

# The Basics of Chemical Phosphorus Elimination with Iron and Aluminum

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## Introduction

The impetus to eliminate phosphorus from sewage came from the heavily polluted lake of Zurich in Switzerland in the 1950s. The lake had suffered from algae growth and an anaerobic deep-water zone since about 1940. Several times it was infested with burgundy algae, the first time in the twenties.

The lake of Zurich was created by the Linth glacier, about 10,000 years ago and forms, together with some neighboring smaller sister-lakes, a typical morainic landscape at the foothills of the Alps. Today on its shores and alongside of its tributaries lives a population of about 330,000 in the midst some farm country. Back in 1950, the population was 185,000.



**Fig 1:** The crescent shaped Lake Zurich. Männedorf, the village on the far shore was the place where worlds first sewage treatment plant with chemical phosphorus elimination went into operation in 1955. In the background you see the Alps.

The lake of Zurich is about 38 kilometers long and its width varies generally between 3 and 4 kilometers. Its maximum depth is 143 meters.

The lake serves as a major source of potable water, not only to the city of Zurich, but also to many villages alongside the lake. Besides its recreational value, there still is some commercial navigation on it. Mostly gravel and stones are shipped.

In the early 1950s, the first sewage treatment plants were built on the lake, with little effect to the water quality. It was the merit of Prof. E. A. Thomas (1912-1986), head of the Hydrobiological Department at the University of Zurich, to prove that phosphorus was the sole limiting factor to algae growth in the lake. Before 1950, it was disputed whether it was potassium, nitrogen or phosphorus or all three of them together.

To prove his thesis, Thomas filled large plastic bags with clear water to which he added the three fertilizers phosphorus, nitrogen and potassium in different concentrations and combinations and let them float on the lake. Thus he found out that the limiting factor to algae growth was phosphorus alone, since potassium and nitrogen were plentiful anyway on natural reasons.

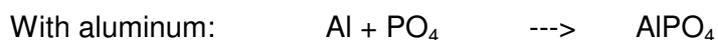
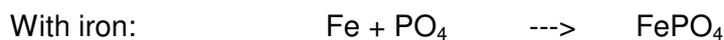
To improve the quality of the lake water, Thomas invented a simple process to eliminate phosphorus in sewage treatment plants: He added iron chloride-solution, and, as an alternative aluminum sulfate, directly to the activated sludge basin of the sewage treatment plant in Männedorf in 1955 (Swiss Patent 361 543). Today, this so called "Simultaneous Phosphorus Elimination" process is widely applied in sewage treatment all over Europe as a standard process. Most engineers today don't know that Thomas was the inventor. (By the way, Thomas never took fees from users of his patent process).



Fig. 2:  
Prof. Eugen A. Thomas in 1983,  
aged 71 years  
Inventor of the simultaneous  
phosphorus precipitation in 1955

### Theory:

Phosphorus is precipitated with iron- or aluminum-salts as ironphosphate or aluminumphosphate according to the following equations:

