



(MARCH TO DECEMBER 2001)

Sylvia REGY

Denis MANGIN

Jean Paul KLEIN

Joseph LIETO

# **PHOSPHATE RECOVERY BY STUVITE PRECIPITATION IN A STIRRED REACTOR**

## **TABLE OF CONTENTS**

<b>TABLE OF CONTENTS.....</b>	<b>2</b>
<b>INTRODUCTION .....</b>	<b>5</b>
<b>1 CRYSTALLISATION &amp; PRECIPITATION (KLEIN AND DAVID).....</b>	<b>6</b>
1.1 GENERALITY .....	6
1.2 SOLUBILITY.....	7
1.3 SUPERSATURATION .....	8
1.4 NUCLEATION.....	10
1.5 INDUCTION TIME.....	11
1.6 GROWTH.....	11
1.7 AGGLOMERATION.....	12
<b>2 PHOSPHATE CHEMISTRY .....</b>	<b>13</b>
2.1 CALCIUM PHOSPHATE.....	13
2.1.1 Solubility.....	13
2.1.2 The thermodynamics “driving force” .....	13
2.1.3 Precursor phases.....	14
2.1.4 Inhibitors.....	14
2.2 STRUVITE (MAP).....	14
2.2.1 Generality and solubility.....	14
2.2.2 Supersaturation .....	15
<b>3 THE DIFFERENT WORKS ON P-RECOVERY (FBR, AIR AGITATED COLUMN, ...).....</b>	<b>16</b>
3.1 BATTISTONI’S WORKS .....	16
3.1.1 Pilot unit (September 1999) in batch mode.....	16
3.1.2 Pilot unit (1998) in a continuous mode.....	17
3.1.3 Treviso plant, Italia (2001).....	18
3.2 UNIKITA RECOVERY PLANT OF STRUVITE (UENO AND FUJII) .....	19
3.3 PRODUCTION UNIT OF MAP (MÜNCH ET AL.).....	20
3.4 A PILOT PLANT STUDY ON USING SEAWATER AS MAGNESIUM SOURCE FOR STRUVITE PRECIPITATION (KUMASHIRO ET AL.).....	21
3.5 THE CRYSTALACTOR® (PIEKEMA AND GIESEN) .....	22
3.5.1 Principle.....	22

---

3.5.2	<i>Crystalactor application (wastewater treatment plant at Geestmerambacht, the Netherlands..</i>	22
3.6	PILOT PLANT OF STRUVITE RECOVERY FROM WASTEWATER HAVING LOW PHOSPHATE CONCENTRATION (MITANI ET AL.) .....	23
3.7	PILOT UNIT OF STRUVITE PRODUCTION (OHLINGER ET AL.) .....	25
<b>4</b>	<b>STIRRED REACTOR: GENERALITY, EXPERIMENTAL SET-UP AND METHODOLOGY</b>	<b>26</b>
4.1	GENERALITY .....	26
4.2	DIFFERENT TYPES OF AGITATORS .....	26
4.3	DESCRIPTION OF THE EXPERIMENTAL SET-UP.....	27
4.3.1	<i>Reaction zone</i> .....	27
4.3.2	<i>Settling zone</i> .....	28
4.4	MATERIALS AND METHODS .....	29
4.4.1	<i>Introduction</i> .....	29
4.4.2	<i>Preparation of the solutions</i> .....	29
4.4.3	<i>Seed materials</i> .....	33
4.4.4	<i>Running conditions</i> .....	33
4.4.5	<i>Analysis</i> .....	33
4.4.6	<i>Experimental methodology</i> .....	33
<b>5</b>	<b>EXPERIMENTS OF SAND COATING (SEMI-BATCH EXPERIMENTS)</b> .....	<b>35</b>
5.1	EXPERIMENT 1 : COARSE SAND .....	35
5.1.1	<i>Operating conditions</i> .....	35
5.1.2	<i>Results</i> .....	36
5.2	EXPERIMENT 2 : THIN SAND.....	37
5.2.1	<i>Operating conditions</i> .....	37
5.2.2	<i>Results</i> .....	37
5.3	DISCUSSION.....	39
<b>6</b>	<b>EXPERIMENTS WITH SEEDING: STRUVITE SUPPLIED BY UNITIKA</b> .....	<b>40</b>
6.1	SEED MATERIALS: UNITIKA STRUVITE .....	40
6.2	EXPERIMENT 3: SEEDING WITH UNITIKA STRUVITE .....	43
6.2.1	<i>Operating conditions</i> .....	43
6.2.2	<i>Results</i> .....	44
6.3	EXPERIMENT 4: SEEDING WITH UNITIKA STRUVITE .....	45
6.3.1	<i>Operating conditions</i> .....	45

---

6.3.2	<i>Results</i> .....	47
6.4	ELUTRIATION OF THE UNITIKA PELLETS .....	47
6.4.1	<i>Description</i> .....	47
6.4.2	<i>Terminal falling velocity</i> :.....	48
6.5	EXPERIMENT 5: SEEDING WITH ELUTRIATED UNITIKA STRUVITE.....	51
6.5.1	<i>introduction</i> .....	51
6.5.2	<i>Operating conditions</i> .....	51
6.5.3	<i>Results</i> .....	53
6.6	DISCUSSION.....	54
<b>7</b>	<b>EXPERIMENTS WITHOUT SEEDING .....</b>	<b>55</b>
7.1	EXPERIMENT 6: NO SEEDING .....	55
7.1.1	<i>Operating conditions</i> .....	55
7.1.2	<i>Results</i> .....	56
7.2	EXPERIMENT 7: NO SEEDING .....	58
7.2.1	<i>Operating conditions</i> .....	58
7.2.2	<i>Results</i> .....	60
7.3	DISCUSSION.....	62
	<b>CONCLUSION .....</b>	<b>63</b>
	<b>BIBLIOGRAPHY .....</b>	<b>64</b>
	<b>APPENDICES.....</b>	<b>65</b>

## **INTRODUCTION**

Phosphorus, which is the eleventh most common element on Earth, is essential to all organisms. In particular, alongside nitrogen, it is one of the main plant nutrient.

Around 80% of phosphate produced by the world's industry today are used in fertilisers, with a further 5% being used to supplement animal feeds. These phosphates are manufactured from phosphate-containing rock mined from deposits in several countries. Around 140 million tonnes of phosphate rock are extracted each year across the world.

The conventional phosphate removal technique applied for the wastewater treatment is based on phosphate fixation in activated sludge. The processes unfortunately generate huge amounts of a water-rich sludge which has to be disposed off at continuous increasing costs.

An alternative would be to intercept a significant proportion of phosphorus by phosphates precipitation in wastewaters. Phosphorus could then be recycled into industrial processes instead as simply being transferred to sewage sludges as a residual. This would also reduce the quantities of sludge generated.

It exists other techniques, for example, the KEPRO process (phosphate –as well as 3 other products- removal from sludge, based on thermal hydrolysis with sulphuric acid), or the REM NUT process (P, NH<sub>4</sub> and K removal through selective ion exchange followed by struvite precipitation in proper conditions).

This work focuses on phosphate removal by precipitation. Numerous studies have been reported in literature on this subject. The reactors tested are mainly fluidised bed reactors (FBR) and the phosphate is mainly recovered as calcium phosphate or struvite (MAP, Magnesium Ammonium Phosphate, principally). Our choice turned to the struvite precipitation. Owing to the need of having a simple and flexible technology, a new reactor was designed. This reactor is composed of a mixing zone in which precipitation takes place and a settling zone to keep the solid particles inside of the reactor. Thus, the reactor is operated in continuous mode with the liquid phase and batchwise with the solid particles. This operating mode is needed by the low phosphate concentration level in wastewater. FBR are also operated with this mode but the reactor developed in this current study is much more easy to operate. It should also accept more easily variations in wastewater works parameter.

After a description of the theory on crystallization and precipitation, a brief description of the calcium phosphate and struvite chemistry will be presented. Then, we will describe the different processes developed in literature for P-recovery.

The last parts deal with the study of the feasibility of our new reactor. Phosphate is recovered as struvite (Magnesium Ammonium Phosphate) which is precipitated by sodium hydroxyde and magnesium chloride addition. The pH studied vary from 8 to 9.2 and the molar ratios Mg/P go from 0.9 to 1.5. Two different seed materials (sand and struvite pellets supplied by Unitika) are tested. The seeded experiments are finally compared with unseeded precipitations.

# **1 CRYSTALLISATION & PRECIPITATION (KLEIN AND DAVID)**

## **1.1 Generality**

Precipitation (also named reaction crystallization) is an area for which aspects of crystallization as well as reaction engineering are very important.

The crystallisation is a change of state, starting from a gaseous or liquid phase and leading to a solid phase called crystal with a regular and organised structure.

In the industry, the crystallization is an important operation of chemical engineering. We distinguish three sorts of crystallization:

- crystallization in gaseous phase or desublimation
- melt crystallization
- crystallization in solution

There are two steps in the solid apparition:

- the nucleation (crystals birth, which can be of several types)
- the growth (crystals development)

Other mechanisms can also occur simultaneously, during a crystallization process:

- ▣ agglomeration
- ▣ breakage
- ▣ Ostwald ripening

The important parameter (i.e; the driving force) of the crystallization is the supersaturation. Several methods can be used to obtain a supersaturated solution.

In classical crystallization, crystals can be obtained from a solution by cooling, by increasing the concentration of the solute through the solvent evaporation, or by combining these two processes when solvent evaporation is used both for cooling and for concentrating.

Precipitation differs from these classical methods in the way that the supersaturation, no longer results from an action on the physical properties of the solution. It is obtained by a chemical reaction between two soluble components, leading to a less soluble product which crystallizes. The reactants used can be molecules or ions. The reactants can lead to an intermediate soluble molecule, which afterward becomes solid, or to a sparingly soluble specie which directly precipitates. However, in both cases, the reaction and the crystallization occur simultaneously and both reaction kinetics and crystallization kinetics have to be taken into account. So it will be necessary to consider the crystallizer as a chemical reactor with complex kinetics and to apply the chemical reaction engineering methodology for its characterization.. The solids generated can be crystalline or amorphous.

Thanks to the way the supersaturation is generated, high supersaturation levels can be reached in precipitation. The supersaturation will be particularly high if the solubility is low (which is often the case with the components produced by precipitation). This induces very high nucleation kinetics. Conversely, growth will be weak, resulting in small particles of generally only few micrometers.

Industrial precipitations are also highly sensible to hydrodynamic conditions which can strongly affect the size distribution of the particles produced. Mixing effects which can occur in precipitation have to be considered in two ways: (a) the global homogeneity of the vessel ; (b) the local mixing effects, particularly at the feed point of the reactants. At this point, the local supersaturation can be very high and high primary

nucleation rates can be observed although particles are already present in the crystallizer. Mixing effects will occur if reaction and crystallization kinetic rates are faster or of the same order of magnitude than the mixing process rates, resulting in competition among mixing, reaction, and nucleation. The mixing kinetics will then have a strong effect on the number of crystals formed and consequently on their size.

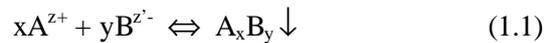
Due to the complexity of the reaction crystallization, the following steps are to be studied:

1. The kinetics of the chemical reaction leading to supersaturation. These kinetics are often very fast, especially when combining ionic species or fast acid-base reactions. In some cases they may be complex for gas-liquid reactions or for organic reactions between molecules, for example.
2. The kinetics of crystallization, including primary and secondary nucleation, growth, agglomeration, breakage and Ostwald ripening. The growth of ionic component, can be rather complicated, because the surface diffusion and integration of several ions have to be taken into account. Ostwald ripening can be an important mechanism during the precipitation of very small particles.
3. The kinetics of mixing, which can have a strong effect if reaction and crystallization kinetic are of the same order of magnitude. In this case macromixing and mixing down to the molecular level, called micromixing, have to be considered.

## 1.2 Solubility

Two different possibilities are to be considered:

1. The chemical reaction leads to a more or less soluble molecule P, which then crystallizes. For such problems, the solubility of component P can be described as the molar concentration  $C_p$  of P in the solution at the thermodynamic solid liquid equilibrium. This concentration generally increases with temperature.
2. The chemical reaction does not lead to an intermediate soluble species, and the solid crystallizes directly from the reaction, leading to a sparingly soluble salt, between a cation  $A^{z+}$  and an anion  $B^{z'-}$ .



with the electroneutrality condition:

$$xz = yz' \quad (1.2)$$

It is necessary to quantify the effect of the concentrations of the two ionic species  $[A^{z+}]$  and  $[B^{z'-}]$ , and the thermodynamic equilibrium will be described by the solubility product  $K_a$ , which is a function of temperature and is defined by:

$$K_a = a_{Ae}^x a_{Be}^y \quad (1.3)$$

where  $a_{Ae}$  is the activity of the cation  $A^{z+}$  and  $a_{Be}$  the activity of the anion  $B^{z'-}$  at equilibrium, given by

$$a_{Ae} = f_z [A^{z+}]_e \quad (1.4)$$

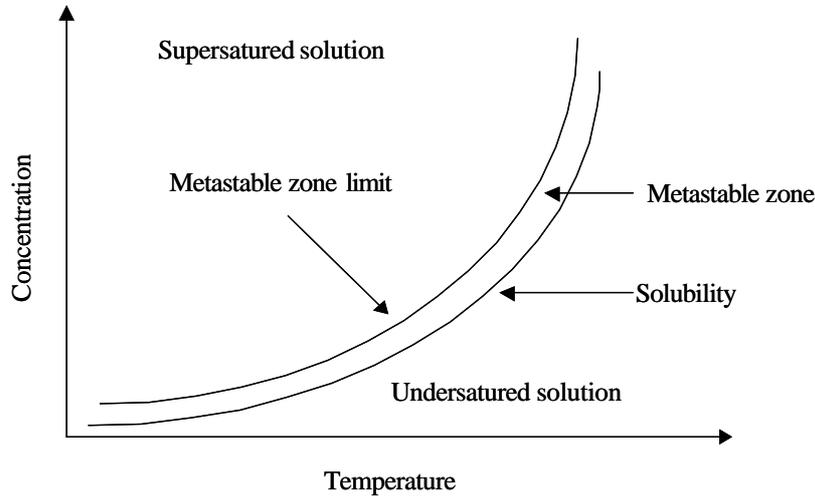
$$a_{Be} = f_{z'} [B^{z'-}]_e \quad (1.5)$$

$[A^{z+}]_e$  and  $[B^{z'-}]_e$  are the molar concentrations of the two ions at equilibrium conditions.  $f_z$  and  $f_{z'}$  are the activity coefficients of ions  $A^{z+}$  and  $B^{z'-}$ .

The solubility of the electrolyte  $A_xB_y$  can be expressed by a concentration  $C^*$  at thermodynamic equilibrium, calculated from

$$c^* = \frac{[A^{z+}]_e}{x} = \frac{[B^{z'-}]_e}{y} \quad (1.6)$$

The representation of this concentration as a function of temperature is called the solubility curve, and generally increases with temperature (see Fig. 1).



**Fig. 1 : solubility and metastable zone**

### 1.3 Supersaturation

In the case of precipitation of molecular components, the driving force of the crystallization is the difference between the chemical potential of the solute in the supersaturated liquid phase and in the solid. At equilibrium conditions, these two chemical potentials are equal. The chemical potential of the solute on the crystal can then be expressed as the potential of the solute in the solution at equilibrium:

$$\mu^* = \mu_0 + RT \ln(a^*) \quad (1.7)$$

where  $T(K)$  is the absolute temperature,  $\mu_0$  is the standard chemical potential of the crystallizing product and  $a^*$  its activity in the solution at equilibrium.

Since the chemical potential of the solute in the supersaturated solution is given by:

$$\mu = \mu_0 + RT \ln(a) \quad (1.8)$$

The driving force of the crystallization is then equal to:

$$\Delta\hat{\mu} = RT \ln \frac{a}{a^*} = RT \ln \frac{f C}{f^* C^*} \quad (1.9)$$

Considering  $f \approx f^*$ , (which is a reasonable approximation if the supersaturation is not too high), the supersaturation can finally be defined by :

$$\hat{a} = C/C^* \\ \text{or } \hat{\sigma} = (C - C^*)/C^* \quad (1.10)$$

In the case of an ionic solid, one has to consider the two ions, with the stoichiometry:



and the chemical potential to be used can be written

$$\mu = x\mu_A + y\mu_B \quad (1.12)$$

where

$$\mu_A = \mu_{A0} + RT \ln(a_A) \quad (1.13)$$

$$\mu_B = \mu_{B0} + RT \ln(a_B) \quad (1.14)$$

are, respectively, the chemical potentials of ions  $\text{A}^{z^+}$  and  $\text{B}^{z^-}$ . The driving force of the crystallization is in this case

$$\begin{aligned} \Delta\mu &= x(\mu_A - \mu_A^*) + y(\mu_B - \mu_B^*) \\ &= RT \ln \frac{a_A^x a_B^y}{a_A^{*x} a_B^{*y}} \end{aligned} \quad (1.15)$$

The last expression can be written

$$\Delta\mu = RT \ln \frac{a_A^x a_B^y}{K_a} \quad (1.16)$$

In this expression,  $\Delta\mu$  is the difference in chemical potential for one salt molecule  $\text{A}_x\text{B}_y$ , and the supersaturation can be defined as:

$$S = \frac{a_A^x a_B^y}{K_a} \quad (1.17)$$

Sometimes, the supersaturation is also defined by:

$$S' = S^{1/(x+y)} \quad (1.18)$$

Assimilating the activities to the concentrations (which is possible at sufficiently reasonable supersaturation),  $S$  can finally be given by:

$$S = \frac{c_A^x c_B^y}{K_c} \quad (1.19)$$

However, in precipitation processes, the supersaturation can have very high local values, particularly at the introduction points of reactants if the reaction kinetics are fast. Expression (1.19) can then no longer be applied and equation (1.17) or (1.18) has to be used in the expressions of the primary nucleation kinetics and of the growth rate of the formed nuclei. This high supersaturation explains the difference between precipitation and classical crystallization and allows us to understand the effects of mixing on crystal size. A high complexity level and difficulties in modelling the obtained phenomena result.

## 1.4 Nucleation

The nucleation corresponds to the apparition of new particles. Several mechanisms are possible, depending on the supersaturation level in the crystallizer.

Homogeneous primary nucleation corresponds to nuclei apparition directly in the supersaturated solution.

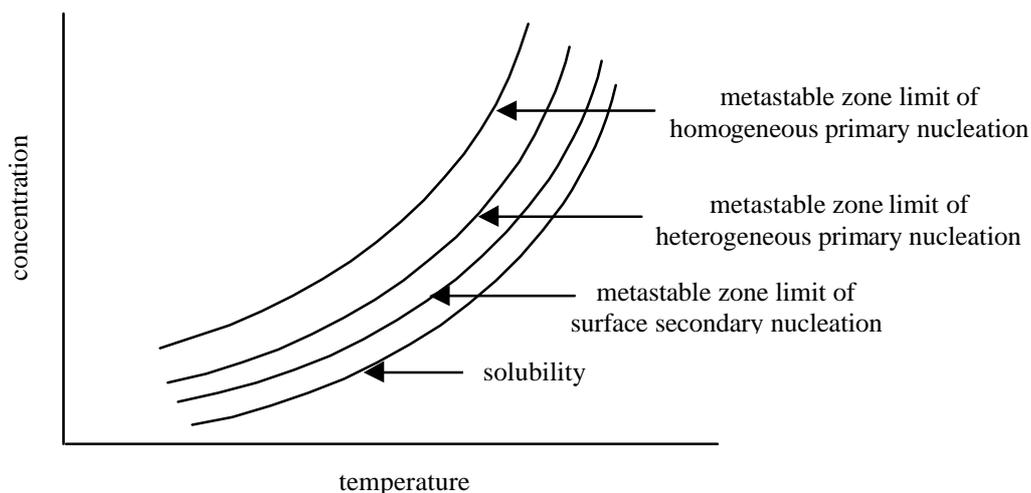
Heterogeneous primary nucleation takes place on foreign surfaces which can be dust in suspension or parts of the crystallizer itself.

