

PHOSPHORUS RECOVERY FROM WASTEWATER BY STRUVITE CRYSTALLISATION: A REVIEW

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Abstract

The present review provides an understanding of principles of struvite crystallisation and examines the techniques and processes experimented to date by researchers at laboratory, pilot and full scale to maximise phosphorus removal and reuse as struvite from wastewater effluents. Struvite is mainly known as a scale deposit causing concerns to wastewater companies. Indeed struvite naturally occurs under specific condition of pH and mixing energy in specific areas of wastewater treatment plants (e.g. pipes, heat exchangers) when concentrations of magnesium, phosphate and ammonium approach an equimolar ratio 1:1:1. However, thanks to struvite composition and its fertilising properties, the control of its precipitation could contribute to the reduction of phosphorus levels in effluents while simultaneously generate a valuable end by-product. A number of processes such as stirred tank reactors, air agitated and fluidised bed reactors have been investigated as possible configurations for struvite recovery. Fluidised bed reactors emerged as one of the promising solutions for removing and recovering phosphorus as struvite. Phosphorus removal can easily reach 70% or more, although the technique still needs improvement with regards to controlling struvite production quality and quantity to become broadly established as a standard treatment for wastewater companies.

Keywords: phosphorus removal, struvite, crystallisation technologies, fertiliser

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1. Introduction

Phosphorus (P) is the eleventh in order of abundance element on Earth; under most conditions, it is exclusively combined with four oxygen molecules, forming the phosphate oxyanion. Phosphorus is essential for all living organisms, as it represents the energy currency for organisms at cell level, and its availability often controls biological productivity; for that reason, in excess quantities it is the cause of eutrophication. Eutrophication can be described as nutrient enrichment of surfaces waters, leading to an excessive production of toxic algae, and is responsible for turning water green in lakes, reservoirs, rivers, coastal waters and the marine environment in general (Burke *et al.*, 2004).

Phosphates represent the main source of P and are commonly used in fertilisers, detergents or insecticides. Morse *et al.* (1993) reported that the overdose of P in European Union (E.U) countries water essentially comes from human sources in sewage and from live stock.

Since 1991, European legislation has approached this pollution problem by establishing a new directive (EC Urban Waste Water Treatment Directive 91/271/EEC, UWWTD, 1991). The removal of P in wastewater discharged to sensitive areas is now regulated and minimum P concentrations in effluents are imposed, depending on the size of discharge (Table 1).

Table 1. Requirements of P concentration for discharges from urban waste water treatment plant (UWWTD, 1991)

Population (population equivalents)	Phosphorus limit	Minimum percentage of reduction *
10 000-100 000 p.e.	2 mg. L ⁻¹	80 %
More than 100 000 p.e.	1 mg.L ⁻¹	80 %

* related to the load of the influent

The legislative pressure has led to more discussions on how to integrate P removal processes in wastewater treatment plants (CEEP, 1971- to present). Traditional P removal processes are based on phosphorus fixation in activated sludge either by a biological (biological nutrient removal, BNR) or chemical (precipitation by metal salts) method. These processes are efficient in the sense that they can reduce the P concentration in wastewater effluents to less than 1 mg.L^{-1} (Booker *et al.*, 1999), but they lead to the accumulation of phosphorus in sludge, an increase in sludge volumes, and contribute by reaction with magnesium and ammonium ions to the precipitation of magnesium ammonium phosphate hexahydrate most commonly known as struvite.

Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) scale deposits are causing significant concern to wastewater treatment plants (Doyle *et al.*, 2003). The problem is not necessarily new, as struvite was first observed as a crust of crystalline material in 1937 in a multiple-stage sludge digestion system (Rawn *et al.*, 1937). Often perceived as a nuisance affecting the efficiency of treatment processes and causing maintenance problems, the control of struvite deposition has been widely investigated, including the dilution of struvite crystals with water effluents (Borgerding, 1972); preventive action by chemical dosing of iron salts (Mamais *et al.*, 1994) or addition of chemical inhibitors (Doyle *et al.*, 2003; Snoeyink and Jenkins, 1980).

In the past 10 years struvite precipitation has gained interest as a route to phosphorus recovery (Doyle *et al.*, 2003). Its composition (nitrogen (N), phosphorus (P) and magnesium (Mg) ions in equal molar concentrations) makes it a potentially marketable product for the fertiliser industry, provided that its nucleation and the quality of crystals recovered can be controlled (Booker *et al.*, 1999). Research in struvite formation is now widespread and includes studies towards the prevention of scaling, alternative phosphorus removal and recovery from waste water effluents and potential exploitation to the benefit of wastewater companies and industries as a fertiliser.

Several studies have been carried out to assess potential methods of phosphorus recovery as struvite at a bench and pilot scale, and few processes, integrated in treatment plants, already exist and are effective in Japan (Ueno and Fujii, 2001), The Netherlands (Giesen, 1999) and Italy (Cecchi *et al.*, 2003, Battistoni *et al.*, 2005a).

