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Investigations on Phosphorus Removal from Waste Water

Progress Report

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Abstract

This paper describes the research work on phosphorus removal which was done in the Water Technology Division of the Nuclear Research Center in Karlsruhe.

Two goals were covered:

- Improvement of the commonly used simultaneous precipitation process to minimize the increase of the salt concentration in the water and the sludge amount obtained
- Development of two different alternative processes which avoid an additional salt increase of the water and allow a reuse of the phosphorus
    - Development of a process for direct precipitation of calciumphosphate from waste waters induced by seeding crystals
    - Development of a process applying activated alumina for phosphorus removal and recovery

Untersuchungen zur Phosphatentfernung aus Abwässern

Zusammenfassung

Es werden die Forschungs- und Entwicklungsarbeiten zur Phosphatentfernung aus Abwässern, die im Institut für Radiochemie, Abteilung Wassertechnologie, des Kernforschungszentrums Karlsruhe durchgeführt wurden, beschrieben.

Die Arbeiten gliederten sich in zwei Gebiete, nämlich

- der Optimierung des zur Phosphatentfernung üblicherweise verwendeten Simultanfällungsprozesses mit dem Ziel, die Aufsalzung der Gewässer und den Schlammehranfall durch Minimieurng des Fällmitteleinsatzes möglichst weitgehend zu reduzieren

- der Entwicklung von zwei Alternativverfahren, die eine Aufsalzung des Wassers vermeiden und eine Rückgewinnung des abgeschiedenen Phosphors erlauben

    - ein Verfahrens zur direkten Abscheidung von Calciumphosphat aus Abwässern unter Einsatz von Calcit als Impfkristall

    - ein Verfahrens zur Phosphatentfernung und -rückgewinnung aus Abwasser durch Einsatz von Aktivtonerde

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General Introduction

The deterioration of the water quality especially of slowly running rivers and lakes due to eutrophication caused by too high phosphorus concentrations is well known and often described in literature /1,2/.
Therefore, in the Federal Republic of Germany some measures were ordered:

1) Phosphorus limitation in detergents was decreed in 1975 /3/ by the Government and a reduction of the phosphorus content in the detergents in two steps was ordered which effected an estimated relief of about 10-15 % but was only specified on the phosphorus inflow of some selected sewage treatment plants /4/.

2) Phosphorus removal was ordered by the local authorities in two main areas by limiting the phosphorus outflow concentration of the sewage treatment plants

A) For the Lake Constance which is used as a recreation area and as a drinking water reservoir already in 1967 the phosphorus outflow concentration of all sewage treatment plants discharging into the water system of the lake was limited to 1 mg/l P in accordance with the neighbours, Switzerland and Austria. But, although this measure caused an improvement of the water quality the eutrophication of the lake could not be stopped. Therefore, the limit was changed in 1985 as follows /5/:

- For sewage treatment plants from 600 to < 3.000 population equivalents 85 % phosphorus removal, ≤1.5 mg/l P
- For sewage treatment plants from 3000 to < 30.000 population equivalents 87 % phosphorus removal, ≤1.0 mg/l P
- For sewage treatment plants ≥ 30.000 population equivalents 93 % phosphorus removal, ≤0.3 mg/l P

B) For Berlin, because all wastewater is discharged into a river system which essentially consists of a series of shallow lakes and which is used intensively as recreation area, in 1982 a water protection agreement was contracted with the German Democratic Republic to lower step by step the total phosphorus effluent of all Berlin waste water treatment plants to ≤ 2 mg/l P until 1986 /6/. But, however, this phosphorus reduction will probably not be sufficient for a restoration of the rivers and lakes. This is confirmed by the experiences on the Lake Constance mentioned above as well as by other countries, e.g. Switzerland and Sweden, with limits of ~ 0.2 mg/l P.

3) Besides, phosphorus removal is ordered for a lot of sewage treatment plants depending on their receiving water body. These limits are set by the local authorities.

4) The phosphorus concentration of the waters will be included in the minimum requirements from 1992 onwards, i.e. phosphorus will be considered as a noxious substance for the water and will be charged according to the waste water charges act. This measure will be valid for sewage treatement plants larger than 50.000 inhabitant equivalents if the effluent concentration exceeds 2 mg/l P.

Phosphorus removal in Germany is normally effected with precipitation using Fe and Al salts or lime, respectively /7,8/, and was applied in 1983 for the treatment of the sewage of about 9 millions inhabitants + population equivalents which amounts to 7.7 % of the total installed treatment capacity /9/ or 1.9 % of all sewage treatment plants, respectively. This is of course far away from the situation in Sweden where phosphorus removal with precipitation already in 1978 was effected on about 80 % of all secondary effluents /10/. The average outflow concentrations obtained vary to some extend on the method applied - simultaneous precipitation, pre- or postprecipitation - but are normally not less than about 1 mg/l P, especially if simultaneous precipitation is applied which is the most frequently used method in Germany (about 50 %). For a further decrease of this value either a high excess of the precipitating agent has to be applied or filtration has to be added as an additional treatment step /11/. And, furthermore, the precipitation process has some great disadvantages:

- The anion concentration of the water, i.e. chloride or sulfate is increased
- A precipitation sludge is obtained which must be incinerated or disposed
- A recovery of the phosphorus is nearly impossible. This seems to become a very important point for the future, too, because the Federal Republic of Germany generally dependens on imports. According to /1/ in 1978

85.000 tons of phosphorus were discharged into the waters which could be saved and thus an import in the same order of magnitude could be spared.

Therefore, it is still an urgent task to develop phosphorus removal processes avoiding the disadvantages mentioned above as far as possible and this policy is followed by the Federal Ministry for Research and Technology. Some major projects concerning Advanced Waste Water Treatment especially in view of phosphorus and partly nitrogen removal are sponsored. The research is mainly concentrated on biological processes for phosphorus removal in connection with nitrification and denitrification.

Research work on phosphorus removal was done on two different ways:

- Improvement of the precipitation process, i.e. investigations on simultaneous precipitation in a research project in cooperation with the Berliner Entwässerungswerke /12/ in order to optimize the process by dosage control of the precipitating agent and, therefore, to minimize the increase of the salt concentration in the water and the sludge amount obtained

- Development of processes which avoid an additional salt increase of the water and allow a reuse of the phosphorus

  - Development of a process for direct precipitation of calcium phosphate from waste waters induced by seeding crystals/13-15/ which is known in Japan as crystallization /16-19/

  - Development of a process applying activated alumina for phosphorus removal and recovery /20/

PART 1

Investigations on Phosphorus Removal from Waste Water by Precipitation of Calcium Phosphate Induced by Seeding Crystals

/10,13,15/

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Abstract

Phosphorus removal by means of direct precipitation of calcium phosphate induced by seeding crystals was investigated. For this, jar tests as well as throughput experiments were carried out.
If calcium phosphate, either as hydroxylic apatite or as tricalcium phosphate is used as seeding material, amorphous precipitation products are obtained which transform only extremely slow to defined crystallinic calcium phosphate compounds.
Residual concentrations of about 0.1 mg/l P are obtainable dependent on the pH-value of the water, but the process is strongly retarded if carbonate or magnesium ions are present in the water.
If calcite is used as seeding material instead of a calcium phosphate compound no deterioration of the phosphorus elimination due to the presence of carbonate or magnesium ions in the water takes place. Jar tests as well as throughput experiments with artificial waste water showed that the residual phosphorus concentration depends only on the pH value of the water and on its calcium content.
Throughput experiments with secondary effluent of a sewage treatment plant lasting about 40 days confirmed these results. Using 500 g/l of limestone as seeding material its phosphorus content was reduced from 8.7 mg/l P to 0.44 mg/l P if the pH of the water was adjusted to 9.7 with lime water.
The use of calcite as seeding material for the direct precipitation of calcium phosphate seems to be a very promising method for phosphorus removal from waste waters especially because in contrary to other investigated seeding materials like apatite or other calcium phosphate compounds calcite has the great advantage that the carbonate and the magnesium content of the water does not influence the process.

1. Introduction

The idea of the precipitation of phosphorus induced by seeding crystals is: The domestic sewage effluents are supersaturated with regard to most calcium phosphate species because both, phosphorus and calcium, are present in concentrations which are far above the solubility product. If it would be possible to obtain an equilibrium with hydroxylic apatite, the most stable and least soluble calcium posphate compound, nearly all the phosphorus present in the water would precipitate already in the sewage treatment plant and the phosphorus problem would not exist in waste water technology which is demonstrated by the following example:

Calculation for a Representative "German" Waste Water
for 15°C and pH = 8
HAP = hydroxylic apatite

waste water	0.262×10^{-3} moles/l P = 8.1 mg/l P
equilibrium with HAP	6.000×10^{-8} moles/l P = 0.002 mg/l P

In reality no precipitation of calcium phosphate even after long times takes place, but, it is known on the other hand, that calcium phosphates precipitate if seeding crystals are present in the water /21/.

2. Previous Investigations

This idea, i.e. to initialize the crystallization of calcium phosphate by means of seeding crystals, was further intensively investigated especially in Japan and in the Netherlands. Regarding the high/low lime process, i.e. precipitation with lime, the main difference is that only an appropriate pH is adjusted, but neither lime nor lime slurry are added and, theoretically, a pure calcium phosphate is obtained.

2.1 Investigations in Japan

Research work in Japan was already done since 1977 and was presented on the 2nd and 3rd Japanese-German workshop on waste water treatment about the Tokyo pilot plant /16/ and about the results in the Public Works Research Institute, Ministry of Construction, in the laboratory scale /18/ as well as in a pilot plant study in Kyoto /17/ summarized in /19/.

In Tokyo the process is carried out in the following way:

- acidification of the water for decarbonization
- addition of gypsum and lime to a pH of 8.5-9.2
- sand filtration
- phosphorus removal in a crystallization reactor with bone char or phosphorus rock as seeding material

The results indicate a reduction from about 1.4 mg/l P to an average of 0.35 mg/l P.

The Public Works Research Institute did a lot of experiences with phosphorus rock and bone char, but, however, the results were not as good as in Tokyo probably because decarbonization was not carried out completely.
It would be difficult to apply this "Japanese" process in Europe because both, the carbonate and the phosphorus concentrations in the waters, are much higher, i.e. the demand of chemicals would increase in comparison to Japan. Thus the process would become uneconomic. Furthermore, an additional increase of the sulfate concentration in the water must be avoided due to corrosion problems concerning the concrete.

2.2 Investigations in Europe

The investigations were carried out in the Netherlands by Trentelmann and Eggers /22,23/. Water was adjusted to a pH of 9 with NaOH and then pumped into a sand fluidized bed. The result was a reduction from 3-13 mg/l P to about 2.5-4 (total phosphorus) corresponding to 0.6-1.2 mg/l dissolved phosphorus.

Similar experiments /23/ were carried out in a pilot scale plant (40 m^3/h) using pellets of calcium phosphate or sand, respectively. Effluent concentrations of < 1 mg/l P were only obtainable by an additional filtration step.

Obviously the high effluent concentrations in the Netherlands are due to the carbonate content of the water, i.e. the same situation as in Japan where only a sufficient phosphorus removal is obtained if decarbonation of the water was carried out as the preliminary step.

Both principles, the European as well as the Japanese, give a great importance to the nature of the seeding material although it is not well defined and agree that a formation of "amorphous calcium phosphate" must be avoided.

Caused by these problematics it seemed impossible to apply this method which is very attractive seen from the chemical point of view.

3. Prevailing Knowledge about the Crystallization of Calcium Phosphate from Supersaturated Solutions

3.1 Solubility Behaviour of the Calcium Phosphates

According to the literature /24,25,26/ a lot of slightly soluble compounds may be formed listed in table 1.

Table 1

Calcium Phosphate Compounds

name	formula	abbrevation	Ca/P-ratio
Calciumhydrogenphosphatedihydrate (Dicalciumphosphatedihydrate)	$CaHPO_4.2H_2O$	(DCPD)	1.0
Calciumhydrogenphosphateanhydride (Dicalciumphosphatanhydride)	$CaHPO_4$	(DCPA)	1.0
Tetracalciummonohydrogentriphosphate	$Ca_4H(PO_4)_3 \times 2.5\ H_2O$	(OCP)	1.33
Amorphous "Tricalciumphosphate"	"$Ca_3(PO_4)_2 \times\ xH_2O$"	(ATCP)	1.5
β-Tricalciumphosphate	$Ca_3(PO_4)_2$	(TCP)	1.5
Hydroxylic apatite	$Ca_{10}(PO_4)_6(OH)_2$	(HAP)	1.67

The names of these compounds are not always in accordance with the systematic technical terms, they derive from the molar ratio Ca/P.

3.2 Formation of Calcium Phosphates

The compounds listed in table 1 are reported in the literature to be formed in an X-ray amorphous form first if a fast precipitation is carried out, but crystallize if they are allowed to stand for some time in the mother liquor solution. Therefore, the whole procedure will be called "crystallization" without a further mentioning of these facts.

A lot of other papers were published also focusing the formation of calcium phosphates from supersaturated solutions by crystallization which partly are contradictory /27-31/. It was reported, that the products initially formed change their crystallographic structure dependending on the conditions of the environment. Additionally, foreign ions are of great influence, especially carbonate /32,33/ and magnesium /34,35/ which prevent the precipitation of calcium phosphates.

Summarizing it must be stated that the informations obtainable regarding the formation of calcium phosphates from supersaturated solutions are in no way helpful for the development of a technology for phosphorus removal by precipitation. And, however, this technology was not developed up to a satisfying degree up to now.
Therefore, also investigations were carried out in order to obtain basic information regardless of experiences of other authors.

4. Experimental Part

4.1 Artificial Waste Water

In the preliminary experiments in the laboratory scale artificial waste waters were used listed below, a "German" and a "Japanese" one in order to enable a comparison with the experiments in the literature.

4.1.1 "German" Artificial Waste Water

The concentrations listed in table 2 are the mean concentrations of 12 important sewage treatment plants in Baden-Württemberg /36/ and represent the principal constituents of a waste water although accessory constituents as well as the "organic substance" are missing. It will be called "KAW" in this manuscript.

Table 2

Mean Concentrations of "German Waste Water" and the Amount Weight of Salts for its Preparation /36/

cations mmoles/l		anions mmoles/l	
Na	3.7318	Cl	2.4560
K	0.4870	tCO_3	4.9890
NH_4	2.0782	NO_3	0.1879
Mg	0.8670	SO_4	0.9698
Ca	1.0331	tPO_4	0.2624

salt	mg/l
NaCl	5.30
$NaHCO_3$	245.40
Na_2SO_4	14.60
Na_2HPO_4	37.25
KCl	22.30
KNO_3	19.00
NH_4HCO_3	164.30
$MgSO_4 \times 7H_2O$	213.70
$CaCl_2 \times 2H_2O$	151.90

4.1.2 "Japanese" Artificial Waste Water

In /37/ some datas are given about Japanese Waste waters. Therefore, the concentrations in table 3 were chosen. This water will be referred as "KJAW" in this manuscript.

Table 3

Mean Concentrations of "Japanese Waste Water" and the Amount Weight of Salts for its Preparation /35/

cations mmoles/l		anions mmoles/l	
Na	2.494	Cl	2.4560
K	0.4870	tCO_3	1.6130
NH_4	0.696	NO_3	0.1879
Mg	0.590	SO_4	0.9698
Ca	0.700	tPO_4	0.08

salt	mg/l
NaCl	44.24
$NaHCO_3$	82.07
Na_2SO_4	53.98
Na_2HPO_4	28.65
KCl	22.30
KNO_3	19.00
NH_4HCO_3	55.03
$MgSO_4 \times 7H_2O$	145.42
$CaCl_2 \times 2H_2O$	102.91

4.2 Performance of the Crystallization Experiments

The experiments were started by addition of the seeding crystals in 1 l of a suspension of 20 % by weight. The pH of the water with a ionic strength of 0.01 mol/l was kept constant throughout the experiment with a combination titrator - pH-electrode - personal computer by regulated addition of NaOH. The personal computer was a very efficient help, on the other hand, for collecting and and managing the datas throughout the experiment.
Furthermore, samples were taken in the course of the experiments and analyzed as described in section 4.3 after filtration through a membran filter with a porous size of 0.1 µ.

4.3 Analytical Methods

The methods used were

- the photometric method "molybdene blue" for phosphate /38/
- titration with EDTA for calcium and magnesium /39/
- pH following /40/
- ion chromatography for chloride, nitrate and sulfate

4.4 Determination of the Composition of the Calcium Phospate Precipitates

The amount of the precipitataed calcium phosphate was in most cases much lower than the amount of the seeding crystals. Therefore, the composition of the "products" was determined by the calculation of the differences of the initial and the residual concentrations of calcium and magnesium, respectively, i.e. $\Delta c(Ca)/\Delta c(P)$, in the following shortly named as $\Delta Ca/\Delta P$ which is usually done in the literature, too.
A change in this ratio in the course of the experiment was an indication that

- either different calcium phosphate compounds had precipitated or
- that a transformation of such a calcium phosphate compound had taken place.

This indirect way was the only practocable method because mostly only X-ray amorphous products were obtained (section 5.1.1.2).

5. Results

5.1 Phosphorus Elimination with Calcium Phosphate Compounds as Seeding Crystals

A lot of different calcium phosphate compounds (table 1) was tested in preliminary experiments for the applicability as seeding material, but only TCP and HAP yielded satisfactory phosphorus elimination rates. Therefore the investigations, were limited to these two compounds.

5.1.1 Phosphorus Elimination with HAP-Seeding Crystals

5.1.1.1 The Influence of the Concentration of the Seeding Crystals

Phosphorus elimination was investigated applying 2 different concentrations of HAP with 2 pH-values of 8 and 9, respectively:

- 0.2 g/l HAP corresponding to a slow reaction velocity
- 1.0 g/l HAP corresponding to a fast reaction velocity

The results up to a time of reaction of 3 hours are shown in figure 1 and indicate that a higher pH as well as a larger concentration of the seeding material HAP favours the reaction.

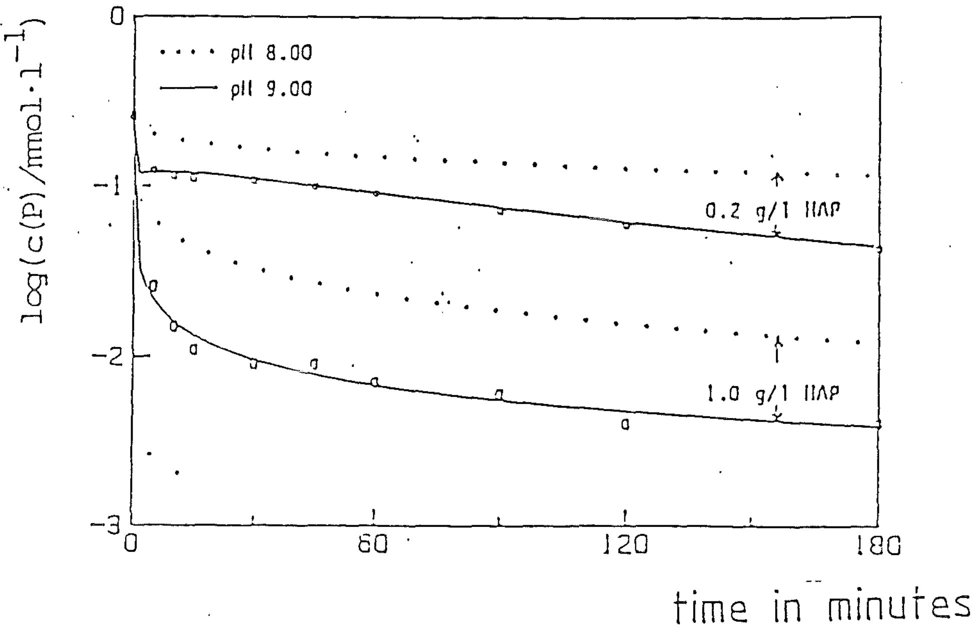

Figure 1: Phosphorus Elimination with 0.2 g/l and 1 g/l HAP at a pH of 8 and 9 and 20°C

5.1.1.1.1 The Composition of the Precipitated Products Induced with 0.2 g/l HAP

After 16 hours the equilibrium concentration of OCP was obtained, i.e. $c(P)^{\infty}$ = 0.055 mmoles/l P. The stoichiometric ratio $\Delta Ca/\Delta P$ enhanced from about 1.27 30 minutes after the start to about 1.45 after 2 hours and remained then constant.