Surface secondary nucleation, also called true secondary nucleation, needs to have already in suspension particles of the same specie as the solid which is crystallized. Indeed, surface secondary nucleation corresponds to the nuclei formation on the surface of these particles. The new born surface nuclei are then detached by the shear exerted by the fluid or by shocks undergone by the particles.

These three nucleation types are “activated processes”. This means that, we will have a metastable zone for each of these mechanisms. The nucleation rate of the mechanism under consideration is negligible within its own metastable zone and increases rapidly if its metastable zone limit is exceeded. Figure 1bis shows the relative positions of the metastable zone limits relating to the different nucleation mechanisms. Among the different nucleation mechanisms, homogeneous primary nucleation requires the highest supersaturation level to spontaneously develop. It is followed by heterogeneous primary nucleation and surface secondary nucleation, respectively.

Contact secondary nucleation is also induced by particles of the same specie as the solid which is crystallized. It is simply due to the attrition of these particles, essentially provoked by the shocks undergone by the particles. This mechanism is not an activated process and exists then whatever the supersaturation is. However, it is generally negligible compared with the other mechanisms, when the supersaturation is sufficiently high to induce these other mechanisms.

The last nucleation type is the apparent secondary nucleation. It occurs with seeded crystallizations, when fines, issued from crystal attrition, are “stick” on the seed crystals by static electricity. These fines, which existence in the seed is generally not detected, correspond in fact to crystals which will grow during the crystallization process and which will then affect the final crystal size distribution.

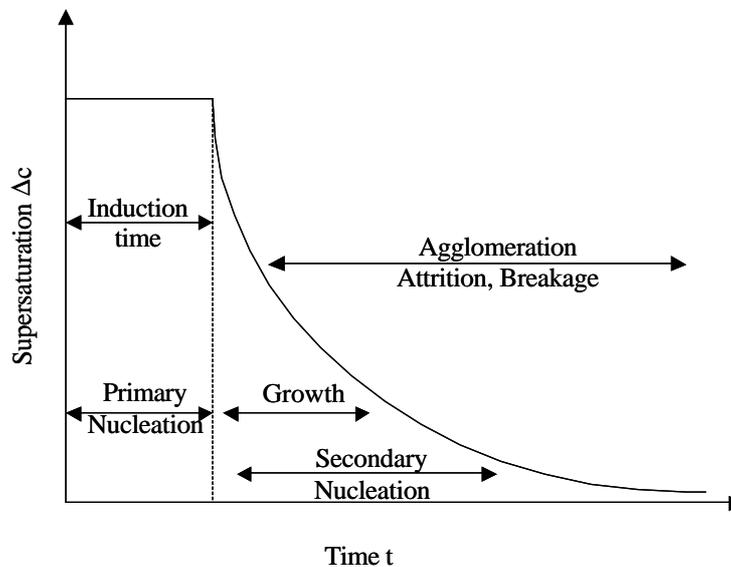


**Fig.1 bis: the different metastable zone widths**

## 1.5 Induction time

Let us consider a batch crystallization performed under perfect mixing conditions. Fig.2 represents the evolution of the supersaturation. All the reactants are introduced at  $t=0$ . Then, a certain lapse of time called induction time is necessary for the crystallization to begin on an observable level. This initial period obviously depends on the kinetics of the different processes involved:

1. The kinetics of mixing.
2. The chemical reaction kinetics.
3. The nucleation rate, which leads to the apparition of crystals.
4. The growth rate of particles formed. Indeed, the initial nuclei are too small and do not contain enough mass to be detectable. It is necessary for them to growth to become observable.



**Fig. 2 : supersaturation versus time during a batch reaction crystallization with premixed reactives, induction time, and relevant mechanisms**

If the reaction and mixing kinetics are very rapid, the induction time can be shared in two parts:

$$t_{\text{ind}} = t_N + t_G \quad (1.20)$$

where  $t_N$  is the time necessary for nucleation and  $t_G$  is the time necessary for sufficient growth.

In fact, significant induction time can be observed only if the initial supersaturation is such that we are in the metastable zone of primary nucleation. Indeed, for supersaturation exceeding the metastable zone limit, the induction time becomes too short to be observable.

If mixing and reaction kinetics are not rapid, they will introduce their own time scale in the value of  $t_{\text{ind}}$ . Reaction time  $t_R$  and mixing time at both macroscopic and microscopic scales will then influence the initial induction of the reaction crystallization processes.

## 1.6 growth

Growth is generally described as a two-steps process: a mass transfer process across the diffusion layer surrounding the crystal, followed by a surface integration mechanism of the solute into the crystal. The global growth kinetics depend then on the kinetics of each step. Thus, if the mass transfer kinetics are much

lower than the integration kinetics, growth is controlled by diffusion. On the contrary, growth will be controlled by surface integration if the solute transfer is much more rapid than the solute surface integration.

In the case of direct precipitation of ionic crystals without any dissolved intermediate, models used for crystal growth are more complicated. Indeed, classically described surface integration and diffusion apply simultaneously to the different ionic species, with respect to the electric neutrality of the crystal and the solution.

## **1.7 Agglomeration**

Unlike nucleation and growth, agglomeration is not a phenomenon occurring in all crystallization processes. Its existence depends on the crystallizing system in terms of physicochemistry and technology, and on crystallization conditions. It arises if crystals stick together to generate new, larger particles. Three types of agglomeration processes may be distinguished:

1. If the cohesion forces are weak, the agglomeration is called flocculation.
2. If the supersaturation sticks the agglomerating crystals strongly together, the processes is called agglomeration.
3. For intermediate processes and for processes arising without supersaturation, one speaks of aggregation.

During crystallization processes, agglomeration in the presence of supersaturation or aggregation without supersaturation are essentially observed. To obtain agglomerates, three successive steps have to occur: (a) the collision of two particles, (b) a sufficient period during which the two particles stay together, and (c) adherence of the two particles with the help of supersaturation. The key parameters of this operation are then:

1. The hydrodynamic conditions (mixing, local turbulence, etc.)
2. The nature of the solvent (viscosity, density, etc.).
3. The size and habit of the crystals, which may have a strong influence on the first two steps. So, for small particles, agglomeration will be very important.
4. The population density of the crystals, which has a very important direct influence on the collision frequency, and so on the first step of the agglomeration process.
5. Supersaturation and the related growth rate, with an effect on the sticking step.
6. The cohesion forces between the solvent, impurities, and the crystals, which are very important for the second step.

Agglomeration is a very important process during reaction crystallization since the particles are very small and rather insoluble.

## **2 PHOSPHATE CHEMISTRY**

### **2.1 Calcium phosphate**

Phosphate calcium can exist as several forms (cf. [Table 1](#)), depending on the pH and the solution composition. The phase which precipitates mainly is the most thermodynamically stable phase, i.e. hydroxylapatite (HAP). The calcium phosphate recovered in the waste water are used in the phosphorus industry.

#### **2.1.1 Solubility**

The different forms of calcium phosphate are reported in the Table 1.

Compounds	Formula	Molar ratios	pK*	pK à 20°C
DCPD (dicalcium phosphate dihydrate)	CaHPO <sub>4</sub> *2H <sub>2</sub> O	1	pK <sub>DCPD</sub> =3649.6/T-18.181+0.04203T	6.59
DCPA (monetite)	CaHPO <sub>4</sub> (Anhydrous DCPD)	1		
OCP (octacalcium phosphate)	Ca <sub>4</sub> H(PO <sub>4</sub> ) <sub>3</sub> *2.5H <sub>2</sub> O	1.33	pK <sub>OCP</sub> =50.606 à 20°C	
ACP (amorphous calcium phosphate)	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	1.5	No solubility product for an amorphous	
HAP (hydroxylapatite)	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH	1.67	pK <sub>HAP</sub> =8219.41T+1.6657+0.098215T	58.5
TCP (tricalcium phosphate)	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	undefined	pK <sub>TCP</sub> =45723.26/T-287.4536+0.546763T	28.8

**Table 1 : Different forms of calcium phosphate**

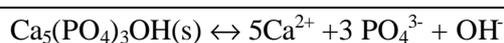
\*reference : Y. Song, H.H. Hahn, and E. Hoffmann.

The solubility of calcite decreases when the temperature increases whereas the solubility of calcium phosphate increases when the temperature increases.

In the wastewater, where ion association is significant (due to high ionic strength), the free ion concentrations contributing to saturation will be lower than the total ion concentration, and thus significant supersaturation is necessary for precipitation to occur.

The different phases of calcium phosphate depend on the pH and the composition of the solution.

Dissolution of HAP:



#### **2.1.2 The thermodynamics “driving force”**

The most important factors are the temperature of the reaction, the chemical speciation of the solution and the solubility product of the mineral. As stated before, the solubility of calcite decreases with increasing temperature whereas the solubilities of calcium phosphate minerals increase with the temperature. However for both HAP and OCP, the solubility trends reverse at higher temperatures in the region 15-20°C (W.A. house).

The degree of saturation,  $\Omega$  (which corresponds in fact to the supersaturation denoted  $S$  in part 1), and the saturation index,  $SI$ , of a solution with respect to mineral phase, are defined as :

$$\dot{U} = \frac{I_{AP}}{K_{sp}} \text{ is the thermodynamic solubility product and } I_{AP} \text{ the ion activity product}$$

$$SI = \log(\dot{U})$$

The formation of calcium phosphate salts in aqueous solutions takes place following the development of supersaturation. Supersaturation is a measure of the deviation of a dissolved salt from its equilibrium value. Supersaturation may be developed by increasing the aqueous medium content in calcium and/or the pH. Moreover, a temperature increase contributes to solution supersaturation development because the sparingly soluble calcium phosphate salts have reverse solubility (Koutsoukos).

### **2.1.3 Precursor phases**

Primary nucleation, or spontaneous nucleation may not involve the formation of the most thermodynamically stable phase but normally the formation of a “precursor phase” with a higher solubility than the stable phase. Then, eventually, this precursor phase recrystallizes as HAP, the most thermodynamically stable phase. Depending on the conditions, precursor phases are : DCPD ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ), OCP ( $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 2.5\text{H}_2\text{O}$ ), TCP ( $\text{Ca}_3(\text{PO}_4)_2$ ), ACP ( $\text{Ca}_3(\text{PO}_4)_2$ ).

At  $\text{pH} > 9$  ACP transforms directly in HAP.

At a pH range of 7-9, the transformation is the following:  $\text{ACP} \rightarrow \text{OCP} \rightarrow \text{HAP}$ , the conversion rate depends on the temperature and the pH.

At very high supersaturation,  $SI > 10$ , it is difficult to think that HAP precipitates alone because of the spontaneous formation of the precursor phase as ACP or OCP.

### **2.1.4 Inhibitors**

A number of ions have been shown to act as inhibitors to precipitating phases, by forming a surface complex on the newly forming surfaces, and blocking further precipitation. These effects depend on the saturation of the solution. The inhibitor ions are mainly carbonate and magnesium. In principle, the inhibitors effects can be annihilated by an increase of the supersaturation degree. Natural amino acids with hydrophobic non-polar groups were found to inhibit HAP growth blocking active growth sites.

## **2.2 Struvite (MAP)**

Struvite in the waste water treatment plants was identified in 1939 because of deposits in the pipes. The blockage of pipes leads to an increase in pumping costs (maintenance, workforce, ...). The phosphate recovery as struvite permits its recycling in the fertiliser industry because struvite is a good slow release fertiliser.

### **2.2.1 Generality and solubility**

Struvite which crystallizes as a white orthorhombic crystalline structure is composed of magnesium, ammonium and phosphate in equal molar concentrations ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ). A general description of struvite is given in appendix 1. The specific gravity is 1.7.

The formation reaction is shown below :



Other components with potassium ( $\text{K}^+$ ) or nickel ( $\text{Ni}^{2+}$ ) can exist, but they are more rare in the waste water treatment plants.

Struvite precipitation is controlled by pH, supersaturation, temperature and impurities as calcium (Bouropoulos and Koutsoukos, 2000) and can occur when the concentrations of magnesium, ammonium and phosphate ions exceed the solubility product ( $K_{sp}$ ) for struvite. The  $K_{sp}$  is given by the following expression:

$$K_{sp} = [\text{Mg}^{2+}][\text{NH}_4^+][\text{PO}_4^{3-}] \text{ and } pK_s = 13.26 \text{ (Ohlinger).}$$

The relationship between  $K_{sp}$  and pH indicates that struvite solubility, in mg/L, decreases with increasing pH, which in turn leads to an increase in the precipitation potential of a water. A number of chemical equilibrium based models have been developed and allow reasonable prediction of struvite precipitation (Musvoto and al., 2000).

In wastewater, the struvite is highly soluble at acidic pH and highly insoluble at alkaline pH. When the pH increases the orthophosphate concentration increases whereas the magnesium and ammonium concentration decrease. So, it exists an optimum pH to precipitate struvite, the pH range is between 7 and 11. The minimum solubility in the waste water is around pH9. The minimum solubility implies a maximum potential for struvite formation. Thus, the optimal precipitation is located between pH 8 and 8.5. The turbulence influences the struvite formation. Increased turbulence leads to  $\text{CO}_2$  liberation, so an increase in pH and hence in struvite precipitation.

### **2.2.2 Supersaturation**

The supersaturation ratio  $\Omega$  can be defined as follow:

$$W = \left[ \frac{(\text{Mg}^{2+})(\text{NH}_4^+)(\text{PO}_4^{3-})_{init}}{K_{so}} \right]^{1/3}$$

### **2.2.3 Induction time**

A pH and temperature increase leads to reduce the induction time. At  $\text{pH} < 8$ , the struvite precipitation is very slow et can take several days. The induction time is significantly influenced by the supersaturation, and is also influenced, to a much lesser degree, by mixing energy (Ohlinger). This is not surprising since up to now, nothing could explain any influence of mixing on primary nucleation.

### **2.2.4 Scaling**

The surface roughness and materials of pipes influence struvite scaling. The accumulation rates is significantly lower on a plastic coupon than on a stainless-steel ones. However, the struvite accumulation rate is much more dependent on surface roughness. Surface roughness may affect the ability of nuclei to anchor, may cause local turbulence and increase local mixing, or may affect the number of surface nucleation sites available for crystal growth by increasing the total surface area.

### **3 THE DIFFERENT WORKS ON P-RECOVERY (FBR, AIR AGITATED COLUMN, ...)**

#### **3.1 Battistoni's works**

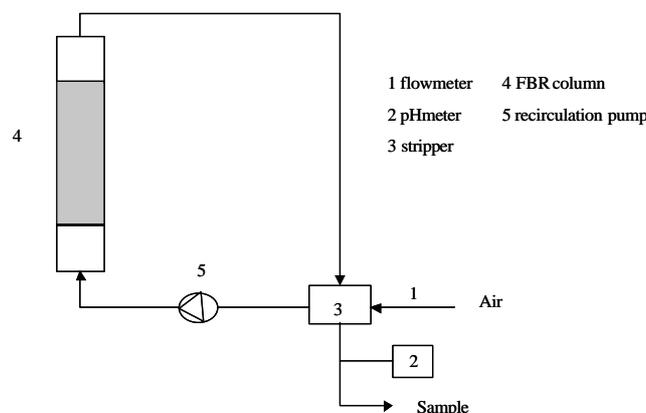
##### **3.1.1 Pilot unit (September 1999) in batch mode**

The medium alkalinity induces a high buffer capacity (effet tampon) demanding large amounts of chemical reactants to reach the operating pH (8-8.3). However, a pH of 8.0-8.5, sufficient to obtain a co-precipitation of HAP and MAP, can be easily reached by CO<sub>2</sub> stripping. The crystallization technique (i.e; for the authors crystallization on the seed material), contrary to the precipitation technique (i.e; precipitation of new fine particles in the suspension itself), allows to work in the metastable zone and requires then a lower pH. Battistoni's technique is based on fluidised bed reactor without the addition of alkali chemicals. The only CO<sub>2</sub> stripping is enough to reach the operating pH. No addition of calcium or magnesium salt is needed.

The anaerobic supernatant used for the experiments was obtained from the dewatering section (belt-press) of a 85000 equivalent inhabitants civil wastewater treatment plant, with a combined carbon oxidation and nitrogen nitrification-denitrification and anaerobic digested sludge (composition of liquors of BNR processes: 60-100 mg P/L as a consequence of the release during the digestion of waste activated sludge, a strong ammonia concentration 300-700 mg/L, magnesium ion is connected to polyphosphate release  $\Delta\text{Mg}/\Delta\text{P} = 0.26$ , calcium concentration is not correlated with P content of the sludge).

The pilot unit works in batch mode and its characteristics are the followings :

- glass column
- 58 mm internal diameter and 0.42 m high
- a fixed amount (610g) of quartz sand with size ranging from 0.21 to 0.35 mm
- a compressed bed 0.15 m high, the bed was expanded to 0.3 m
- flow rate ranging from 0.11 to 0.3 m<sup>3</sup>/h
- a stripping tank (V=5L), provided with pH measurement, was utilized with an air flow rate of 0.9m<sup>3</sup>/h
- the starting supernatant volume was three times the expanded bed



**Fig. 3 : FBR apparatus**

The scheme of the pilot unit is shown in Fig. 3.

**Problem:** Sludge liquors used contained only 24mg/L in P, corresponding to the typical phosphate concentration of a process without biological phosphorus removal. For this reason phosphates are added up to about 160 mg/L.

Three stripping configurations were used :

- outside discontinuous (OD) aeration
- outside continuous (OC) aeration
- internal continuous (IC) aeration

As already stated above, the authors distinguish the “crystallization” on seed material and the “precipitation” as fines.

For a process time (defined as the time spent in the FBR and the stripper section) comprised between 100-210 min, the global removal of phosphate (crystallized and precipitated) goes from 61.7 to 89.6, the precipitated fines representing 8.7 to 24.5% of the total phosphate removal.

The different aeration configurations affected the process time. The best operating conditions were obtained by using OC aeration for 70-100 min.

The process performance is essentially controlled by the growth rate on the seed. It is not affected by the initial concentration.

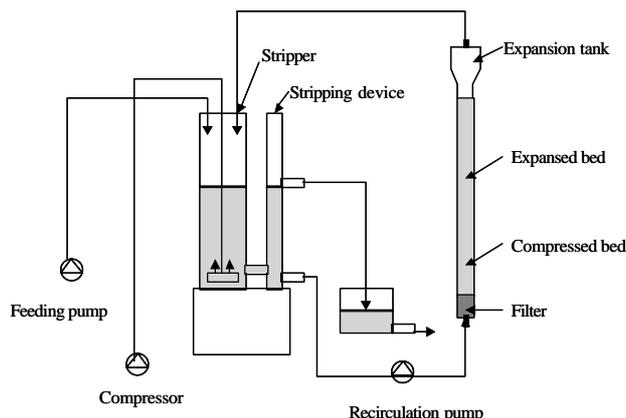
With this batch operating mode, it was not possible to avoid “precipitation” of fines. But, obviously, the results obtained can not be extrapolated to a continuous operating mode.

### **3.1.2 Pilot unit (1998) in a continuous mode**

The characteristics of of the treated water are (anaerobic liquors from A<sub>2</sub>O process):

- pH=7,7
- PO<sub>4</sub>=139 mg/L
- NH<sub>4</sub>=914 mg/L
- Ca=153 mg/L
- Mg=24 mg/L
- HCO<sub>3</sub>=3550 mgCaCO<sub>3</sub>/L
- CO<sub>3</sub>=0 mgCaCO<sub>3</sub>/L
- Ca/PO<sub>4</sub>=2,6 mol.mol<sup>-1</sup>
- Mg/PO<sub>4</sub>=0,7 mol.mol<sup>-1</sup>
- NH<sub>4</sub>/PO<sub>4</sub>=35 mol.mol<sup>-1</sup>

The pilot unit is divided in two sectors, a stripping tank (18+3 L), composed of a stripper and a stripping device, and a fluidised bed reactor ( $\phi_{int}=0.09$  m and H=1 m). This reactor is initially filled with 3.3 kg of quartz sand (0.21-0.35 mm) leading to a compress bed height of 0.4 m, and fed with anaerobic supernatant through a peristaltic pump. The flow rate varied in the range 4-19 L/h, the air flow rate in the range 15-50 L/h and the pH in the range 6.9-8.7. The recycle flow rate (230L/h) remained constant allowing a fixed expanded bed height of 1 m.