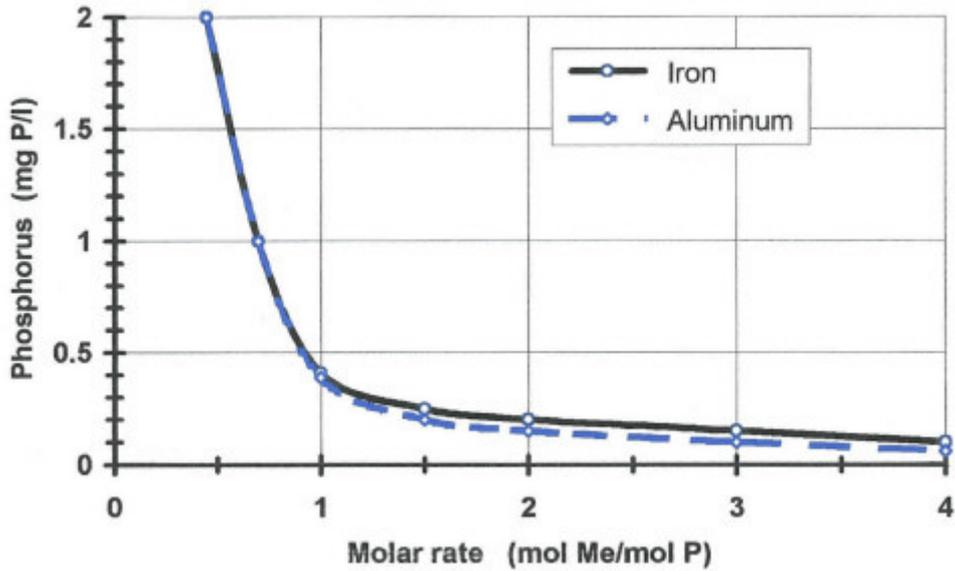


The precipitation with aluminum is slightly better than with iron. Look [Fig. 2](#).

According to the mass-action law the remaining phosphorus concentration is inversely proportional to the molar surplus of metal salt. So the solubility (Sol) may be computed as:

$$\text{Sol} = K \cdot \frac{[\text{mol Me}]}{[\text{mol P}]} = \text{mg P/l} \quad (\text{whereby K is the solubility constant and "Me" stands for "metal", - iron or aluminum})$$

That means: By doubling the metal concentration the remaining phosphorus concentration is always cut by half as demonstrated in [Fig. 2](#).



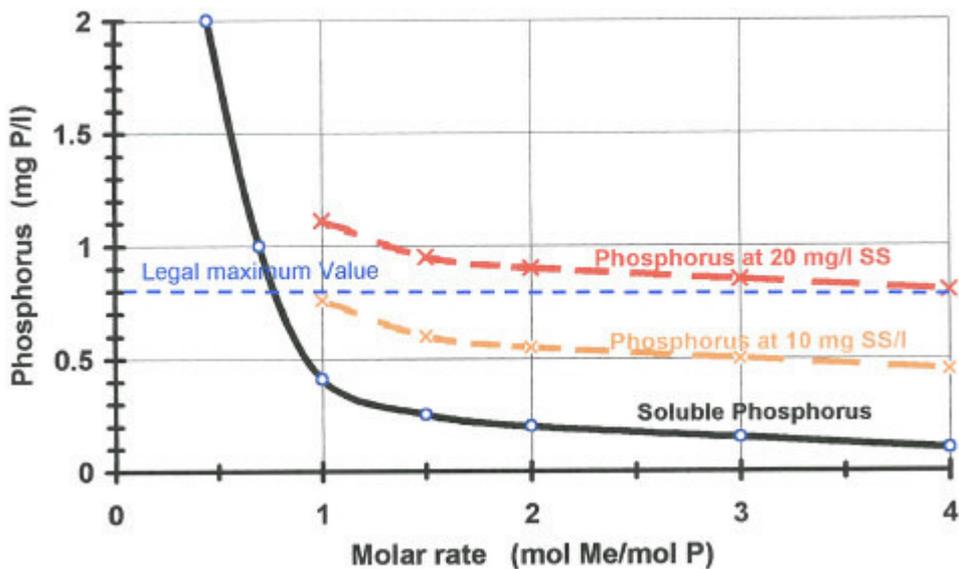
**Fig. 2:** Precipitation of a  $\text{NaH}_2\text{PO}_4$ -solution with Iron chloride and Aluminum sulfate at pH 7.5 Among Swiss sewage engineers, the mol-rate is called  $\beta$ -value

### Practical Application:

The role of the suspended solids on the final effluent of the plant

The phosphorus concentration of the final effluent of sewage treatment plants firstly depends on the surplus of the added metal-salt as demonstrated in Fig. 2. But finally it is governed by the concentration of the suspended solids.