This review paper focuses on phosphorus removal and recovery by struvite crystallisation. It provides an understanding of principles of struvite crystallisation and reviews the techniques and processes experimented to date by researchers at laboratory, pilot and full scale to maximise phosphorus removal and reuse as struvite.

2. Struvite chemistry

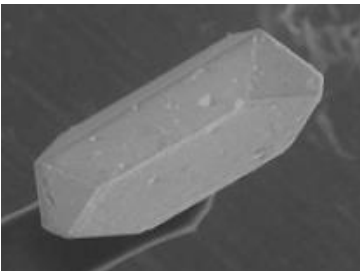
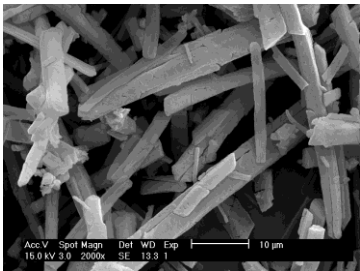
2.1 Struvite characteristics

Struvite is an orthophosphate, containing magnesium, ammonium, and phosphate in equal molar concentrations. The general formula for minerals of the struvite group is:

$AMPO_4 \cdot 6H_2O$ where **A** corresponds to potassium (K) or ammonia (NH₃) and **M** corresponds to magnesium (Mg), cobalt (Co), or Nickel (Ni) (Bassett and Bedwell, 1933).

Struvite in the form of a magnesium ammonium phosphate hexahydrate crystallises as an orthorhombic structure (*i.e.* straight prisms with a rectangular base). Table 2 summarises the main chemical and physical properties of struvite crystals.

Table 2. Properties of struvite.

Nature	Mineral salt
Chemical Name	Magnesium ammonium phosphate hexahydrate
Formula	$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$
Aspect	White glowing crystal, (Bassett and Bedwell, 1933).
Structure	Orthorhombic (space group $\text{Pmn}2_1$): regular PO_4^{3-} octahedra, distorted $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ octahedral, and NH_4 groups all held together by hydrogen bonding, (Abbona and Boistelle, 1979).
	<div style="display: flex; justify-content: space-around; align-items: flex-end;"> <div style="text-align: center;">  <p>Dunn <i>et al.</i> (2004)</p> </div> <div style="text-align: center;">  <p>Le Corre <i>et al.</i> (2007a)</p> </div> </div>
Molecular weight	245.43 g.mol ⁻¹
Specific gravity	1.711 ($\rho=1.711 \text{ g.cm}^{-3}$), (Borgerding, 1972)
Solubility	<p>Low in water: 0.018g.100 ml⁻¹ at 25°C in water</p> <p>High in acids: 0.033g.100 ml⁻¹ at 25°C in 0.001 N HCl;</p> <p style="padding-left: 100px;">0.178g.100 ml⁻¹ at 25 °C in 0.01 N HCl</p> <p>(Bridger <i>et al.</i>, 1961).</p>
Solubility constant	$10^{-13.26}$ (Ohlinger <i>et al.</i> , 1998)

Struvite crystals occur spontaneously in various biological media. For instance, it has been found in rotting organic material such as guano deposits and cow manure, where it is produced through the microbiological combination of NH_4^+ ions from bacterial metabolisms with Mg and P already present in the media (Ben Omar *et al.*, 1994). It has also often been studied in the medical field as it can spontaneously form calculi in human kidneys (Coe *et al.*, 2005), and lately in soil sciences as a way to entrap nitrogen in compost (Jeong and Kim, 2001; Jeong and Hwang, 2005)

2.2 Spontaneous precipitation of struvite in wastewater environments

In the wastewater treatment area, struvite is well-known as a scale problem. In their study about digestion system published in 1937, Rawn *et al.* (1937) mentioned the occurrence of a “*crust of crystalline material*” in areas of a pipe that was carrying supernatants liquors and identified it as magnesium ammonium phosphate in a purity ratio of 96 %. Struvite as a source of scale deposits in wastewater treatment plants (WWTP) was then confirmed by Borgerding (1972) who identified it on the walls of an anaerobic digestion system at the Hyperion treatment plant, Los-Angeles, 1963. This scale problem was first considered to be solved successfully as the struvite deposit was dissolved by an acidic treatment. Unfortunately it reappeared a few years later and reduced significantly the diameter of pipes in the same plant. Since then, struvite as a scale agent had been the theme of several studies (Snoeyink and Jenkins 1980, Mohajit *et al.*, 1989, Doyle *et al.*, 2002), but most authors have considered struvite as a ‘problem’ to eliminate and not as a product which could be of economic interest.