**Fig. 4: pilot unit in a continuous mode**

The precipitation of phosphates in these tests was very low whereas the crystallization varied from 59 to 88%. Efficiency is strongly related to the operating pH, the lowest result being 58.2% at pH 7.94, but even in this case no significant increase of precipitated fines is observed.

The different molar ratios exercise a strong control on HAP or MAP formation:

- If the ratio Ca/Mg increases, the HAP formation increases and MAP formation decreases.
- For a ratio Ca/Mg equal to 3.1, the HAP/MAP formation is 50-50.
- A ratio Ca/Mg equal to 1.8 gives a MAP formation ranging from 80 to 100%.
- If the ratio Ca/Mg is equal to 3.6, the MAP/HAP formation is 35/65.
- If Mg is superior at 53 mg/L, only MAP precipitates, the magnesium ions exert a strong inhibitory effect on HAP formation and the ratio Mg/PO<sub>4</sub> increases.

The low operating pH induced by the air stripping limits the lost of fines. The contact time and the pH are the main operating parameters to define the process efficiency.

### **3.1.3 Treviso plant, Italia (2001)**

The plant was built up after the tests presented above. The influent is an anaerobic supernatant produced by an A<sub>2</sub>O process.

The characteristics of the waste water are :

- Q=19600 m<sup>3</sup>/j
- Q<sub>max</sub>=1225 m<sup>3</sup>/h
- SS=4900 kg TS/j
- N<sub>tot</sub>=843 kg N/j
- P<sub>tot</sub>=118 kg P/j

The plant SCP (Struvite Crystallization Process) is composed of a pre-treatment section and of two operative sections: a stripping tank and a fluidised bed reactor. The pre-treatment section is composed of a suspended solid apparatus and of a reservoir tank to operate the FBR in a continuous mode. The stripping section is composed of a stripper connected to a de-aeration column. The anaerobic supernatant issued from pre-

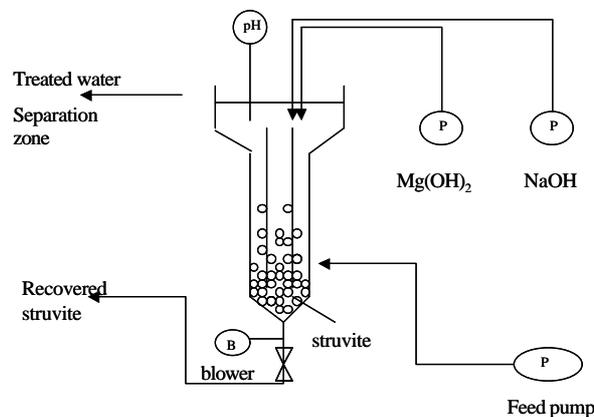
treatment, feeds the stripper, together with the recycle flow coming from FBR. The air flow rate needed for CO<sub>2</sub> stripping is injected at the bottom using ceramic aerators to obtain an operating pH of 8.3-8.7.

The reactor is a steel column ( $\phi_{in}=0.6$  m,  $H=3$  m) filled with 700 kg of virgin silica sand (0.21-0.35mm,  $\phi_m=0.265$  mm) to obtain a compress bed of 1.5 m height. At the bottom of the column a steel cylinder ( $\phi_{in}=0.6$  m,  $H=1$  m) works as a filter in order to avoid that sand returns to the pump. At the top of the column an expansion tank is added in order to avoid a loss of sand.

Note : The phosphate concentration was too low to simulate the conditions obtained in the digester, so the concentration was adjusted in adding (NH<sub>4</sub>)HPO<sub>4</sub>.

When the phosphate concentration is low, the calcite formation is coupled with MAP and HAP formation, independently of the alkalinity (1000-2500 mg/L). Moreover, the calcite formation is always coupled with a great loss of fines.

### **3.2 Unikita Recovery plant of struvite (Ueno and Fujii)**



**Fig. 5**

The site is composed of two struvite crystallization plants (500 m<sup>3</sup>/d and 150 m<sup>3</sup>/d).

The reactor used is a fluidised bed reactor agitated with air. The reactor is a vertical tower composed of two concentric cylinders. The digester effluent is introduced at the bottom of the reactor. The reactants, Mg(OH)<sub>2</sub> et NaOH, are introduced at the top of the column in order to obtain a Mg/P ratio of 1 and an operating pH of 8.2-8.8. Air is injected at the bottom of the column to provide the “mixing” and the CO<sub>2</sub> stripping. “The struvite prepared is fluidised in a fine crystal condition which grows by mutual contact”. After a residence time of the solid in the reactor of about 10 days, the crystals grow in a granular shape of 0.5 to 1.0 mm. The residence time calculated for the liquid is about 28 min ( $H=2/3 \times 9$  m, influent 500 m<sup>3</sup>/d). The struvite is extracted from the lower part of the reaction tower. The fine granular struvite contained in the separated liquid is returned to the reaction tower as seed crystal. The influent contains about 100 to 110 mg/L phosphoric acid ion (NH<sub>4</sub>-N=200 to 250 mg/L). The elimination rate is about 90% with a struvite production of 500 to 500 kg/d.

Characteristics	Struvite plant (500 m <sup>3</sup> /d)	Struvite plant (150 m <sup>3</sup> /d)
Diameter of the reaction tower (m)	1,43	0,96
Diameter of precipitating portion(m)	3,6	2,6
Total height(m)	9	5,5

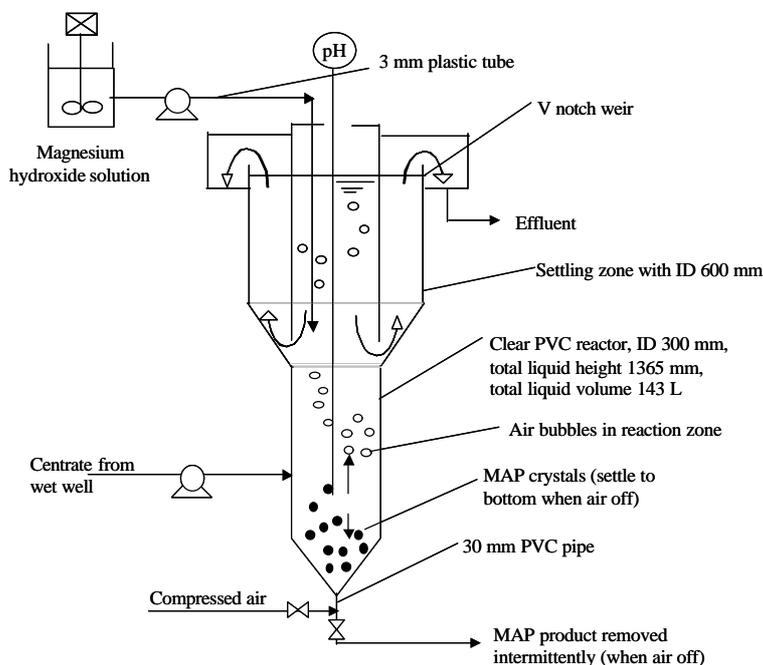
**Table 2 :** Specification of struvite plant

### **3.3 Production unit of MAP (Münch et al.)**

The influent to the MAP reactor was centrate from the centrifuge that dewateres anaerobically digested sludge at the Oxley Creek wastewater treatment in Brisbane.

A discussion on the reagents that can be used showed that :

- The advantage of using magnesium chloride (MgCl<sub>2</sub>) is that it dissociates faster than magnesium hydroxide Mg(OH)<sub>2</sub> leading to shorter reaction times.
- Magnesium hydroxide is generally cheaper.
- Magnesium hydroxide has the advantage of raising the pH but, in that case, pH and magnesium concentration can not be controlled independently.
- The addition of NaOH is more efficient than the addition of lime or Mg(OH)<sub>2</sub>.
- Aeration itself can achieve the desired pH increase but it requires longer residence times.



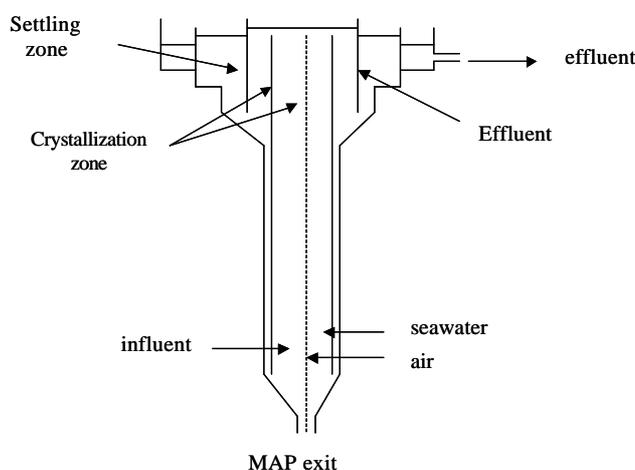
**Fig. 6 :** Diagram of pilot-scale MAP reactor with ancillary equipment

The reactor lies in the same principle as that of Unitika's reactor. The pilot-scale MAP reactor consists in a plexi-glass reactor, an influent pump, an air compressor, a magnesium/ alkali dosing pump, a pH probe and an air flowmeter (cf. Fig. 6). The total reactor volume is 143 L (reaction zone and settling zone). The internal diameters of the reaction zone and the settling zone are 300 mm and 600 mm, respectively. The total liquid height is 1365 mm.

The magnesium source used  $\text{Mg}(\text{OH})_2$  (55% w/w  $\text{Mg}(\text{OH})_2$  and 42% w/w water) provides a ratio Mg/P of 1:1.3 and induces an increase of the pH value. At the bottom of the reactor air (7 L/min in order to avoid air bubbles in the separation zone) is injected to provide the “mixing” and to put the particles in suspension. The reactor was initially seeded with 500 g of crushed and sieved (1 mm) struvite particles issued from a deposit on a pipe. The pilot-scale MAP process achieved an ortho-P removal of 94% from an influent of 61 mg/L (i.e.; effluent ortho-P concentration of 4 mg/L). A fraction of the MAP produced in the reactor was removed every five days of operation by turning the air off.

In the range of about 1-8 h, the hydraulic residence time (HRT) has no effect on the effluent ortho-P concentration (at sufficiently high magnesium dose). This is important as it means that small reactor volumes are sufficient (1-2 h HRT).

### **3.4 A pilot plant study on using seawater as magnesium source for struvite precipitation (Kumashiro et al.)**



**Fig. 7: pilot plant using seawater as magnesium source**

Seawater is a cheap magnesium source. The objective is to treat wastewater from sidestreams, such as dewatering effluent containing high concentration of ammonium ( $\text{NH}_4^+$ ) and orthophosphate ions ( $\text{HPO}_4^{2-}$ ). The dissolved phosphorus (D-P) concentration varies from 50.5 to 110 mg/L.

The reactor is composed of 2 concentric cylinders ( $H_{\text{total}}=3.7$  m,  $\phi_{\text{inner cylinder}}=200$  mm,  $\phi_{\text{outer cylinder}}=350$ mm). The reactor upper part is a settling zone of larger diameter. Air is blown into the inner cylinder at the bottom of the column. This air injection causes an upward flow in the inner cylinder and a downward flow in the annular zone. Baffles are added to guide the downward flow. Seawater represents about 10% of the total influent and contains around 1250 mg/L of  $\text{Mg}^{2+}$ . The volume of the inner cylinder is 99L while the outer cylinder has a volume of 218 L. The volume of the settling zone is of 792 L. The produced MAP particles are drawn off from the bottom of the reactor along with water by opening the solenoid valve during about 30 seconds. The produced MAP particles measure about 1 mm of diameter. The pH was controlled from 7.66 to 8.4 using NaOH to study the relation between pH and P removal efficiency. The linear velocity (LV) in the inner cylinder varied from 9.5 to 76.4 m/h and the air supply of airlift for circulation was 130 m/h.

With a feed stream containing 50.5 to 110 mg/L of dissolved phosphorus, a pH over 7.77 (not controlled), a seawater inflow representing 9.0 to 10% of the total input, a residence time of 29 minutes and a solid concentration between 4.3 and 13% in volume, more than 70% of dissolved phosphorous was removed. It was also observed that the higher the operating pH was, the better the removal efficiency was. A Mg/P ratio over 1.5 was required to achieve this efficiency of 70%.

## **3.5 The Crystalactor® (Piekema and Giesen)**

### **3.5.1 Principle**

DHV, a multi-national group of consulting engineers and general contractors with headquarters in the Netherlands, has developed and patented a fluid-bed type of crystallizer in which phosphate is removed and recovered from the wastewater while phosphate pellets with a typical diameter of 1 mm are produced. The major advantage of the crystallization technology, the so-called Crystalactor®, is that in the compact high-purity phosphate pellets are produced which have proven to be reusable. Phosphate has been successfully recovered in the form of calcium phosphate, magnesium phosphate and magnesium ammonium phosphate.

The pellet reactor is partially filled with a suitable seed material like sand or minerals. The wastewater is pumped in an upward direction maintaining the pellet bed in a fluidized state. In order to crystallize the target component on the pellet bed, a driving force is created by a reagent dosage and pH-adjustment. By selecting the appropriate process conditions, co-crystallization of impurities is minimized and high-purity crystals are obtained. The pellets grow and move towards the reactor bottom. At regular intervals, a quantity of the largest fluidized pellets is discharged from the reactor and fresh seed material is added. After atmospheric drying, readily handled and virtually water-free pellets are obtained.

The appropriate process conditions are chosen in order to minimize the primary nucleation in acting on :

- reagent overdose and pH
- supersaturation (in the reactor bottom, the supersaturation must be maintained under a critical value in order to avoid the primary nucleation)
- the hydraulic reactor load

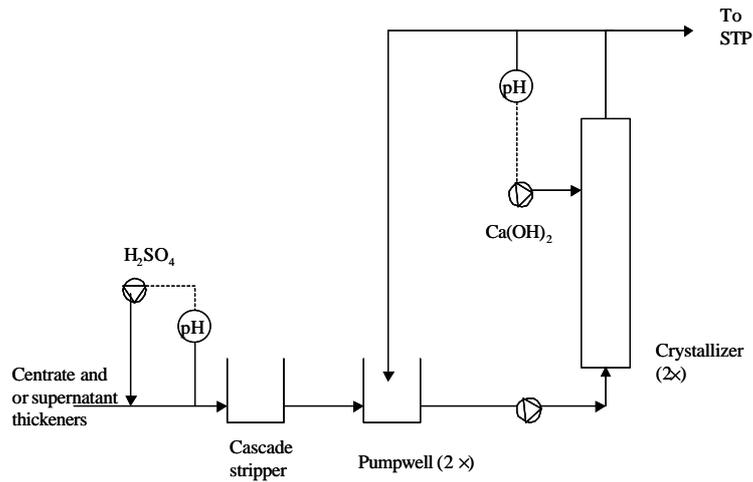
The problem of the crystalactor is due to influent flow rate. The influent rate must be constant during the treatment. An increase can lead to an increase of the secondary nucleation or a decrease not sufficient to maintain the particles in a fluidized state.

Furthermore, some amorphous phosphate is lost in a suspended form (carry-over), therefore a dual media filtration is required, that incurs additional capital and operational costs.

The crystalactor has also successful applications for removal/recovery of heavy metals, phosphate, fluoride and the softening of drinking and process water.

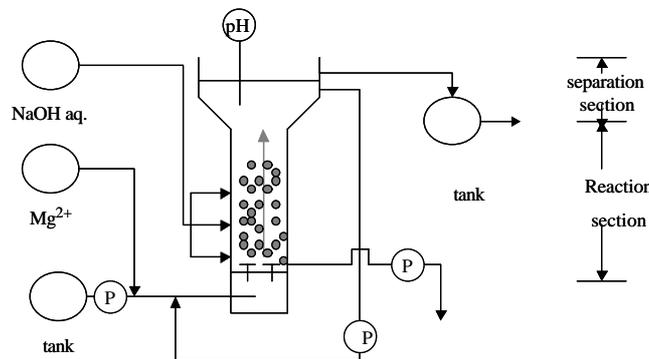
### **3.5.2 Crystalactor application (wastewater treatment plant at Geestmerambacht, the Netherlands)**

The treated effluent is an anaerobic supernatant. In order to reduce the calcite formation in the crystallizer,  $\text{CO}_3^{2-}$  is removed in a cascade stripper after having adjusted the pH value to 5 (easier stripping of  $\text{CO}_2$ ) by sulphuric acid addition (96% solution). The supernatant is then stocked in a buffer tank before entering the crystalliser. The reactor is a crystalactor®. The seed material is quartz sand. The influent is pumped through nozzles into the reactor (vertical velocity about 40 m/h). Also in the bottom  $\text{Ca}(\text{OH})_2$ -solution is added via separate nozzles, to provide an elevation of the pH-level and Ca-ions. Through the high turbulence a good mixing of P-rich water and solution is obtained. Crystallisation of calcium phosphate takes place mostly on the seeding sand, and the pellets grow. The flow rate of calcium hydroxide is controlled by pH-measurement (pH # 8). The crystallisation efficiency is enhanced by recirculation over the pump wells, by recirculation 2.5-3 times the crystallisation efficiency is about 70%. The bed height is controlled at 4-4.5 meter. The height is adjusted by extracting pellets near the bottom and subsequently adding new seeding sand.



**Fig. 8:** crystalactor application (WWTP at Geestmerambacht)

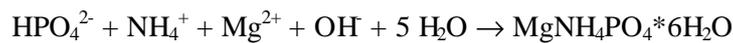
**3.6 Pilot plant of struvite recovery from wastewater having low phosphate concentration (Mitani et al.)**



**Fig. 9:** pilot plant for low phosphate concentration

P concentration was around 40 mg/L.

In batch tests, it was confirmed that the condition where struvite precipitates prior to calcium phosphate in wastewater requires the condition of  $[Ca^{2+}]/[Mg^{2+}] < 0.25$  in the influent. The formation struvite reaction is the following :



$$\log K_{sp} = -14,1$$

$$K_{sp} = r_1[Mg^{2+}] * r_2[HPO_4^{2-}] * r_3[NH_4^+] * r_4[OH^-] = 7.8 \times 10^{-15} (\text{mol/L})^4$$

This equation shows that a high pH is necessary to treat wastewater having a low phosphate concentration.

The reactor is a liquid-solid two-phase fluidized bed reactor seeded with struvite particles of about 1 mm in diameter.

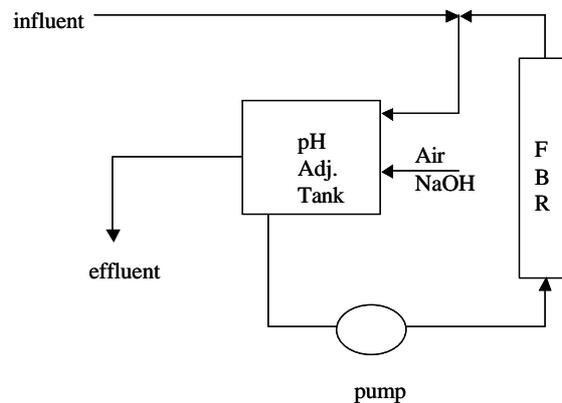
Reaction section	Diameter	0.6 m
	LV(influent and recirculation)	60 m/h
Separation section	Diameter	0.85 m
	Overflow rate	20 m/h
	Height	5.3 m
	Aeration	no
	Operating pH	8.8

**Table 3 : pilot scale reactor**

The treated flow rate was equal to 266 m<sup>3</sup>/day and the circulating effluent flow rate was equal to 133m<sup>3</sup>/day. No aeration was used.

The pH is adjusted by injecting NaOH (in the bottom of the reactor) to obtain an operating pH of 8.8 and MgCl<sub>2</sub> is added to adjust the Mg/PO<sub>4</sub> ratio. The used seed material is struvite. The struvite recovery rate is about 62%.

### **3.7 Pilot unit of struvite production (Ohlinger et al.)**



**Fig. 10 : Schematic of pilot FBR Struvite Precipitation System**

The FBR reactor works in continuous feed (with residence hydraulic times in the range of 0.7 to 7.3 hours). The influent is SRWTP (Sacramento Regional Wastewater Treatment Plant) SSB (Sludge Storage Basins) supernatant.

