

CHEMICAL AND ENGINEERING ASPECTS OF PHOSPHATE ELIMINATION

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Background

In the North German Coastal Plain, the effective ageing process of a lake includes the following stages: fertilisation by nutrients, silting up, and then development to swamp, moor, and forest. This process is speeded up by increased introduction of nutrients, resulting in accelerated eutrophication. The restoration of a lake involves reduction of nutrients, either down to a natural level, or even lower.

Lake Tegel is located in Berlin in a North German glacial moraine. Its natural influent is a glacial drainage channel called the Tegeler Fliess. During the 1930's it was provided in addition with an artificial inlet in its natural inflow area, called the Nordgraben. Lake Tegel empties into the Havel River, at its south-west end, opposite both inlets. There is a good bit of agriculture activity in the catchment areas of the Lake Tegel inlets. In addition, numerous sewage farms have been in operation in this area for the past 90 years as part of the metropolitan sewage disposal system for several million people. As a result, the mean phosphate concentration of the inlet is now $150 \text{ mmolm}^{-3} \text{ P}$ (5 mg l^{-1}). This situation means that the lake can no longer be optimally used for extracting potable water by bank filtration and artificial recharge of the surrounding groundwater, or for bathing, aquatic sports, and recreation.

The most favourable procedure for restoring Lake Tegel for all purposes of use as mentioned, was determined to be elimination of phosphates from the tributaries down to a concentration of $0.3 \text{ mmolm}^{-3} \text{ P}$ ($0.01 \text{ mg l}^{-1} \text{ P}$). At the same time, precautionary measures have to be taken to ensure that nutrient loads from sediments and diffuse tributaries will remain ineffective.⁽¹⁾

Chemical Aspects Of Phosphate Elimination

As far as the solubility of phosphate minerals is concerned, it is impossible to achieve the very low concentration of 0.3 mmolm^{-3} mentioned above. According to thermodynamic considerations at least 10 mmolm^{-3} (0.3 mg l^{-1} of $\text{PO}_4\text{-P}$) still remain soluble. For this reason, one must consider two elimination models:

- the precipitation model, and
- the ion-exchange, or chemisorption, model.

Both of these models use the same kinetic procedure as a starting point: the very fast intermolecular condensation of the HO-P group of soluble phosphate with the MO-Me = group of soluble Me-hydroxocomplexes (me = Al or Fe) or of the solid particles of these compounds⁽²⁾.

This condensation occurs very rapidly. Up to now, it has not been possible to obtain kinetic data on this reaction. In our experiments, as shown in Fig. 1, we found that after 0.12 s (the first sampling point in a kinetic flow apparatus), the reaction was completed⁽³⁾. Great influences of the calcium ions were determined by measurement. Furthermore, immediately after mixing acid agents with the water, the natural water acts as a non-buffered solution, and the pH falls to a range of 3.5 ... 5.5. Within 1 ... 5 s, it rises to a pH which corresponds to the alkalinity of the water and the amount of the flocculant agent added. The reason for this behaviour is the restrained dehydration of carbonic acid to carbon dioxide and water. The brief pH depression promotes phosphate precipitation, but if there is no calcium in the water, the precipitates become soluble as the pH rises. Fortunately, calcium is present at all times.

Stumm and Sigg⁽²⁾ found negatively charged and thus stable particles such as colloids in the reaction of phosphate with goethite. In natural waters the precipitates show rather a positive surface charge. There is no additional need for flocculants for destabilisation of the precipitates or of the turbid matter in the water. For very low concentrations of phosphate in the outlet of the plant, it is necessary to provide ion exchange (or chemisorption) of phosphate on Me- hydroxocomplex precipitates in a sand filter. A filter is thus essential for phosphate elimination. Table 1 outlines the P concentrations in the outlets of different treatment plants. Owing to organic phosphorus compounds, it is impossible to eliminate the total P of sewage plant effluent to less than 0.7 mmolm^{-3} water), then the total P in the effluent of a filter may be less than 0.1 mmolm^{-3} ($0.003 \text{ mg l}^{-1} \text{ P}$). This explains the contradictory findings in the professional literature.