Struvite precipitates in a 1:1:1 molar ratio following the general equation (with n= 0, 1, or 2):



The occurrence and development of struvite crystals follows two chemical stages: nucleation (crystal birth) and crystal growth (development of crystals until equilibrium) (Jones, 2002). Predicting or controlling these mechanisms is complex as it is controlled by a combination of factors including the crystal state of initial compounds, thermodynamic of liquid-solid equilibrium, phenomena of matter transfer between solid and liquid phases (Jones, 2002; Mullin, 1992), and kinetics of reaction (Ohlinger *et al.*, 1999) as well as several physico-chemical parameters such as: pH of the solution from which struvite may precipitate (Bouropoulos and Koutsoukos, 2000), supersaturation (Doyle *et al.*, 2002), mixing energy

(Ohlinger *et al.*, 1999), temperature (Aage *et al.*, 1997) and presence of foreign ions (Le Corre *et al.*, 2005). To illustrate, according to equation (1), the reaction between magnesium, ammonium and phosphate ions causes the release of hydrogen ions in solution, and induces a drop of pH. As a result, spontaneous precipitation of struvite always occurs in specific areas of WWTP (Ohlinger *et al.*, 1999). As struvite solubility decreases when pH increases, and increases with phosphate concentration, most of struvite scales have been observed in areas of high turbulence (*i.e.* elbows, valves, propellers, pumps) and in parts of sludge treatment processes where phosphates concentrations are the highest that is to say in digested sludge and sludge liquors pipeline (Table 3).

Table 3. *Locations of struvite deposits and relative damages caused.*

Authors	Location of deposit	Effects	Type of plant
Rawn <i>et al.</i> (1937)	Digestion sludge process: pipes carrying supernatants liquors	Accumulation in some places to the thickness of an inch (~ 2.5 cm)	Wastewater treatment plant, (USA)
Borgerding (1972)	Activated/digested sludge process: suction side of pump onto separating screen	310 mm diameter of the suction side reduced to 150mm	Hyperion waste water treatment plant, (USA)
Booram <i>et al.</i> (1975)	Items in contact with anaerobic liquids: pump impellers, pipes...	-	Livestock waste treatment and management plant, (U.S.A)
Mohajit <i>et al.</i> (1989)	In floating aerators, raw waste pumps, pipelines and outfall pipelines.	Accumulation: from 5.88 up to 14.44 mm in aerators from 8 up to 28mm in pipes carrying digester effluents	Pig waste treatment plant, (Singapore)
Ohlinger <i>et al.</i> (1998)	Accumulation on pipe walls from sludge basins supernatant system	Accumulation along 5.6 km of pipes.	Wastewater treatment plant, (USA)
Williams (1999)	Accumulation of struvite crystals in pipelines from the sludge holding tank to the centrifuges	Bore of pipes reduced from 100 to 50 mm	Wastewater treatment plant, (UK).
Doyle <i>et al.</i> (2000)	Pipes carrying centrate liquors	Pipe diameter reduction from 150 to 60 mm in 12 weeks.	Sludge destruction plant, (UK)
Battistoni <i>et al.</i> (2004)	Pipes carrying anaerobic supernatants.	Reduction of pipes diameter	Demonstrative Fluidised Bed Reactor plant, WWTP , (Italy)
Neethling and Benisch (2004)	Streaming pipes controlling polymer feed - flowmeters	2 months build up in a 3" rubber lined 90° elbow	WWTP, (USA)

2.3 Notion of solubility and solubility product

2.3.1 Definition

As for other mineral salts, the presence of struvite is controlled by its solubility (Taylor *et al.*, 1963, Burns and Finlayson, 1982, Webb and Ho, 1992, Aage *et al.*, 1997).

Solubility of a chemical compound can be quantified as the maximum quantity (gram or mole) of solute dissolved in one litre of saturated solution under precise conditions of temperature, nature of solvent and nature of solute. It is generally expressed in gram per litre (g.L^{-1}) or mole per litre (mol.L^{-1}). Solubility is a function of temperature and pressure (Mullin, 1992), and every salts is characterised by its own solubility curve representing the concentration of the salt in a solvent versus temperature. Figure 1 represents the solubility curve for struvite determined by Borgerding (1972).

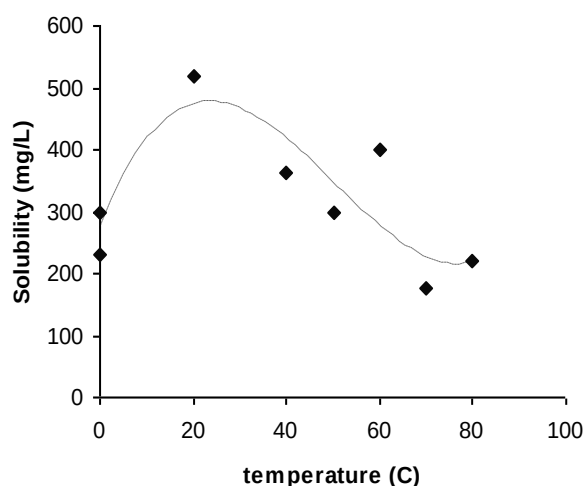
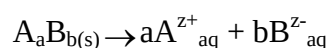


Figure 1. Solubility curve of struvite, adapted from Borgerding (1972).