The process is composed of :

- tank to adjust the pH
- FBR
- feed and recirculation pumps
- pH controller
- aeration pump
- chemical feed pump

The system configuration (cf. Fig. 10), allowed for long FBR contact time with a relatively small reactor by recirculating the process fluid, enabling multiple passes through the FBR. With these conditions, the reactor works quite like a continuous feed stirred-tank reactor (CFSTR).

The FBR was constructed from acrylic plastic, with 6.35 cm inside diameter and 100 cm height dimensions (3.17 L). The unexpanded bed height was 31cm. Struvite was collected from surfaces in the SRWTP SSB, pulverised and segregated using sieve screens for use as nucleation media.

The circulation flow rate through the FBR was regulated to maintain 100% bed expansion. The required upflow velocity was 11 cm/s, which resulted in a circulation flow rate of 21 L/min. Flow was circulated through the pH adjustment tank, using a centrifugal pump. The flow rate was regulated by throttling the pump discharge using a ball valve. Adjustment of pH ( $8.3 \pm 0.03$ ) was accomplished using medium-bubble aeration to strip excess  $\text{CO}_2$ , supplemented in some cases by feeding 0.1 N NaOH solution. Aeration was the primary pH adjustment method, and chemical feed was employed only when high process fluid feed rates were treated. The seed material was struvite. A part of the produced struvite was crushed in order to be reused as seed material.

The mixing energy in the FBR was sufficient to overcome the transport limitations in growth process. Growth was identified as being controlled by the solute integration kinetics.

## **4 STIRRED REACTOR: GENERALITY, EXPERIMENTAL SET-UP AND METHODOLOGY**

The different systems developed to recover phosphate in the waste water treatment plant are mainly based on fluidised bed reactor or air agitated column reactor. However, the control of such reactors is difficult. The flow rate must be maintained constant during the operation to keep the bed in a fluidised state. A simpler approach, would be to use a stirred reactor, as it is often the case in industrial crystallization.

### **4.1 Generality**

Because of the complexity of kinetic competitions in a reactor, the agitator is one of the major component to control the final crystal size. The agitation functions in a stirred reactor are the following:

- to maintain the crystals in a homogeneous suspension
- to assure the heat transfer
- to assure mass transfer towards the growing particle
- to control the nucleation
- to crush the suspended particles

The choice of the agitator type and the determination of its size is difficult. Indeed, for a given mobile, an increase of the agitation rate increases the homogeneity degree in the apparatus and the heat and mass transfers, which is positive, but also increases the secondary nucleation and the breakage, leading to a smaller final size and a larger size distribution. So, it is necessary to find a compromise.

In a precipitator, even if it is well mixed, three zones have to be differentiated:

1. A zone near the reactant feed point. In the case of a fast chemical reaction leading to supersaturation, this zone will be more supersaturated than the average volume of the vessel; primary nucleation will occur at a high rate in this area.
2. A zone near the stirrer, especially if it is an agitator like a turbine, in which the energy dissipation is much higher than in the average volume of the vessel. Breaking, agglomeration, secondary nucleation, or diffusion-controlled growth will be influenced.
3. A zone comprising the average volume of the vessel.

(In our case, zone 2 is eliminated because the chosen mobile is a profiled propeller inducing a low shearing.)

Industrial vessels are generally less well mixed, since they are intermediates between mixed and plug-flow reactors, in which dead zones or bypasses cannot be excluded.

### **4.2 Different types of agitators**

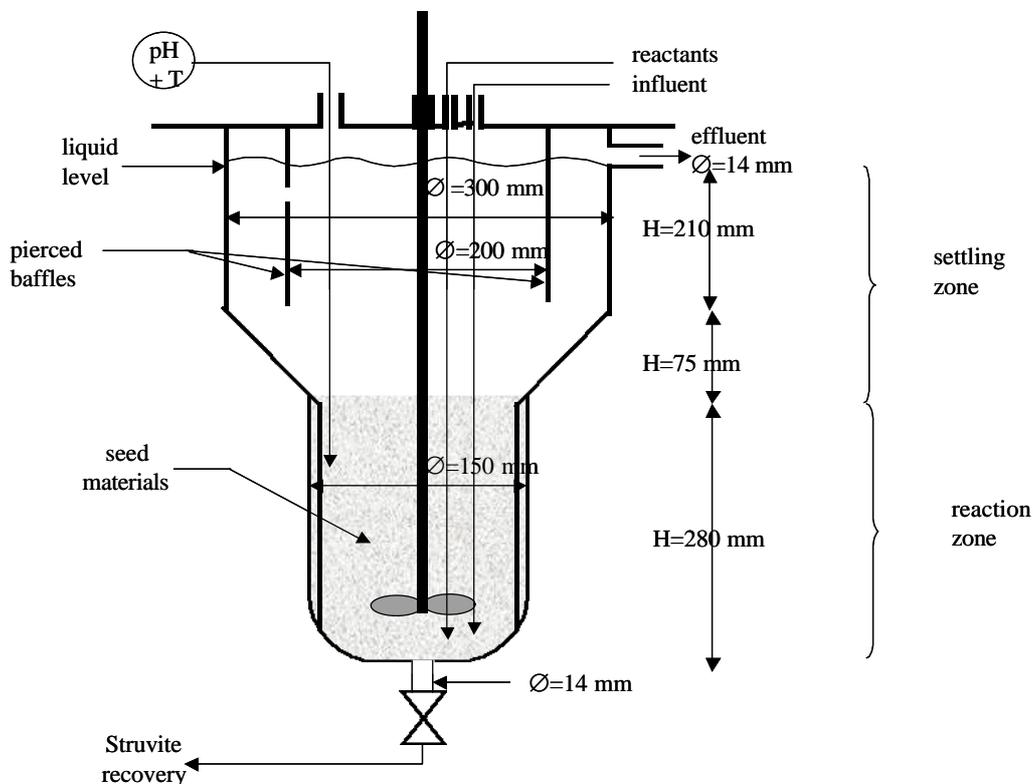
The agitators are classified in two categories, turbine or propeller depending on the flow.

The turbines cause a radial flow with an intensive turbulence zone in the blade output, leading to an important fluid shearing. Turbines are only used if fine particles are wanted.

Propellers cause an axial flow with a low shearing. The profiled propellers are more efficient and less shearing than the marine-type propellers are. Profiled propellers will favour a large final crystal size. Their diameter must be such that the ratio (propeller diameter / reactor diameter) is comprised between 0.5 and 0.6.

### 4.3 Description of the experimental set-up

To study the recovery of phosphorus in the waste water, we built a reactor to crystallize phosphate as struvite. It is a glassware reactor. The reactor is composed of two parts. The bottom part of the reactor is the reaction zone, and the top part is a settling zone, to avoid having fines in the effluent.



**Fig. 11 : stirred reactor**

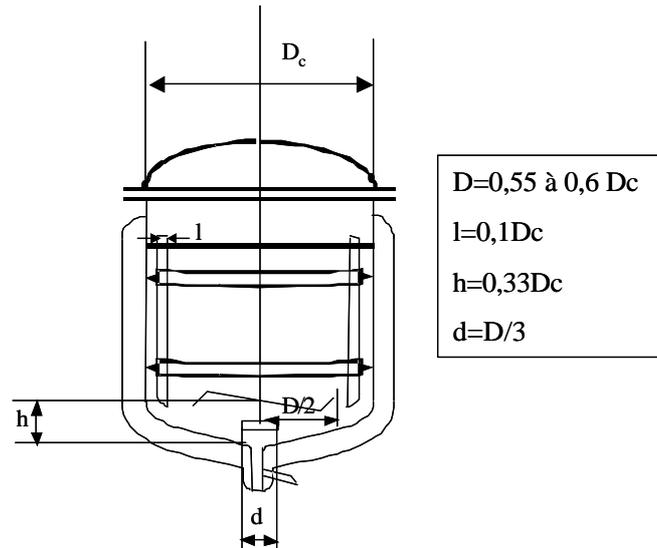
The different volumes are the following:

Reactor zones		Volume (litter)
Reaction zone	Perfectly mixed zone	2.65
	Badly mixed zone	2.3
Settling zone	Cone-shaped section	1.6
	Straight section	14
<b>Total</b>		<b>20.55</b>

**Table 4 : different volumes of the reactor**

#### 4.3.1 Reaction zone

The reaction zone was designed according to the typical dimensions of a “perfectly mixed reactor”. These typical dimensions are given in Fig. 12. The reaction zone diameter is equal to 150 mm and its height is equal to 250 mm. Intensive mixing is obtained until  $H=D_c=150\text{mm}$ . The reaction zone is equipped with four baffles to avoid the formation of a vortex and to favour the mixing.



**Fig. 12 :rules of sizing**

The chosen agitator is a profiled propeller of TT type from Mixel company. It is equipped with three shaped blades ( $D/2=90\text{cm}$ ). It is an axial flow propeller which induces a low shearing and favours a large final particle size. The agitation axe extremity is fitted with a small blade ( $d=50\text{mm}$ ). The baffle are  $l=15\text{mm}$  width and  $H=250\text{mm}$  high. The baffles, the stirrers and the agitation axe are all made of stainless steel.

The stirring rate is fixed at 300 rpm, which corresponds to a specific power input of  $0.5 \text{ KW/m}^3$ .

#### **4.3.2 Settling zone**

The settling zone is situated above the reaction zone. The settling zone is cone-shaped. The angle between the reaction zone and settling zone is  $45^\circ$ . The angular part is 75 mm high and the straight part is 300 mm in diameter and 210 high. The size of this part was sized following to the Stoke's law:

$$u_{0A} = \frac{d_A^2 g (\bar{n}_A - \bar{n})}{18\mu}$$

$u_{0A}$  is the climbing speed

$d_A$  : particle diameter

$\bar{n}_A$  : particle density

$\bar{n}$  : liquid density

$\mu$  : viscosity

In the  $\phi 300$  part, the up speed is  $10.4\mu\text{m/s}$ . Stoke's law is applicable, so the particles with a diameter inferior to  $5 \mu\text{m}$  are driven by the upward flow in the effluent. In the opposite, the particles larger than  $5 \mu\text{m}$  settle in the reactor. The settling zone is a security zone to avoid to drive fines particles in the effluent.

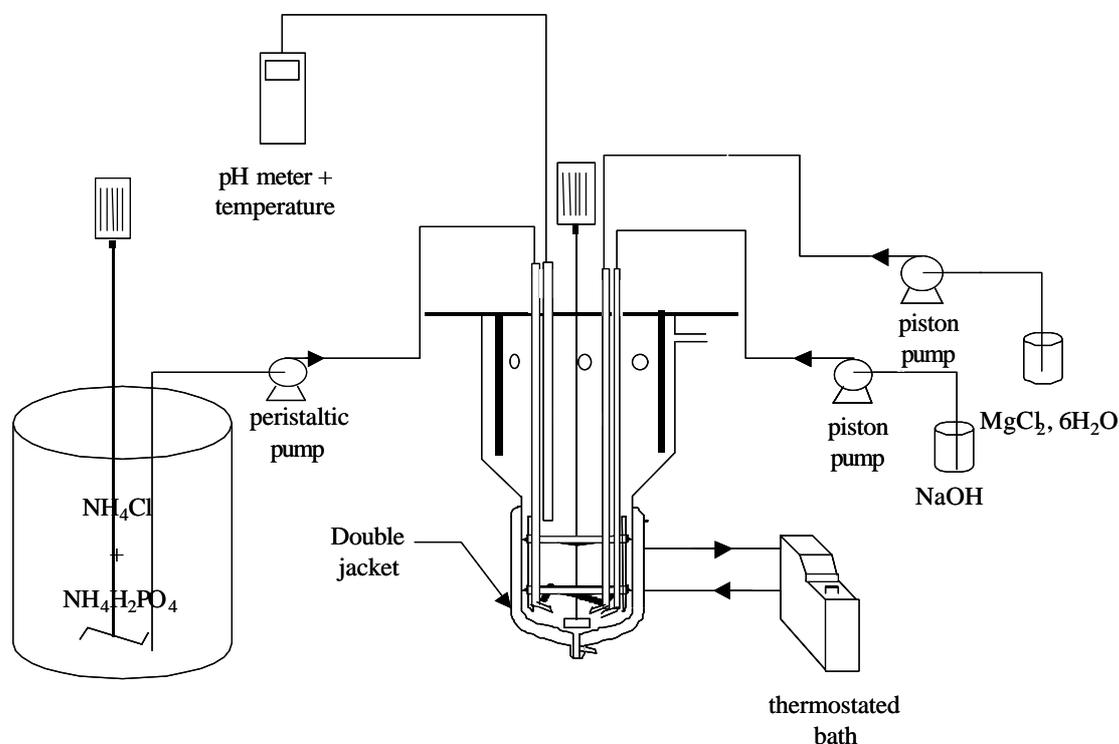
This part is also equipped with a baffle to guide the flow.

The effluent flows out at the top of the settling zone.

## 4.4 Materials and methods

### 4.4.1 Introduction

The experimental device (see Fig. 13) is composed of the reactor presented above, three injection tubes (stainless steel tubes), a thermostated bath, and a pH-probe.



**Fig. 13** : scheme of the installation

A storage tank contains the phosphate solution. The phosphate solution is composed of ammonium dihydrogenophosphate and ammonium chloride, the concentrations being such that ammonium is in large excess. A peristaltic pump injects this solution in the reactor through a 4mm in diameter stainless steel tube. The pH is adjusted with a hydroxide sodium solution through a piston pump. A pH-probe is plunged into the reactor in the reaction zone. The magnesium solution is added through a 2 mm diameter stainless steel tube by means of a second piston pump. We chose magnesium chloride rather than magnesium hydroxide because magnesium hydroxide also acts on the pH and its control is then more difficult. The three flows are injected under the propeller to avoid the fouling of that one.

### 4.4.2 Preparation of the solutions

#### 4.4.2.1 Phosphate solution

About 175 liters of drinking water are poured into the storage tank and the following reagents are added:

- $\text{NH}_4\text{H}_2\text{PO}_4$  to fix phosphate concentration
- $\text{NH}_4\text{Cl}$  to have an excess of ammonium ions.
- NaOH pellets to adjust the pH to about 7.1 in order to compensate for the buffer solution of ammonium dihydrogenophosphate.

The composition of the using drinking water is the following:

- P= 0 mg/L
- $Mg^{2+}$ = 6 mg/L
- $Ca^{2+}$ = 70 mg/L

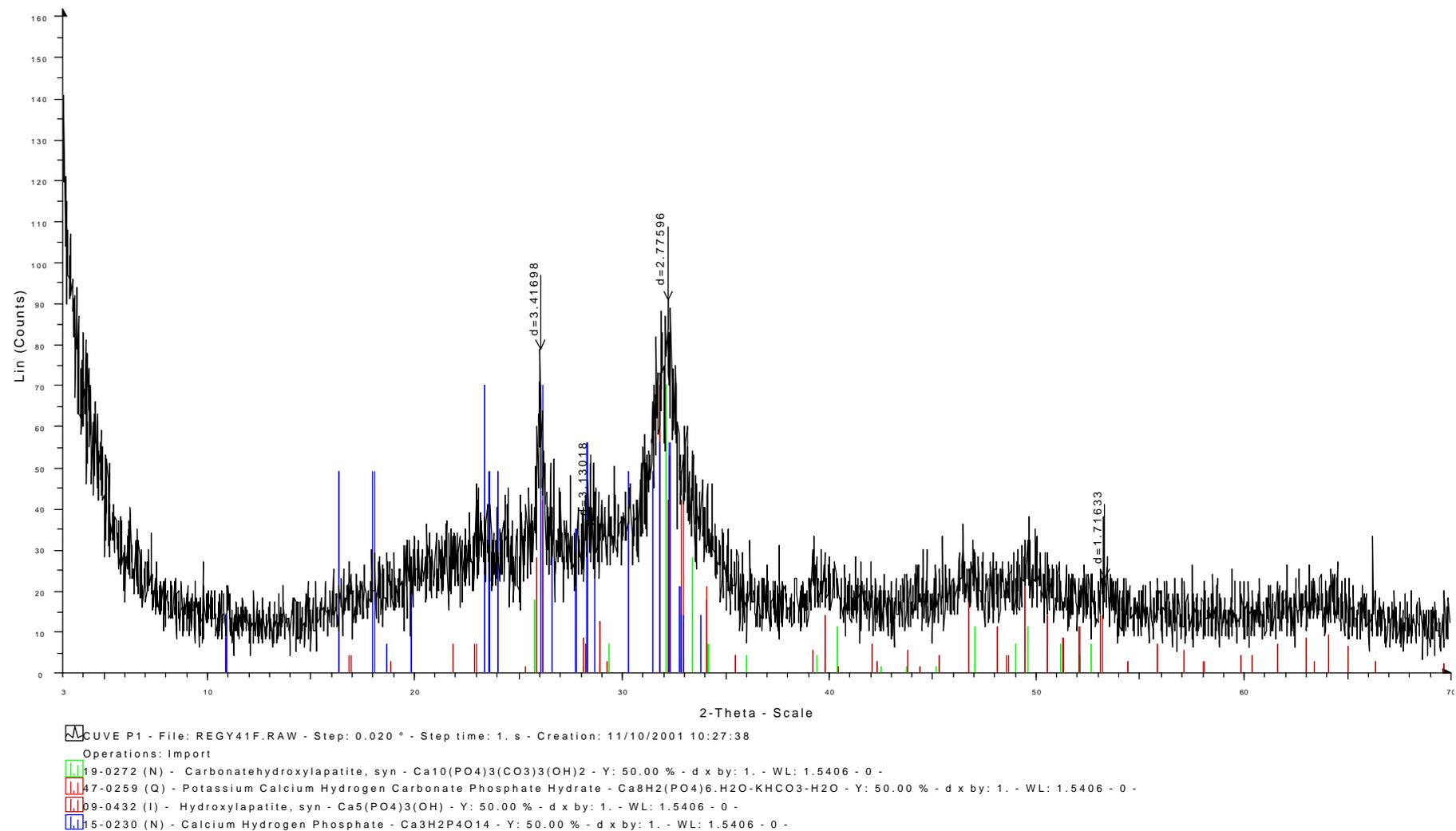
The added quantities of reagents are about:

- $NH_4H_2PO_4$ =74.2 g
- $NH_4Cl$ =83.2 g(molar ratio=11/3) and 12 g (molar ratio=11/6)
- NaOH pellets =16g

The molar ratio N- $NH_4$ /P- $PO_4$  is chosen equal to 11/3 to have about the same ratio as waste water treatment plant.

The initial pH of the drinking water is about 7.2, after the reagents addition the pH decrease to 6.3 and increase to 7.1 after caustic soda addition. After the caustic soda addition , the solution makes cloudy. A solid precipitates. The solid was analyse to X-ray diffraction. The XRD pattern obtained is reported in Fig. 14.

## CUVE P1



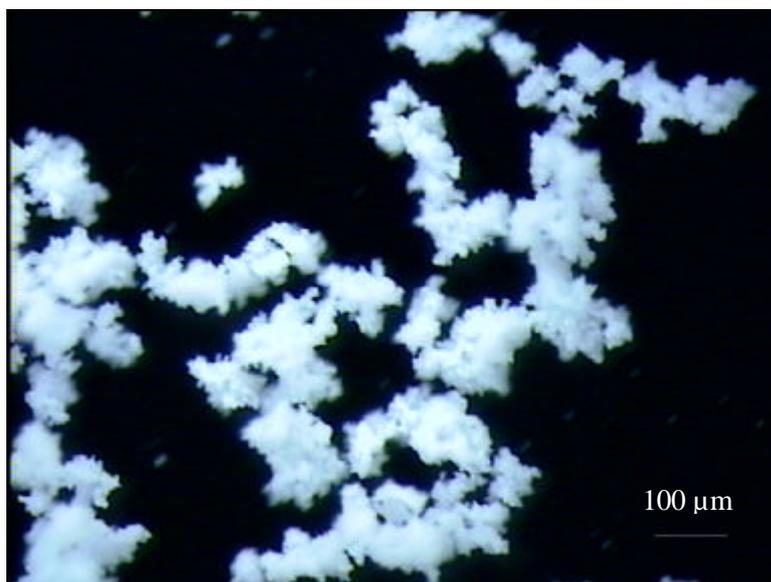
**Fig. 14 : X-ray diffraction of solid formed in storage tank and data base corresponding**

The comparison with the data base allowed to identify a phosphate calcium form (probably HAP). This result was confirmed by ICP-AES analysis. After the precipitation, the composition of phosphate solution is about:

- P = 87 mg/L
- Mg = 6 mg/L
- $\text{Ca}^{2+}$  = 17 mg/L

This method presents the advantage of eliminating a lot of calcium. So, the competition between calcium and magnesium in the reactor is eliminated. So, the struvite precipitation is favoured and calcium phosphate precipitation insignificant.