This change of the ratio $\Delta Ca/\Delta P$ indicates that 2 different species of calcium phosphate are precipitated one after the other or become assimilated in the course of the reaction with an increased uptake of calcium ions. Either OCP or an ATCP with a calcium deficit are possible phases formed.

The time point of this change corresponds to the moment where the surface of the HAP is completely covered with a monomeleculare layer of the precipitated product.

5.1.1.1.2 The Composition of the Precipitated Products Induced with 1.0 g/l HAP

The ratio $\Delta Ca/\Delta P$ increased during the first 15 minutes from 1.23 to 1.33 and remained constant throughout 16 hours. After 10 minutes of reaction the phosphorus concentration was below the solubility product of OCP, after 16 hours a final concentration of 0.003 mmoles/l P was found corresponding approximately to the solubility of TCP which is higher than the solubility of HAP. Possibly again an ATCP with a deficit of calcium was initially precipitated which was not transformed within 16 hours because this would have been remarked by a gradual increase of $\Delta Ca/\Delta P$.

This increase of $\Delta Ca/\Delta P$ during the beginning of an experiment was reported by other authors, too, but no satisfying explanation could be given.

5.1.1.2 The Influence of Other Substances Present in the Water

5.1.1.2.1 Magnesium and Carbonate

Both, magnesium and carbonate, are present in the water up to a certain extent, i.e. that investigations disregarding their influence on the process would be of less interest for a practical application. According to the results (table 4) the influence of the carbonate is much more significant than the influence of the magnesium but mainly the kinetics of the precipitation is retarded but no remarkable influence on the final concentration of phosphate obtainable was detected. This may be derived from figure 2 because the slope of the phosphorus concentration versus the time does not indicate an approach to saturation.

Both, magnesium and carbonate, showed besides the influence on the kinetics of the precipitation an influence on the composition of the reaction products, too. An increase of the ratio Ca/P was effected by carbonate, whereas a decrease of this ratio was caused by the presence of magnesium.
Regarding the magnesium obviously only at the beginning of the reaction an elimination of magnesium was effected similar to adsorption.
In the case of a high carbonate content in the water the most probable reaction is a precipitation of calcite instead of calcium phosphate.

This means that according to the results obtained and in accordance with the results from Japan /16-19/ the carbonate content of the water seems to be the entire problem of the phosphorus removal induced by seeding crystals especially because the average carbonate content in the waters is much higher and the influence much stronger than of magnesium as shown in table 4.

Table 4

The Influence of Carbonate and Magnesium on Phosphorus Elimination Induced by HAP Seeding Crystals

Experimental conditions: I = 0.01 moles/l, 1 g/l HAP-seeding crystals, pH = 8
20°C, c(P) = 0.262 mmoles/l, c(Ca) = 0.984 mmoles/l

		Addition of		
	---	+ 1 mmole/l	+ 1.68 mmoles/l	
	---	$NaHCO_3$	Mg	time of reaction
c(P)fin.(% removal) mmoles/l	0.033 (87.4)	0.081 (69.1)	0.069 (73.7)	30 minutes
	0.012 (95.4)	0.052 (80.2)	0.039 (85.1)	180 minutes

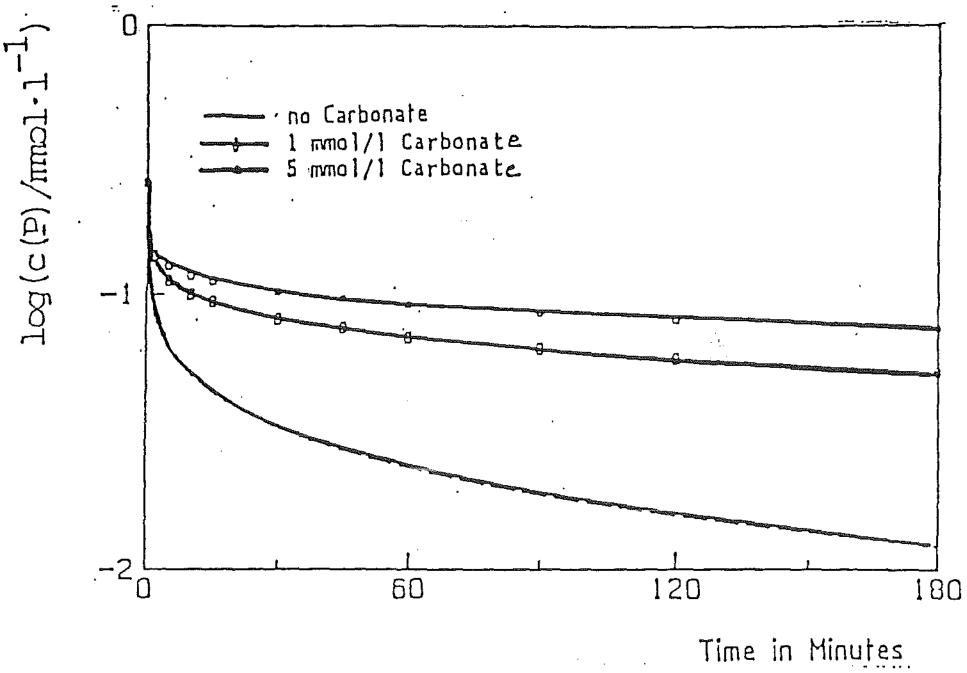

Figure 2: The Influence of Carbonate on the Calcium Phosphate Precipitation Induced with 1 g/l HAP, pH=8.0, 20°C

5.1.1.2.2 Chloride, Sulfate, Lignosulfonic Acid

In comparison with the effects of carbonate and magnesium the influence of the 3 ions was negligible small. This means an interesting result regarding the lignosulfonic acid:

The phosphorus elimination is obviously independent from the the degree of the organic pollution of the water.

5.1.1.3 The Influence of the Working Conditions

The conditions investigated were the initial ratio Ca^0/P^0, the temperature and the pH-value of the water.

5.1.1.3.1 The pH-Value of the Water

According to table 5 the phosphorus elimination is improved by an increase of the pH-value of the water due to an increase of the supersaturation regarding OCP, TCP and HAP, respectively, because the concentration of the species PO_4^{3-} increases by raising the pH of the water if the concentration of the total phosphorus remains constant.

At a higher pH of the water products are obtained at a higher pH which contain more calcium than at a lower pH. The composition of these products lies between TCP and HAP and moves towards HAP with increasing time of reaction, i.e. increasing phosphorus elimination, but, the residual phosphorus concentration conforms to the solubility of TCP.

Table 5

The Influence of the pH-Value of the Water on Phosphorus Elimination Induced by HAP Seeding Crystals

Experimental conditions: I = 0.01 moles/l, 1 g/l HAP seeding crystals, 20°C
c(P) = 0.262 mmoles/l, c(Ca) = 0.984 mmoles/l

	pH = 8	pH = 9	time of reaction
c(P)fin. (rem. %)	0.033 (87.4)	0.009 (96.6)	30 minutes
(mmoles/l)	0.012 (95.4)	0.004 (98.5)	180 minutes

5.1.1.3.2 The Influence of the Temperature

Phosphorus elimination decreases as expected with a lower reaction temperature according to the results listed in table 6.

The stoichiometry of the product obtained - $\Delta Ca/\Delta P$ - was independent of the reaction temperature applied up to 3 hours of reaction, but changes occured after a time of reaction of 16 hours:
The ratio $\Delta Ca/\Delta P$ increased from 1.33 at 20°C to 1.55 at 5°C, i.e. that at lower temperatures products with a higher calcium content are formed.

Table 6

The Influence of the Temperature on Phosphorus Removal Induced with HAP Seeding Crystals

Experimental conditions: I = 0.01 moles/l, 1 g/l HAP seeding crystals, pH = 8
c(P) = 0.262 mmoles/l, c(Ca) = 0.984 mmoles/l

	5°C	10°C	20°C	time of reaction
c(P)fin. (rem. %)	0.073 (72.1)	0.061 (76.7)	0.033 (87.4)	30 minutes
(mmoles/l P)	0.037 (85.9)	0.025 (90.5)	0.012 (95.4)	180 minutes

5.1.1.3.3 The Influence of the Initial Ratio Ca^0/P^0 in the Solution

The formation of the precipitated product is not remarkable influenced by a change of the initial ratio Ca^0/P^0, but phosphorus elimination is favoured by a higher ratio, i.e. a surplus of Ca versus the phosphorus (table 7).

Table 7

The Influence of the Initial Ratio Ca^0/P^0 on Phosphorus Elimination with HAP as Seeding Crystals

Experimental conditions: I = 0.01 moles/l, 1 g/l HAP as seeding crystals, pH = 8
c(P) = 0.262 mmoles/l, 20°C

Ca^0/P^0	1.9	3.8	time of reaction
c(P)fin. (rem. %)	0.132 (49.6)	0.033 (87.4)	30 minutes
(mmoles/l P)	0.069 (73.7)	0.012 (95.4)	180 minutes

5.1.1.4 Comparison of the Single or the Multiple Use of the Seeding Material

In the experiments previously described always unused HAP was applied and its surface was covered with an X-ray amorphous product not definitely identified in the course of the experiment. This is of course far away from the reality because in a technical device the seeding material should be used as long as possible. This means, on the other hand, that its surface would be completely covered with the precipitated product, i.e. the original surface would no longer take an influence on the reaction, perhaps, even if the surface is only partially covered, i.e. changed by effects of adsorption. Therefore, the "aging" of the HAP seeding material was investigated in special experiments.

5.1.1.4.1 Performance of the Experiments

It was not possible to carry out continuous throughput experiments because HAP was not sufficiently settleable. Therefore, the reaction solution was quickly separated and the seeding material was again used with a fresh phosphorus solution.

5.1.1.4.2 Results

The main result of the experiments (table 8) is a deterioration of the elimination efficiency of the HAP seeding material caused by its multiple use, but fastly a steady state is obtained leading to final phosphorus concentrations near the solubility TCP within 1 to 2 hours. I.e., that this final concentration is obtained within 50 minutes with unused HAP and only after about the doubled time of reaction with multiple used one. But it should be possible, on the other hand, to obtain times of reaction practicable in the technical scale ($\leq$ 30 minutes) using a higher concentration of seeding crystals.

Table 8

The Influence of the Multiple Use of HAP on the Phosphorus Elimination

Experimental conditions: I = 0.01 moles/l, 1 g/l HAP as seeding crystals, pH = 8
$c(P)^0 = 0.257$ mmoles/l, $c(Ca)^0 = 1.033$ mmoles/l, 20°C

HAP reused	0	several times	time of reaction
c(P) in mmoles/l P (final concentration)	0.04	0.2	15 minutes
	0.035	0.13	30 minutes
	0.025	0.09	50 minutes

5.1.2 Phosphorus Elimination with TCP-Seeding Crystals

The experiments with TCP gave nearly analogous results in comparison to the experiments with HAP although the TCP contained impurities such as HAP, i.e. no pure TCP was available. Again an amorphous calcium phosphate was precipitated on the surface of the TCP as investigations with the surface electrone microscope showed. And, furthermore, the deteriorating effect of magnesium and carbonate, respectively, remained.

- X-Ray Investigations

In experiments carried out with a low concentration of 0.2 g/l TCP weak X-ray reflexes of HAP were detected after a time of reaction of 16 hours, otherwise, as already mentioned, only X-ray amorphous products were obtained. This is not surprising due to the fact that the times of reaction were only short and all investigations reported in the literature indicate that the formation of crystalline calcium phosphate compounds is a very slow process.
Regarding a technical application of apatite for phosphorus removal by "crystallization" only an amorphous precipitation product would be obtained because the detention periods are still shorter than in the batch experiments carried out. But, this amorphous product could possibly change into a crystalline one due to the long periods the material is used.

5.1.3 Conclusions Regarding Calcium Phosphate Compounds as Seeding Material

Regarding the applicability of the "crystallization" of calcium phosphate the results obtained were less encouraging because carbonate deteriorated considerable the phosphorus removal as told by authors especially from Japan /16/. But the "Japanese" method described therein did not seem an alternative for the European circumstances. Maybe, that an increase of the seeding crystal concentration which was not investigated would have improved the process.

5.2 Phosphorus Elimination with Calcite as Seeding Crystals

It was the aim of the investigations now to find a suitable way to escape the "carbonate problem" which seemed to be a very severe one. For this, some methods which seemed applicable from the technical point of view were tried. One of these chosen methods was the precipitation of the carbonate with calcite crystals with a constant pH value of the water.

5.2.1 Preliminary Experiments

The experiments were performed in the device used already for the experiments with the apatites (section 4.2) with artificial waste water. The pH was adjusted to 9 and 10 g/l calcite was added. During the experiments the pH-value of the water was kept constant throughout the whole time of reaction of 30 minutes.

The results were surprising because only a small amount of the carbonate (~ 2 % instead of ≥&rb.99 % as expected) but the main part of the phosphorus (~ 77 %) had been removed. The expected effect had not been attained, but a much more interesting one had been detected:
the use of calcite instead of apatite as seeding material seemed a practicable method to develop a process for phosphorus removal regardless of the carbonate content of the water /14/.

5.2.2 Jar Tests for Phosphorus Elimination with Calcite

Therefore, the experiments were concentrated on this new principle and basic investigations were carried out again to detect the influences favouring or deteriorating it.

5.2.2.1 The Influence of the Liquor Applied

In the course of particular experiments on the effects of different liquors it was found that the phosphorus elimination process is favoured by a high calcium content of the water, i.e. that it is advantageous to use lime water, a clear $Ca(OH)_2$-solution, instead of a lime suspension or NaOH for the pH adjustment of the water. This is shown in table 9 in experiments where fresh, i.e. not reused calcite, was applied. In these experiments another improvement of the removal efficiency was obtained if the calcium content of the water was raised further by addition of a $CaCl_2$-solution.
The results turned out to improve if the calcite was used several times (section 5.3.2.4).

During the experiments it was found advantageous to use lime water, i.e. a clear solution of lime instead of a lime suspension which is well known in the chemical technology.

Table 9

Phosphorus Elimination from Artificial "German" Waste Water with Calcite . Influence of Different Liquors

Experimental conditions: artificial waste water, pH = 9.0, time of reaction 1 hour, 20°C
100 g/l unused calcite as seeding material

liquor applied	$Ca(OH)_2$+ $CaCl_2$	$Ca(OH)_2$	NaOH 0.1 m
c(Ca) liquor	32.0	22.9	0.0
c(Ca) added	1.469	1.390	0.000
c(Ca) total	2.558	2.454	1.064
$c(P)^0$ (mmoles/l P)	0.274	0.255	0.255
c(P) end (mmoles/l P)	0.051	0.097	0.154
phosphorus elimination (%)	81.4	62.0	39.6
$\Delta Ca/\Delta P$	3.63	12.30	7.81
$\Delta Ca_{calcite}$ 1)	0.8	1.6	0.6

1) calculated assuming a stoichiometry Ca/P = 2.0 of the precipitated calcium phosphate

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5.2.2.2 The Influence of the Concentration of the Calcite Seeding Crystals

According to the results listed in table 10 a sufficient phosphorus removal is obtained already with low concentrations of calcite which is improved if the concentration of the seeding crystals is raised. Generally, better elimination rates were obtained with secondary effluent than with artificial waste water with the same dependencies.

In experiments with 100 g/l calcite a $\Delta Ca/\Delta P$ ratio of 5.63 was found which may be explained by a simultaneous precipitation of calcium phosphate and calcite. If it is assumed that an amorphous calcium phosphate with a ratio $\Delta Ca/\Delta P = 2.0$ is precipitated one may calculate:

- for 10 g/l calcite a precipitation of ~ 0.08 mmoles/l calcium carbonate
- for 100 g/l calcite a precipitation of ~ 0.8 mmoles/l calcium carbonate

This estimation proves the results obtained, i.e. the advantage of the apply of a higher calcite concentration which favours both, the precipitation of the carbonate together with phosphorus precipitation.

Table 10

The Influence of the Concentration and the Grain Size of the Calcite Seeding Crystals on Phosphorus Elimination
Single Use of the Crystals

Experimental conditions: jar tests, pH = 9.0, time of reaction 1 hour
c(P) ~ 0.262 mmoles/l P, 20°C
KAW = "German" artificial waste water or
secondary effluent of a trickling filter

kind of material	marble	marble	marble	limestone	dolomite
grain size	>20 mm	1-1.4 mm	20µm	5µm	2µm
degree of purity	r.g.	r.g.	r.g.	techn.	techn.
concentration of seeding material	phosphorus elimination from KAW in %				
1 g/l	60.8	61.3	65.6	63.6	----
10 g/l	61.3	64.8	74.8	67.4	72.6
100 g/l	----	----	89.7	85.1	87.1
250 g/l	----	----	----	86.3	97.3
	phosphorus elimination from secondary effluent in %				
1 g/l	----	88.3	85.8	86.9	----
10 g/l	----	89.2	87.7	87.6	----
100 g/l	85.8	90.1	88.7	89.7	----

5.2.2.3 Experiments with Different Calcites as Seeding Crystals

Table 10 contains experiments with different kinds of calcites, i.e. with different grain sizes as well as with different degrees of purity. The applicability of dolomite was tested, too.
According to the results the degree of purity of the calcite as well as its grain size distribution show only a slight influence on the phosphorus removal. The main point is the calcite concentration in the water as described in the previous section.
The dolomite generally gave better yields than all the different calcites investigated.

5.2.2.4 Experiments on the Multiple Use of the Calcite Seeding Crystals

As already stated previously (5.1.1.4) it was necessary to carry out experiments reusing the seeding material several times because its surface is covered within a certain time of reaction with the precipitated calcium phosphate, i.e. completely different conditions regarding phosphorus precipitation may appear.

According to the results in table 11 phosphorus elimination is improved by a multiple use of the calcite, and simultaneously the amount of the calcium carbonate precipitated is lower. This can be seen from the amount $\Delta Ca_{calcite}$ calculated which is listed in the same table, too.
From these results one may assume that during the multiple use of the calcite caused by the deposition of calcium phosphate on its surface the precipitation of calcium carbonate is pushed back.

But, however, the calcite was only reused for three times which does probably not represent the stationary state. Therefore, it was decided to verify the results obtained with throughput experiments.

