measure of the improvement of effluent quality resulting from the precipitation. As is readily seen, this improvement was particularly significant when the removal of BOD by biological treatment only was in the range of 75–90 per cent.

It may be mentioned that the overall depth of the trickling filter system was far too large. In the quoted series, and in most of the other series too, the dominating part of the bio-oxidation took place in the first of the three filters. A correct comparison of the two systems with respect to cost and effectiveness would require that the quoted loadings of the trickling filter (0.7–1.5 $m^3/m^3 \cdot h$) were multiplied by a factor between two and three.

Pulp and paper mill systems of the combined type may be quite complex, and operational disturbances are therefore almost of daily occurrence in many of them. The disturbances are reflected in the composition and volume of the effluent. This may occasionally change its properties both rapidly and drastically. Such changes may in turn influence any system employed for biological effluent treatment. It is well known that a badly disturbed activated sludge plant may require days or even weeks to recover, while trickling filters are more sturdy in this respect. One purpose of our study was therefore to examine whether or not this assumed difference would be very much in favour of the trickling filter–chemical precipitation combination in practical situations when it is important to know the average or minimum efficiency of performance rather than the performance obtainable only when there is a coincidence of ideal conditions. *Figure 10* illustrates this point.

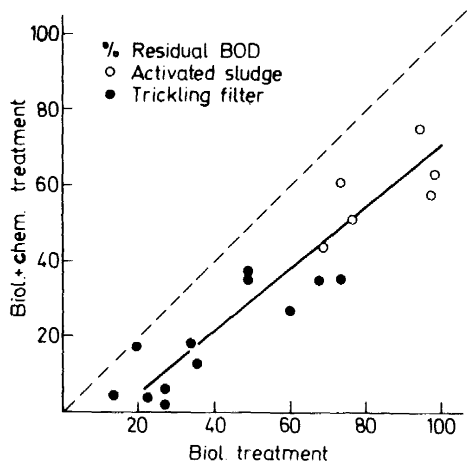

Figure 10. Biological versus combined biological-chemical treatment of pulp mill effluents.

The substrate had its principal source on the plant for production of semichemical (NSSC) pulp and paper. There was a regular and indispensable use of slimicides in this plant. Now and then it was necessary to store pulp and this was not possible without using a preservative. Formaldehyde was used for this purpose and of course, found its way to the treatment plant. Certain dyes may have added to the problems. In other words, the resulting effluent would appear to be incompatible with biological treatment. It is also evident from the figure that an activated sludge process would have no chance of maintaining a steady performance under such conditions. Subsequent precipitation did not bring much improvement. The trickling filter gave significantly better results at loadings similar to those applied in the series quoted above. The required amount of precipitant was, however, quite high in this instance, around 300–400 mg/l. It has not yet been calculated whether the corresponding cost per ton of product is acceptable or not. The question of the consumption of chemicals, on the other hand, has no direct bearing on the principle underlying the discussion.

One main purpose of our study was to examine the capacity of different precipitants to remove different kinds of waste lignins present in important types of pulp mill effluents. Previous work at our Institute showed clearly that some types of waste lignins, above all those from the bleaching of kraft pulp and from the production of sulphite pulp, could impair the quality of the receiving water with regard to its fitness as a source of drinking water when the purification process involves flocculation with alum. A significant increase of alum is evident in such cases, also at a fairly high dilution. These two types, furthermore, are virtually completely resistant to biological degradation in an aquatic environment. The indications obtained in our previous work were corroborated in the present study. Effluents from sulphite mills and from plants for kraft pulp bleaching are not amenable to combined biological and chemical treatment, as unrealistic quantities of alum or iron salts would have to be added before a precipitate forms. This kind of treatment seems to be applicable in the pulp industry only to effluents from the production of unbleached kraft pulp.

The data presented derive from a study which is not yet complete in all details. I have discussed them not because they deal with environmental problems within the pulp and paper industry, but because they appear to present some generally applicable aspects on combined biological and chemical treatment of industrial effluents. My discussion has been based on a limited number of experimental series, however, and should thus be considered as tentative rather than conclusive. In spite of this there may be reason to pursue the studies of potential applications along lines which differ slightly from those prevalent today.

CONCLUDING REMARKS

The conclusions of this paper may be formulated as follows:

(i) To consider chemical treatment of urban sewage merely as a method for the removal of phosphorus is equivalent to an erratic, unjustified limitation of its field of application.

(ii) It appears to be profitable to look upon chemical precipitation of urban sewage as an attractive alternative in instances when a final effluent with a particularly low and stable level of residual BOD is called for.

(iii) When the biological treatment of industrial waste waters is not sufficient for achieving the desired effluent quality, chemical treatment is sometimes a useful supplement. When applicable, it allows a wider choice of biological treatment methods. Hence conditions for optimization are improved.

(iv) It is more interesting to know what a given process will leave behind in the treated water than what it is capable of removing. This holds also for precipitation processes. Such an approach will help the decision-maker without expert knowledge to know what he will get for the money involved. This is certainly of interest to the owner of the money, whether an industrial company or an ordinary taxpayer.