The light microscope observation (see Fig. 15) shows an amorphous and agglomerated structure.



**Fig. 15 : phosphate calcium**

#### **4.4.2.2 Magnesium solution**

The magnesium is added as magnesium chloride ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ). The solution is prepared by dissolving 30.45 g of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  in 5 liters of distilled water. The magnesium concentration is thus equal to  $720 \text{ mg} \cdot \text{L}^{-1}$ . This chosen magnesium concentration is quite high. The magnesium flow rate will then represent less than 10% of the total flow rate.

#### **4.4.2.3 Sodium hydroxide solution**

Two solutions of sodium hydroxide were prepared,  $0,5 \text{ mol} \cdot \text{L}^{-1}$  and  $0,1 \text{ mol} \cdot \text{L}^{-1}$ . For the 0,5 M solution, 100 g pellets NaOH were added in 5 liters of distilled water. For the 0,1 M solution, 20 g pellets NaOH were added in 5 liters of distilled water.

Because of the low sodium hydroxide flow rate it requires, the 0.1 M solution is better to adjust the pH in the reactor.

### **4.4.3 Seed materials**

We used two types of seed materials: sand and struvite supplied by Unitika struvite crystallization plant. Two kinds of sand were also considered: coarse sand with size range between 200 and 300 $\mu$ m and fine sand with size range between 150 and 200  $\mu$ m. The quantity of seed materials introduced represents 5 to 10 percent in volume and 10 to 20 percent in mass.

### **4.4.4 Running conditions**

The total flow rate is calculated to have a residence time in the perfectly mixed zone of about one hour. So the total flow rate is about 2,65 L/h and the total residence time in the reactor is 7h45.

The reactor is operated in continuous mode for the liquid phase and batchwise for the solid phase. The stirring speed is fixed at 300 rpm that is to say power of 0.5kW/m<sup>3</sup>.

The range of initial concentrations is reported in Table 5:

[P-PO <sub>4</sub> ] mg.L <sup>-1</sup>	80-90
[N-NH <sub>4</sub> ] mg.L <sup>-1</sup>	170-85
[Mg <sup>2+</sup> ] mg.L <sup>-1</sup>	720
[Ca <sup>2+</sup> ] mg.L <sup>-1</sup>	10-20
Hydroxide sodium mol.L <sup>-1</sup>	0.5 or 0.1

**Table 5 : initial concentrations**

The pH varies between 8 and 9.2 and the molar ratio Mg/P varies between 0.9 and 1.5.

### **4.4.5 Analysis**

Two main analysis methods were used. The concentrations in liquids were analysed by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry) and solid by X-Ray Diffraction.

Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) is a major technique for elemental analysis. The sample to be analysed, if solid, is normally first dissolved and then mixed with water before being fed into the plasma. The ICP-AES is able to quantitatively determine a wide range of elements in a number of geological, environmental and archaeological matrices. Major, minor and trace elements (including rare earth elements) can be determined typically down to  $\mu$ g.l<sup>-1</sup> in solution. The ICP-AES technology is described in appendix 2.

Magnesium, phosphorus as phosphate form and calcium were analysed by ICP-AES. Ammonium ions were added in excess, so ammonium ions were not analysed. Furthermore, the reactor being close, the atmosphere above liquid is saturated in ammoniac gas.

R-X diffraction is a technique to determinate the nature of compounds particles and their geometric layout in the space.

The pH is measured with a pH-probe plunged in the reactor and a pH-meter.

### **4.4.6 Experimental methodology**

All experiments were conducted at a temperature of 25°C (regulated by a thermostated bath).

During the experiment, the pH in the reactor was adjusted to the chosen value by correcting the sodium hydroxide flow rate. The resulting sodium hydroxide flow rate was then regularly measured. The magnesium flow rate was also regularly measured and adjusted as necessary. Eventually, the effluent flow rate was regularly measured too. This allowed us to readjust the inlet water flow rate if a drift was observed.

Samples of the effluent (50 mL) were taken for ICP analysis of the remaining magnesium, calcium and phosphorus concentrations. Half of the sample (25 mL) was filtered through pre-weighed filter to measure dissolved phosphorus, dissolved magnesium and dissolved calcium concentrations. The other part of the sample (25 mL) was acidified with nitric acid (1%) to dissolve the fines present in the effluent and to measure total phosphorus, magnesium and calcium concentrations.

Solids precipitate in the reactor were recovered by filtration and dried at ambient temperature. The mass precipitated was recorded. Small samples of the precipitate were analysed by XRD technology. The position and intensity of peaks generated from the XRD patterns were compared with the standard database lines (MASTER-noICSD).

Further samples of precipitate were weighed, dissolved in nitric acid and filtered. These samples were analysed for magnesium and phosphorus concentrations using ICP analysis. The theoretical concentrations were calculated from the masses dissolved assuming the precipitate formed was pure struvite and compared with the results generated from the ICP analysis. The theoretical mass composition of struvite is:

- 9.9 % in magnesium
- 5.7 % in nitrogen
- 12.6% in phosphorus
- 44 % in water

## **5 EXPERIMENTS OF SAND COATING (SEMI-BATCH EXPERIMENTS)**

Two sands were tested, a coarse sand with a distribution size range of 200 to 300  $\mu\text{m}$  and a thinner sand with a distribution size range of 150 to 200  $\mu\text{m}$ . These experiments were performed in semi-batch mode.

### **5.1 Experiment 1 : coarse sand**

#### **5.1.1 Operating conditions**

##### **5.1.1.1 Composition of solutions**

The initial concentrations of the solutions (analysis ICP-AES) after calcium phosphate precipitation are given in Table 6.

Solution	Species	Concentration (mg/L)	Concentration (mmol/L)
Phosphate solution	[P-PO <sub>4</sub> ]	86	2.77
	[N-NH <sub>4</sub> ]	175 (calculated)	12.5
	[Ca <sup>2+</sup> ]	/	
	[Mg <sup>2+</sup> ]	6	0.25
	pH	7.2	
Hydroxide sodium	NaOH		0.5
Magnesium solution	[Mg <sup>2+</sup> ]	720	30

**Table 6: composition of solutions (experiment 1)**

The molar ratio N/P is 4.5.

##### **5.1.1.2 Start-up**

2.5 liters of phosphate solution were taken from the phosphate storage tank. 300 g of coarse sand were added in the solution. The density of sand is of about 2650 kg/m<sup>3</sup>. So, the added sand represents 11.3% in mass (or 4.3% in volume) of the perfectly mixed zone. The mixture was transferred into the reactor and mixed at 300-550 rpm. The magnesium was progressively added at a flow rate of 0.33L/h. The addition lasted one hour. The solution was stirred at 300-550 rpm during this period. The pH was kept to 9 by NaOH addition.

##### **5.1.1.3 Running period**

After an hour corresponding to the magnesium addition, the three flow rates, magnesium flow rate of 0.33 L/h, phosphate flow rate of 2.25 L/h and sodium hydroxide flow rate of 0.25 L/h (total flow rate of 2.83 L/h) were added in the reactor during 3 hours. The pH was maintained to about 9. The concentration in the reactor after dilution were:

Species	Concentration (mg/L)	Concentration (mmol/L)
P-PO <sub>4</sub>	68.4	2.21
N-NH <sub>4</sub>	139.1	9.94
Mg <sup>2+</sup>	83.9	3.5

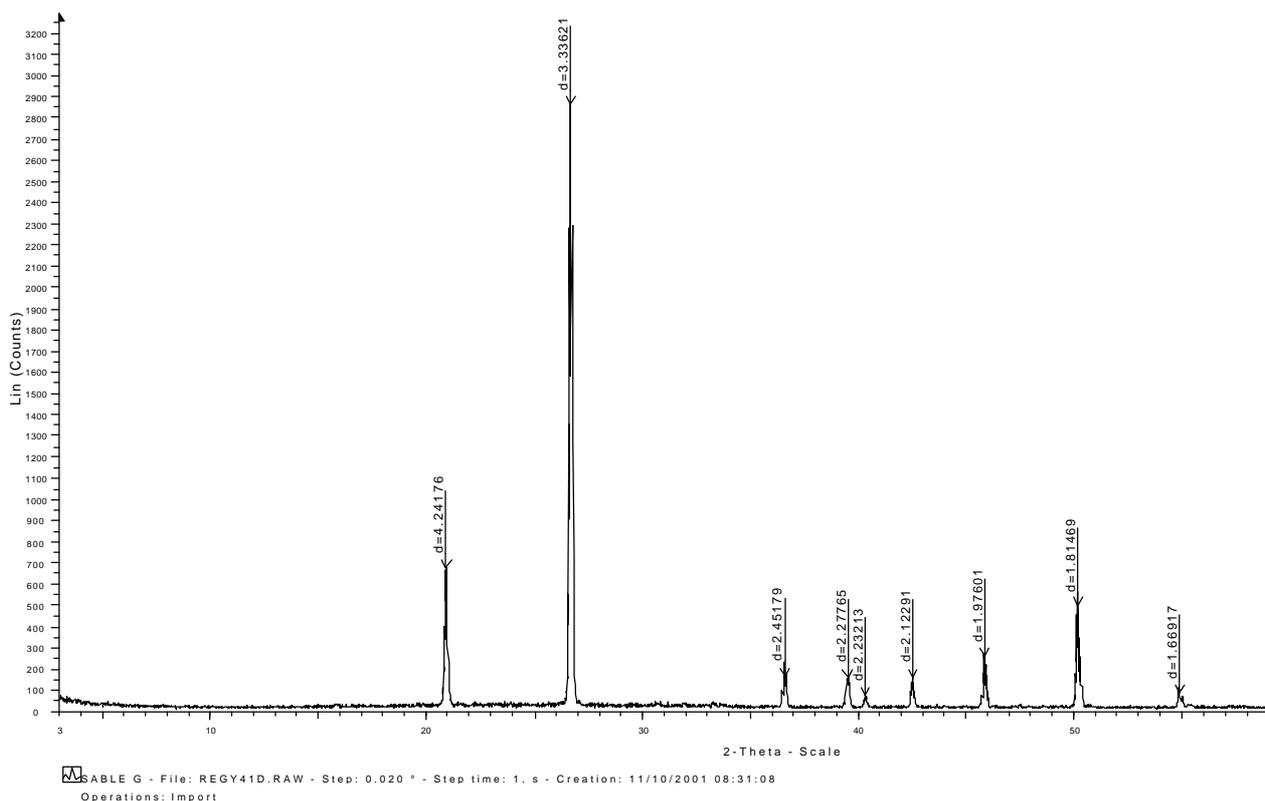
**Table 7: “initial” concentrations in the reactor (assuming no crystallization) (experiment 1)**

The molar ratio Mg/P was 1.6. The high molar ratio N/P is due to a loss of phosphate as calcium phosphate in the storage tank. This loss was not expected at the beginning.

## 5.1.2 Results

### 5.1.2.1 Analysis

A sample of sand taken in the reactor was analysed by X-ray diffraction. The spectrum is presented in Fig. 16. The X-ray diffraction shows not mixture of sand and struvite, but just a spectrum of quartz.



**Fig. 16: X-ray diffraction of coarse sand after reaction**

The residual magnesium and total phosphate concentrations in the solution at the end of the experiment were 3.2 mg/L and 28 mg/L respectively.

### **5.1.2.2 Observations**

The first notice concerns the stirring speed. Indeed, at a stirring speed of 300 rpm, the sand was not maintained in a homogeneous suspension. A part of sand is stayed in the bottom of the vessel. The minimum stirring speed to have a sand in homogeneous suspension was of 540 rpm. At the end of the experiment, the solid settled and we could notice two different phase of solid, underneath a layer of sand and above a white layer of struvite analysed by X-ray diffraction. So, the struvite didn't succeed to fix on the sand. Furthermore, the X-ray diffraction shows just the spectrum of sand and not a mixture of sand and struvite. The stirring speed was too high to favour the deposit of struvite on the sand. Since a too high agitation speed was required to totally put the sand in suspension, we chose thinner sand "sable de Fontainebleau" with a distribution size ranging from 150 to 200  $\mu\text{m}$ .

## **5.2 Experiment 2 : thin sand**

The test was conducted at a higher concentration, ten times the usual concentration, in order to force the coating of the struvite on the sand.

### **5.2.1 Operating conditions**

#### **5.2.1.1 Start-up**

200 g of "sable de Fontainebleau" were added in 2 litter of distilled water (10% in mass and 3.8% in volume) and mixed at 300 rpm. After the three flow rate addition (phosphate, magnesium and sodium hydroxide), the composition in the reactor was :

Species	Concentration (mg/L)	Concentration (mmol/L)
P-PO <sub>4</sub>	1000	32.3
N-NH <sub>4</sub>	1029	73.5
Mg <sup>2+</sup>	775	32.3

**Table 8: "initial" concentrations in the reactor (assuming no crystallization) (experiment 2)**

The molar ratio Mg/P was 1/1.

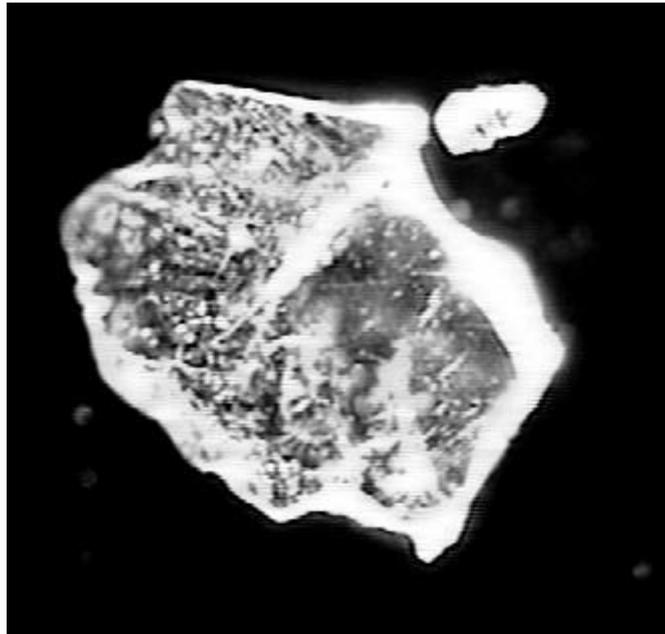
The pH varied between 8,5 and 9.

### **5.2.2 Results**

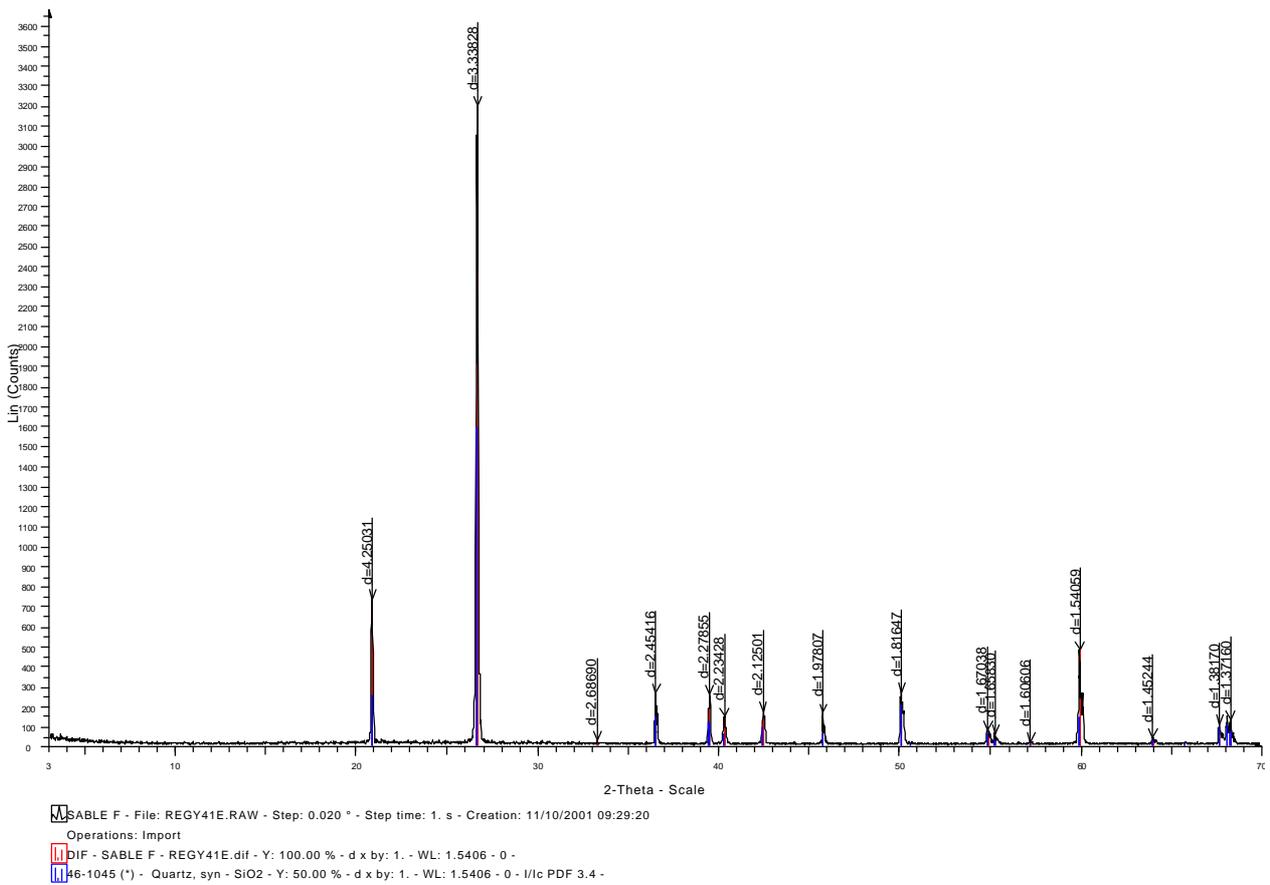
#### **5.2.2.1 Analysis**

The X-ray diffraction spectrum of sand after reaction is given in Fig. 18.

The light microscope photo of "sable de Fontainebleau" is given in Fig. 17.



**Fig. 17** : “sable of Fontainebleau” (magnification  $\times 20$ )



**Fig. 18** : X-ray diffraction of “sable de Fontainebleau” after reaction

The residual magnesium and phosphate concentration in the solution after filtration was 8 mg/L and 32 mg/L respectively.

### **5.2.2.2 observations**

With “sable de Fontainebleau”, the stirring speed of 300 rpm was enough to keep the sand in homogeneous suspension in the vessel. But when agitation was stopped, two solid phases were observed, underneath sand and above precipitated struvite. The spectrum of X-ray diffraction shows no mixture of sand and struvite.

In these conditions, no deposit on the sand was observed but a strong primary nucleation occurred and only fines were produced.

## **5.3 Discussion**

In the working conditions, it was not possible to coat sand with struvite. In the case of coarse sand, an explanation can be the high stirring speed which favoured not the fixation of formed nuclei on sand particles. If nuclei are fixed, they are pulled out by the agitation. Furthermore, the molar ratio was too high and favours fooling at reactant feed point.

The operating conditions generated a high supersaturation (pH, ratio molar Mg/P, ...). In these conditions, primary nucleation is very important and growth does not occur.