To analyse organic phosphorus, ice-cold samples are exposed to ultraviolet irradiation (184 nm) after addition of peroxodisulfate. The molar ratio $b = \text{Me}/\text{P}$ is 1.3 for the precipitation and, further, is 0.4 for the filtration step. Actually, this means $b = 3 \dots 5$ for the filtration step, with regard to the reduced P concentration in the filter outlet, instead of the inlet to the plant.

In practice, the total b ranges from 1.7 ... 2.5. It depends mostly on the mixing device and the quality and velocity of P analysis in the raw water.

Table 1
Total phosphorus in the outlet of treatment plants

$-\log$ (molar)	$\text{PO}_4 \text{ mmol m}^{-3}$	as $\text{PO}_4 \text{ mg l}^{-1}$	as P mg l^{-1}	Type of treatment
3.5	316	30	9.8	Biol. treatment
4.5	31.6	3	0.98	Precipitation
5	10	0.95	0.31	Adsorption to aluminium oxide
6	1	0.095	0.03	Filtration with organic P
7	0.1	0.01	0.003	Filtration w/o organic P

Engineering Aspects of Phosphate Elimination

As mentioned, the chemical aspect of phosphate elimination end one second after mixing the agents with the water. Then coagulation, flocculation, sedimentation, and filtration take place, all of them determined by the engineering aspects.

The most common value for comparing and scaling up of laboratory or pilot plant experiments is the mean velocity gradient in the water until the flocs are ready for sedimentation.

There are no vessels with stirrers in the Berlin plant. For the first time, flocculation in pipes has been implemented on such a large scale ⁽⁴⁾. Typical values for the operation units are listed in Table 2.

In Berlin, sedimentation occurs in a new type of cylindrical tank, with tangential inflow at its external circumference. ^(5,6)

Uniformity of flow is obtained by lateral vanes installed around the sedimentation region (see Fig. 2). This vane reverses the water flow to a stable and slow rotation, extending over the whole sedimentation region. The incoming water is directed from the circumference to the centre of the tank, thus providing an accelerated flow. It has in fact been proven that accelerated flows are more stable than retarded ones ⁽⁷⁾.

At the outlet of the tank there is a secondary dosing of Al of Fe salts. Residual phosphates are thus fixed in double layer filters pumice (2.5 to 3.5 mm) and sand (0.6 to 0.8 mm).

The diagram in Fig. 3 gives an overall impression of the plant, which is designed for a treatment capacity of 3 ... 6 m^3s^{-1} .

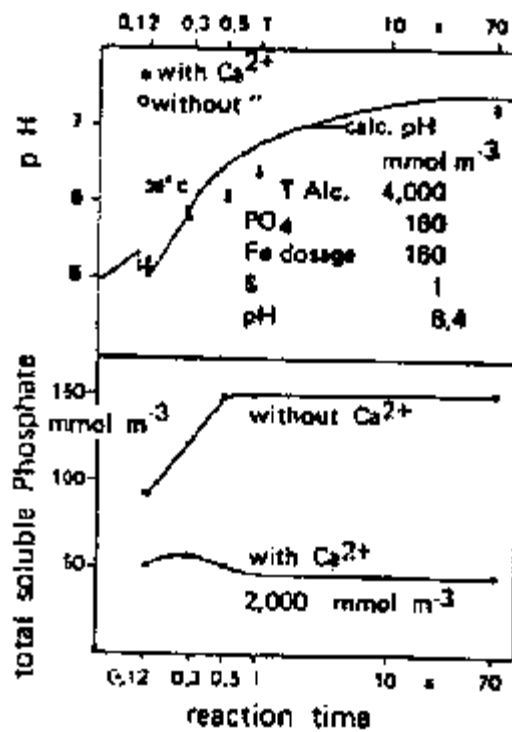


Figure 1: Phosphate precipitation compared with briefly pH depression during mixing.