Table 11

The Influence of the Multiple Use of Calcite Seeding Crystals on Phosphorus Elimination

Experimental conditions: artificial "German" waste water

pH = 9.0, time of reaction 1 hour

T=25°C , $c(Ca)^0$=1.036 mmoles/l , $c(P)^0$=0.256 mmoles/l

concentration of the liquor:

22.9 mmoles/l $Ca(OH)_2$ (saturated)

concentration of the seeding crystals:

100 g/l calcite

calcite reused	0	1	2	3
c(P) end (mmoles/l P)	0.087	0.066	0.052	0.052
phosphorus elimination (%)	66.0	74.2	79.7	79.7
$\Delta Ca/\Delta P$	12.43	6.82	3.80	2.43
c(Ca) total	2.562	2.228	1.950	1.855
$\Delta Ca_{calcite}$ 1)	1.762	0.916	0.367	0.087

1) calculated assuming a stoichiometry Ca/P = 2.0 for the precipitated calcium phosphate

---

5.2.3 Throughput Experiments with Limestone as Seeding Material

These experiments were carried out to prove the encouraging results obtained in the jar tests:

- the tendency to obtain a good phosphorus elimination, regardless of the carbonate and magnesium content of the water, by using calcite as seeding material and lime water, a clear solution of $Ca(OH)_2$, for the pH adjustment of the water

Thus, this method could become an interesting alternative to guarantee certain phosphorus elimination concentrations in sewage treatment plants

The experiments were performed in a reactor shown in figure 3 consisting of a reaction part with 1300 ml and a sedimentation part with 300 ml volume. pH adjustment was effected with saturated $Ca(OH)_2$-solution and kept constant throughout the experiment.

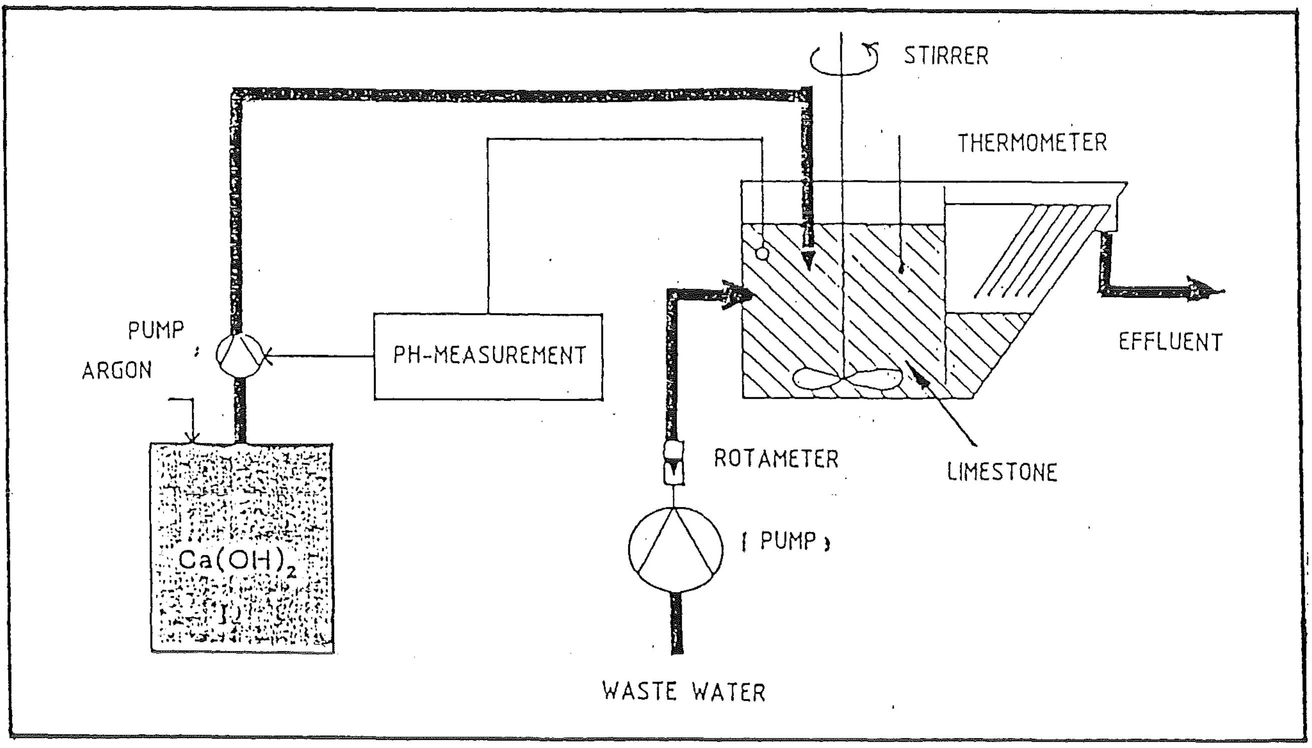

Figure 3: Reactor for Phosphorus Removal with Powdered Limestone as Seeding Material

5.2.3.1 Throughput Experiments with Artificial Waste Water

First experiments with artificial waste water were carried out to get a direct connection to the results obtained in the batch tests and to obtain informations about optimal running conditions as pH and detention period.

Furthermore, it was of interest to carry out experiments with both kinds of water, the "German" and the "Japanese" one (table 2 and 3).

5.2.3.1.1 Preliminary Experiment with "German" Artificial Waste Water

The first experiment was carried out with 230 g/l calcite and confirmed the results obtained in the batch tests:

- at a pH of 9 adjusted with lime water a residual concentration of 1 mg/l P was obtained which did not depend on the detention period
- adjusting the same pH of 9 with NaOH resulted in a much lower phosphorus elimination, the residual concentrations were in the range of 3 - 4 mg/l P.
- the higher the pH, the better the phosphorus elimination independent from the kind of liquor applied
- no preliminary decarbonization was necessary to obtain these results

Thus it was proven that calcium carbonate could be applied as seeding material for phosphorus elimination preferably together with a saturated $Ca(OH)_2$-solution for the adjustment of the pH of the water.

5.2.3.1.2 Throughput Experiments with "German" Artificial Waste Water

For the following experiments which are summarized in table 12 only $Ca(OH)_2$-solution was applied for the adjustment of the pH. It was the aim of these experiments to investigate mainly the influence of the grain size and of the concentration of the calcite. Furthermore, dolomite was again investigated for its applicability.

The results of the batch tests (table 10) were confirmed. It is especially remarkable that using calcite at a pH of 9 a phosphorus elimination of about 80 % was obtained although 1.673 mmoles/l HCO_3-ions were present in the water.
By substituting calcite by dolomite an even better phosphorus elimination rate of 86 % was obtained under the same experimental conditions.
The grain size and the concentration of the calcite seeding material were of less influence on phosphorus elimination, on the other hand.

Table 12

The Influence of the Concentration and Grain Size of the Seeding Crystals on Phosphorus Elimination from Artificial "German" Waste Water

Experimental conditions: throughput experiments, pH = 9.0,
31 hours of reaction, 20°C
throughput: 4 l/h ~ a detention period of 30 minutes
pH-adjustment with 0.02 molar $Ca(OH)_2$-solution

kind of seeding crystal	marble	limestone	dolomite
grain size	1-1.4 mm	20µm	2µm
degree of purity	r.g.	techn.	techn.
concentration of the seeding crystals	phosphorus elimination from KAW in % ~ 0.265 mmoles/l, pH = 9.2 - 9.3		
5 g/l	----	82.5	----
50 g/l	76.4	80.8	----
250 g/l	----	81.6	86.4

5.2.3.1.3 Throughput Experiments with "Japanese" Artificial Waste Water

For these experiments only dolomite which had turned out to effect the best phosphorus elimination from "German" waste water (previous section) was used.

The results listed in table 13 show two significant differences compared with the results of the "German" waste water:

- a higher pH-value of the water is necessary to obtain a phosphorus elimination in the same order of magnitude

- the pH-dependence is more distinctly marked

The addition of calcium and magnesium ions improved the phosphorus elimination significantly, e.g at pH = 9.6 68.6 % vs. 58.0 % without addition.

Table 13

The Influence of the pH on Phosphorus Elimination with Calcite Seeding Crystals from Artificial "Japanese" Waste Water

Experimental conditions:

throughput experiments
31 hours of reaction, 20°C
throughput: 4 l/h ~ a detention period of 30 minutes
pH-adjustment with 0.02 molar $Ca(OH)_2$-solution
seeding material: 250 g/l dolomite (2µm)
KJAW, c(P) ~ 0.085 mmoles/l

pH	phosphorus elimination in %
9.30	45.5
9.60	58.0
9.90	86.3
10.55	95.5

c(P) ~ 0.085 mmoles/l, pH = 9.9 - 10.7
Addition of 0.33 mmoles/l Ca und 0.28 mmoles/l Mg

pH	phosphorus elimination in %
8.83	38.8
9.50	64.5
9.60	68.6

5.2.3.2 Throughput Experiments with Secondary Effluent

For these experiments the same type of reactor (figure 3) in a larger scale was applied:
The reactor volume was 47 l, i.e. a reaction tank of 30 l and, divided by a scum-board, a clarification part of 17 l designed as a parallel plate separator.

The concentration of the seeding material limestone was 500 g/l. The results according to figure 4 show that the phosphorus effluent concentration was only depending on the pH of the water which was adjusted again with lime water regardless of the carbonate content and the content of organic impurities (DOC 15-35 mg/l).

Obviously the solubility equilibrium of the precipitated amorphous calcium phosphate was obtained, because the final phosphorus concentration was independent from the time of reaction.

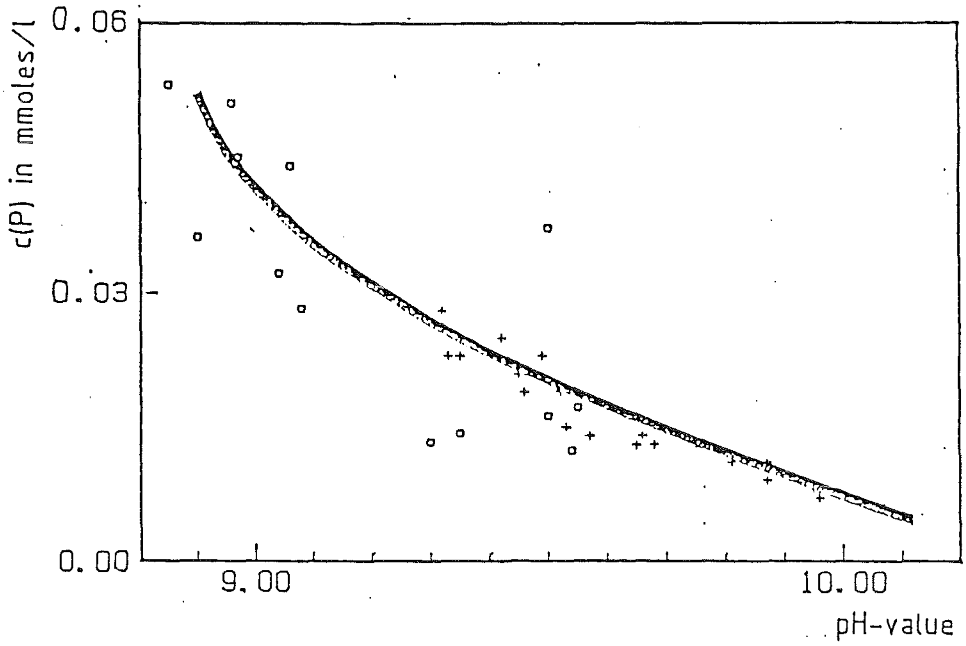

Figure 4: The Phosphorus Elimination from Secondary Effluents with Powdered Limestone as Seeding Material at Different pH-Values

The X-ray investigations which were carried out at the end of the experiments gave no hint on the nature of the products precipitated, i.e. that after an experimental period of more than 2 months no crystalline product had been formed. The specific surface area increased from 0.6 m^2/g to 9.4 m^2/g which leads again to the conclusion that an amorphous product was formed which is not transferred into a crystalline one, at least not on the surface.

On the other hand, it was impossible to get more information by means of IR-analysis.

The average stoichiometric ratio of the precipitate amounted to $\Delta Ca/\Delta P \sim 4.4$, i.e. that a precipitation of calcite had taken place, too.

5.2.3.3 Review on the Throughput Experiments

A new process for phosphorus precipitation from waste waters was developed using calcite or dolomite as seeding material. It has the advantage that it is only necessary to increase the pH of the water with a solution of $Ca(OH)_2$ No deteriorating influence was detected due to the carbonate and magnesium content of the water.

It is advantageous to apply a high concentration of preferably fine grained seeding material ($\geq$ 100 g/l) in order to provide a sufficient amount of active centers for precipitation.

6. General Conclusions

For the investigation of phosphorus removal from water by calcium phosphate precipitation induced by seeding crystals of calcium phosphate jar and continuous running tests were carried out.

1) The results of jar tests under constant pH-values 8 and 9, respectively, in absence of foreign ions may be summarized as follows:

- If hydroxylic apatite (HAP) or tricalcium phosphate (TCP) are used as seeding material an X-ray amorphous calcium phosphate is obtained as precipitation product which cannot be characterized among the known spezies

- The stoichiometry of this product depends on the temperature, the concentration of the seeding crystals, the pH-value and to some extent on the time of reaction.

- This product is only very slowly transformed into crystallized calcium phosphate.

- If the seeding material, e.g. HAP, is reused for several times a constant velocity of the precipitation is obtained.

- The original seeding material has only a remarkable influence on the elimination process before its surface is completely covered by the precipitation product, afterwards only the properties of the calcium phosphate precipitated on the original seeding material are of influence on the reaction. Therefore, any material may be used which enables the precipitation of calcium phosphate on its surface.

- The lowest phosphate concentrations obtainable are 0.2 mg/l P for a seeding crystal concentration of 1 g/l HAP and a pH of 9.

2) Investigations regarding the influence of foreign ions showed that both, magnesium and carbonate, retard the precipitation of calcium phosphate, the latter to a significantly higher extent. This effect seems to have an upper limit at 5 mmoles/l total carbonate.

3) Experiments for a preliminary removal of carbonate showed, that calcite, limestone powder and dolomite, respectively, can be used for phosphorus removal with about the same efficiency than HAP and TCP. Investigations of this new process gave the following results:

- In jar tests with an artificial waste water using 100 g/l calcite residual phosphorus concentrations of about 0.05 mmoles/l P were obtained at a pH of 9 within a time of reaction of 30 minutes. Throughput experiments under the same conditions gave even better results with an average effluent concentration of about 0.03 mmoles/l P.

- In experiments concerning the multiple use of the calcite the phosphorus elimination increased up to 6 cycles and remained constant afterwards.

- the determining parameter for phosphorus removal is the pH of the water, i.e. the higher the pH the higher the removal efficiency.

- apart from the pH of the water a good phosphorus removal can only be obtained if the calcium concentration in the water is sufficiently high which may be adjusted, if necessary, by adding solutions of $Ca(OH)_2$- or $CaCl_2$.

- the process was successfully demonstrated by a throughput experiment continuously running for a period of 40 days using 500 g/l powdered lime stone and a detention period of 30 minutes. At a pH of 9.7 which was adjusted with lime water a reduction of the phosphorus content of the secondary effluent of a sewage treatment plant from 0.28 mmoles/l P to 0.014 mmoles/l P ≡ 95.0 % removal efficiency was obtained.

The use of calcite as seeding material for the direct precipitation of calcium phosphate seems to be a very promising method for phosphorus removal from waste waters especially because in contrary to other investigated seeding materials like apatite or other calcium phosphate compounds calcite has the great advantage that the carbonate and the magnesium content of the water does not influence the process.
Regarding the precipitation process using iron or aluminium salts this new concept has the advantage that there is no additional increase of the salt concentration. Regarding the high/low lime process only about 25 % of the lime used in those processes is necessary. Furthermore, instead of a precipitation sludge a high concentrated calcium phosphate is obtained which allows the recovery of the phosphorus removed from the water.

But, however, the pH of the effluent does not allow a direct discharge and more research work is necessary on this point e.g. to lower this pH by the application of carbon dioxide. Thus a cost elimination is not yet possible.

PART 2

Simultaneous Precipitation with Concentration-Dependent Dosage of $FeSO_4$ Results of Field Tests /12/

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Abstract

In order to prepare the treatment plant of Berlin Marienfelde for simultaneous precipitation, field tests with half of its capacity (60.000 m^3/d) were carried out in the course of a research project comparing dosage dependence on phosphorus load and on waterflow.

The required outflow concentration of < 2mg/l P-total may be obtained by using a molar ratio Fe/P of 1.1. By using phosphorus load instead of waterflow to determine the dosage up to 16 % of the precipitating agent are saved, and, furthermore, the outflow concentrations are more constant, i.e the consistency of the whole process is improved. Regarding the elimination of other parameters such as DOC, COD, BOD_5 and suspended solids, no significant difference between the two dosing methods was detected.
The precipitant requirement increased remarkably in the presence of bulking sludge regardless of which dosing method was employed.

1. Introduction

One of the outstanding problems of the rivers and lakes of Berlin is the increasing eutrophication due to the high phosphorus content originating from the discharge of large amounts of waste waters, mainly effluents from sewage treatment plants. Although these waters are treated mechanically as well as biologically phosphorus removal is not sufficient to prevent these effects. Therefore, in addition to direct phosphorus elimination from surface waters (Wannsee, Nordgraben) starting from 1986 the phosphorus outflow concentration of the sewage treatment plants of Berlin (East and West) has to be reduced from about 7 to ≤ 2 mg/l P-total according to an agreement with the GDR. This reduction of the phosphorus may easily be effected with simultaneous precipitation which has two main advantages - the cheap $FeSO_4$ may be used as the precipitating agent and no additional facilities are necessary /41-45/.

However, difficulties concerning mainly the sludge treatment occurred during the first field tests in Marienfelde /41/ due to the altered properties of the sludge as well as to the larger sludge amount obtained. Therefore, a research project was started in the sewage treatment plant Berlin - Marienfelde aimed at minimizing the consumption of the precipitating agent and consequently of the amount of additional sludge. This goal should be accomplished by dosing in accordance to the load of dissolved phosphorus in the inflow, i.e. in dependence of the concentration of the dissolved phosphorus of the primary effluent of the sewage treatment plant and the waterflow, rather than only in dependence of the waterflow, the state of the art.

Some research work with pre- and post-precipiation and other precipitating agents has been done, but a lot of problems remained, especially concerning the measurement of the phosphorus concentration and the changes of the sludge characteristics /42-44/.

2. Description of the Sewage Treatment Plant Berlin - Marienfelde

2.1 Waste Water Treatment

The sewage treatment plant Berlin-Marienfelde where the research project is carried out is designed for a dry weather flow of 125.000 m^3 per day. The biological waste water treatment is accomplished in 4 units completely mixed and aerated with mammoth rotors (figure 1).

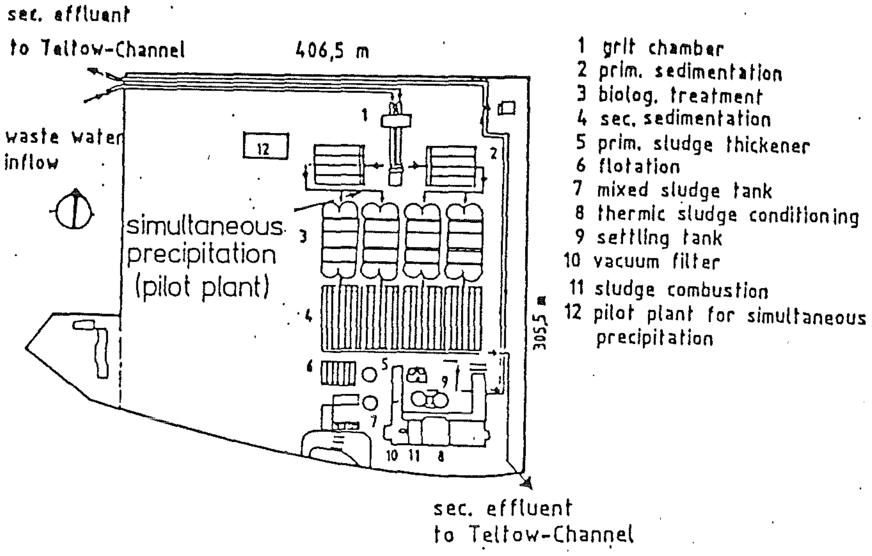

Figure 1: Scheme of the Sewage Treatment Plant
Berlin - Marienfelde

2.2 Sludge Treatment

Both, the primary sludge and the surplus sludge are prethickened by applying gravity thickening and flotation, respectively. After mixing one part of the mixed sludge is thermally conditioned at 200°C and 16 bars and dewatered together with the untreated part of the sludge by centrifuges. The old treatment chain with vacuum filters had to be changed in the course of the experiments caused by the larger amount of sludge obtained as well as by its changed properties due to the simultaneous precipitation (section 5.4). Finally, the sludge cake is incinerated at about 850°C, above the temperature of desodoration.