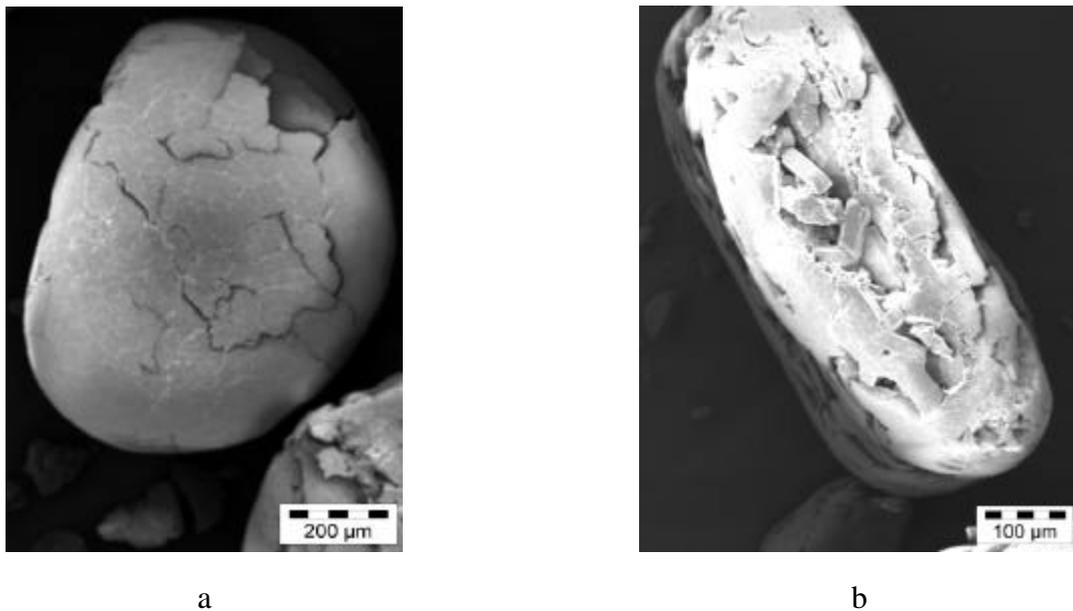
Another explanation can be the roughness of the sand. Indeed, in Fig. 17, the sand surface seems to be smooth. So, the fixation of nuclei is more difficult. The affinity between sand and struvite is low.

These two experiments are not enough to conclude that coating sand with struvite is impossible. Other experiments with a lower supersaturation (decrease pH, decrease molar ratio Mg/P, ...) could be interesting to complete these results.

## **6 EXPERIMENTS WITH SEEDING: STRUVITE SUPPLIED BY UNITIKA**

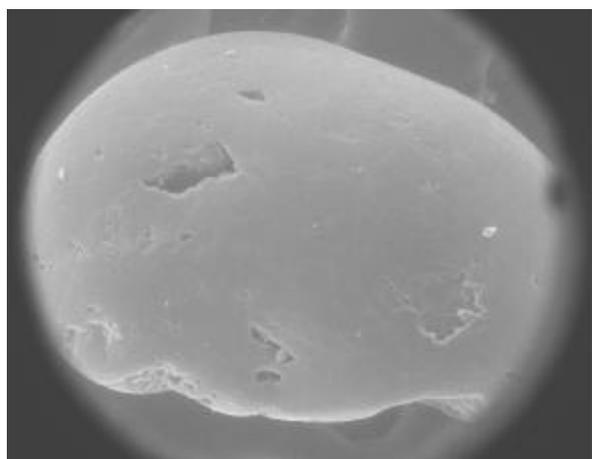
### **6.1 Seed materials: Unitika struvite**

To favour the crystallization on particles and affinity between particles, sand was replaced by struvite solid pellets. Struvite solid pellets were supplied by Unitika struvite crystallization plant. Particles are spherical. Struvite were analysed by X-ray diffraction (see Fig. 22) and observed at electron scanning microscope (see Fig. 19 and Fig. 21) and environmental microscope (see Fig. 20).



**Fig. 19: Unitika struvite pellets**

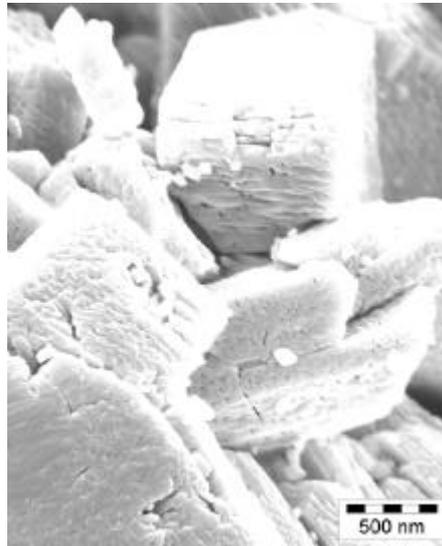
Fig. 19 a. shows a spherical pellet with fractures. The electron scanning microscope observation requires a preparation, the sample is metallized to make it conductor. During this process, the sample is subjected to a high pressure which caused certainly these fractures. Indeed, the environmental microscope observation (see Fig. 20) of a struvite pellet shows no fracture. In this technique, metallization is not necessary and the sample is not subjected to high pressure.



**Fig. 20: struvite Unitika observed in environmental microscope**

The pellets surface is smooth. The fluidised bed reactor favours the formation of smooth pellets because of the numerous collisions between particles.

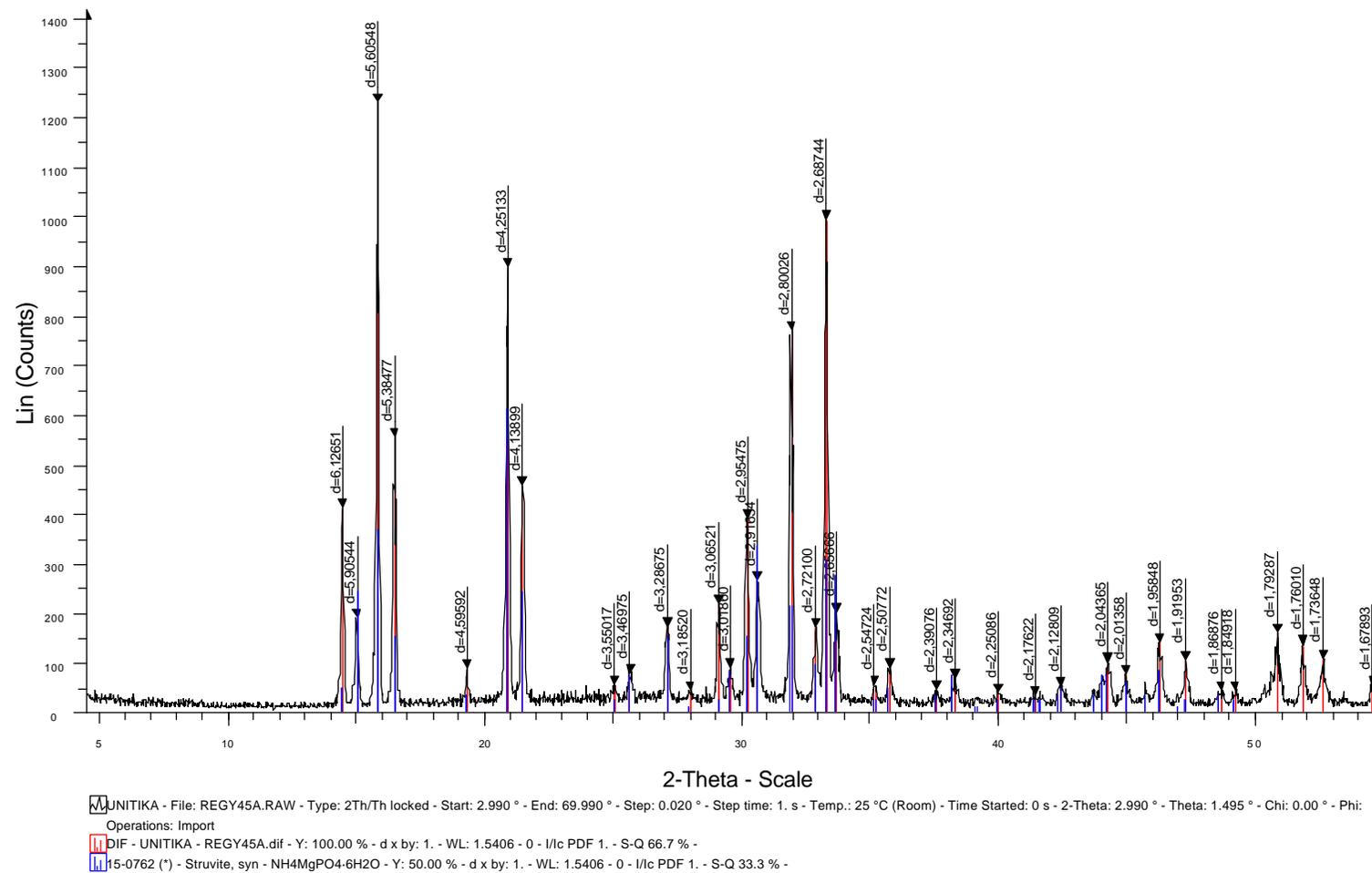
Fig. 21 shows a zoom of the pellet surface. We can see agglomerated particles.



**Fig. 21: zoom on Fig. 19b**

The X-ray diffraction analysis (Fig. 22) confirms the composition of magnesium ammonium phosphate.

# UNITIKA



**Fig. 22: X-ray diffraction of Unitika struvite**

## **6.2 Experiment 3: seeding with Unitika struvite**

### **6.2.1 Operating conditions**

#### **6.2.1.1 Composition of the solutions**

The composition of the different solutions used is reported in the following table:

Solution	Species	Concentration (mg/L)	Concentration (mmol/L)
Phosphate solution	[P-PO <sub>4</sub> ]	86	2.77
	[N-NH <sub>4</sub> ]	175 (calculated)	12.5
	[Ca <sup>2+</sup> ]	/	
	[Mg <sup>2+</sup> ]	6	0.25
	pH	7.6	
Sodium Hydroxide solution	NaOH		0.5
Magnesium solution	[Mg <sup>2+</sup> ]	720	30

**Table 9: composition of the solutions (experiment 3)**

#### **6.2.1.2 Start-up**

2.5 liters of phosphate solution and 265 g of Unitika struvite were introduced into the reactor. The density of struvite is of 1710kg/m<sup>3</sup>. The seed materials represent 10% in mass and 5.9% in volume of the perfectly mixed zone. The initial pH of 7.6 was adjusted to 9 with sodium hydroxide at 0.5 mol/L. The suspension has then been mixed at 300 rpm during one hour to “wet” the struvite pellets. The struvite pellets were totally in suspension and we could observe the formation of foam due to impurities in seed materials. Magnesium (flow rate =0.25 L/h) and NaOH were finally added during one hour to reach the continuous conditions. At the end of the addition, the pH increased up to 9.2.

#### **6.2.1.3 Running period**

The three flow rates, magnesium flow rate of 0.25 L/h, phosphate flow rate of 2.4 L/h and sodium hydroxide flow rate of about 0.04 L/h (total flow rate of 2.69 L/h) have been fed in the reactor during 22.5 hours. The pH was maintained to about 9-9.2. The “inlet” concentrations (calculated by considering the mixing of the 3 feed flows) were:

Species	Concentration (mg/L)	Concentration (mmol/L)
P-PO <sub>4</sub>	76.7	2.48
N-NH <sub>4</sub>	156.1	11.2
Mg <sup>2+</sup>	66.9	2.8

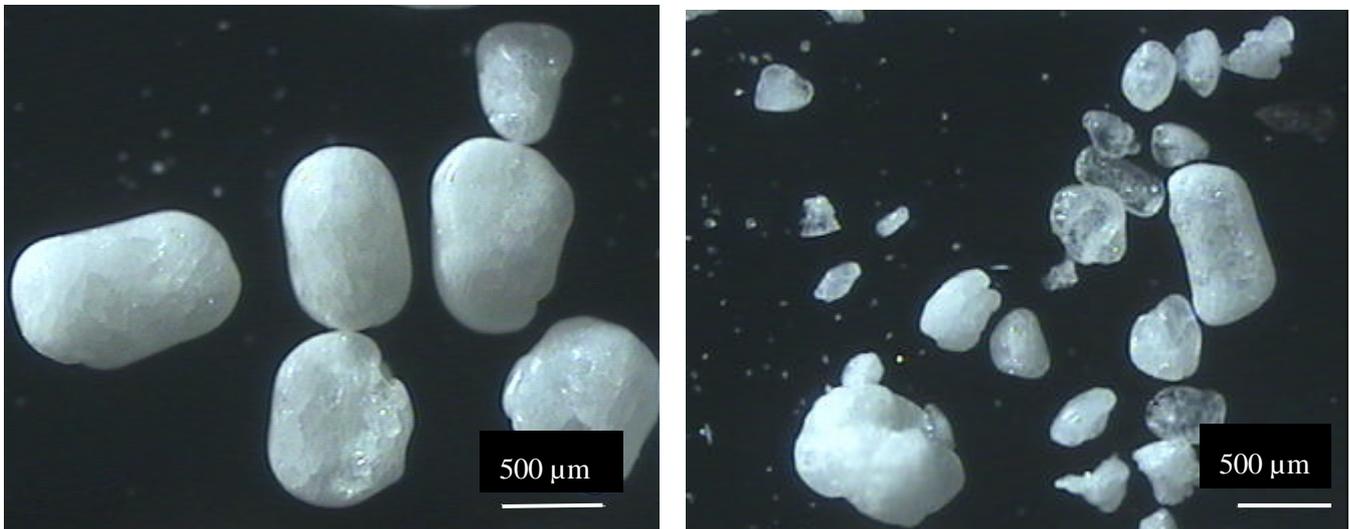
**Table 10: feed concentrations which would be obtained by mixing the 3 flows (experiment 3)**

The molar ratio Mg/P was equal to 1.15. The stirring speed was maintained to 300 rpm.

## **6.2.2 Results**

### **6.2.2.1 Analysis**

The residual magnesium and dissolved phosphate concentrations of the effluent after filtration were equal to 7 mg/L and 6.2 mg/L respectively. The solid formed was struvite (analysed by X-ray diffraction). The light microscope observations (Fig. 23) show the Unitika pellets obtained at the end of the experiment.



**Fig. 23: Unitika struvite after residence in the reactor**

### **6.2.2.2 Observations**

The observations are the following:

- Lots of fines
- Fines settling on the cone-shaped section
- Some fines are driven in the effluent (cloudy solution)
- Seed materials stay in the mixing zone and are not driven by the upward flow

Fines can have 2 main sources: (i) high primary and/or secondary nucleation due to high supersaturation or (ii) fines contained in seed materials or coming from disintegration of seed materials. To eliminate the second possibility, the fines contained in the reactor were eliminated and the experiment was continued in the same conditions.

Fig. 23 shows that the final pellet are similar to the seed pellets. No deposit of precipitated struvite can be observed.

At pH 9.2, the conversion rate of phosphate reaches 92%.

### **6.3 Experiment 4: seeding with Unitika struvite**

Because of the large quantity of fines present in the reactor, fines were eliminated and the test was continued to know the source of fines (fines produced by nucleation or fines coming from seed materials). The pH was also decreased to study the influence of pH on struvite precipitation.

#### **6.3.1 Operating conditions**

##### **6.3.1.1 Composition of the solutions**

Phosphate solution	[P-PO <sub>4</sub> ] meas.	86.9 (mg/L)	2.80 mmol/L
	[N-NH <sub>4</sub> ] cal.	167.6 (mg/L)	11.97 mmol/L
	[Ca <sup>2+</sup> ] meas.	19.5 (mg/L)	0.49 mmol/L
	[Mg <sup>2+</sup> ] meas.	5.6 (mg/L)	0.23 mmol/L
	PH	7	
Sodium hydroxide	NaOH		0.5 (mol/L)
Magnesium solution	[Mg <sup>2+</sup> ]	720 (mg/L)	30 mmol/L

**Table 11: composition of solutions (experiment 4)**

##### **6.3.1.2 Start-up**

To eliminate the fines, a high flow rate (about 20 L/h) of saturated solution (filtrate of effluent) were injected in the reactor (principle of elutriation). After this process, the solution was less cloudy. The initial composition of the solution in the reactor is similar to the effluent of experiment 3.

[P-PO <sub>4</sub> <sup>3-</sup> ]dis. (mg/L)	6.2
[Mg <sup>2+</sup> ] (mg/L)	7
[Ca <sup>2+</sup> ] (mg/L)	8
pH	9.12

**Table 12: initial composition of the solution in the reactor (experiment 4)**

### 6.3.1.3 Running period

Magnesium flow rate of 0.25 L/h, phosphate flow rate of 2.4 L/h and sodium hydroxide flow rate of 0.013 or 0.026 L/h (total flow rate of about 2.7 L/h), calculated flow rate, have been added in the reactor during 40 hours. The “inlet” concentrations calculated by considering the mixing of the 3 feed flows are then:

Species	Concentration (mg/L)	Concentration (mmol/L)
P-PO <sub>4</sub>	77.2	2.49
N-NH <sub>4</sub>	149	10.64
Mg <sup>2+</sup>	71.6	2.98
Ca <sup>2+</sup>	17.3	0.43

**Table 13:** feed concentrations which would be obtained by mixing the 3 flows (experiment 4)

The molar ratio Mg/P is 1.2. During the test, some fluctuations were observed (Table 14):

Running	Operating conditions						
	time	pH	Mg flow rate (L/h)	NaOH 0.5M flow rate (L/h)	effluent flow rate (L/h)	P flow rate (L/h)	ratio Mg/P
	0-9h	8.2	0.25	0.026	2.8	2.52	1.14
	6h-12h	8.1	0.21	0.01	2.9	2.68	0.92
	12h-16h	8.15	0.21	0.01	2.72	2.50	0.98
	16h-33h	8.7	0.22	0.03	2.77	2.52	1.02
	33h-40h	8.7	0.220	0.03	2.77	2.52	1.02
	average	8.37	0.222	0.021	2.79	2.55	1.02

**Table 14:** flow rate fluctuations (experiment 4)

### **6.3.2 Results**

#### **6.3.2.1 Analysis**

Sample	Concentrations (mg/L)					
	Mg tot.	Mg dis.	P tot.	P dis.	Ca tot.	Ca dis.
9h	19.5	14.1	30	21	21.5	/
12h	19	14.7	28	21.2	18.7	18.4
16h	19.4	/	26.7	/	18.3	/
33h	13.6	10.9	17.7	13.1	17.2	16.6
average	17.9	13.2	25.6	18.4	18.9	17.5

**Table 15: analysis results (experiment 4)**

#### **6.3.2.2 Observations**

We have still observed a lot of fines on the cone-shaped section, in the effluent and in the reactor. The fines do not seem to come only from seed materials. Fines are produced during the experiment. The nucleation is still high under these conditions.

In Table 15, we can see the pH influence on the phosphate conversion. When the pH decreases the phosphate precipitation decreases, too. At pH 8.2, about 73% of phosphate is eliminated and about 64% of phosphate is recovered, whereas at pH 8.7, these rates are 78% and 76% respectively. The difference between pH 8.2 and 8.7 is not significant in comparison with the reactants high cost.

After having emptied the reactor, we could observed fouling on propeller, blades, glassware and reduction of the magnesium tube. These observations are in agreement with a high supersaturation. The supersaturation must be decreased.

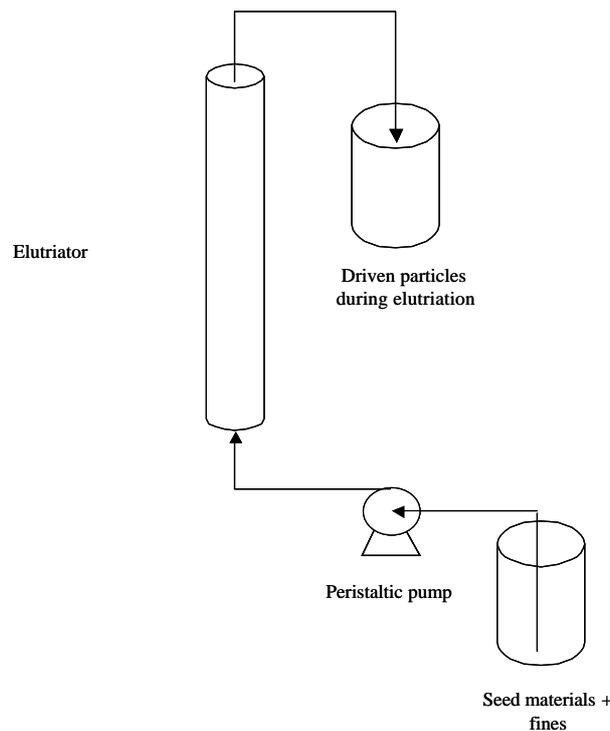
## **6.4 Elutriation of the Unitika pellets**

### **6.4.1 Description**

The seed materials supplied by Unitika contains a lots of fines. To eliminate the fines, the seed materials have been elutriated.