2.3.2. Solubility product

Given the general equation of dissolution of a salt in water:



The constant solubility product K_{sp} can be expressed as:

$$K_{sp} = [A^{z^+}]^a \cdot [B^{z^-}]^b \quad (2)$$

where: - $[A^{z^+}]$ and $[B^{z^-}]$ are the total concentrations of ions in solution

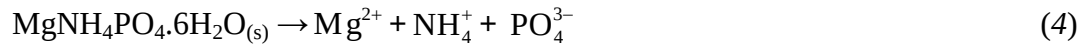
- z^+ , z^- are the valencies of the considered ions.

If we call c^* the equilibrium solubility of each ion in a way that $a=b=1$, and $c^*=[A^{z^+}]=[B^{z^-}]$, then for a salt producing two ions, we have:

$$K_{sp} = (c^*)^2 \text{ or } c^* = K_{sp}^{\frac{1}{2}}$$

$$\text{Or more generally: } K_{sp} = (c^*)^{a+b} a^a b^b \leftrightarrow c^* = \left(\frac{K_{sp}}{a^a b^b} \right)^{\frac{1}{a+b}}, \text{ (Mullin, 1992)} \quad (3)$$

By applying equation (2) and (3) to struvite dissolution (4), we have:



$$K_{sp} = [Mg^{2+}] \cdot [NH_4^+] \cdot [PO_4^{3-}] \text{ or } C^* = \left(\frac{K_{sp}}{1} \right)^{\frac{1}{3}} \quad (5)$$

Equation (5) shows that if the product of the concentrations of Mg^{2+} , NH_4^+ , PO_4^{3-} is greater than the value of K_{sp} , then the solution is supersaturated with respect to struvite and precipitation will occur.

Several studies have been carried out to assess the solubility product of struvite, and numbers of K_{sp} values are available in the literature (Table 4). These are usually expressed using its negative log, noted pK_{sp} for practical reasons.

Table 4. pK_{sp} values and respective concentrations of ions required to reach them

Authors	K_{sp}	pK_{sp}	Mg^{2+} (mg.L ⁻¹)	NH_4^+ (mg.L ⁻¹)	PO_4^{3-} (mg.L ⁻¹)
Bube (1910)	$2.50 \cdot 10^{-13}$	12.60	1.51	1.13	5.98
Taylor <i>et al.</i> (1963)	$7.10 \cdot 10^{-14}$	13.15	0.99	0.74	3.93
Borgerding (1972)	$3.90 \cdot 10^{-10}$	9.40	17.53	13.15	69.40
Burns and Finlayson (1982)	$7.50 \cdot 10^{-14}$	13.12	1.01	0.76	4.01
Loewenthal <i>et al.</i> (1994)	$2.50 \cdot 10^{-13}$	12.60	1.51	1.13	5.98
Buchanan <i>et al.</i> 1994	$4.32 \cdot 10^{-13}$	12.36	1.81	1.36	7.18
Aage <i>et al.</i> (1997)	$1.15 \cdot 10^{-13}$	12.94	1.17	0.87	4.62
Ohlinger <i>et al.</i> (1998)	$5.49 \cdot 10^{-14}$	13.26	0.91	0.68	3.61

As a thermodynamic constant, K_{sp} translates to real sludge or liquors with difficulty, due to the presence and influence of many dissolved species other than the struvite components, the net effect of other species in solution is a reduction in the precipitation potential of struvite (*e.g.* Ca^{2+} which can combine with phosphates).

A more practical way of assessing saturation is in the form of the activity solubility product, K_{so} , which takes into account the ionic strength (I) and the activity (a_i) of the ionic species. As pH, I and a_i are not considered in a K_{sp} calculation, the value generated by a K_{sp} is lower than the one generated by a K_{so} calculation. For struvite, K_{so} is calculated via the following formula (Snoeyink and Jenkins, 1980):

$$K_{so} = a_{Mg^{2+}} \times a_{NH_4^+} \times a_{PO_4^{3-}} \quad (6)$$

where: a_i is the activity of the i^{th} ion in solution defined as $a_i = \gamma_i \cdot [C_i]$