3. Description of the Installations for the Research Project

The experiments were carried out in two units of the treatment plant which received the same waste water, using phosphorus load in one and waterflow in the other to determine dosage. Thus a direct comparison of the 2 principles was possible. In order to get a dosage as exact as possible and to collect all data of importance automatically, a computer controlled installation was used as shown in figure 2.

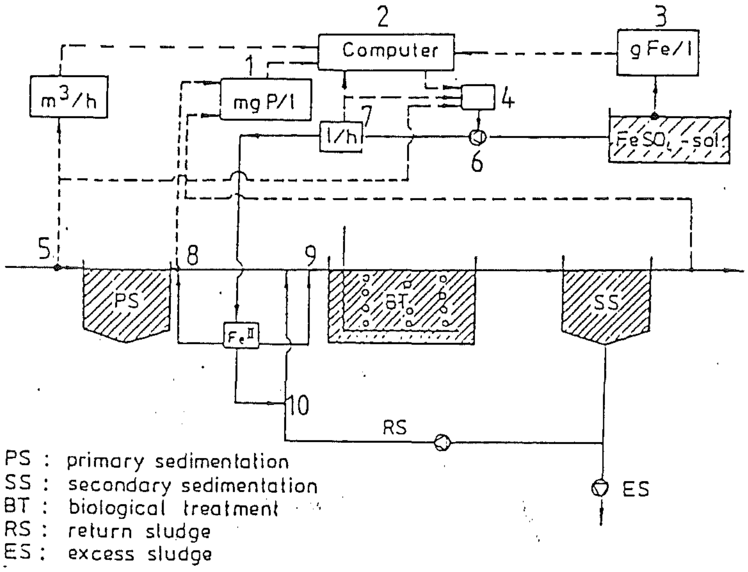

Figure 2: Scheme of the Control System for Phosphorus Load Dependent Simultaneous Precipitation

A phosphorus value is sent to the computer (2) from the automatic phosphatometer (1) every 30 minutes. Every hour this value corresponds to the phosphorus content of the primary effluent and is used for the dosage calculation. The Fe-concentration of the $FeSO_4$-solution (3) is continuously monitored by measurement of its density and temperature. From these data the exact amount of the precipitating agent required is calculated by the computer and sent to a controller (4) as an analoguous signal. The signal from the water flow (5) goes directly to the controller, which regulates the dosing pumps with a motor (6) and is registered together with the signal of the flow of the $FeSO_4$- solution (7) by the computer, too.

The dosing of the $FeSO_4$-solution was carried out on different sites - the effluent of the primary sedimentation tank (8), the influent of the activated sludge tank (9) or the return sludge (10). Besides the phosphorus concentrations of the in- and outflow of the treatment plant many other data of the units 3 and 4 and the primary effluent, respectively, were collected by the computer. The whole project was accompagnied by numerous laboratory analysis.

4. Survey of the Planned Experiments

The following steps were planned for the research project:

- preliminary experiments
    - monitoring of the Fe content of the $FeSO_4$-solution
    - automatic filtration of the primary effluent
    - test of the phosphatometer
- detection of the optimal dosing site
    - primary effluent
    - inflow return sludge
    - inflow to the activated sludge tank
- variation of the molar ratio Fe/P on the optimal dosing site

The following questions were investigated:

- to what extent is the "new" dosing principle (proportional to the phosphorus load of the inflow) better in comparison with the "normal" waterflow dependent dosage concerning
    a) the elimination of the phosphorus (effluent concentration, stability of the process, consumption of $FeSO_4$ to obtain a distinct outflow concentration)
    b) the elimination of other parameters (COD, BOD_5, DOC etc)
    c) the amount of sludge and its properties

- is it sufficient for the purpose of an automatic operation to apply a phosphorus load dependent dosage or is it necessary to take the outflow concentration into account, too

5. Results

5.1 Monitoring of the Fe-Concentrations

The automatic monitoring of the Fe-concentrations of the precipitating solution was routinely checked in the laboratory and showed a very precise accordance of about ± 1 %. The range of the Fe-concentrations (46.3 to 58.2 g/l Fe) show the importance of a monitoring for the plant. The assumption that the Fe-concentration is constant leads to incorrect results as shown in table 1. That is, in the extreme cases more than 14.3 % less or 7.8 % more than the required amount of $FeSO_4$ would have been dosed, an order of magnitude which would make the effects of the different dosing methods indistinguishable (5.3.2).

Table 1

Results of the Monitoring of the Fe-Concentrations (Waste Water Flow 100.000 m^3/d)

	specified value	minimum value	maximum value
density (kg/l)	1.153	1.135	1.167
Fe-conc. (g/l Fe)	54.0	46.3	58.2
dosage of 27% $FeSO_4$-sol. (m^3/d)	36.7	36.7	36.7
quantity (kg Fe/d)	1982	1699	2136
deviation (%)		- 14.3	+ 7.8

5.2 Monitoring of the Phosphorus Concentrations

5.2.1 Automatic Filtration of the Samples of the Primary Effluent

In order to determine the $FeSO_4$-dosage based on phosphorus load the concentration of the total dissolved phosphorus in the primary effluent has to be known. For this purpose samples taken with an automatic sampler were filtrated with the help of a provisional construction through folded filters. These were replaced by membran filters /45/ in the course of the research project.

5.2.2 Phosphate Analysis

- automatic determination

An automatic device is used which takes a sample automatically every 30 minutes and determines the total phosphorus concentration after digestion with sulfuric acid.

- phosphate analysis in the laboratory

The method used is described in /46/. The digestion is performed with dilute sulfuric acid in combination with an oxidizing agent.

- correlation of the values obtained in the automatic device and in the laboratory

1) samples of the secondary effluent

If the results of the 24-hour mixed samples analyzed in the laboratory and the mean value of 8 single P values from the phosphatometer are compared, it is obvious that only the dissolved phosphorus is detected by the automatic measurement, probably due to its method of digestion without an oxidizing agent. The correlation coefficient for 229 values of the filtrated samples measures r = 0.94.

If the phosphorus content of the suspended solids (ab. 0.03 mg/mg SS) is added to the results of the phosphatometer, a correlation of 218 'automatic' values with the results of the laboratory analysis of the unfiltrated samples leads to r = 0.90.

2) filtrated samples of the primary effluent

Reference samples analyzed by both methods showed a correlation coefficient of r = 0.88, the results obtained in the laboratory were about 3 % higher. This deviation may be explained by the different methods of digestion, too, because the samples have different contents of organic phosphorus which is probably not detected by the digestion in the phosphatometer without an oxidizing agent.

It was not possible, on the other hand, to obtain a correlation between the 24-hours mixed samples (laboratory results) and the average of the corresponding single values (phosphatometer). Possible explanations are the different taking and handling of the samples - the samples of the phosphatometer are filtrated immediately, the samples for the laboratory are stored for at least 24 hours at 4°C. During this time dissolution as well as adsorption effects may occur.

5.2.3 Statistical Evaluation of the Phosphorus Concentrations of the Primary Effluent

$FeSO_4$ dosing was done according to the phosphorus concentrations of the primary effluent, however time dependent variations of the phosphorus concentration of the primary effluent as well as for working days in view of working days and sundays were also of interest. In this regard an estimate of the phosphorus concentration should be available if the phosphatometer should go out of action.

These results do not allow any conclusions about living habits in Berlin (e.g. bathing time, washing days) to be drawn because the water which comes to the sewage treatment plant has an age between 6 and 18 hours due to the discharge pipe system in Berlin. The results are shown in figure 3 and table 2.

5.2.3.1 Classification According to the Time of the Day

The phosphorus content of the primary effluent varied considerably. Generally, an increase was to be seen between 18 - 24 h, between 0 and 6 h the values were nearly constant and decreased from 6 h onwards.
This curve of the phosphorus concentration remained constant throughout the whole research project and is now used as a substitute for phosphorus load dependent dosage in case of a damage of the phosphatometer.

5.2.3.2 Classification According to Week-days and Day-time

The curve for phosphorus concentrations is also related to the day of the week. This is illustrated in figure 3, for example, for all saturdays 12 - 18 h and all mondays 18 - 24 h where the highest and the lowest phosphorus concentrations occurred. The week-days having these maximum and minimum concentrations varied throughout the research project, therefore, it is not possible to substitute P concentrations on the week-days for phosphorus load dependent dosage.

Table 2

Mean Values of the Phosphorus Concentrations of the Primary Effluent of the Sewage Treatment Plant Berlin-Marienfelde

time	0 - 6	6 - 12	12 - 18	18 - 24	0 - 24
	mean values of the P-conc. in mg/l P-total,diss.				
weekday	50% 16% 84%	50% 16% 84%	50% 16% 84%	50% 16% 84%	50% 16% 84%
all days	8.14 6.86 9.43	8.02 6.71 9.34	7.16 5.93 8.40	8.00 6.80 9.21	7.84 6.55 9.14
number	2403	2357	2385	2438	9583
sunday	8.21 7.00 9.42	8.10 6.74 9.47	7.15 5.87 8.43	7.80 6.67 8.94	7.82 6.53 9.11
number	361	362	362	369	1454
monday	8.00 6.80 9.20	7.99 6.71 9.27	7.30 6.14 8.47	8.37 7.06 9.70	7.94 6.64 9.25
number	345	342	332	354	1373
tuesday	8.33 6.92 9.74	8.05 6.79 9.31	7.15 5.96 8.36	8.08 6.97 9.20	7.91 6.60 9.23
number	329	316	330	359	1334
wednes-day number	8.18 6.94 9.42 314	7.95 6.58 9.33 309	7.16 5.87 8.45 335	8.14 7.03 9.26 352	7.85 6.55 9.16 1310
thursday	8.01 6.76 9.26	8.06 6.95 9.18	7.17 5.90 8.45	7.83 6.59 9.08	7.77 6.53 9.02
number	316	309	334	352	1311
friday	8.28 7.00 9.57	8.10 6.58 9.63	7.11 5.85 8.38	7.72 6.57 8.88	7.83 6.46 9.20
number	336	332	337	342	1347
satur-day number	7.99 6.70 9.30 375	7.88 6.72 9.04 375	7.08 5.97 8.19 368	8.00 6.83 9.18 368	7.77 6.54 9.00 1486

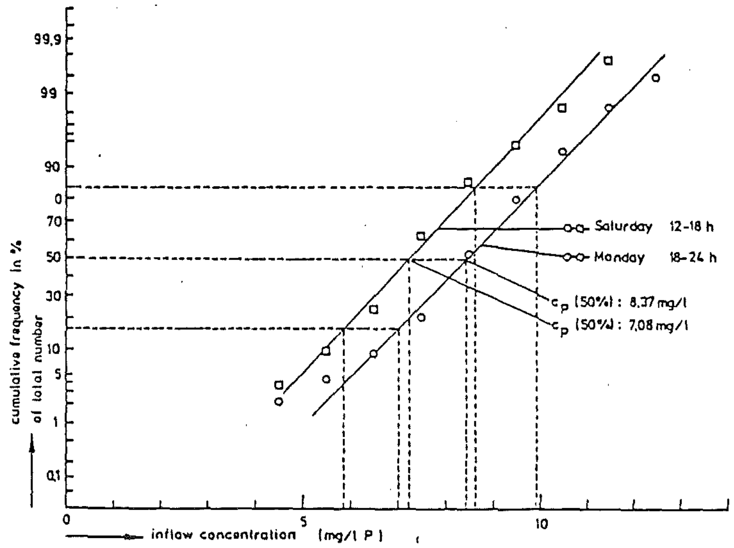

Figure 3: Cumulative Frequency of Total Number vs P-Concentration of the Primary Effluent of the Treatment Plant Berlin-Marienfelde (Phosphorus Concentration mg/l P-Total, Dissolved)

5.3. Results of the Precipitation Experiments

5.3.1 The Influence of the Dosing Site on Phosphorus Elimination

3 different dosing points were used - primary effluent, return sludge and inflow to the biological treatment - in order to investigate their possible influence of the efficiency of the precipitation. The results are illustrated in figure 4 and show that there is no significant dependence of the phosphorus removal efficiency on the dosing site.

5.3.2 Results of the Experiments with Variation of the Molar Ratio Fe/P

Since the dosing site had no effect on phosphorus removal efficiency, all further experiments were carried out by dosing the $FeSO_4$ into the inflow of the activated sludge tank.

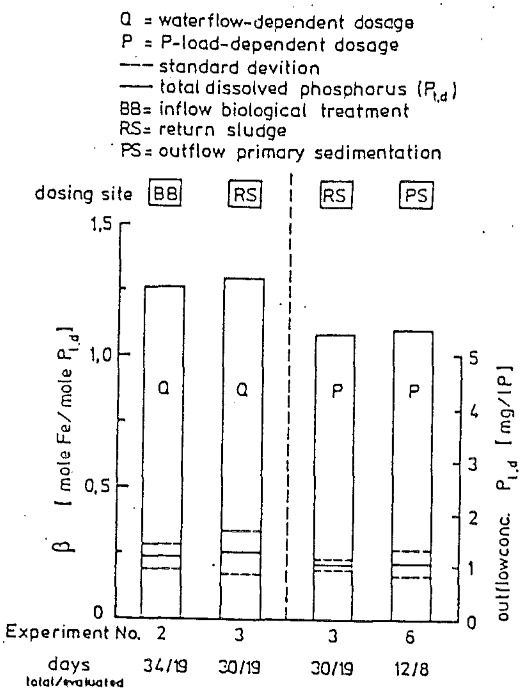

Figure 4: Results of Experiments with Simultaneous Precipitation in the Sewage Treatment Plant Berlin-Marienfelde with Different Dosing Sites

5.3.2.1 Results of the Phosphorus Elimination

- comparison between phosphorus load and waterflow dependent dosage in parallel operation

The results of 6 experiments carried out in parallel operation with both dosage methods under the same conditions are shown in figure 5. The first 5 histograms show that $FeSO_4$ is saved if dosage is based on phosphorus load as the molar ratio Fe/P increases (from 5.2 % for $\beta = 0.9$ to 17.3 % for $\beta = 1.3$). Besides this, the phosphorus outflow concentrations are more constant, expressed by a lower standard deviation of the mean value. Similar savings are reported in /48,49/ for the application of phosphorus load dependent dosage in pre-precipitation experiments with AVR, a basic Al-Fe-salt.

Figure 5 shows the total phosphorus concentrations obtained after addition of the suspended solids phosphorus concentration in each experiment (5.2.2). In order to attain the demanded outflow concentration of

≤ 2 mg/l P total a molar ratio Fe/P of 1.1 (phosphorus load dependent) or 1.3 (waterflow dependent) must be used.

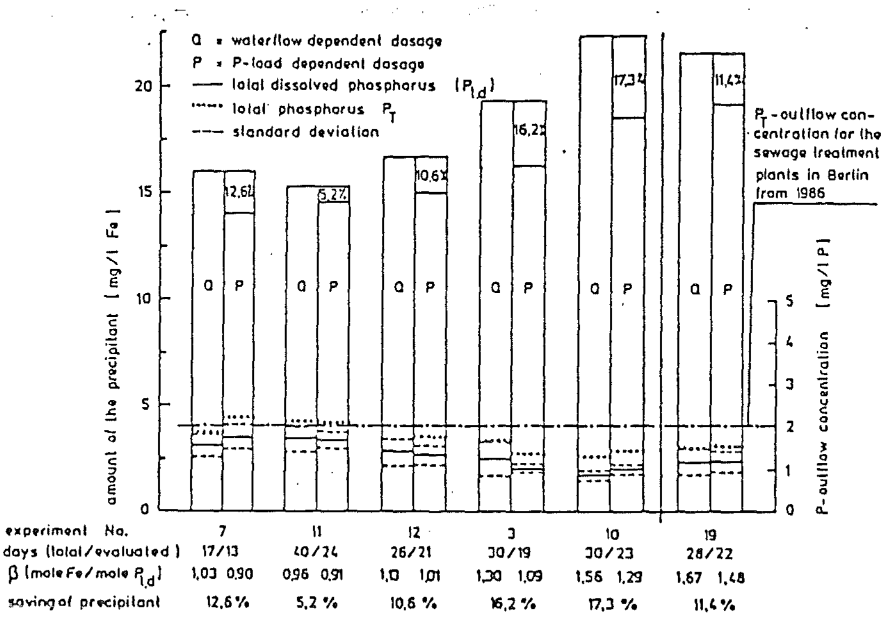

Figure 5: Results of Experiments with Simultaneous Precipitation in the Sewage Treatment Plant Berlin-Marienfelde

- evaluation of all experiments

In figure 6 the measured outflow concentrations of dissolved total phosphorus are plotted vs the molar ratio Fe/P applied. For this figure all experiments, whether carried out in parallel operation or not, were considered.

The results confirm that dosage dependence on phosphorus load yields better phosphorus elimination than waterflow-dependent dosage using the same molar ratio. This improvement increases between a molar ratio Fe/P of 0.9 to 1.1 and remains steady to about 2.3, but, for higher molar ratios applied only one experiment exists. The minimum outflow concentration obtainable by simultaneous precipitation is about 0.7 mg/l dissolved P-total. This is in accordance with results obtained by other authors /43-47/.

- occurence of bulking sludge

The occurence of bulking sludge after 15 months of operation was registered with great surprise (5.4.1).

Phosphorus elimination by means of silmultaneous precipitation deteriorated considerably when bulking sludge was present, the advantages of phosphorus load dependent dosage diminished or disappeared completely. This is illustrated by the experiments 19 and 10 which are plotted in figure 5 together with some other experiments carried out when bulking sludge was present.

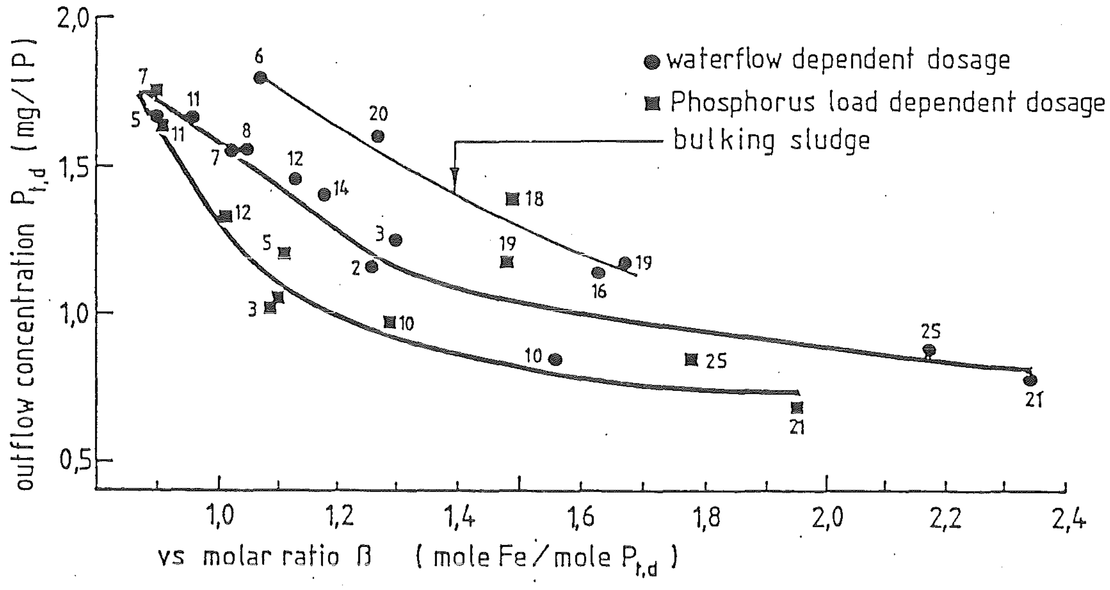

Figure 6: Dependence of the Outflow-Concentration (mg/l P-Total, Dissolved) on β (Molar Ratio Fe/P) in Experiments for Simultaneous Precipitation in the Sewage Treatment Plant Berlin - Marienfelde

	molar ratio Fe/P	effluent concentration (mg/l dissolved P-total)	
with bulking sludge	1.48	1.2	(experiment 19)
without bulking sludge	1.29	1.0	(experiment 10)

The reasons for these effects cannot be explained completely, according to some investigations carried out in this direction 2 effects seem to occur:

- the amount of suspended solids which are containing phosphorus increases in the effluent causing thus an increase of its total phosphorus concentration
- obviously the phosphorus precipitation in the activated sludge tank has the normal efficiency due to the β applied, but a redissolution in the secondary clarifier occurs which causes the higher effluent concentration of dissolved phosphorus. But, however, this explanation is not complete and further experiments are necessary.