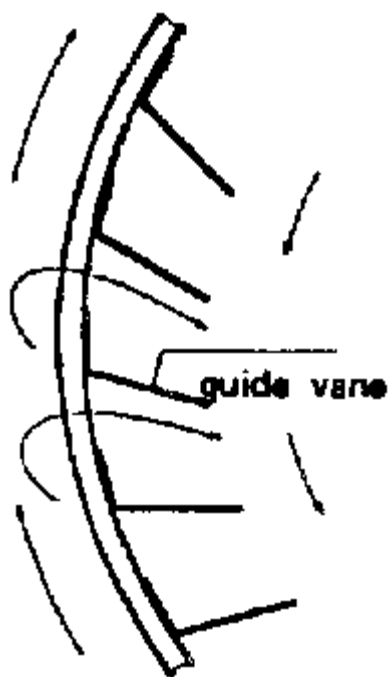


Figure 2: Construction of the guide vanes in the sedimentation

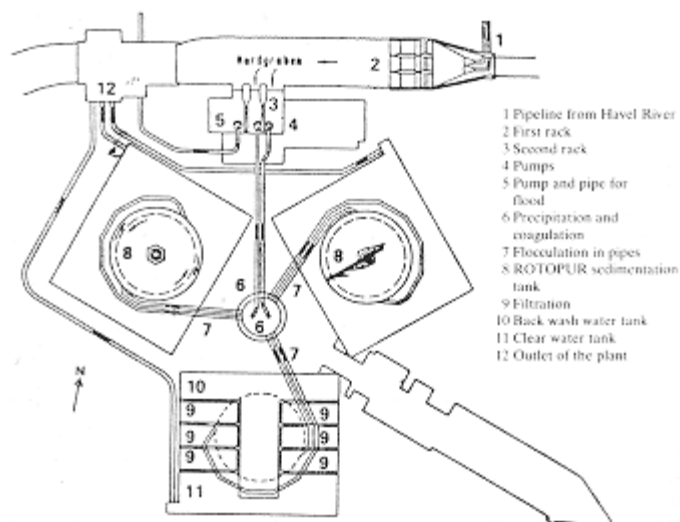


Figure 3: Schematic of the Phosphate Elimination Plant in Berlin (Tegel)

Table 2

Mean velocity gradient and detention time in the flocculation process

Operation unit	G in s ⁻¹	t in s	Pipe diameter in mm for Q=1.5 m ³ s ⁻¹
Mixing	500 ... 1000	1	1000
Destabilization	1000 ... 5000	0.5 ... 0.1	600
Aggregation to micro-flocs (coagulation)	200 ... 500	14 ... 30	1000
Aggregation to micro-flocs (flocculation)			
a. Without flocculant aids	20 ... 50	300 ... 1000	—
b. With flocculant aids	50 ... 120	20 ... 200	2 x 1200

A pipeline has been laid along the bottom of Lake Tegel from the Phosphate Elimination Plant across to the opposite outlet of the lake (approx. 6 km). This line serves to compensate for extremes in the flow through the two tributaries served by the plant: at peak periods of tributary flow the untreated excess is pumped under the lake into the Havel River at the other end; at slack periods, water is pumped in the reverse direction, from the Havel River, and through the plant for treatment.

The Tegel Phosphate Elimination Plant in Berlin will be put into operation in July of 1985. The first results will be available in a few months.

References

1. U. Hasselbach, "Phosphoreliminierung aus den Zuflüssen Berliner Seen", Z. Wasser Abwasser Forsch., 12, 88-102 (1979).
2. W. Stumm and L. Sigg, "Kolloidchemische Grundlagen der Phosphor-elimination", Z. Wasser Abwasser Forsch., 12, 37-46 (1979).
3. A. Grohmann, H.W. Althoff, and P. Koerfer, "Geschwindigkeit der Phosphatfallung mit Eisen (III) und der Einfluss von Calciumionen", Vom Wasser, 62, 171-180 (1984).
4. A. Grohmann, "Flocculation in Pipes: Design and Operation", Chemical Water and Wastewater Treatment, editors A. Grohmann, H.H. Hahn, and R. Klute, Gustav Fischer Publishers, Stuttgart, 1985.
5. K. Engel, "The ROTOPUR System", Chemical Water and Waste Water Treatment, editors A. Grohmann, H.H. Hahn, and R. Klute, Gustav Fisher Publishers, Stuttgart, 1985.
6. H.G. Moll, Gas- und Wasserfach, Wasser, 124, 295-301 (1983).
7. S.K. Banjeri, J. Environ. Eng. Div., 105, p. 803 (1979).

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