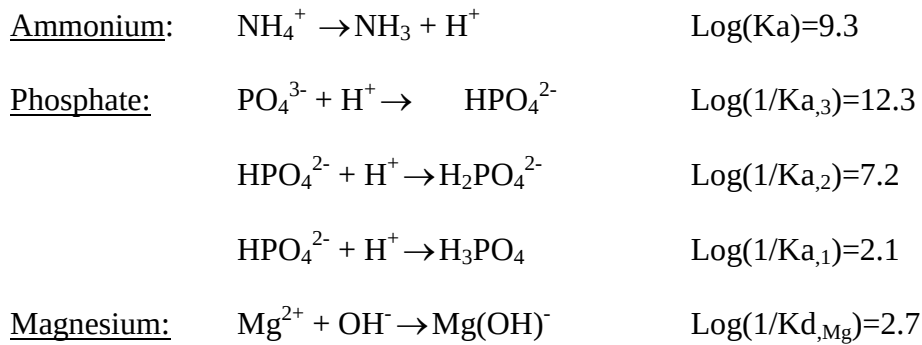
with γ_i representing the activity coefficient of the ionic specie i and $[C_i]$ its respective total concentration.

K_{so} can also be expressed as a pK_{so} value, such as $pK_{so} = -\log K_{so}$.

Hence when the solutions are infinite diluted ($\gamma_i=1$), we have $K_{sp}=K_{so}$. This condition occurs in practise for concentrations of the ionic species up to 10^{-3} mol.L⁻¹, as A_i depends on all other ions in solution (Mullin, 1992).

The main difficulty in predicting struvite formation in media such as wastewater is that many ionic species (*e.g.* Ca^{2+} , K^+ , CO_3^{2-}) can influence the saturation of struvite by reacting with its component ions, Mg^{2+} , PO_4^{3-} and NH_4^+ . It is therefore necessary to know the availability of free ions, i.e. the ionic activity, for a given pH. A variety of empirical equations have been proposed in the literature.

For instance, Snoeyink and Jenkins (1980) used the following equations and constants to estimate ions concentrations in solution:



From them, they deduced:

$$K_{so} = a_{Mg^{2+}} \times a_{NH_4^+} \times a_{PO_4^{3-}} \quad (7)$$

$$K_{so} = (\gamma_{Mg^{2+}} [Mg^{2+}])(\gamma_{NH_4^+} [NH_4^+])(\gamma_{PO_4^{3-}} [PO_4^{3-}])$$

Snoeyink and Jenkins (1980) also introduced the notion of conditional solubility product defined as:

$$C_{sp} = C_{T, Mg^{2+}} \times C_{T, PO_4^{3-}} \times C_{T, NH_4^+} \quad (8)$$

$$\text{where: } C_{T, Mg^{2+}} = \left(\frac{[Mg^{2+}]}{\alpha_{Mg^{2+}}} \right) \text{ is the total analytical concentration of magnesium} \quad (9)$$

with α symbolising the ionisation fraction that can continue to form struvite

From (7) and (8) and (9),

$$C_{sp} = \left(\frac{K_{so}}{\alpha_{Mg^{2+}} \alpha_{NH_4^+} \alpha_{PO_4^{3-}} \times \gamma_{Mg^{2+}} \gamma_{NH_4^+} \gamma_{PO_4^{3-}}} \right) = \left(\frac{K_{sp}}{\alpha_{Mg^{2+}} \alpha_{NH_4^+} \alpha_{PO_4^{3-}}} \right) \quad (10)$$

This conditional solubility product is a function of pH, so it is at its minimum when the product of the ionisation fractions is at its maximum. This minimum value corresponds also to a pH minimum usually called in the literature **pH of minimum solubility** (e.g. Snoeyink and Jenkins, 1980, $pH_{\min}=10.7$). This notion of conditional solubility product is useful as it allows a quick assessment of the crystallisation state of a solution (Table 5):

Table 5. Comparison of K_{sp} and C_{sp} value taken from the literature

Authors	Source	[Mg] mol.L ⁻¹	[NH ₄] mol.L ⁻¹	[PO ₄] mol.L ⁻¹	pH	C _{sp}	K _{sp}	Consequences
Booram <i>et al.</i> (1975)	A.T.*	1.97.10 ⁻³	26.8.10 ⁻³	2.63.10 ⁻³	7.5	10 ^{-7.54}	10 ^{-6.87}	C _{sp} <<K _{sp}
Snoeyink and Jenkins (1980)	R*	5.10 ⁻³	5.10 ⁻³	4.10 ⁻²	5.5	10 ⁻⁴	10 ⁻⁶	Struvite precipitation should take place C _{sp} >>K _{sp}
	D*	5.10 ⁻³	1.10 ⁻¹	7.10 ⁻²	7.5	10 ^{-7.5}	10 ^{-4.5}	Undersaturated solution/ No precipitation C _{sp} >K _{sp}
	D.D*	1.10 ⁻³	2.5.10 ⁻²	2.10 ⁻²	7.5	10 ^{-7.5}	10 ^{-6.3}	Oversaturated solution C _{sp} <K _{sp} Supersaturation

* A.T.: Anaerobically treated sludge, R: raw sludge, D: digested sludge, D.D: diluted digested sludge.