5.3.2.2 Reduction of DOC, BOD_5 and COD

No additional reduction of COD, BOD_5 and DOC was obtained by simultaneous precipitation. This confirms results of earlier experiments /41/.

5.3.2.3 The Influence of the Simultaneous Precipitation on the pH, the Conductivity and the Turbidity

As expected, no changes of the pH-value and of the conductivity of the water due to the simultaneous precipitation were found.
Turbidity values exceeding 10 FE corresponded to effluent concentrations > 1.5 mg/l dissolved total P but phosphorus concentrations in the same order of magnitude were found when the turbidity values were around the norm of about 4 FE.

5.4 The Influence of the Simultaneous Precipitation on the Sludge Properties

5.4.1 Sedimentation Behaviour

When the experiments for the simultaneous precipitation were started, bulking sludge was present in the activated sludge tanks. The addition of the precipitating agent caused a tremendous improvement of the sedimentation behaviour of the sludge. No bulking sludge formation occured for 15 months as it had in earlier experiments /41/. At this time no significant difference of the sedimentation behaviour of the sludge as well as of the content of suspended solids in the effluent between the two units was found when different amounts of $FeSO_4$ were dosed.

The occurence of bulking sludge after 15 months of operation (5.3.2.1) came as a great surprise because the addition of $FeSO_4$ is usually recommended /50/

to prevent bulking sludge from forming. The time factor, therefore, seems to be of great importance for experiments with biological systems and it is necessary to provide enough time in order to get correct informations and results.

5.4.2 Amount of Sludge

Unfortunately it was not possible to measure the amount of excess sludge from 24-hour-mixed-samples with an accuracy sufficient to allow a calculation of how much precipitant agent was saved by phosphorus load-dependent dosage method. It was assumed, therefore, thad the addition of 1 g Fe effects the formation of 2.6 g dry matter based on a comparison of 2 units, one in which was precipitated while the other remained untreated.

5.4.3 Sludge Treatment

The dewatering of the sludge deteriorated when simultaneous precipitation was carried out as it happened in the previous experiments /41/. Therefore, the sludge treatment had to be changed from vacuum filters to centrifuges (2.2).

5.5 Availability of the Experimental Device

In the course of the research project problems with the automatic filtration and the phosphatometer occured. Thus, in some cases only waterflow dependent dosage could be carried out. All other installations worked satisfactory and caused no problems.

6. Cost Evaluation

Using the results of the previous experiments, an evaluation was made for the additional cost of a simultaneous precipitation comprising the cost of the precipitating agent and the increase of the cost for slugde treatment and combustion, respectively.

According to previous experiments it may be assumed that 2.6 g dry solids are formed by adding 1 g Fe and for this addition of 1 g Fe costs of 0.005 DM mainly due to the sludge treatment must be calculated. Then the addition of 20 g/m^3 Fe will cost about 0.1 DM / m^3. If phosphorus load is used to determine dosage, 16 % of these additional costs may be saved, i.e. for the 2 treatment plants of Berlin a savings of about 2 mio DM/year. On the other hand investment costs of about 125.000 DM - for the phosphatometer and maintenance - are necessary in each plant.

7. Final Remarks

The device was put into industrial operation from 1986 onward and the results obtained during the research project were confirmed during 1.5 years of operation. A molar ratio Fe/P of 1.1 is applied to attain the preset effluent concentration of ≤ 2 mg/l P-total in the treatment plant if no bulking sludge appears.

As already mentioned (5.3.2.1), the phosphorus outflow concentrations in the case of bulking sludge are higher than in the normal case. This is due to a deterioration of the elimination of the dissolved phosphorus as well as to a higher content of suspended solids in the effluent which contain about 0.03 mg P/mg SS (5.2.2).

In these cases, the dosage of $FeSO_4$ is regulated according to the outflow concentration, too, i.e. dosage of the precipitant will be automatically increased to an upper limit with increasing outflow concentrations. If this upper limit is reached, the water throughput is reduced to get better phosphorus effluent values by reduction of the content of suspended solids.

The limit for the effluent concentration is set to 1.3 mg/l P to meet the required value of ≤ 2 mg/l P-total because only the dissolved phosphorus content may be measured automatically.
The dewatering of the sludge was completely changed to centrifugation to avoid further difficulties with the vacuum filters.

PART 3

Application of Activated Alumina for Phosphorus Removal and Recovery from Waste Waters /51-57,64,65/

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Abstract

The application of activated alumina for phosphorus removal from secondary effluents was tested with continuous running experiments in Berlin with a throughput of 10 - 20 m^3 per day. The device consisted of 4 stirred reactors each with a volume of 441 liters containing 50 to 75 kg of fine grained activated alumina. The experiments were run automatically by means of an automatic phosphatometer and a process computer.

During one year of operation, a mean effluent concentration of 0.6 mg/l P was obtained. It was shown that the effluent quality can be adjusted by isolating one of the reactors from the process stream for regeneration at an appropriate effluent concentration. The normal influent phosphorus concentration had no influence on the effluent quality. Besides the phosphorus the COD of the influent was reduced up to about 20 %.

Coarse activated alumina was applied in fixed bed filters with a throughput of about 600 m^3 per day for phosphorus removal of a fish culture pond. At the beginning of the experiment, a reduction of the total phosphorus of about 95 % was achieved which slowly decreased to about 40 % after 2 years of operation without regeneration.

Results of the running experiments, as well as of experiments concerning the regeneration of the loaded activated alumina, and the recovery of phosphorus from the regeneration liquors by lime precipitation are given.

1. Introduction

In /51/ first results were given on experiments concerning the development of a process for phosphorus elimination from waste waters employing activated alumina which effects not only a sufficient water purification but also a recovery of the phosphorus in a suitable form. The reason for these investigations was the special situation of the Federal Republic of Germany which is generally dependent on imports of phosphate. Thus a recovery of the phosphorus from the secondary effluents as well as from sewage treatment sludges would help to reduce imports up to 25 % /1/.

The research work was started with jar tests and experiments on the laboratory scale /52,53/. Afterwards a device for experiments on a pilot scale was constructed employing fine grained activated alumina in stirred reactors. The stirred reactor system was equipped for automatic operation of the adsorption and regeneration process steps according to the signal of a phosphatometer and a process computer /54,55/. In addition, a large scale experiment with coarse activated alumina in fixed bed filters was carried out.

2. Process Scheme

The process comprises three steps, i.e.

- adsorption of the phosphorus on the activated alumina
- regeneration of the loaded alumina with NaOH and
- recovery of the phosphorus from the regeneration liquors

In the adsorption step water is brought into contact with the activated alumina, this step is followed by the regeneration, i.e. the redissolution of the phosphorus from the alumina with NaOH, and, finally, the recovery of the phosphorus is effected by precipitation with lime from the regeneration liquors. Both, the alumina and the NaOH, are recycled. Therefore, in the ideal case only lime is used as a reagent. Furthermore, the salt concentration of the treated water is not increased, as in the usual processes for phosphorus removal, such as precipitation with iron or aluminium salts.

3. Properties of the Activated Alumina

3.1. Mechanical Properties of the Activated Alumina

Activated alumina may be purchased in technical quantities in a fine grained and in a coarse form. Both forms were tested in the preliminary experiments. Difficulties occurred with secondary effluents in fixed bed filters with coarse activated alumina. The suspended solids in the water frequently caused clogging of the filters requiring frequent backflushing /51/. Therefore, fine grained activated alumina was used in the further investigations.
Experiments with coarse grained alumina were first only run in some special cases. The main application concerned the effluent of a fish pond with a low content of solids. This will be described in section 6 of this paper.
But on practical reasons a new concept was built up to enable the use of coarse material in fixed bed filters:

- to apply simultaneous precipitation as the first step
- to make a filtration of the effluent
- to apply activated alumina filtration as a polishing step (section 7).

3.2. Adsorption Properties of the Activated Alumina

Shaking experiments with a variety of organic compounds /56,57/ showed, that both acids and bases are adsorbed, the latter ones to a lower extent, whereas neutral compounds are not adsorbed from water. As is shown in figure 1a, every compound is best adsorbed at a distinct pH. Acidic substances are preferably adsorbed in the acidic pH-range, e.g. phosphoric acid at pH about 4, basic substances in the basic pH-range.

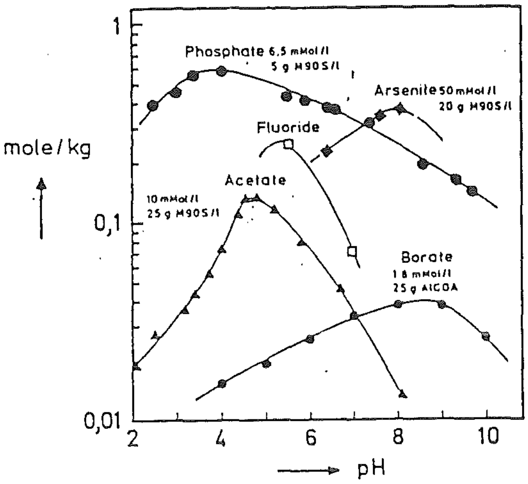

Figure 1a: pH-Dependence of the Adsorption on Activated Alumina

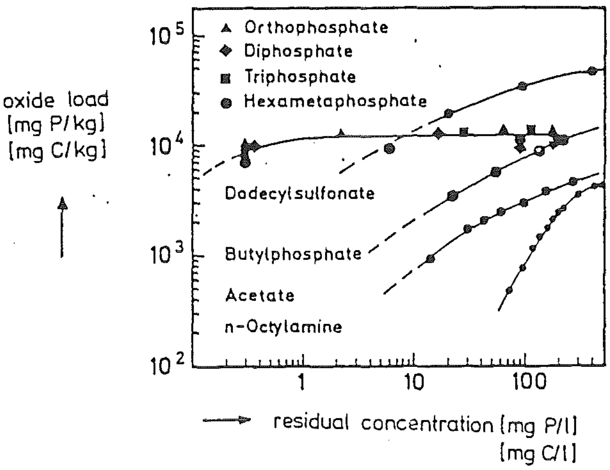

Figure 1b: Adsorption of Different P-Species on Activated Alumina

Due to this pH-dependence a redissolution of the adsorbed phosphorus from the activated alumina with NaOH is possible. In this way a concentrated phosphorus solution may be obtained giving a basis for recovery.

In the same way different species of phosphorus, such as ortho-, di-, tri- and polyphosphate were tested (figure 1b). They all had the same adsorption affinity for activated alumina/52/. Compared to organic compounds /57/, inorganic acids /58/, and organophosphoric compounds /52/, the phosphates were much better adsorbed, i.e. the activated alumina has a selective affinity for phosphate. The capacity of the activated alumina for phosphorus is strongly influenced by its inner surface area. The greater the surface area, the greater the phosphorus load obtained. The loading can be described by the equation /59/.

$$\text{oxide load } Q \text{ (mg P/kg)} = 112 \times S \text{ (surface area in m}^2\text{/g)}.$$

3.3 Conclusions

Operational conditions which were identified in these preliminary experiments for phosphate removal by activated alumina included:

- use an alumina with a surface area as high as possible
- lower the pH of the secondary effluents to about 5.5
- an alternative application is the aeration in the reaction tank

Due to the preference of phosphorus compounds for adsorption on Al_2O_3 compared with other organic or inorganic substances no diminishing of the phosphorus adsorption should occur as a result of interference from other compounds. Furthermore, there should be no influence of the preceding hydrolysis of the detergents in the water.

4. Stirred Reactors as Contacting Units

Among several possibilities the stirred reactor principle was chosen and developed for the application of fine grained activated alumina. Starting from units in the laboratory scale a device for a throughput of about 20 m^3 per day was constructed where the process steps adsorption and regeneration are carried out automatically. This is done, as shown in figure 2, by means of an automatic phosphatometer and a process computer /54,55/.

4.1 Stirred Reactor

Each reactor had a volume of 440 liters and each was divided by a scum board into 2 parts: a mixing zone, where the alumina was contacted with the water and an adjacent inclined settling part where oxide and water were separated. The water flowed without any pressure to the next reactor.

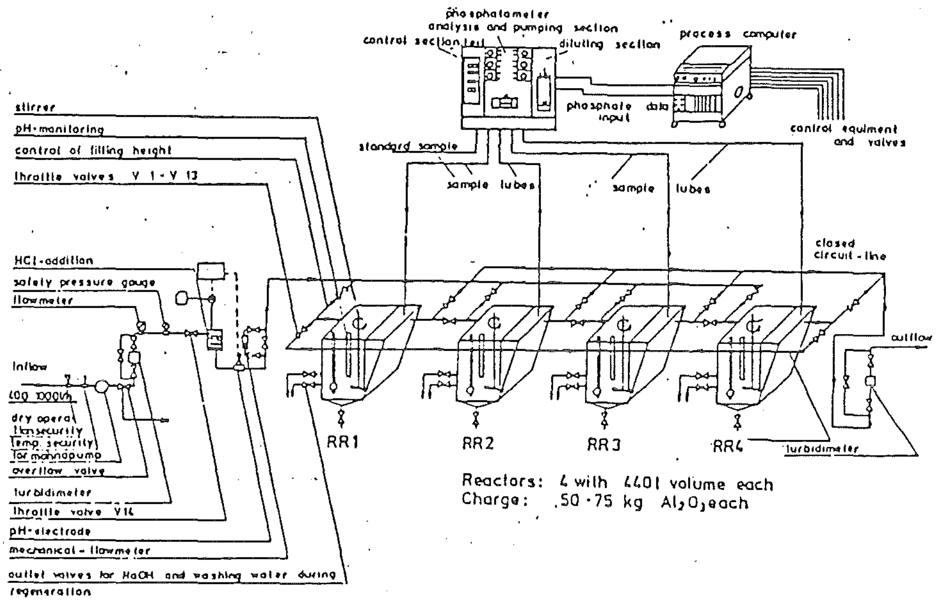

Figure 2: Design of the Stirred Reactor Device

4.2. Closed Circuit-line, Change of the Phase

The device contained 4 reactors which were connected by a circuit pipe (figure 3). The outflow of each reactor could be switched on or off to the next reactor by electropneumatic valves which were controlled by the process computer. Thus each reactor could be isolated from the adsorption process. All the time three of the reactors were connected to a cascade. Raw water was introduced into the first reactor and treated water left the unit after the third reactor.

After exceeding a preset phosphorus concentration in the outflow, the first reactor was removed from the adsorption train and the fourth reactor was connected to the cascade as number 3. The reactor taken out of operation was subjected to a regeneration cycle and afterwards remained in standby position until the next switch of the cascade. Therefore, 4 different arrangements of the reactor system occured which are shown in figure 3.

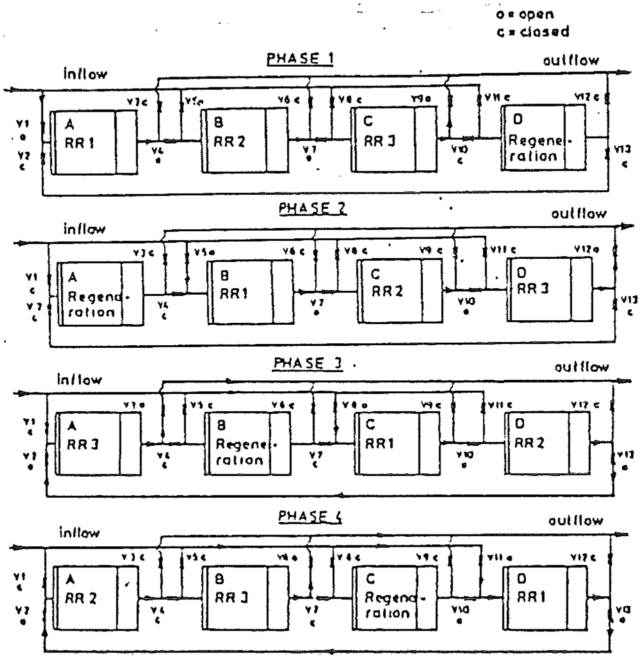

Figure 3: Flow Scheme of the Reactors in a Closed Circuit-Line

4.3. Operating and Monitoring Instruments

The water, which was transported with a mohnopump, first passed a turbidimeter to detect a high content of activated sludge in the water especially in raining periods, then a pressure controller to detect blockings in the line and at last a flowmeter before entering the reactors. For operation during the winter periods, the inlet and outlet were heated to prevent freezing.

Initially, a mixer was used for the addition of HCl to adjust the pH of the inflow. Later, CO_2 and air was used, respectively, and introduced into the water in the mixing zone of the first reactor.

The phosphorus concentration was continuously monitored by an automatic phosphatometer which was connected to the inflow and to the outflow of each reactor and measured these 4 samples sequentially. Before the water left the unit, it passed a turbidimeter to detect a rinsing loss of alumina in the outflow.

5. Experiments in Stirred Reactors

The device was tested at Kernforschungszentrum and run on two different waste water treatment plants in Berlin, at Berlin-Marienfelde and Berlin- Ruhleben.

The goal in Marienfelde was a competitive test with different precipitation processes for phosphorus removal to get a direct comparison of the phosphorus removal efficiency and the process cost /60/.

The experiments in Ruhleben were run besides a device for post-precipitation, thus a direct comparison of these 2 processes was possible again.

5.1 General Running Conditions

The running conditions, which are listed in table 1, were in accordance with preliminary experiments in stirred reactor units on the laboratory scale /52/.

Table 1

Running Conditions of the Experiments in
Berlin-Marienfelde and Berlin-Ruhleben

Adsorption
- 3 reactors with 441 l volume, charged with 75 kg CHI-Al_2O_3
- adjustment of inflow-pH with HCl, CO_2 or aeration
- throughput 500-720 l/h
- inflow: secondary effluent

Regeneration
- 2 (3) cycles with 210 l 0,5 molare NaOH, fresh or reused
- 4 cycles with 210 l water
- adjustment of the pH of the washing water with CO_2
- addition of 2,5 % Al_2O_3

Lime Precipitation
- 2 cycles with 1,5 moles $Ca(OH)_2$ per mole P
- addition of 30 % NaOH

The regeneration was first, i.e. in Marienfelde and during the first time in Ruhleben, performed with fresh NaOH with a ratio of 12 moles NaOH per mole of phosphorus. Technical 50% NaOH was pumped into a tank with a volume of 6 liters and was introduced into the reactor filled with 210 liters of water. After 45 minutes of stirring, and one hour of settling, the regeneration liquor was discharged and the whole procedure repeated, followed by 2 to 4 cycles of washing with water. The number of cycles, the NaOH addition as well as the washing water cycles, were chosen by the process computer. Finally the pH of the oxide-water-suspension was readjusted to pH = 7 with HCl or CO_2.