The elutriation method is based on the fact that the terminal falling velocity of a particle in a fluid increases with particle size.

This method is in fact a reverse sedimentation process in which the particles are dispersed in an upward flowing stream of fluid. All particles with terminal falling velocities less than the upward velocity of fluid will be carried away. A complete size analysis can be obtained by using successively higher fluid velocity. Fig. 24 shows the experimental set-up.



**Fig. 24 : elutriation device**

Materials are separated by means of an elutriator, which consists of a vertical tube up which fluid is passed at a controlled velocity. The particles are introduced before in the cell, and the smaller particles are carried over in the fluid stream while the large particles settle against the upward current.

#### **6.4.2 Terminal falling velocity:**

If a spherical particle is allowed to settle in a fluid under the action of the gravity, it will increase in velocity until the accelerating force is exactly balanced by the resistance force. Although this state is approached exponentially, the effective acceleration period is generally of short duration for very small particles. This terminal falling velocity depends on the flow, so Reynolds,  $Re$ .

$$Re = \frac{\rho_f u d_p}{\mu}$$

where  $\rho_f$  is the density of fluid

$u$  is the velocity of the fluid relative to the particle

$d_p$  is the diameter of the particle

$\mu$  is the viscosity of the fluid

In case of laminar flow ( $Re < 1$ ), the terminal falling velocity is given by the following expression:

$$u = \frac{d_p^2 (\rho_s - \rho_f) g}{18 \mu}$$

where  $\rho_s$  is the density of solid

$g$  is the acceleration due to gravity

In case of intermediate flow ( $1 < \text{Re} < 10^3$ ), the terminal falling velocity is given by the following expression:

$$u = \frac{d_p^{1.14} [(\rho_s - \rho_f)g]^{0.714}}{6.55 \mu^{0.428} \rho_f^{0.286}}$$

With our elutriator, if the flow is laminar:

particles size ( $\mu\text{m}$ )	terminal falling velocity (m/s)	section elutriator ( $\text{m}^2$ )	Flow rate ( $\text{m}^3/\text{s}$ )	Flow rate (L/h)	Re	
100	3.33E-03	1.96E-03	6.54E-06	23.6	0.3	Re < 1
200	1.33E-02	1.96E-03	2.62E-05	94.2	2.7	Re > 1
300	3.00E-02	1.96E-03	5.89E-05	212.1	9.0	Re > 1
400	5.33E-02	1.96E-03	1.05E-04	377.0	21.3	Re > 1
500	8.33E-02	1.96E-03	1.64E-04	589.0	41.7	Re > 1
600	1.20E-01	1.96E-03	2.36E-04	848.2	72.0	Re > 1
700	1.63E-01	1.96E-03	3.21E-04	1154.5	114.3	Re > 1
800	2.13E-01	1.96E-03	4.19E-04	1508.0	170.7	Re > 1
900	2.70E-01	1.96E-03	5.30E-04	1908.5	243.0	Re > 1
1000	3.33E-01	1.96E-03	6.54E-04	2356.2	333.3	Re > 1

**Table 16: terminal falling velocity in laminar flow**

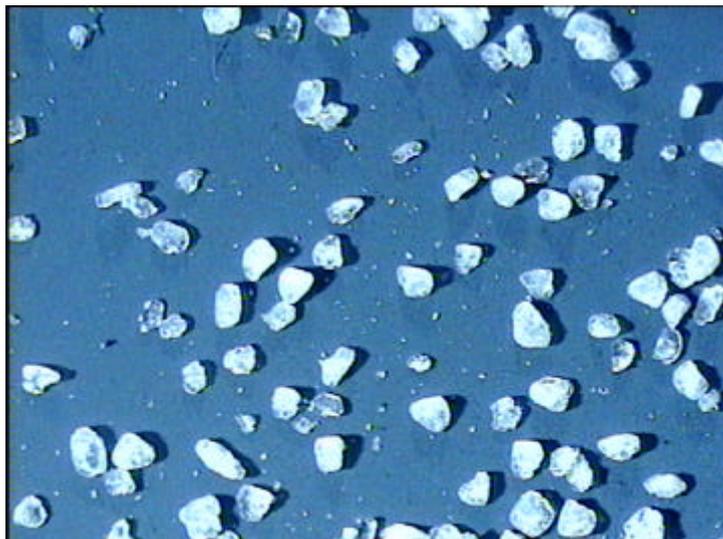
For particle sizes superior to 200  $\mu\text{m}$ ,  $\text{Re} > 1$ , so we must apply the expression of terminal falling velocity relating to intermediate flow. The terminal falling velocity is reported in Table 17.

If the flow is intermediate:

particles size ( $\mu\text{m}$ )	terminal falling velocity (m/s)	section elutriator ( $\text{m}^2$ )	Flow rate ( $\text{m}^3/\text{s}$ )	Flow rate (L/h)	Re
200	1.23E-02	1.96E-03	2.42E-05	87.1	2.5
300	1.96E-02	1.96E-03	3.84E-05	138.2	5.9
400	2.71E-02	1.96E-03	5.33E-05	191.9	10.9
500	3.50E-02	1.96E-03	6.87E-05	247.5	17.5
600	4.31E-02	1.96E-03	8.46E-05	304.6	25.9
700	5.14E-02	1.96E-03	1.01E-04	363.2	36.0
800	5.98E-02	1.96E-03	1.17E-04	422.9	47.9
900	6.84E-02	1.96E-03	1.34E-04	483.6	61.6
1000	7.72E-02	1.96E-03	1.51E-04	545.4	77.2

**Table 17:** terminal falling velocity in intermediate flow

The elutriated particles are shown in Fig. 25.



**Fig. 25:** elutriated Unitika struvite

The size of the largest particles is equal to about  $200\mu\text{m}$ . The smallest particles measure about  $15\mu\text{m}$ .

## **6.5 Experiment 5: seeding with elutriated Unitika struvite**

### **6.5.1 introduction**

Following the previous results, that is to say a production of lots of fines, the supersaturation was decreased. Supersaturation is function of magnesium, ammonia and phosphate concentrations. So, ammonia concentration was divided by 2 and the molar ratio Mg/P was decreased from 1.2 to 1 to reduce supersaturation at feed point. The pH was also decreased from 9.2 to 8.7 since pH contributes to supersaturation too.

The previous experiments were performed with an initial solution in the reactor of same composition as the feed solution. The initial supersaturation at the feeding point was then high supersaturation and favoured primary nucleation and production of fines. In order to reduce this initial supersaturation, we chose then to begin with a step of saturated solution in the reactor.

### **6.5.2 Operating conditions**

#### **6.5.2.1 Composition of the solutions**

Phosphate solution	[P-PO <sub>4</sub> ] mes.	89.9 (mg/L)	2.9 (mmol/L)
	[N-NH <sub>4</sub> ] cal.	71 (mg/L)	5.07 (mmol/L)
	[Ca <sup>2+</sup> ] mes.	24.4 (mg/L)	0.61 (mmol/L)
	[Mg <sup>2+</sup> ] mes.	6 (mg/L)	0.25 (mmol/L)
	pH	7.1	
Sodium hydroxide	NaOH		0.1 (mol/L)
Magnesium solution	[Mg <sup>2+</sup> ]	720 (mg/L)	30 (mmol/L)

**Table 18: composition of the solutions (experiment 5)**

#### **6.5.2.2 Start-up**

3 liters of filtrate of the last experiment were taken and introduced in the reactor. The composition of the filtrate is the following:

[P-PO <sub>4</sub> <sup>3-</sup> ] (mg/L)	21.5
[Mg <sup>2+</sup> ] (mg/L)	13.4
[Ca <sup>2+</sup> ] (mg/L)	13.2
PH	8.26

**Table 19: initial composition of the solution in the reactor (experiment 5)**

The pH was adjusted to 8.66 with sodium hydroxide 0.1 M; 240 g of elutriated Unitika struvite, that is to say 9% in mass and 5.3% in volume, were added in the reactor. The solution was mixed during an hour to favour the absorption of the solution on the pellets.

### 6.5.2.3 Running period

The three flow rates (average on the running period), magnesium flow rate of 0.210 L/h, phosphate flow rate of 2.37 L/h and sodium hydroxide 0.1 mol/L flow rate of about 0.103 L/h (total flow rate of about 2.68 L/h) were added in the reactor during 69 hours. The different fluctuations during the running period are listed in the following table:

Running time	Operating conditions					
	pH	Mg flow rate (L/h)	NaOH 0.1M flow rate (L/h)	effluent flow rate (L/h)	P flow rate (L/h)	ratio Mg/P
0h-13h40	8.75	0.195	0.11	2.73	2.43	0.92
13h40-22h30	8.8	0.183	0.11	2.74	2.45	0.86
22h30-36h50	8.67	0.245	0.10	2.72	2.38	1.15
36h50-39h40	8.67	0.213	0.10	2.66	2.35	1.02
39h40-60h	8.79	0.220	0.10	2.55	2.23	1.11
60h-68h20	8.7	0.206	0.10	2.70	2.39	0.98
average	8.73	0.210	0.103	2.68	2.37	1.01

**Table 20: operating conditions fluctuations (experiment 5)**

The pH was maintained at about 8.7. The “inlet” concentrations calculated by considering the mixing of the 3 feed flows are reported in Table 21.

Species	Concentration (mg/L)	Concentration (mmol/L)
P-PO <sub>4</sub>	79.5	2.56
N-NH <sub>4</sub>	62.9	4.48
Mg <sup>2+</sup>	61.7	2.57
Ca <sup>2+</sup>	21.6	0.54

**Table 21: feed concentrations which would be obtained by mixing the 3 flows (experiment 5)**

The molar ratio Mg/P is equal to about 1.

### 6.5.3 Results

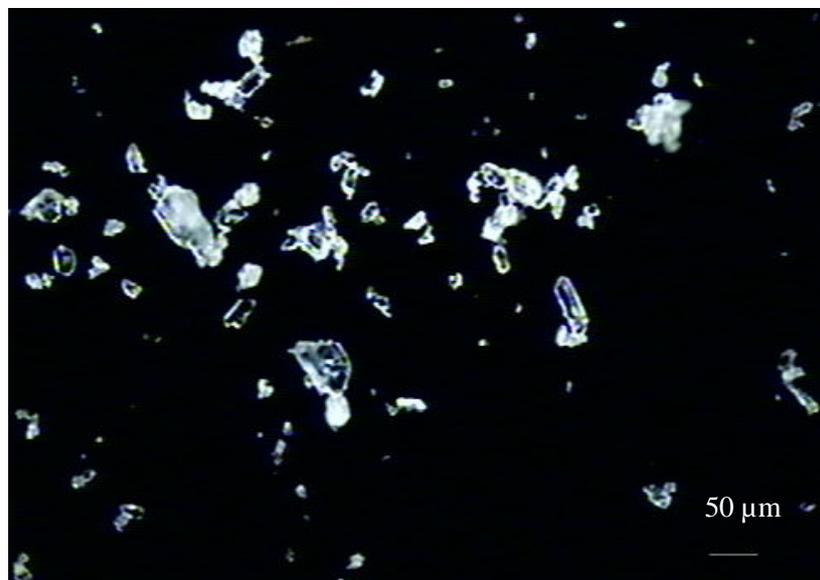
#### 6.5.3.1 .Analysis

The effluent concentrations during the test are reported in the following table:

Sample	Concentrations (mg/L)					
	Mg tot.	Mg dis.	P tot.	P dis.	Ca tot.	Ca dis.
time						
13h40	15.9	9.81	28.5	15.5	17.4	10.1
22h30	15.7	9.36	29.3	15.3	16.5	9.38
36h50	25.7	17.9	27.1	12.7	18	13.8
39h40	24.2	16.1	26.9	11.8	17.4	13.2
60h	20.1	14.1	24.1	11.5	14.2	13.5
68h20	19.7	14	28	15.7	14	12.8
Average	20.2	13.5	27.3	13.8	16.3	12.1

**Table 22:** analysis results (experiment 5)

The following figure (Fig. 26) shows the particles in the “upper solid phase” (see following section).



**Fig. 26:** precipitated struvite during experiment with elutriated Unitika struvite

### **6.5.3.2 Observations**

Fig. 27 shows the reactor during the experiment.



**Fig. 27: View of the reactor during experiment with elutriated Unitika struvite**

A lot of fines can be seen. These fines stay in the mixing zone, settle on the conical zone or are driven in the effluent. Indeed, in the Fig. 27, we observe a white settling on the cone-shaped section and a cloudy solution in the settling zone. In the reaction zone, we see seed materials and other thinner particles in suspension.

If agitation is stopped, the solid particles settle and form two different solid layers: the seeds materials in the lower part and precipitated struvite in the upper part (see Fig. 26).

## **6.6 Discussion**

For the three experiments the same observations were noticed:

- Production of a lot of fines
- Fines settling on the cone-shaped section
- Some fines driven in the effluent by the upward flow
- No deposit of precipitated struvite on struvite pellets

The operating conditions generate a lot of fines (high nucleation) which are driven by the upward flow and have no time to grow in the mixed zone. This nucleation can be primary or secondary nucleation. In fact, the Unitika pellets are too large to agglomerate together. They can neither collect the fines. If fines are collected or if nuclei appear on the pellets surface, they are immediately pulled out by the shearing forces (this last mechanism corresponding to secondary nucleation). Finally, the Unitika pellets have probably reached their maximum size. The existence of a maximum size is often observed in agglomeration. This size is essentially linked to hydrodynamics.

## **7 EXPERIMENTS WITHOUT SEEDING**

Two experiments without seeding were performed because of the difficulties to coat sand and struvite pellets.

### **7.1 Experiment 6: no seeding**

#### **7.1.1 Operating conditions**

##### **7.1.1.1 Compositions of the solutions**

Phosphate solution	[P-PO <sub>4</sub> ] meas.	86 (mg/L)	2.77 mmol/L
	[N-NH <sub>4</sub> ] cal.	175 (mg/L)	12.5 mmol/L
	[Ca <sup>2+</sup> ] meas.	/	
	[Mg <sup>2+</sup> ] meas.	6 (mg/L)	0.25 mmol/L
	pH	7.2	
Sodium hydroxide	NaOH		0.5 (mol/L)
Magnesium solution	[Mg <sup>2+</sup> ]	720 (mg/L)	30 mmol/L

**Table 23: composition of solutions (experiment 6)**

##### **7.1.1.2 Start-up**

2.5 L of phosphate solution were introduced in the reactor, pH (equal to 7.16 at the beginning) was adjusted with sodium hydroxide 0.5 mol/L at pH 9.1. Magnesium flow rate of 0.36 L/h was added in the reactor during an hour with a stirring speed of 300 rpm. After a latent time of few minutes, the solution became cloudy, indicating that solids had precipitated. The stirring speed was maintained during few hours before the addition of the reactants.

##### **7.1.1.3 Running periods**

The three flow rates, magnesium flow rate of 0.36 L/h, phosphate flow rate of 2.5 L/h and sodium hydroxide flow rate of about 0.04 L/h (total flow rate of 2.9 L/h) were added in the reactor during 14 hours. The pH was maintained to about 9-9.2. The inlet concentrations if the 3 flows were mixed would be:

Species	Concentration (mg/L)	Concentration (mmol/L)
P-PO <sub>4</sub>	74	2.39
N-NH <sub>4</sub>	150.9	10.78
Mg <sup>2+</sup>	89.4	3.72

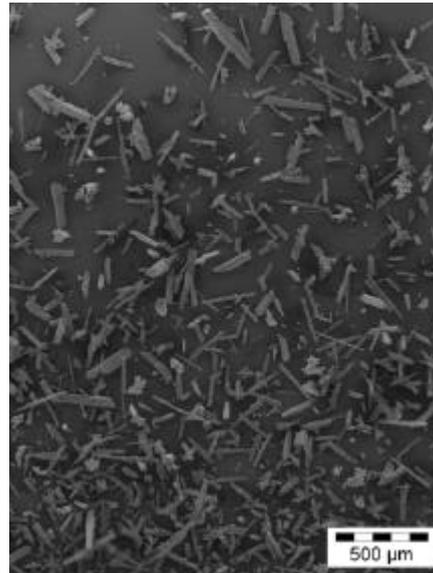
**Table 24: feed concentrations which would be obtained by mixing the 3 flows (experiment 6)**

The molar ratio Mg/P is 1.5.

## **7.1.2 Results**

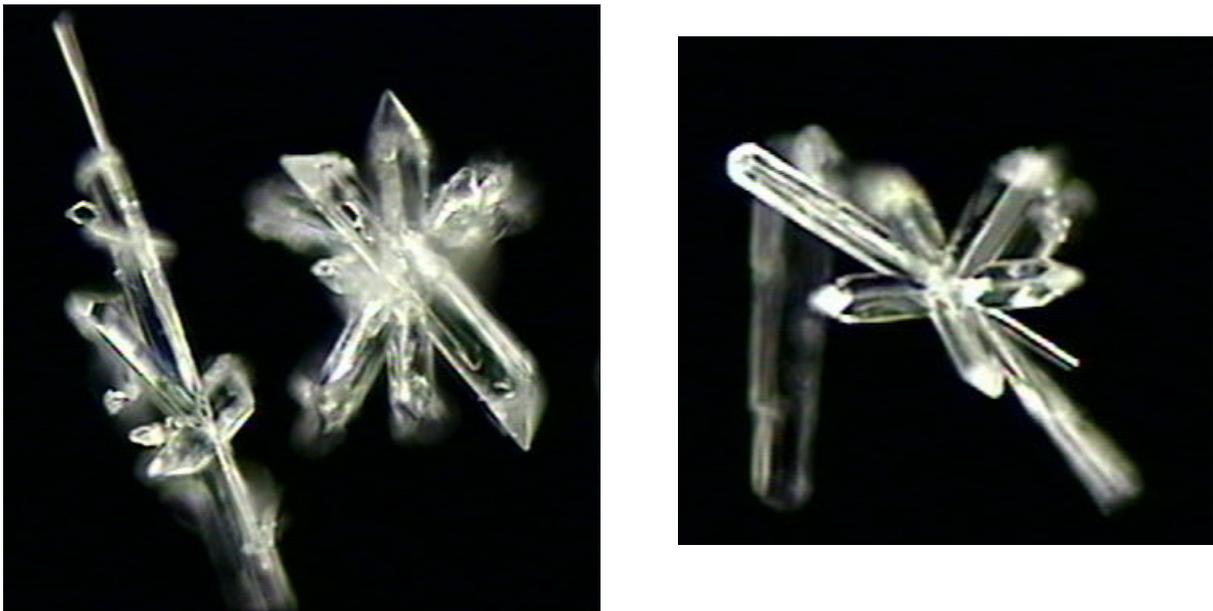
### **7.1.2.1 Analysis**

The residual magnesium and phosphate dissolved concentration of the effluent after filtration was 9 mg/L and 4 mg/L respectively. The formed solid was struvite, analysed by X-Ray diffraction. The purity of solid formed was analysed too. A sample of precipitate were weighed, dissolved in acid nitric and filtered to analyse by ICP-AES the magnesium and phosphorus composition. The measured mass composition of struvite precipitated was similar to theoretical mass composition, that is to say 9.9 % in magnesium and 12.6 % in phosphorus.