- if $C_{sp} \leq C_{T, Mg} \times C_{T, PO_4} \times C_{T, NH_4}$, the solution is oversaturated, and struvite should precipitate until equilibrium.

- if $C_{sp} \geq C_{T, Mg} \times C_{T, PO4} \times C_{T, NH4}$, the solution is undersaturated with respect to struvite, no precipitation will occur.

2.4 Saturation

Saturation is the parameter describing the potential for crystal formation in a solution. For example, given a solution A containing variable quantities of solute, three states are possible (Figure 2):

- undersaturated (in the undersaturated zone), meaning that crystals can dissolve when added to the solution. Crystallisation is thus impossible.
- metastable (in the metastable zone situated between the solubility curve $[A_1A_2A_3]$ and the supersaturation curve $[B_1B_2B_3]$), meaning that the solution is saturated. Spontaneous nucleation can not occur, but growth can be induced by seed addition.
- oversaturated (in the labile or unstable zone), meaning that solute concentration exceeds the equilibrium value substantially and causes spontaneous nucleation. Crystallisation can be rapid and abundant without the need for seeding.

Supersaturation can be achieved by cooling a solution (A to C_1), by evaporating the solvent at constant temperature (A to C_3) or by combining these two methods (A to C_2).

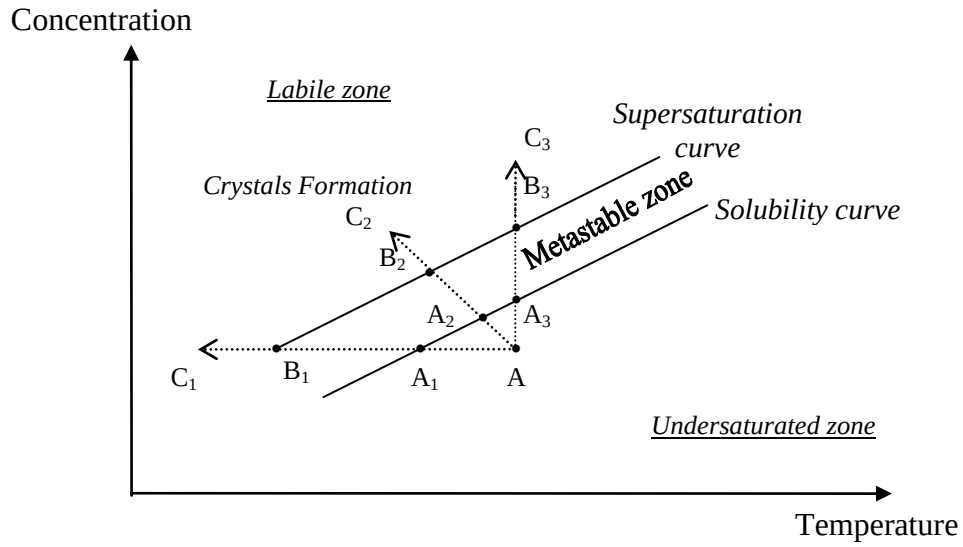


Figure 2. States of a solution during the crystallisation process (adapted from Mullin, 1992).

The characteristics of the metastable zone (*i.e.* width, limits) define the optimum mode of crystallisation for a given process. These characteristics are strongly linked to a parameter, called supersaturation ratio Ω . Ω can be defined in relation with the concentration driving force ΔC . $\Delta C = C - C^*$ with C the concentration of the solution (*e.g.* C_1 , C_2 or C_3), and C^* the equilibrium saturation at a given temperature (*e.g.* B_1 , B_2 , B_3). Thus $\Delta C / C^* = \Omega - 1 = \sigma$ where σ represents the relative supersaturation (Mullin, 1992). However, the application of this expression is limited, and can not be directly used in complex ionic systems (*i.e.* wastewater where many ionic species are in solution).

Bouropoulos and Koutsoukos (2000) defined the supersaturation Ω as a representation of the driving force of the crystallisation. The latter is defined as the difference $\Delta\mu$ of the chemical potential of struvite in the supersaturated solution compared to its value at equilibrium. To calculate the supersaturation they used the following expression:

$$\Omega = \left(\frac{a_{\text{Mg}}^{2+} \cdot a_{\text{NH}_4}^+ \cdot a_{\text{PO}_4}^{3-}}{K_{\text{so}}} \right) \quad (11)$$

where a represents the activity of the ionic species relative to struvite components in solution and K_{so} the struvite solubility product.

The activities of ionic species and the supersaturation Ω are determined by taking into account a series of chemical reactions relevant to the system studied. These are then generally determined using iterative calculations with modeling software based on chemical equilibrium (Doyle and Parsons, 2002).

3. Mechanisms of struvite crystallisation

Crystal formation is a complex process leading to the occurrence of a solid phase made of regular structures named crystals. Despite its complexity, crystallisation is commonly used in industrial applications aiming to separate a desirable solid phase.