Later NaOH reuse was performed in Ruhleben (section 5.3)

5.2 Results of "Berlin-Marienfelde"

As already mentioned, the experiments were run in Marienfelde for about 1 year in 1980/81 within a research project for a competitive test of several methods of phosphate elimination from waste waters (post-precipitation, tube flocculation and filtration and a biological method with iron salts). In this running period three important changes were performed,

- change of the Al_2O_3-modification (CHI-Al_2O_3 instead of GAMMA-Al_2O_3),
- enlarging of the filling capacity of the reactors from 50 kg to 75 kg and
- the application of CO_2 instead of HCl for pH-adjustment of the inflow.

Therefore, the experiment may be divided into 3 parts

1. 50 kg GAMMA-Al_2O_3 per reactor, HCl for pH-adjustment
2. 50 kg CHI-Al_2O_3 per reactor, HCl for pH-adjustment
3. 75 kg CHI-Al_2O_3 per reactor, CO_2 for pH-adjustment

The results of these 3 sections are listed in table 2.

5.2.1. Phosphorus Adsorption on the Activated Alumina

Figure 4 shows the first two cycles of the experiment Berlin-Marienfelde. In cycle 2 one of the main advantages of this process is demonstrated, i.e. attaining a uniform phosphorus outflow concentration independent of the quality of the inflow. In this cycle, a sudden increase of the phosphorus concentration in the inflow occurred, exceeding the range of measurement of the phosphatometer (> 15 mg/l P). The phosphorus concentrations of the outflows of the first and second reactor increased, but the outflow concentration of the third reactor remained constant.

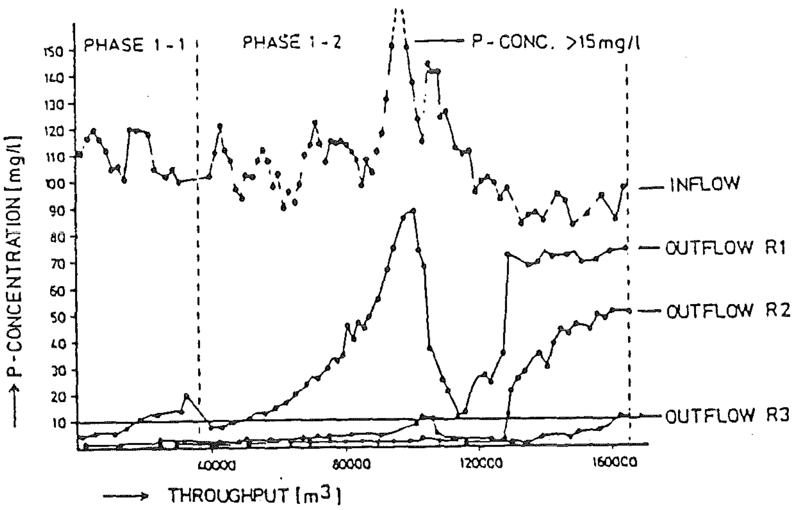

Figure 4: The First 2 Cycles of the Experiment Berlin-Marienfelde

Figure 5 shows three cycles of the same experiment are shown. After switching of the reactors indicated by a vertical line, the outflow concentration decreases to 0.2 - 0.3 mg/l P and increases continuously with increasing saturation of the activated alumina up to the maximum value of the phosphorus concentration. It is an outstanding property of this process that the effluent quality may be chosen between the minimum value depending on the operating conditions and the maximum value for the changing of the phase. The minimum value could be lowered by adding a fourth reactor to the adsorption stream or the application of a better adsorbing activated alumina.

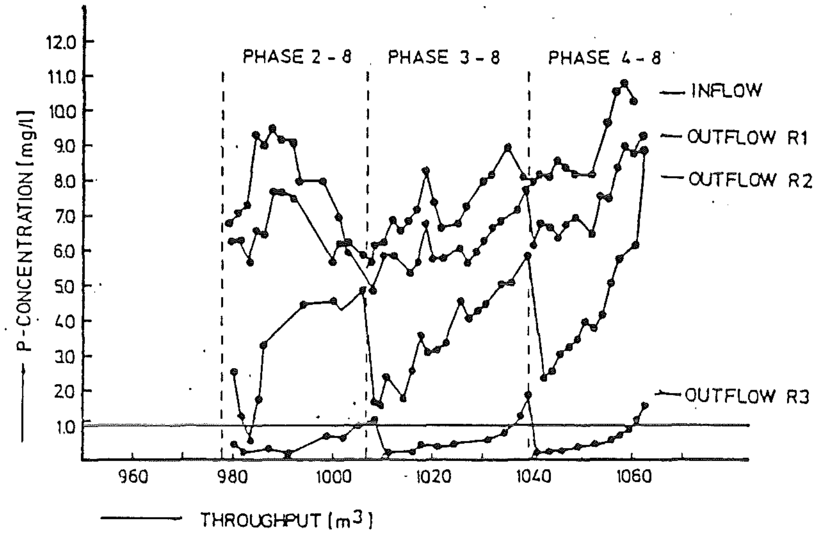

Figure 5: Three Cycles of the Experiment Berlin-Marienfelde

5.2.2. COD and DOC Removal

The DOC was reduced with an effectiveness of about 20 % throughout the experiment. The COD was removed between 25 and 40 %. The differences in the COD reduction in the 3 sections of the experiment Berlin-Marienfelde are probably due to the great variations of the inflow concentration. In the first section of this experiment, the COD-content was very high due to the high content of suspended solids, caused by bulking sludge. Therefore the higher COD removal resulted from an additional retention effect of the activated alumina.

According to table 2 an outflow concentration of < 1 mg/l P was obtained throughout the experiment. Thus an effectiveness of about 90 % removal of the total phosphorus from the water was obtained. The percental removal was independent of the quality of the applied activated alumina and of the use of HCl or CO_2 for adjusting the pH, but these parameters had an influence on the cycle periods (see e.g. 5.2.3).

Table 2

Results of the Experiments in Berlin-Marienfelde

switching limit	section 1 50 kg activ. alum. GAMMA per reactor pH-adjustment of inflow with HCl throughput: 500 l/h 1.0 mg/l P	section 2 50 kg activ. alum. CHI per reactor pH-adjustment of inflow with HCl throughput: 500 l/h 1.0 mg/l P	section 3 75 kg activ. alum. CHI per reactor pH-adjustment of inflow with CO2 throughput: 500 l/h 1.0 mg/l P
duration of test	121 days	69 days	93 days
total throughput	1448 m^3	761 m^3	669 m^3
number of cycles	45	17	11
mean length	3 days(32.0 m^3)	4.5 days(44.7 m^3)	6.5 days(75.9 m^3)
inflow phosphorus	9.6 ± 2.20 mg/l P	8.0 ± 1.80 mg/l P	8.45 ± 2.67 mg/l P
outflow phosphorus R3	0.65 ± 0.44 mg/l P	0.81 ± 0.51 mg/l P	0.72 ± 0.56 mg/l P
efficiency of phosphorus-elimination	93.1 %	90.0 %	88.4 %
inflow COD	260 ± 215 mg/l	103 ± 23 mg/l	131 ± 47 mg/l
outflow COD	145 ± 102 mg/l C	77 ± 18 mg/l	95 ± 25 mg/l
efficiency of COD-elimination	39.4 %	23.3 %	27.5 %
inflow DOC	41 ± 15 mg/l C	42 ± 15 mg/l C	26 ± 5 mg/l
outflow DOC	33 ± 14 mg/l C	33 ± 14 mg/l C	21 ± 4 mg/l
efficiency of DOC-elimination	19.5 %	21.5 %	19.3 %
oxide load before regeneration	7290 ± 1290 mg P/kg 4260 ± 1160 mg C/kg	8321 ± 566 mg P/kg 5465 ± 703 mg C/kg	9019 ± 1428 mg P/kg 5660 ± 1759 mg C/kg
oxide load after regeneration	3153 ± 775 mg P/kg 1872 ± 670 mg C/kg	2786 ± 617 mg P/kg 1809 ± 758 mg C/kg	3612 ± 644 mg P/kg 2514 ± 364 mg C/kg
efficiency of regeneration	56.5% related to P 56.0% related to C	66.5% related to P 66.7% related to C	60.0% related to P 55.6% related to C

	cost of chemicals und energy					
	demand per m^3	DM	demand per m^3	DM	demand per m^3	DM
activ. alumina	0.039 kg	0.047	0.028 kg	0.034	0.037 kg	0.044
NaOH	10.82 mol	0.227	7.75 mol	0.163	6.68 mol	0.119
HCl	12.1 mol	0.218	12.1 mol	0.218	----------	-----
CO2	----------	-----	----------	-----	7.0 mol	0.077
energy	0.1 kWh	0.01	0.1 kWh	0.01	0.1 kWh	0.01
total		0.502		0.425		0.250

5.2.3. Oxide Load and Effectiveness of the Regeneration

The experiments in Berlin-Marienfelde were started with GAMMA-Al_2O_3 with a relatively low surface area of 120 m^2/g, which was obtainable in technical quantities in the grain size 0.08 to 0.2 mm required for application in the stirred reactors. Later on, CHI-Al_2O_3 was available with a surface area of about 200 m^2/g which had been proven in laboratory scale tests /54/ to effect higher loads and to give better regeneration yields. Therefore, it was used starting with section 2 "Marienfelde".

The oxide loads, obtained in all sections of both experiments (table 2), are lower than those obtained in previous experiments (0.7 - 0.9 % P compared with >1.1 % P)/51/. The probable explanation is the high COD content of the inflow due to a high content of activated sludge. By changing the species of the activated alumina, a great improvement of the oxide load was obtained and the regeneration effectiveness increased.

This may be best seen by the prolongation of the mean cycle period which increased from 3 days (32 m^3 throughput) for GAMMA-Al_2O_3 to 4.5 days (44.7 m^3 throughput) for CHI-Al_2O_3 (table 2). The residual oxide load increased during the first 2 regeneration cycles and did not increase afterwards, i.e. no decrease of the yield of redissolution was observed during several regenerations.

The application of 75 kg CHI-Al_2O_3 instead of 50 kg in the reactors resulted in a further increase of the mean cycle period to 6.5 days or 75.9 m^3 throughput.

5.2.4. Adjustment of the Inflow-pH

In the first 2 sections of the experiment, HCl was used for the lowering of the inflow pH to 5.5. Simultaneously, the chloride content was raised. This additional increase of the salt concentration was avoided by using CO_2 and moreover, no deterioration of the results occurred, although the inflow-pH only decreased to about 6.5 according to results previously obtained /61/.

5.2.5. Loss of Activated Alumina

In the first two sections of the experiment "Marienfelde" 2.25 kg (4.5 % from 50 kg) activated alumina were added after each regeneration. This was done to cover the losses of Al_2O_3 by dissolution in NaOH during regeneration as well as by rinsing out during adsorption. For experimental control the activated alumina of one reactor was collected, dried and weighed after 9 regenerations. The yield was 58.8 kg instead of 50 kg, the filling quantity of the reactor at the beginning of the experiment. Thus the actual loss amounted only to 2.5 % (1.25 kg) after each regeneration.

5.3 Results of "Berlin-Ruhleben"

After finishing the experiments in Marienfelde, the unit was run for about 2 years in the treatment plant at Berlin-Ruhleben, in parallel operation to a pilot plant device for post-precipitation. One goal was a further optimization of the device and a comparison of the results with post-precipitation. The other goal was to complete the unit, i.e., to carry out experiments with NaOH-recycling. The running conditions are listed in table 1 and are optimized according to the results previously described.

The experiments may be divided into 2 main parts, namely

1. Experiments without reuse of the NaOH
   - 75 kg CHI-Al_2O_3 per reactor with differential increasing throughput rates, CO_2 for pH-adjustment,
   - 75 kg CHI-Al_2O_3 per reactor, aeration, i.e. no pH-adjustment
2. Experiments with reuse of the NaOH
   - 75 kg CHI-Al_2O_3 per reactor, CO_2 for pH-adjustment
   - 75 kg CHI-Al_2O_3 per reactor, aeration

5.3.1 Results of the Experiments without NaOH Reuse

5.3.1.1 Experiments with Different Throughput Rates

The goal of this experimental series was to get more knowledge about the kinetical behaviour, which had not yet been investigated. It was started with 720 l/h, i.e. a detention period of 1.84 hours. This was the maximum velocity which could be run in the device without considerable losses of activated alumina by rinsing out. Then the throughput rate was lowered to 600 l/h and finally to 480 l/h, i.e. a detention period of 2.21 hours and 2.75 hours, respectively.

The results are listed in table 3 and show no significant difference in the elimination rates of phosphorus as well as DOC and E_{254} (extinction at 254 nm). That means that the maximum throughput was determined by the settling behaviour of the activated alumina and not by the kinetics of the phosphorus removal.

The quality of the mean effluent was raised during these experiments by lowering the preset maximum outflow concentration of the effluent from 1.0 mg/l P in Marienfelde - i.e. a mean outflow concentration of 0.8 mg/l P - to 0.6 mg/l P in Ruhleben - i.e. 0.4 mg/l P as average outflow concentration. Therefore, the mean throughput between 2 regenerations was reduced from about 75.9 m^3 to about 38.5 m^3.

Oxide load and effectiveness of the regeneration are nearly identical. That is, the qualtiy of the inflow water has no remarkable effect on the phosphorus and the COD removal.

Table 3

Results of Continuous Running Experiments without NaOH Reuse in Berlin-Ruhleben

Comparison of Different Throughput Rates

	section 1	section 2	section 3
	75 kg activ. alum. CHI per reactor pH-adjustment of the inflow with CO2		
	throughput: 720 l/h	throughput: 600 l/h	throughput: 480 l/h
duration of test	9 days	19 days	22 days
total throughput	182 m^3	267 m^3	227 m^3
number of cycles	5	7	6
mean length	2.5 days(36.4 m^3)	2.6 days(38.3 m^3)	3.2 days(37.8 m^3)
inflow phosphorus	7.0 ± 0.90 mg/l P	6.5 ± 1.14 mg/l P	5.54 ± 2.53 mg/l P
outflow phosphorus R3	0.43 ± 0.13 mg/l P	0.43 ± 0.13 mg/l P	0.40 ± 0.14 mg/l P
efficiency of phosphorus-elimination	93.9 %	93.4 %	92.8 %
inflow DOC	13.0 ± 0.8 mg/l C	12.2 ± 0.6 mg/l C	12.1 ± 1.2 mg/l C
outflow DOC	10.0 ± 0.9 mg/l C	9.3 ± 0.5 mg/l C	9.0 ± 1.2 mg/l C
efficiency of DOC-elimination	23.7 %	23.3 %	25.6 %
inflow E254	34.3 ± 2.8 m -1	32.1 ± 1.5 m -1	33.4 ± 3.8 m -1
outflow E254	23.2 ± 2.4 m -1	23.4 ± 2.0 m -1	22.5 ± 3.0 m -1
efficiency of E254-elimination	32.3 %	27.2 %	32.6 %
oxide load before regeneration	7389 ± 86 mg P/kg 2425 ± 234 mg C/kg	7094 ± 173 mg P/kg 2295 ± 205 mg C/kg	6505 ± mg P/kg 2660 ± mg C/kg
oxide load after regeneration	3741 ± 109 mg P/kg 1856 ± 60 mg C/kg	3643 ± 179 mg P/kg 1950 ± 127 mg C/kg	3618 ± 147 mg P/kg 2200 ± 201 mg C/kg
efficiency of regeneration	49.4% related to P 23.5% related to C	48.7% related to P 15.0% related to C	44.4% related to P 17.3% related to C

5.3.1.2 Experiments with pH-Adjustment and Aeration

Table 4 shows the results of an experimental series of 92 days. Additionally, a cost calculation is given for the 3 sections carried out. A considerably high NaOH consumption had to be calculated because no recycling was performed in this period.

In the first section the throughput rate was raised to 720 l/h and the maximal phosphorus effluent concentration was set to 1.0 mg/l P again. The average cycle length was raised to 42.5 m^3 throughput which is definitely lower than in Marienfelde. Possibly there is an influence of the retention time in contrary to the results obtained in the last section or the inflow quality had changed, i.e. more phosphonic acids have been used instead of phosphates in the detergents.

In the second part, the maximal outflow concentration was reduced to 0.6 mg/l P which resulted in a reduction of the mean cycle length to 32.0 m^3. Therefore, the operating cost raised considerably.

During the experiments, a cost calculation showed that the pH adjustment with CO_2 covered a considerable part of the total operation cost. Therefore, the system was changed to aeration, i.e. the pH-adjustment of the inflow was no longer performed. This was done according to results of experiments performed on the laboratory scale /61/ which had shown that phosphorus removal from waste waters could be enhanced by aeration in comparison to pH-adjustment with both, HCl and CO_2.

Section 3 shows the results: the mean throughput rate was higher than in section 2 which was run under the same conditions with CO_2 and a considerable saving of the cost was attained.

Table 4

Results of Continuous Running Experiments without NaOH Reuse in Berlin-Ruhleben

Comparison of pH-Adjustment with CO_2 and Aeration

	section 1		section 2		section 3	
	75 kg activ. alum. CHI per reactor					
	pH-adjustment of the inflow with CO2				aeration	
switching limit	throughput: 720 l/h 1.0 mg/l P		throughput: 720 l/h 0.6 mg/l P		throughput: 720 l/h 0.6 mg/l P	
duration of test total throughput number of cycles mean length	41 days 698 m^3 17 2.6 days(42.5 m^3)		37 days 674 m^3 21 1.8 days(32.0 m^3)		14 days 222 m^3 6 2.3 days(37.0 m^3)	
inflow phosphorus outflow phosphorus R3 efficiency of phosphorus-elimination	5.93 ± 1.64 mg/l P 0.69 ± 0.40 mg/l P 88.4 %		6.88 ± 2.24 mg/l P 0.47 ± 0.30 mg/l P 93.2 %		6.84 ± 1.63 mg/l P 0.45 ± 0.14 mg/l P 93.4 %	
inflow DOC outflow DOC efficiency of DOC-elimination	12.4 ± 1.5 mg/l C 9.8 ± 1.4 mg/l C 21.0 %		14.7 ± 1.5 mg/l C 11.6 ± 2.1 mg/l C 21.1 %		14.4 ± 2.1 mg/l C 11.5 ± 1.5 mg/l C 20.1 %	
inflow E-254 outflow E-254 efficiency of E-254 elimination	29.7 ± 3.6 m -1 21.4 ± 3.1 m -1 27.8 %		33.5 ± 2.9 m -1 23.8 ± 3.3 m -1 29.0 %		31.8 ± 4.0 m -1 24.2 ± 5.9 m -1 23.9 %	
oxide load before regeneration oxide load after regeneration efficiency of regeneration	7106 ± 86 mg P/kg 2774 ± 234 mg C/kg 3782 ± 109 mg P/kg 1740 ± 60 mg C/kg 46.8% related to P 37.3% related to C		6905 ± 173 mg P/kg 2478 ± 205 mg C/kg 3433 ± 179 mg P/kg 1943 ± 127 mg C/kg 50.3% related to P 21.6% related to C		6505 ± mg P/kg 2660 ± mg C/kg 3618 ± 147 mg P/kg 2200 ± 201 mg C/kg 44.4% related to P 17.3% related to C	
	cost of chemicals and energy					
	demand per m^3	DM	demand per m^3	DM	demand per m^3	DM
activ. alumina	0.035 kg	0.042	0.047 kg	0.056	0.041 kg	0.049
NaOH	8.14 mol	0.171	10.82 mol	0.227	9.36 mol	0.197
CO2	4.5 mol	0.05	4.5 mol	0.05	---------	-----
energy	0.1 kWh	0.01	0.1 kWh	0.01	0.1 kWh	0.01
total		0.273		0.343		0.256

5.3.2 Results of the Experiments with NaOH Reuse

In order to fulfill the goal of the experiments, i.e. to complete the device in Berlin with the lime precipitation step, further research work was necessary. First investigations were carried out to optimize the recovery of the phosphorus from the regeneration liquor, afterwards an experiment was carried out on the laboratory scale.