The phosphorus concentration of suspended solids (SS) averages 3.5% total phosphorus. Typically, a secondary clarifier discharges an effluent of 10 mg/l SS (In USA the legal limit) Maximum is 20 mg/l SS (Legal limit in Switzerland)



**Fig. 3:** Influence of the suspended solids on the concentration of total phosphorus of the effluent of a sewage treatment plant

Projected on the solubility curve in [Fig. 2](#) it can be demonstrated that the suspended solids govern the quality of the effluent far more than the concentration of the added chemicals. This graph explains why it's impossible to comply with the rules, when a plant's effluent has 20 mg/l SS (Suspended solids). Hence, a sewage treatment plant has to provide at least 15 mg/l SS or less!

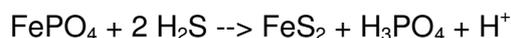
An expected phosphorus concentration may be calculated with the following equation:

$$\text{mg P/l} = \frac{0.4}{\beta} + (\text{SS} \cdot 0.035)$$

## How Phosphorus bonds to the digested sludge

In the early 1960's the simultaneous chemical phosphorus elimination theory came under heavy enemy fire. Karl Wuhrmann, then professor for waste water biology at the 'Swiss Federal Institute of Technology' in Zurich, joked about Thomas and claimed that through the digesting process of the biological surplus sludge, phosphorus will be released again to the plant. (See publication Thomas: "Phosphat-Elimination in der Belebtschlammanlage von Männedorf und Phosphat-Fixation in See- und Klärschlamm" (Vierteljahresschrift der Naturforschenden Gesellschaft in Zurich, pages 419-434 (1965)), where he argued against it. I was a student of Prof. Karl Wuhrmann then, so I'm reporting this firsthand.

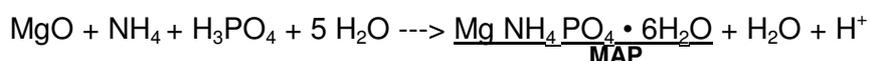
That would mean the precipitated phosphorus would return to the activated sludge process with the supernatant from the digester again and again, which would call for ever more ironchloride to precipitate it. Here we will see "a cat, chasing it's own tail". The argument that sounds convincing to a chemical engineer is:



H<sub>2</sub>S (hydrogen sulfide-gas) is plentiful and omnipresent in any digester. It is a product of the decomposition of proteins and sulfate in digesters. The solubility of iron sulfide is far worse than that of iron phosphate what shifts the above equation towards the iron sulfide-side of the equation. Here we see the phosphorus released indeed. I admit, some of the phosphorus of the digested sludge is bound by the surplus Iron after all hydrogen gas is consumed. But the surplus iron added to the activated sludge never would compensate the released phosphorus.

As a consequence of Wuhrmanns argument, Thomas made digesting tests in his laboratory with sewage-sludge and also with lake-sediments. He could prove, that the phosphorus was not released on digesting. With this finding everyone went back to normal and no one ever investigated why phosphorus remained fixed in the digested sludge. (When something goes well, why investigate why it does so?)

In the 1980s, - twenty years later, I was involved in a study to precipitate ammonium simultaneously with the digesting process. By adding magnesia and phosphoric acid to the fresh sludge, ammonium reacts as



MAP is the short for '**m**agnesium **a**mmonium **p**hosphate'. It forms characteristic triangular, flat plates, most about half a millimeter in size. Through my weeks long study I became familiar with this type of crystal.

To my surprise I later found the same crystals were abundant in any digester. That explained why Thomas was right and Wuhmann surprisingly erred. Magnesium and ammonium are plentiful in all digesters, so the released phosphorus binds as MAP. Secret solved!



**Fig. 4:**

Typical MAP crystals in the digested sludge of the sewage treatment plant Tobl, S. Lorenzen (South Tyrol, Italy). Original size: 0.2 mm.  
Photo courtesy Dr. K. Engl, general manager

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