This chemical engineering process can be divided in two parts:

- *Nucleation:*

It corresponds to the crystal birth into a liquid or a gaseous media. Ions combine together to form crystal embryos which are the first state of crystals. Nucleation is mostly governed by kinetics of reaction.

- *Crystal growth:*

It corresponds to the development of crystals until the equilibrium is reached. The crystal growth determines the final size of crystal according to the crystallisation kinetics (rate of growth).

To crystallise a compound such as struvite, the supersaturation, as the driving force, need to be reached, in order to trigger the first occurrence of crystals.

3.1. Struvite nucleation

3.1.1. Nucleation and nucleation rate

The nucleation process occurs in a solution when ions combine to form embryos (Mullin, 1992). As illustrated in Figure 3, there are two types of nucleation: the homogeneous primary process causes the spontaneous occurrence of crystals in highly purified or highly supersaturated solution, while the heterogeneous process where crystal formation occurs due to the presence of foreign particles or impurities which function as substrates. Due to the high impurities content of wastewaters, struvite crystal formation is likely to be a heterogeneous nucleation process.

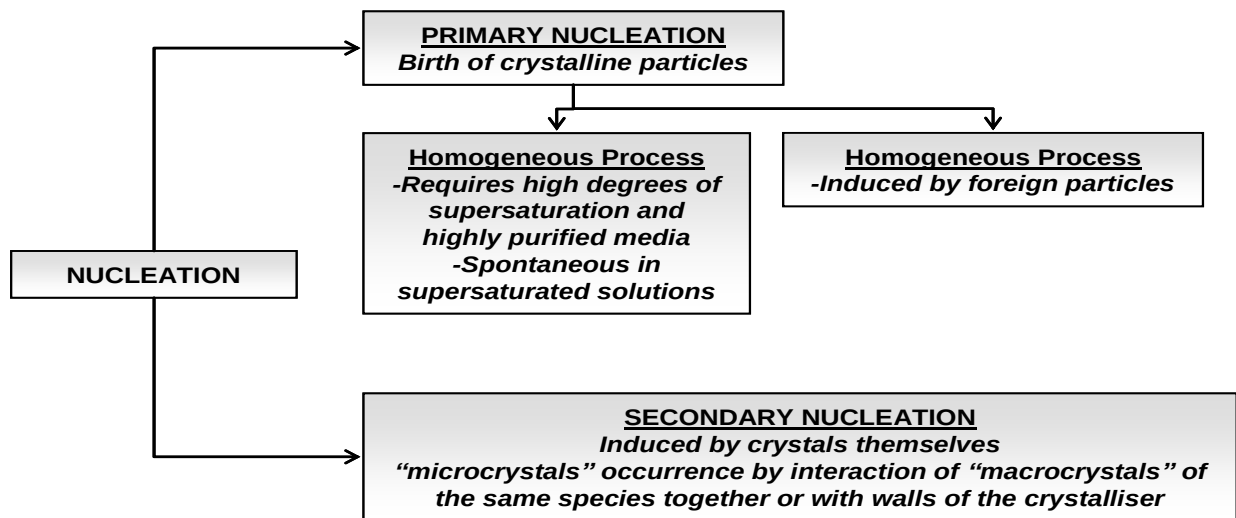


Figure 3. The nucleation process.

According to nucleation theory (Mullin, 1992; Jones, 2002), the rate of nucleation J or number of struvite nuclei formed per unit time (second) and unit volume (cm^3) follows the general equation:

$$J = A \exp \left[- \frac{16 \pi \gamma^3 v^2}{3 k^3 T^3 (\ln \Omega)^2} \right] \quad (12)$$

where A is a kinetic factor, k is the Boltzmann constant (1.38 J. K^{-1}), Ω is the supersaturation ratio, γ is the interfacial tension between a crystal and the solution (mJ.m^{-2}), v the molecular volume (cm^3), and T the absolute temperature (K).

The nucleation rate therefore closely depends on supersaturation Ω of the solution in which crystals occurs, as well as on the kinetic factor A which is usually assumed to be $10^{17} \text{ nuclei.cm}^{-3}$ (Abbona and Boistelle, 1985; Bouropoulos and Koutsoukos, 2000)

Equation (12) has been used to determine the interfacial tension (*i.e.* surface energy) γ of the struvite crystal formed. According to Abbona and Boistelle (1985) a rate of $J = 1 \text{ nucleus.cm}^{-3}$ is characteristic of supersaturations at which nucleation takes place within 1 min. Using this value they obtained an interfacial tension for struvite of 50 mJ.m^{-2} .