After the successful completition of these two important steps, an automatic device for the lime precipitation was installed in Berlin-Ruhleben.

5.3.2. Results of the Experiments with NaOH Reuse

5.3.2.1. Recovery of the Phosphorus from the Regeneration Liquors by Lime Precipitation

Previous experiments /52/ had shown that a total elimination of the phosphorus could be effected only with a large excess of lime yielding a product with a low phosphorus content. Therefore, a two step precipitation was applied using a ratio of 1 to 2.5 moles $Ca(OH)_2$ per mole of phosphorus. According to the results listed in table 5 the best way to carry out the lime precipitation is as follows:

- add a suspension of $Ca(OH)_2$ in water to the regeneration liquor with a molar ratio P : $Ca(OH)_2$ = 1.5 to 2
- stirr for about two hours
- add again a suspension of $Ca(OH)_2$ in water with the same molar ratio referred to the residual phosphorus content in the liquor
- stirr for about two hours
- filter the precipitate and wash it with water

Thus, about 75 % of the phosphorus of the NaOH liquor is eliminated in the first and about 10 % in the second step, yielding a product with a phosphorus content between 11 and 13 %.

Table 5

Results of Lime Precipitation Experiments

Two step lime precipitation
4 l NaOH "Ruhleben"

P-content of the liquor: 378 mg/l P

molar ratio P : lime	1. precipitation		2. precipitation		total P precipitated (%)	Ca-P product obtained	
	residual P-content (mg/l P)	P precipitated (%)	residual P-content (mg/l P)	P precipitated (%)		(g)	(% P)
1 : 1	250,2	33,8	107,0	57,3	71,7	8,2	13,2
1 : 1,5	146,9	61,2	47,0	68,1	87,7	10,2	12,9
1 : 2	96,7	74,4	1,6	72,6	99,6	12,6	12,0
1 : 2,5	99,9	73,6	0,13	99,5	99,8	15,8	9,6

5.3.2.2 Experiment for NaOH Reuse on the Laboratory Scale

In order to complete the device in Berlin with the lime precipitation step to enable the reuse of the NaOH, a throughput experiment was started on the laboratory scale. The running conditions and the main results are listed in table 6.

30 % of fresh NaOH was added after each regeneration according to determinations of the OH^--concentration by titration. 10 regenerations were carried out with the reuse of NaOH. In the beginning, the results indicated a slight decrease of the regeneration yield which remained constant in the course of the experiment.

5.3.2.3 Experiment for NaOH Reuse on the Technical Scale in Berlin-Ruhleben

According to the good results in the preliminary experiments, the device in Berlin-Ruhleben was completed with a unit for the lime precipitation of the regeneration liquor (figure 6). Thus, the complete process could be run as planned.

Table 6

Experiment for NaOH-Reuse on the Laboratory Scale

Experimental Conditions

Adsorption
4 reactors with 44 l volume, charged with 7,5 kg CHI-Al_2O_3
adjustment of the inflow-pH with CO2
throughput 50 l/h
inflow: secondary effluent of the treatment plant of the Nuclear Research Center Karlsruhe

Regeneration
2 cycles with 25 l 0,5 molare NaOH (fresh or reused)
2 - 3 cycles with 25 l water
adjustment of the pH of last backflush water with CO2
adding of 2,5 % Al_2O_3 for the lost oxide

Lime Precipitation
2 step precipitation with 1,5 or 2 moles $Ca(OH)_2$ per mole P

Results

Adsorption

Running time	196 days (50 cycles)
inflow concentration	7,00 ± 1,50 mg/l P
	191 ± 20 mg/l COD
outflow concentration	0,77 ± 0,33 mg/l P
	141 ± 20 mg/l COD
removal efficiency	89 % P
	26 % COD

Regeneration (mean values of 5 cycles)

NaOH appl.	content in NaOH		oxide load	residual load	% P
	mg/l P	mg/l Al	mg P/kg oxide	mg P/kg oxide	rediss.
fresh NaOH	------	----	8870 ± 1185	2684 ± 677	69,4
1 x reused	40,0	2212	8670 ± 688	2784 ± 657	66,7
2 x reused	50,8	2293	8751 ± 553	2992 ± 414	59,2
3 x reused	104,9	2266	8550 ± 314	2886 ± 406	54,1
4 x reused	42,1	1916	7498 ± 456	3608 ± 892	49,8
fresh NaOH	------	----	7553 ± 463	3752 ± 589	51,1
1 x reused	5,1	324	7755 ± 436	2678 ± 446	54,6
2 x reused	10,8	567	7775 ± 367	2342 ± 106	55,7
3 x reused	37,0	755	7515 ± 602	2248 ± 365	52,3
4 x reused	48,0	1005	7353 ± 102	2053 ± 301	55,1
5 x reused	44,3	1160	7171 ± 356	1992 ± 133	58,0

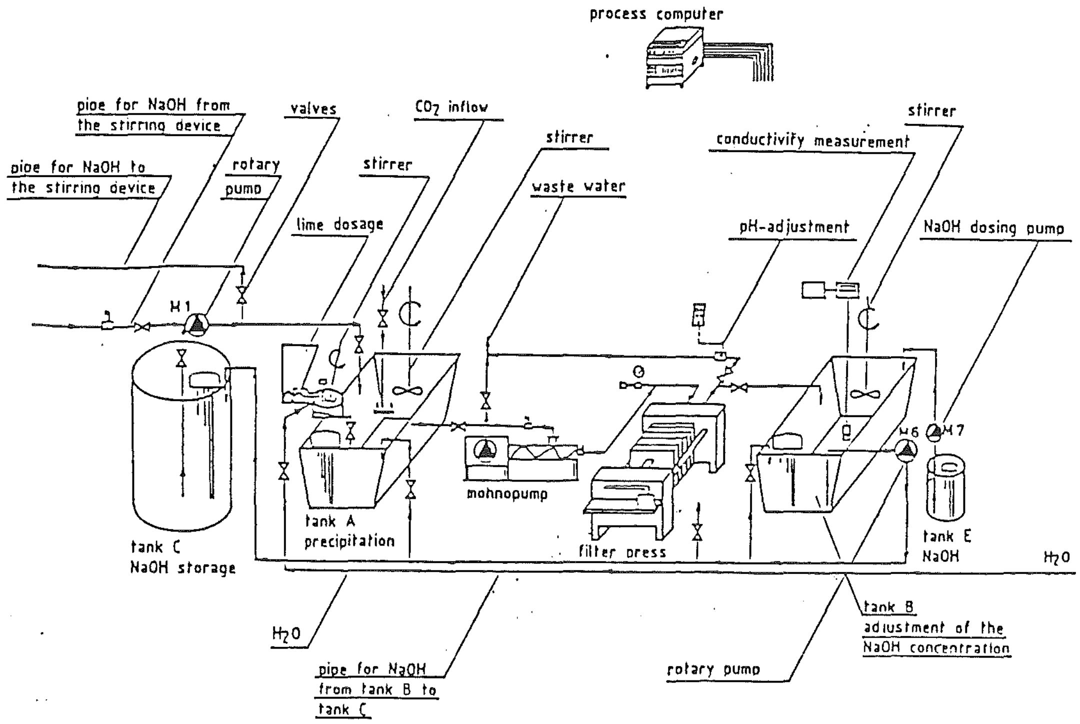

Figure 6: Automatic Device for Lime Precipitation of the Regeneration Liquor in Berlin-Ruhleben

The device consisted of a precipitation tank with a volume of 1000 liters. After stirring the regeneration liquor with lime, the whole suspension was filtrated through a filter press and adjusted to the initial concentration with NaOH. The parameter used for this adjustment was the conductivity which had turned out to be a reliable parameter.

The results of the automatic operation throughout 109 days are listed in table 7, together with the chemical cost.

In order to be able to compare the results with those obtained without the reuse of NaOH, CO_2 was applied again for pH-adjustment of the inflow followed by a section of aeration.

The results indicate the following:

1. no decrease of phosphorus removal resulted in the integration of the lime precipitation step, i.e. the reuse of the regeneration liquor in the process

2. no deterioration of the phosphorus removal occured if pH adjustment with CO_2 was substituted by aeration, i.e. the results of the previous experiments (5.3.1.2) were confirmed.

3. a considerable saving of the cost was obtained.

Table 7

Experiments with NaOH-Reuse in Berlin-Ruhleben

	section 1	section 2
	75 kg activ. alum. CHI per reactor	
	pH-adjustment of the inflow with CO2 throughput: 500 l/h	aeration throughput: 500 l/h
switching limit	0.6 mg/l P	0.6 mg/l P
duration of test	46 days	63 days
total throughput	473 m^3	704 m^3
number of cycles	13	18
mean length	3.5 days(41.7 m^3)	3.5 days(39.0 m^3)
inflow phosphorus	7.62 ± 2.02 mg/l P	7.43 ± 2.10 mg/l P
outflow phosphorus R3	0.43 ± 0.33 mg/l P	0.41 ± 0.17 mg/l P
efficiency of phosphorus-elimination	94.4 %	94.5 %
inflow DOC	14.4 ± 1.3 mg/l C	11.8 ± 2.5 mg/l C
outflow DOC	11.3 ± 1.3 mg/l C	9.6 ± 1.4 mg/l C
efficiency of DOC-elimination	21.5 %	18.6 %
inflow E-254	34.8 ± 4.3 m -1	30.6 ± 2.5 m -1
outflow E-254	24.6 ± 2.5 m -1	22.8 ± 3.2 m -1
efficiency of E-254 elimination	29.5 %	25.5 %
oxide load before regeneration	8136 ± 538 mg P/kg 2560 ± 354 mg C/kg	7581 ± 373 mg P/kg 2283 ± 171 mg C/kg
oxide load after regeneration	3822 ± 279 mg P/kg 2020 ± 528 mg C/kg	3935 ± 326 mg P/kg 1906 ± 142 mg C/kg
efficiency of regeneration	53.0% related to P 21.1% related to C	48.1% related to P 16.6% related to C
	cost of chemicals and energy	
	demand per m^3 DM	demand per m^3 DM
activ. alumina	0.036 kg 0.043	0.047 kg 0.056
NaOH	2.76 mol 0.058	2.95 mol 0.062
CO2	4.5 mol 0.05	--------- -----
lime	0.65 mol 0.011	0.69 mol 0.011
energy	0.1 kWh 0.01	0.1 kWh 0.01
total	0.172	0.139

5.3.2.4 COD and DOC Removal

The results in Ruhleben regardless of NaOH reuse or not are nearly identical with those obtained in the section 3 of "Marienfelde". The same efficiency, i.e. an average removal of 20 % DOC and COD was obtained.

5.3.2.5 Estimation of Losses, Possibilities of Further Improvements of the Process

5.3.2.5.1 Loss of Activated Alumina

The regeneration liquors as well as the washing waters were analyzed, the average content was 480 mg/l Al and 110 mg/l Al, respectively, which is adequate to a total loss of 1100 g Al_2O_3 per cycle. Additionaly, 400 g of activated alumina was lost due to rinsing out which was estimated according to the increase of suspended solids in the effluent.

5.3.2.5.2 Loss of NaOH

The consumption of NaOH was 115 moles in each cycle. This was estimated on 2 methods:

- the analysis of the regeneration liquors

- the NaOH demand detected during the experiment

These losses are due to the following:

- chemical losses

1) dissolution of the COD: ~10 moles of NaOH per cycle, i.e. 640 g COD per cycle with a molar mass of about 200, NaOH demand estimated to 3 moles NaOH/mole COD

2) dissolution of Al: ~20 moles of NaOH per cycle conforming to 480 g Al dissoluted per cycle

3) dissolution of the phosphorus: ~30 moles per cycle conforming to 320 g P dissoluted per cycle

- mechanical losses

4) losses if the NaOH is decanted from the activated alumina: ~30 moles of NaOH per cycle (about 60 liters of 0.5 m NaOH)

5) NaOH remaining in the activated alumina: ~25 moles of NaOH per cycle (0.6 liters of 0.5 m NaOH remain in 1 kg Al_2O_3)

6) NaOH remaining in the lime precipitation product: ~10 moles NaOH per cycle

Therefore, about 55 moles NaOH per cycle could be saved, i.e. 30 moles NaOH according to 4) and 25 moles NaOH according to 5 and 6). This will be considered in the next section for the cost evaluation.

5.4. Cost Evaluation

The chemical cost according to the results of "Berlin-Ruhleben" with reuse of the regeneration liquor are listed in table 8 together with an estimated optimization by improvement of the device, i.e. a reduction of the losses of activated alumina and NaOH as described in the previous section.

No bonus was calculated for the Ca-phosphate product obtained. It was only assumed that no cost for a disposal will arise.

Table 8

Chemical Cost Evaluation of the Process for Phosphorus Removal with Fine Grained Activated Alumina

			experimental cost		optimized cost	
Chemical	Price DM/t	Price DM/mole	demand per m^3	cost DM/m^3	demand per m^3	cost DM/m^3
Al_2O_3	1180	0.194	0.047 kg	0.055	0.028 kg	0.033
NaOH	260	0.021	2.65 moles	0.056	1.96 moles	0.041
$Ca(OH)_2$	250	0.020	2.69 moles	0.014	2.69 moles	0.014
CO_2 1)	1000	0.55	1000 l	0.001	1000 l	0.001
Energy			0.1 kWh	0.010	0.1 kWh	0.010
total cost in DM per m^3				**0.136**		**0.099**

1) CO_2 is used for the neutralization of the calcium phosphate precipitate

5.5 Conclusions on the Stirring Reactor Experiments

The possibility for the application of activated alumina for phosphorus removal was demonstrated successfully, and the cost, which do not include the investment costs are in the same order of magnitude as those given for precipitation processes /62,63/. On the other hand, one has to consider the recycling aspect as well as the fact that an additional increase of the salt content is avoided if the alumina-process is applied.

Table 9 shows a comparison between the pilot plant for post-precipitation and filtration with a dosage of about 35 mg/l Fe and the activated alumina device.

According to these results, the removal efficiency of the activated alumina was in the same order of magnitude which surely would have been improved if an additional filtration step would have been applied.

Table 9

Comparison of the Elimination Rates of the Activated Alumina Device and the Pilot Plant for Post-Precipitation in Berlin-Ruhleben

parameter	activated alumina device			post-precipitation device		
	inflow mg/l	outflow mg/l	eliminat. in %	inflow mg/l	outflow mg/l	eliminat. in %
Susp.Sol	4.9±3.8	10.8±7.2	+118.7	4.5±2.9	1.2±0.8	- 72.8
NH_4	9.0±6.4	6.7±5.9	- 26.0	5.9±3.7	4.0±3.1	- 33.4
NO_3	1.3±1.0	1.5±0.9	+ 13.4	1.3±1.0	0.3±0.3	- 76.9
PO_4	23.3±3.0	1.7±1.4	- 92.9	22.9±2.8	5.4±3.9	- 76.7
Cl	141 ±16	138 ±16	- 2.0	140 ±17	197 ±37	+ 40.0
DOC	13.3±6.1	10.6±5.6	- 20.5	13.2±6.6	9.9±1.2	- 24.8
E_{254}	32.1±3.4	22.7±3.2	- 29.3	31.7±3.1	19.6±3.1	- 38.1

The use of activated alumina has advantages, on the other hand, with regard to a precipitation process:

- no addition of anions
- recovery of the phosphorus
- effluent quality may be adjusted independent from the quality of the influent

The simultaneous precipitation is always cheaper because no investment and maintenance costs have to be considered. Therefore, a new concept was made up for the application of activated alumina:

- application of biological removal together with simultaneous precipitation to attain a quality of ≤ 1.5 mg/l P
- application of activated alumina for polishing, i.e. to obtain an effluent concentration ≤ 0.5 mg/l P (section 7).

6. Fixed Bed Filters as Contacting Units

A large scale experiment was carried out in cooperation with the Wahnbachtalsperrenverband employing coarse activated alumina in fixed bed filters. The goal was a reduction of the phosphorus concentration of the effluent of a fish hatchery flowing into the Wahnbach drinking water reservoir in order to prevent eutrophication. The experiment consisted of 3 parts:

1. section 1 of the running experiment with fresh activated alumina "Compalox" /64/ (part 6.1)
2. regeneration of the loaded activated alumina (part 6.2)
3. section 2 of the running experiment with regenerated alumina and reuse of unregenerated material from section 1 /60/ as well as other kinds of activated alumina (part 6.3)

6.1 Section 1 of the Experiment "Wahnbachtalsperrenverband"

The dimensions of the device and the main results are listed in table 10, the elimination of the total phosphorus is shown in figure 7.

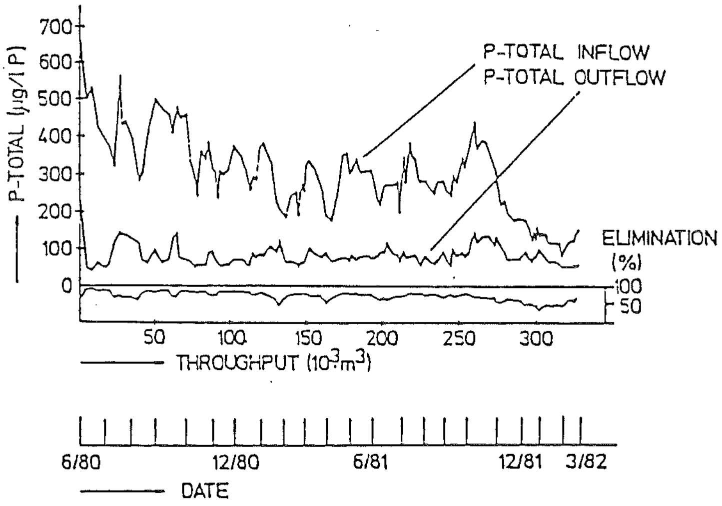

Figure 7: **Experiment "Wahnbachtalsperrenverband"**
Section 1 - Application of Fresh Coarse Al_2O_3
Elimination of the Total Phosphorus

The filters were directly positioned on the bottom of the fish pond being 130 cm deep, the outflow was led through the shutting dam. Due to the hydrostatical pressure, the filtration rate was limited to 1 - 2 m/h to obtain a satisfactory phosphate elimination. This construction of the unit /65/ had several advantages, such as

- operation without electricity
- long operating period of the filters
- decrease of the o-PO_4-concentration in the outflow to < 50 µg/l P and of the P_{tot}-concentration to < 100 µg/l P
- low maintenance and service which includes backwashing of the filters

- operation during the summer period with a large algae growth and during the winter period with ice on the pond
- possibility to replace the individual filters for regeneration or renewal the alumina using a mobile lift.