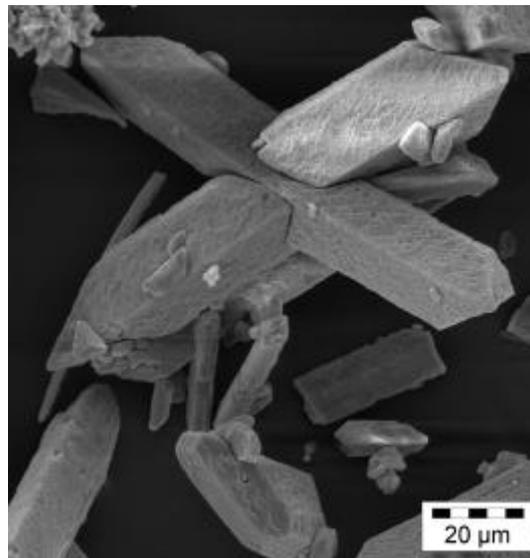
**Fig. 28: struvite formed without seeding**

The scanning electron microscope observations show needle-like particles (Fig. 28). At  $\times 10$  magnification in light microscope, we observe star-like particles, called “macle” (twin crystals). The crystal grow in all directions (see Fig. 29 and Fig. 30).

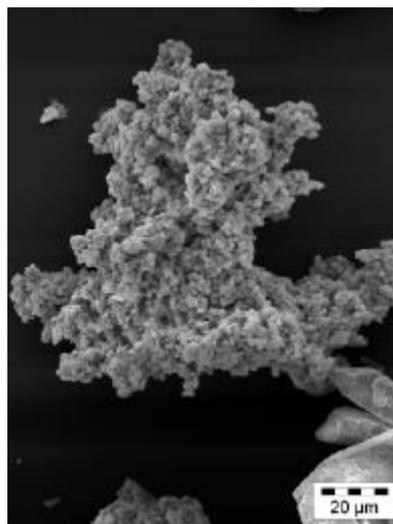


**Fig. 29: struvite crystals in growth (light microscope  $\sim 10$  magnification)**

Agglomerated amorphous crystals were found in the reactor (see Fig. 31). These amorphous crystals are calcium phosphate. Calcium phosphate particles, precipitated in the storage tank of phosphate, were driven by phosphate flow rate in the reactor. The molar ratio Mg/Ca was too low to precipitate calcium phosphate in the reactor and the form of crystals confirms this hypothesis.



**Fig. 30: struvite as form of “macle” (SEM)**



**Fig. 31: amorphous crystal found in the reactor**

### **7.1.2.2 Observations**

Fines were produced during this test, but little were driven in the effluent. Most of the fine particles formed in the reaction zone were driven by the upward flow rate and settled in the cone-shaped section. Only few particles remained in the reaction zone and grew (see Fig. 30). However, the experiment was too short to observe a significant growth of the particles.

During this experiment, several tests were performed to try to drive the settled particles in the reaction zone. The stirring speed was increased. At 600 rpm, we managed to put these particles in suspension but this stirring speed was maybe too high to favour growth. The other test has consisted

in raising the propeller. The new position was 30 cm higher than the old one. Little change was observed with this configuration.

After having emptied the reactor, fouling was observed on Mg feed point and a little on the baffles, the propeller, and the glassware. So, heterogeneous primary nucleation took place on glassware, baffles and propeller and homogeneous primary nucleation took place in the solution volume.

These last observations suggest that supersaturation was too high. So the operating conditions were changed in the following experiment.

## **7.2 Experiment 7: no seeding**

Experiment 6 showed crystals in growth and a production of fines. However, since the initial solution poured in the reactor was a solution relatively concentrated in phosphate (same composition as the solution fed during the semi-continuous process), the initial supersaturation at the feeding point was high and may have favoured the formation of fines. In order to reduce the initial supersaturation, we decided then to operate by following the same initial procedure as in experiment 5. So, this experiment 7 was started with a step of saturated solution in the reactor. Furthermore, to limit the production of fines, parameters influencing the supersaturation as pH, molar ratio Mg/P, ammonia concentration were decreased as in experiment 5.

### **7.2.1 Operating conditions**

#### **7.2.1.1 Compositions of the solutions**

In comparison with the experiment 6 the ammonia concentration was divided by about 2. The concentrations of the feed solutions were the following:

Phosphate solution	[P-PO <sub>4</sub> ] mes.	87.2 (mg/L)	2.81 mmol/L
	[N-NH <sub>4</sub> ] cal.	71 (mg/L)	5.07 mmol/L
	[Ca <sup>2+</sup> ] mes.	17.8 (mg/L)	0.445 mmol/L
	[Mg <sup>2+</sup> ] mes.	6 (mg/L)	0.25 mmol/L
	pH	7.1	
Sodium hydroxide solution	NaOH		0.5 and 0.1 (mol/L)
Magnesium solution	[Mg <sup>2+</sup> ]	720 (mg/L)	30 mmol/L

**Table 25: composition of the solutions (experiment 7)**

The molar ratio N/P is 1.8 that is to say 11/6.

### **7.2.1.2 Start-up**

3 litter of filtrate of the last experiment was taken and introduced in the reactor. The composition of the filtrate was the following:

[P-PO <sub>4</sub> <sup>3-</sup> ] (mg/L)	8,3
[Mg <sup>2+</sup> ] (mg/L)	7,6
[Ca <sup>2+</sup> ] (mg/L)	10,5
pH	8,43

**Table 26: initial solution composition (experiment 7)**

9 g of struvite crystallized during the experiment 6 were added in the solution to absorb the supersaturation. The pH was adjusted to 8.65 with sodium hydroxide 0.5 mol/L . Then, the solution was mixed during one hour before the beginning of the test.

### **7.2.1.3 Running period**

The three flow rates (average on the running period), magnesium flow rate of 0.2 L/h, phosphate flow rate of 2.45 L/h and sodium hydroxide 0.5 mol/L flow rate of about 0.0265 L/h or (sodium hydroxide 0.1 mol/L of about 0.106 L/h (total flow rate of about 2.75 L/h) were added in the reactor during 117 hours. The pH was maintained to about 8.7.

During the experiment, flow rates and pH fluctuated, the operating conditions are summarised in the Table 27:

<b>Running</b>	<b>Operating conditions</b>						
time	PH	Mg flow rate (L/h)	NaOH 0.5M flow rate (L/h)	NaOH 0.1M flow rate (L/h)	effluent flow rate (L/h)	P flow rate (L/h)	ratio Mg/P
0-14h30	8.65	0.16	0.0265		2.8	2.64	0.65
14h30-29h30	8.87	0.181	0.0265		2.74	2.54	0.76
29h30-50h	9.09	0.216	0.0265		2.6	2.43	0.95
50h-69h	8.63	0.21	0.0265		2.7	2.48	0.91
69h-87h	8.55	0.234		0.106	2.71	2.37	1.06
87h-117h	8.55	0.212		0.0795	2.7	2.41	0.94
average	8.72	0.202	0.0265	0.0928	2.71	2.48	0.88

**Table 27: operating condition fluctuations (experiment 7)**

The inlet concentrations calculated by mixing the 3 flow rates are:

Species	Concentration (mg/L)	Concentration (mmol/L)
P-PO <sub>4</sub>	77.7	2.51
N-NH <sub>4</sub>	63.25	4.52
Mg <sup>2+</sup>	52.4	2.18
Ca <sup>2+</sup>	15.86	0.4

**Table 28:** feed concentrations which would be obtained by mixing the 3 flows (experiment 7)

The ratio molar Mg/P is about 0.9.

## 7.2.2 Results

### 7.2.2.1 Analysis

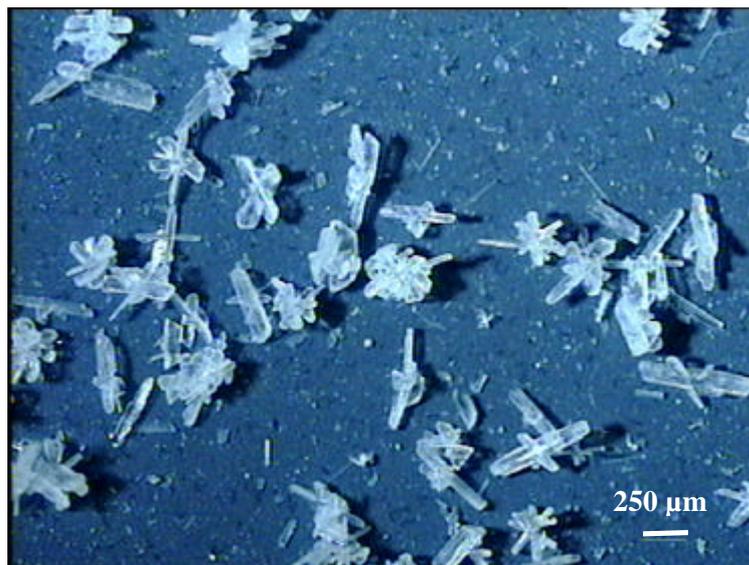
During this different periods, samples were taken to analyse the magnesium, phosphate and calcium (total and dissolved) in the effluent by ICP-AES. The results are summarised in the Table 29:

Sample	Concentrations (mg/L)					
	Mg tot.	Mg dis.	P tot.	P dis.	Ca tot.	Ca dis.
time						
14h30	8.8	4.7	31.4	22	14.6	10.7
29h30	10	5.3	27.6	16.1	17.6	8
50h	14.7	9.4	20.2	8.7	18.6	10.2
69h	16.1	12.7	27	19.8	18.9	12.9
87h	18.9	17	24.6	20.9	18.7	14.9
117h	16.7	14.4	24.1	15.5	13.8	10.1
average	14.2	10.6	25.8	17.2	17.0	11.1

**Table 29:** analysis results (experiment 7)

About 126g of struvite were produced during this experiment of 117 hours, so the production of struvite in these conditions is about 1g/h.

Samples of formed solid during this experiment were taken and observed under light microscope (Fig. 32 and Fig. 33).



**Fig. 32: struvite formed after 5 days**



**Fig. 33: struvite formed after 5 days**

#### **7.2.2.2 Observation**

We still observed particles settled in the cone-shaped section. But, these particles returned in the mixing zone with the stirring flow. The particles are large enough to fall down by gravitation.

In Fig. 33, we observe particles of size over 500 μm. In fact only very few particles of that size have been obtained. These agglomerates were probably formed on the cone-shaped wall and fell down in the reaction zone. In this figure, we also notice a large monocrystal.

A lot of particles larger than 300 μm which have grown (see Fig. 32 in the middle) in form of “macle” and thin particles in form of needle were observed. Particles in form of “macles” are very

interesting because they can grow. Although the experiment has lasted 117h, the experiment time is too short to estimate the maximum size that can be reached.

At pH 8.7, about 78% of phosphate is eliminated and about 67% of phosphate is recovered. In comparison with experiment 5, seed materials have not influence on the conversion rate of phosphate.

After 5 running days, fouling was not observed at reactant feed point. So, the supersaturation was lower enough to prevent fouling.

### **7.3 Discussion**

In comparison with seed materials, sand and struvite pellets, during experiments without seeding particles formed grow.

The generated nuclei grow and agglomerate together. Particles grow by “maclage”, so they have a sufficient size to stay in the reaction zone.

The formed “macles” are interesting because they offer growth site to nuclei. Nuclei can stay attached on the “macles”.

## **CONCLUSION**

The experiments of sand coating didn't succeed. But, these two experiments were not enough to conclude that sand coating by struvite is impossible. It would be interesting to make another test with thin sand at lower supersaturation to limit high nucleation.

As concern experiments with Unitika struvite as seed materials, two solid phases were observed, the seed materials and fines precipitated during the test, even when pH and molar ratio Mg/P were decreased. In fact, Unitika struvite pellets have probably reached their maximum size.

The experiments performed without seeding also produced fines. But the particles manage to grow. Macles (twin crystals) of 300  $\mu\text{m}$  were obtained after 5 days. In comparison with seeding experiments, less fines were driven in the effluent.

In reducing parameters contributing to supersaturation, pH, molar ratio N/P and Mg/P, fouling of baffles, propeller, glassware and magnesium tube was less important.

In the future, it would be interesting to make a longer test in order to evaluate the maximum size that can be reached by the particles and to measure fouling after a long period.

Following to these different experiments, to obtain pellets and not fines, it is better to work without any seed materials.

The advantages of the reactor are that:

- Fines stay in the reactor and few fines are driven in the effluent
- The conception is simple
- The control is easy

The different points to develop are:

- To optimize operating conditions:
  - o increase residence time in the reactor by increasing reactor volume (multiplying volume by 2 just needs to multiply diameter reactor by 1.25)
  - o decrease expensive cost of reactants (sodium hydroxide, magnesium chloride)
- To test reactor with real solution coming from waste water treatment plant to measure influence of impurities on struvite growth. Indeed, impurities are often growth inhibitors.

**BIBLIOGRAPHY**

P. Battistoni, P. Pavan, F. Cecchi, J. Mata-Alvares. Effect of composition of anaerobic supernatants from an anaerobic, anoxic and oxic (A2O) process on struvite and hydroxyapatite formation. *Annali di Chimica*, 88, 1998.

P. Battistoni, P. Pavan, F. Cecchi, J. Mata-Alvares. Phosphate removal in real anaerobic supernatants: modelling and performance of a fluidized bed reactor. *Wat. Sci. Tech.* Vol. 38, No 1, pp. 275-283, 1998.

P. Battistoni, P. Pavan, M. Prisciandaro and F. Cecchi. Struvite crystallization: a feasible and reliable way to fix phosphorus in anaerobic supernatants. *Wat. Res.* Vol. 34, No 11, pp.3033-3041, 2000.

P. Battistoni, R. Boccadoro, P. Pavan, F. Cecchi. Struvite crystallization in sludge dewatering supernatant using air stripping : the new full-scale plant at Treviso sewage works. *Second international conference on Recovery of Phosphate from sewage and animal wastes, Holland*, 12<sup>th</sup> and 13<sup>th</sup> march 2001.

N.C. Bouropoulos and P.G. Koutsoukos. Spontaneous precipitation of struvite from aqueous solutions. *Journal of Crystal Growth*. 213, 381-388, 2000.

I. Celen, M. Türker. Recovery of ammonia as struvite from anaerobic digester effluents. *Second international conference on Recovery of Phosphate from sewage and animal wastes, Holland*, 12<sup>th</sup> and 13<sup>th</sup> march 2001.

J.M. Coulson and J.F. Richardson. *Particle Technology and Separation Processes*. Chemical Engineering. Vol. 2, Fourth Edition, 1991.

D. Donnert and M. Salecker. Elimination of phosphorus from municipal and industrial waste water. *Wat. Res.* Vol. 40, No. 4-5, pp. 195-202, 1999.

J.D Doyle, R.Philp, J. Churchley and S.A. Parsons. Analysis of struvite precipitation in real and synthetic liquors. *Institution of Chemical Engineers*. Vol. 78, Part B, November 2000.

S. Gasstra, R. Schemen, P. Bakker and M. Bannick. Full scale phosphate recovery at sewage treatment plant Geestmerambacht, Holland. *International Conference on Phosphorus Recovery from sewage and Animal Wastes, Warwick University, UK*. May 6<sup>th</sup> and 7<sup>th</sup>, 1998.

W.A. House. The physico-chemical conditions for the precipitation of phosphate with calcium. *Environmental Technology*, Vol. 20, PP. 727-733.

J.A.M. van der Houwen and E. Valsami- Jones. Influence of organic ligands on the precipitation of calcium phosphates. *Second international conference on Recovery of Phosphate from sewage and animal wastes, Holland*, 12<sup>th</sup> and 13<sup>th</sup> march 2001.

J.P. Klein and R. David. *Reaction Crystallization*. Crystallization Technology Handbook edited by Mersmann, 1995.

P. G. Koutsoukos. Current knowledge of calcium phosphate chemistry and in particular solid surface-water interface interactions. *Second international conference on Recovery of Phosphate from sewage and animal wastes, Holland*, 12<sup>th</sup> and 13<sup>th</sup> march 2001.

K.Kumashiro, H.Ishiwatari, Y.Nawamura. A pilot plant study on using seawater as a magnesium source for struvite precipitation. *Second international conference on Recovery of Phosphate from sewage and animal wastes, Holland*, 12<sup>th</sup> and 13<sup>th</sup> march 2001.

D. Matysek, H. Raclavska. Problems of dissolution and crystallization of struvite. *Second international conference on Recovery of Phosphate from sewage and animal wastes, Holland*, 12<sup>th</sup> and 13<sup>th</sup> march 2001.

- Y. Mitani, Y. Sakai, F. Mishina, S. Ishiduka. Struvite recovery from wastewater having low phosphate concentration. *Second international conference on Recovery of Phosphate from sewage and animal wastes, Holland, 12<sup>th</sup> and 13<sup>th</sup> march 2001.*
- K. Moriyama, T. Kojima, Y. Minawa, S. Matsumoto and K. Nakamachi. Development of artificial seed crystal for crystallization of calcium phosphate. *Second international conference on Recovery of Phosphate from sewage and animal wastes, Holland, 12<sup>th</sup> and 13<sup>th</sup> march 2001.*
- E.V. Münch and K. Barr. Controlled struvite crystallization for removing phosphorus from anaerobic digester sidestreams. *Wat. Res.* Vol. 35, No 1, pp. 151-159, 2001-04-13
- E.V. Münch, A. Benesovsky-Scott, J. Josey and K. Barr. Making business from struvite crystallisation for wastewater treatment: turning waste into gold. *Second international conference on Recovery of Phosphate from sewage and animal wastes, Holland, 12<sup>th</sup> and 13<sup>th</sup> march 2001.*
- E.V. Musvoto, M.C. Wentzel, R.E. Loewenthal and G.A. Ekama. Integrated chemical-physical processes modelling-I. Development of a kinetic-based model for mixed weak acid/base systems. *Wat. Res.* Vol. 34, No 6, pp.1857-1867, 2000.
- E.V. Musvoto, M.C. Wentzel, R.E. Loewenthal and G.A. Ekama. Integrated chemical-physical processes modelling-II. Simulating aeration treatment of anaerobic digester supernatants. *Wat. Res.* Vol. 34, No 6, pp.1868-1880, 2000.
- K.N. Ohlinger, T.M. Young and E.D. Schroeder. Predicting struvite formation in digestion. *Wat. Res.* Vol.32, No 12, pp. 3607-3614, 1998.
- K.N. Ohlinger, T.M. Young and E.D. Schroeder. Postdigestion struvite precipitation using a fluidised bed reactor. *Journal Of Environmental Engineering.* August 1999.
- K.N. Ohlinger, T.M. Young and E.D. Schroeder. Kinetics effects on preferential struvite accumulation in wastewater. *Journal Of Environmental Engineering.* April 2000.
- K.N. Ohlinger, T.M. Young and E.D. Schroeder. Struvite characterization and control. *Second international conference on Recovery of Phosphate from sewage and animal wastes, Holland, 12<sup>th</sup> and 13<sup>th</sup> march 2001.*
- P. Piekema, A. Giesen. Phosphate recovery by the crystallization process: experience and developments. *Second international conference on Recovery of Phosphate from sewage and animal wastes, Holland, 12<sup>th</sup> and 13<sup>th</sup> march 2001.*
- L.J. Plant and W.A. House. Precipitation of calcite in presence of inorganic phosphate. *Second international conference on Recovery of Phosphate from sewage and animal wastes, Holland, 12<sup>th</sup> and 13<sup>th</sup> march 2001.*
- Y. Song, H.H. Hahn, and E. Hoffmann. The effects of pH and Ca/P ratio on the precipitation of calcium phosphate. *Second international conference on Recovery of Phosphate from sewage and animal wastes, Holland, 12<sup>th</sup> and 13<sup>th</sup> march 2001.*
- I. Stratful. Conditions influencing the precipitation of magnesium ammonium phosphate. *Second international conference on Recovery of Phosphate from sewage and animal wastes, Holland, 12<sup>th</sup> and 13<sup>th</sup> march 2001.*
- Y. Ueno, M. Fujii. 3 years operating experience selling recovered struvite from full-scale plant. *Second international conference on Recovery of Phosphate from sewage and animal waste, Holland, 12<sup>th</sup> and 13<sup>th</sup> march 2001.*
- M.C. Wentzel, E.V. Musvoto and G.A. Ekama. Application of integrated chemical-physical processes modelling to aeration treatment of anaerobic digester liquors. *Second international conference on Recovery of Phosphate from sewage and animal wastes, Holland, 12<sup>th</sup> and 13<sup>th</sup> march 2001.*

# APPENDICES