Table 10

Working Conditions and Results of the Experiment "Wahnbachtalsperrenverband" Section 1 with Fresh Coarse Activated Alumina

Working conditions

number of filters : 33
each charged with : 0,6 t coarse alumina COMPALOX, 1-3 mm
dimension of the filters : 0,7 m² filtering area
1,0 m filtering height
throughput : 512 ±140 m³/day
filtration speed : 1 - 2 m/h

Results
mean values of each running period

parameter	running period 0 - 200 days			running period 201 - 400 days			running period 400 - 501 days			running period 502 - 638 days		
	concentr. in-flow	concentr. out-flow	% elim.	concentr. in-flow	concentr. out-flow	% elim.	concentr. in-flow	concentr. out-flow	% elim.	concentr. in-flow	concentr. out-flow	% elim.
o-P (µg/l)	254	32	87,8	181	46	73,6	219	55	74,8	114	59	39,3
P-par(µg/l)	110	39	65,6	64	20	60,5	46	13	67,9	50	12	73,8
P-tot(µg/l)	388	83	78,7	277	78	71,1	305	79	74,4	177	78	52,9
DOC (mg/l)	3,4	2,0	39,3	3,1	1,8	41,6	3,1	2,1	33,0	2,1	1,2	41,3
NH4 (µg/l)	1785	663	67,5	1795	781	62,2	1718	976	44,7	1787	469	77,5
NO3 (mg/l)	42,0	44,3	-5,2	43,3	44,3	-3,6	43,0	42,6	1,2	46,4	49,8	-7,1

The outflow concentrations of o-phosphate were in a range of about 50 µg/l P throughout the whole experiment. Furthermore, a 75 % reduction of the total phosphorus which contained a considerable amount of undissolved phosphorus compounds was obtained.

Both values met the elimination target set to prevent eutrophication of the barrage. In addition, organic compounds and ammonia were removed. This removal of the ammonia was obviously due to an unexpected nitrification which occured on the filters.

The experiment was run over a period of 638 days. The elimination rates were constant over a period of about 500 days. Then a sudden decrease of the elimination occured, e.g. the elimination of the total phosphorus decreased from 78 % to 53 %, the o-phosphate elimination from about 75 % to 40 %. Therefore, the experiment was stopped and the unit was started again when the loaded alumina was regenerated.

6.2 Regeneration of the Coarse Activated Alumina

For the regeneration of the loaded coarse activated alumina from section 1 of the experiment "Wahnbachtalsperrenverband" a unit in the pilot scale was constructed /66/ which is shown in figure 8.

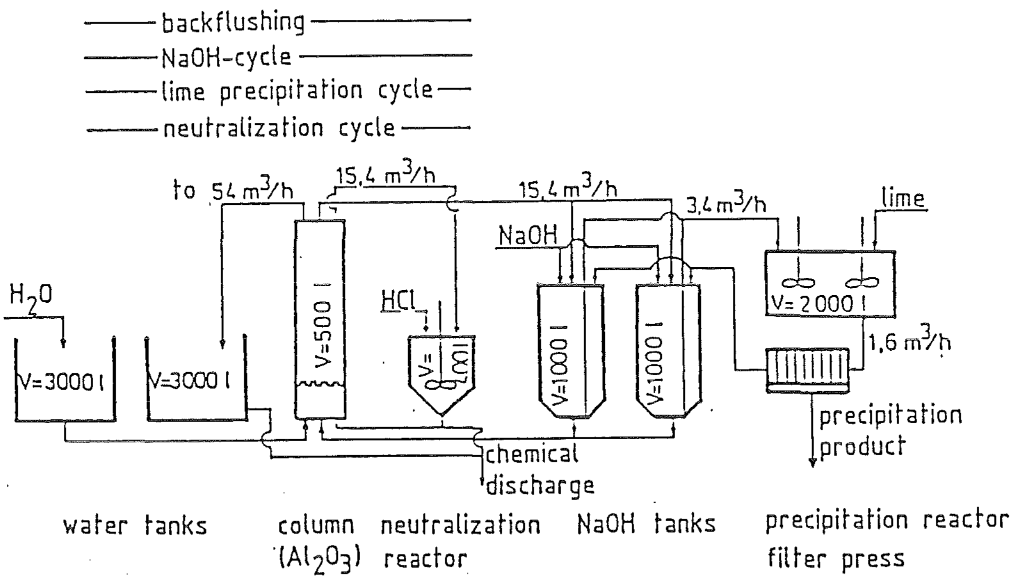

Figure 8: Experimental Device for the Regeneration of P-Loaded Coarse Activated Alumina with NaOH

It consisted of a column with a volume of about 560 liters designed for a charge of 350 kg wet ≡ 260 kg dry activated alumina. Backflushing was effected with water taken from a tank with a volume of 3 m^3, which was collected in a second tank afterwards.

The regeneration was carried out according to the following schedule:

1. backflushing of the filter
2. pumping of the NaOH for some hours through the filter with 15 $m^3/h \equiv 57$ bed volumes/h with permanent readjustment of its concentration according to conductivity measurements with or without lime precipitation for phosphorus removal from the regeneration liquor
3. neutralization of the activated alumina with HCl
4. filtration and neutralization of the lime precipitation product with CO_2

6.2.1 Pumping of the NaOH

- pumping of fresh 0.5 molar NaOH

The results in figure 9 show that an equilibrium of phosphorus solubility was achieved after a time of reaction of 5 hours. The redissolution of the phosphorus was 56 %.

- pumping of 0.5 molar NaOH including lime precipitation (6.2.2) once per hour

The results in figure 9 show the advantage of the application of a lime precipitation step. The redissolution of the phosphorus increased considerably from 56 % to 71 % after 7 hours.

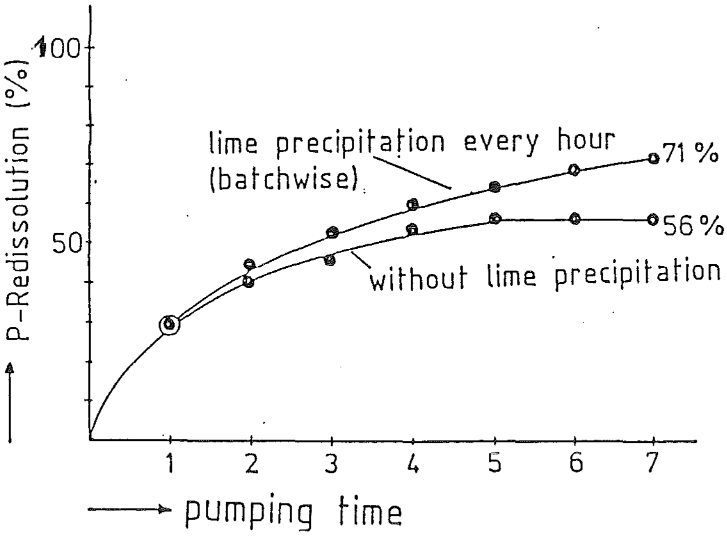

Figure 9: Redissolution of the Phosphorus from P-loaded Coarse Activated Alumina with NaOH Influence of the Time and the Efficiency of the Lime Precipitation

6.2.2 Phosphorus Removal from the NaOH by Lime Precipitation

The lime precipitation was carried out including

- application of a three-fold stoichoimetric excess of lime calculated for $Ca_3(PO_4)_2$
- stirring for 30 minutes after the lime feed

The preliminary investigations in the laboratory showed a very strong dependence of the yield of the precipitation upon the concentration of the regeneration liquor, i.e. this efficiency is significantly deteriorated if the concentration exceeds 0.5 moles/l NaOH (figure 10).

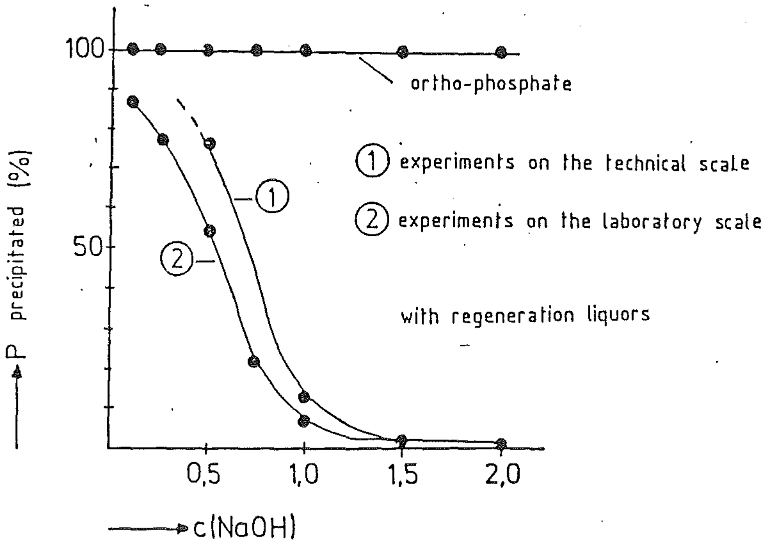

Figure 10: Lime Precipitation of the Phosphorus from the Regeneration Liquor - Influence of the Concentration of the Liquor

6.2.3 Neutralization of the Activated Alumina after Regeneration

This step was carried out by pumping water in a circuit through the column and adjusting its pH to ≤ 6.5 with HCl after passing through the activated alumina. About 0.6 moles of HCl per kg activated alumina were necessary in order to achieve a pH ≤ 6.5 of the washing water.

6.2.4 Optimal Running Conditions of the Regeneration

In order to obtain a satisfactory regeneration yield of the loaded coarse activated alumina, the following steps have to be carried out:

1. the regeneration should be carried out with a pumping of the NaOH for 7 hours with continuous readjustment of the NaOH concentration including a lime precipitation step every hour

2. the concentration of the NaOH applied, should not exceed 0.5 moles/l

3. backflushing should be applied before the neutralization step

6.2.5 Cost Evaluation for the Regeneration of P-loaded Coarse Activated Alumina

The cost calculated for a regeneration cycle with 260 kg activated alumina. are summarized in table 11.

Table 11

Cost Evaluation for the Regeneration of Coarse P-loaded Activated Alumina with NaOH

Chemical	demand	Price (DM/t)	Price (DM/mole)	cost (DM/kg Al_2O_3)
Activated alumina	2% loss	1900	0.194	0.038
NaOH demand (45% NaOH, c=16,62 moles/l)	36 l	260	0.021	0.048
HCl demand (31% HCl, c=9,81 moles/l)	14 l	150	0.018	0.01
$Ca(OH)_2$	6 kg	250	0.020	0.006
CO_2 1)	1000 l		0.55	0.001
total				0.103 DM/kg

1) used for neutralization of the precipitation product

According to the results of the experiment "Wahnbachtalsperrenverband section 1" described previously this would mean a specific cost of 0.007-0.008 DM/m³ for a throughput of 260.000 m³ and 19.800 kg Al_2O_3.

6.3 Section 2 of the Experiment "Wahnbachtalsperrenverband"

The experiments were restarted and run for one year. The main goal was a comparison of different activated aluminas (table 12).

Table 12

Results of the Experiment "Wahnbachtalsperrenverband Section 2" with Different Coarse Activated Aluminas

kind act.alumina		old sect 1 1-3 mm		spheric Granalox		fresh 2-5 mm		fresh 1-3 mm		fresh 0.5-1		regenerat. section 1	
parameter	infl. µg/l	outfl µg/l	elim in %	outfl µg/l	elim in %	outfl µg/l	elim in %	outfl µg/l	elim in %	outfl µg/l	elim in %	outfl µg/l	elim in %
P-ortho	88	30	66	8	91	31	65	11	88	6	93	8	91
P-part.	50	15	68	14	70	20	57	15	68	9	81	11	77
P-hydrol.	20	8	60	9	55	13	35	8	60	6	70	8	60
P-total	155	54	65	32	79	63	59	34	78	21	86	27	83
NH4	1510	390	74	490	68	500	67	500	67	500	67	490	68
	mg/l	mg/l	in %	mg/l	in %	mg/l	in %	mg/l	in %	mg/l	in %	mg/l	in %
DOC	2.8	1.8	36	1.7	39	2.0	29	1.7	39	1.3	54	1.6	43

The results may be summarized as follows:

- the old, i.e. activated alumina of section 1, which was reused, still had a sufficient elimination rate. I.e., in this view section 1 had been stopped too early because the material was not exhausted. The material had a lower elimination rate regarding o-phosphorus, but not regarding particular and organic phosphorus which are generally removed by filtration. Therefore, an average outflow concentration of ≤ 50 µg/l P was observed throughout the whole experiment

- the regenerated material showed no significant differences in the elimination rates in comparison with the fresh one

- better phosphorus removal could be achieved using finer grained Al_2O_3 (0.5-1 mm) but the rates decreased because these filters were more clogged than the others

- the more coarser material (2-5 mm) had better properties regarding the clogging of the filters, but showed a lower phosphorus removal rate

- the nitrification effect, i.e. the ammonia removal was observed again on each filter

6.4 Cost Evaluation for the Application of Coarse Activated Alumina for Phosphorus Removal

The cost for this small device (about 500 m^3/day) without the regeneration cost were calculated to 0.29 DM/m^3 covering:

chemical cost	DM 0.07 per m^3
interest	DM 0.14 per m^3
maintenance	DM 0.08 per m^3
in total	DM 0.29 per m^3

For the large phosphate elimination plant (about 18.000 m^3/h) at the Wahnbach total cost of DM 0.20 per m^3 were calculated, i.e. the cost of the 2 devices are in the same order of magnitude, because one has to consider that generally a large plant is much more economic than a small one.

6.5 Comparison of the "Activated Alumina Process" with Precipitation Experiments with Al-salts /67/

During the time when the regeneration experiments were performed, other investigations were carried out which must be considered:
The goal was to investigate the aptitude of flocculation with iron or aluminium salts /67,68/ for phosphorus removal on the same site. But it was not possible to meet the preset outflow concentration of 50 µg/l P even with an excess of 7 moles Al per mole P, mainly due to the fact that the particular phosphorus was not removed.
Thus, there are 2 additional advantages for the application of activated alumina, a removal of particular compounds by filtration and a removal of ammonia by nitrification. (table 13).

Table 13

Comparison of the Results of the Experiment "Wahnbachtalsperrenverband Section 1" with Precipitation Experiments with Aluminium Sulfate

device	activated alumina device			post-precipitation device		
	20 t Al_2O_3			0.26 - 1g/m^3 Al-sulfate		
throughput	~ 500 m^3/day			~ 600 m^3/day		
	21 months			19 months		
parameter	inflow µg/l	outflow µg/l	eliminat. in %	inflow µg/l	outflow µg/l	eliminat. in %
P-ortho	194	46	76	161	72	55
P-part.	72	23	68	72	76	----
P-hydrol.	28	10	64	25	13	48
P-total	352	79	76	256	160	38
NH_4	1777	709	60	2460	2080	15
	mg/l	mg/l		mg/l	mg/l	
DOC	3.0	1.8	40	3.0	2.4	20

6.6 Conclusions

Evidently the results showed the good applicability of coarse activated alumina for phosphorus removal, especially for the reduction of low inflow concentrations. The device described in the beginning of this section was proved to be a very practical one with a minimum of maintenance, i.e. backflushing every 4 weeks.

Compared to the precipitation, this method seems to be advantageous regarding the phosphorus elimination rate in these low concentrations, as well as regarding the operating cost together with two further advantages:

- no additional increase of the salt concentration of the water
- no sludge disposal problems.

7. Pilot Scale Plant in Berlin-Ruhleben

7.1 Introduction

According to the promising results obtained with the activated alumina a new concept was made up for its application in the sewage treatment plant Berlin-Ruhleben in the course of a new research project comprising biological phosphorus and nitrogen removal together with simultaneous precipitation /6/ as the first step with the goal of a phosphorus reduction to ≤ 2 mg/l P and a finishing step with coarse activated alumina for a further reduction of the phosphorus concentration to ≤ 0.5 mg/l P. The biological experiments are already running in full scale. The device for activated alumina is under construction.

7.2 Planning of the Device for Activated Alumina

The device for the activated alumina filtration was planned for a throughput of about 20 - 40 m^3/h with Preussag AG, Hannover. It consists of four parts (figure 11):

1. filtration part (multi layer filter)
2. adsorption part
3. regeneration part
4. filtration of the precipitation product

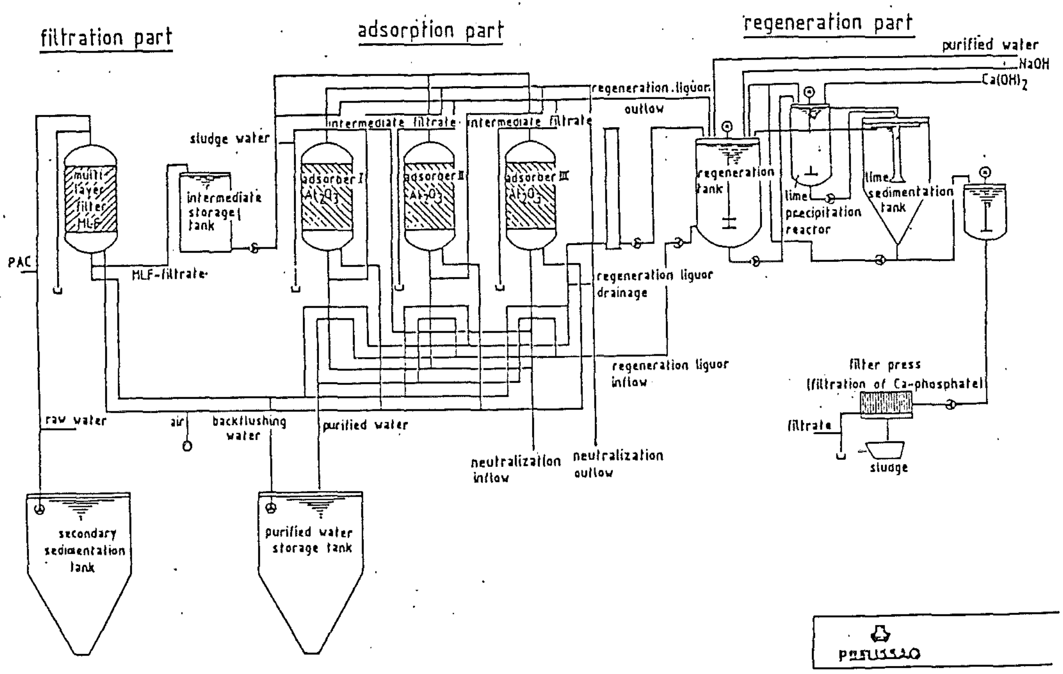

Figure 11: Scheme of the Device in Berlin-Ruhleben for the Application of Coarse Activated Alumina on the Pilot Scale

1. The multi layer filter consists of one column with a height of 3 m and a diameter of 1.6 m charged with multi layer material. Before the water is entering the column a site for the dosage of small amounts of different flocculating agents is provided in order to investigate the influence of a further turbidity removal of the water on the phosphorus removal by activated alumina. After the filter an intermediate storage tank is located in order to enable a continuous working of the filters during the necessary backflushing of the filter.

2. The adsorption part consists of three columns as described above. Each of them is charged with 3.8 tons of activated alumina. Two of the columns are in use as an adsorption cascade, one is isolated from the others and either regenerated or in waiting position. After the preset phosphorus outflow concentration is attained the first reactor will be taken out of operation and a new cascade will be formed with the former second column as the first and the regenerated column as the second one.

3. The regeneration part consists of the regeneration liquor storage tank with a volume of 10 m^3, a lime precipitation reactor with a volume of

2 m^3, a lime sedimentation "Dortmund" tank with a volume of 10 m^3, other facilities as storage tanks for NaOH, lime and CO_2 and a reactor for the preparation of the lime suspension. The regeneration will be carried out by pumping the NaOH through the column with continuous lime precipitation afterwards. The lime and the liquor are then separated in the "Dortmund" tank.
At the end of the regeneration step the activated alumina will be neutralized using CO_2.

4. Partly experiments for the filtration of the precipitation product will be carried out using a filter press.

In the meantime the complete device was completed by Preussag AG and was put into automatic operation with a process computer in August 1988 for the first experiments.

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