Bouropoulos and Koutsoukos (2000) in their study of spontaneous struvite precipitation of struvite from aqueous solution obtained a similar value of the interfacial tension of struvite crystals, and analysed the dependence of rates of nucleation on supersaturation. They concluded that this dependence was of second order suggesting nucleation was controlled by surface diffusion mechanisms. Although they found supersaturation to be the triggering factor of struvite nucleation, they also revealed the great importance of the induction time on the crystallisation process.

3.1.2 Induction time

Ohlinger *et al.* (1999) defined induction time as “the time period between blending of solutions containing precipitant constituents and the first measurable indication of the precipitants”. Induction time can depend on the degree of supersaturation, temperature and the presence of impurities in the solution.

Jones (2002) defined the induction time as:

$$t_{\text{ind}} = t_{\text{N}} + t_{\text{G}} \quad (13)$$

where t_N represents the nucleation time and t_G is the growth time (time necessary to grow to a detectable crystal size).

It appears from this relation that the induction time depends on the different processes involved (nucleation and growth) but also on the kinetics induced by these processes (chemical reaction kinetics, mixing kinetics).

Experimentally speaking, induction time can be determined via different methods such as light scintillation (Gunn and Murphy, 1972), turbidimetry and conductimetry (Söhnel and Mullin, 1982), absorbance measurements (Barrett and Parsons, 1998, Kabdaşlı *et al.*, 2006a), or pH measurements (Bouropoulos and Koutsoukos, 2000).

Bouropoulos and Koutsoukos (2000) demonstrated that induction time was inversely proportional to the supersaturation level Ω , making the supersaturation level one of the most influencing parameter on induction time. This is a general trend in studies that have assessed the variation in struvite induction time, but values can vary depending on condition of precipitation tested (Table 6).

Table 6. Induction times reported for struvite precipitation in a molar ratio Mg:P:N 1:1:1.

Authors	Precipitation method	Induction time measurement method	Supersaturation Ω	Induction time (t_{ind})	Agitation
Abbona and Boistelle (1985)	Spontaneous precipitation (MgSO ₄ .H ₂ O + NH ₄ H ₂ PO ₄)	pH measurement	$\Omega=1.4$ $\Omega=2.5$ $12<\Omega<25$	24 h 24 h 1 min	No agitation
Ohlinger <i>et al.</i> (1999)	Spontaneous precipitation (MgCl ₂ .7H ₂ O + NH ₄ H ₂ PO ₄)	Visual observation of light scintillation	$\Omega=1.6$ $\Omega=2.1$ $\Omega=3.1$	38min 1min 0.25 min	570 rpm
Bouropoulos and Koutsoukos (2000)	Spontaneous precipitation (MgCl ₂ .7H ₂ O + NH ₄ H ₂ PO ₄)	pH measurement	$\Omega=1.13$ $\Omega=2.27$ $\Omega=3.33$	125 min 42 min 6 min	Constant agitation (magnetic stirrer)
Kabdaşlı <i>et al.</i> (2004)	Spontaneous precipitation (MgCl ₂ .6H ₂ O + NH ₄ H ₂ PO ₄)	Light scattering, pH measurement, turbidity, absorbance and particle size measurement	$\Omega=2.346$ $\Omega=3.209$	14 min 3.5 min	Constant agitation (magnetic stirrer)
Kofina and Koutsoukos (2005)	Spontaneous precipitation (synthetic wastewater+ MgSO ₄ .7H ₂ O+ NH ₄ H ₂ PO ₄)	pH measurement	$\Omega=2.1$ $\Omega=3.0$	24.7 min 4.2	Constant agitation (magnetic stirrer)

The mixing speed can also influence nucleation, but its impact on induction time is less significant. To illustrate, Ohlinger *et al.* (1999) showed that for constant supersaturation levels (*e.g.* $\Omega= 2.1, 2.4, 2.7$), a variation of mixing speed from 360 to 1060 rpm only reduced the induction time by about 10 seconds, suggesting that transport influences on struvite precipitation are less important than physico-chemical parameters. However, Abbona and Boistelle (1985) showed that in their system precipitating struvite without any agitation, the induction time at a $\Omega=2.5$ was of 24 h. At a similar supersaturation ratio, but a 570 rpm mixing speed Ohlinger needed only 1 min (Table 6). To reach such an induction period in a static environment, Abbona and Boistelle (1985) needed extremely high supersaturation levels ranging between $12<\Omega<25$.

3.2 Crystal growth

Crystal growth is the step following nucleation, through which crystals embryos increase in size until they form detectable crystals (and beyond).

Growth rate is essentially controlled by processes of mass transfer and by surface integration mechanisms that means by kinetics involved by these processes. The mass transfer process corresponds to the transport of solutes from the solution to the crystal surface by diffusion, convection or both; while the surface reaction process corresponds to the incorporation of material into the crystal lattice through mechanisms of surface integration.

From a theoretical point of view, crystal growth rate G can be expressed as a variation of the increasing size L versus time (t) (Jones, 2002). As for nucleation kinetics, the expression of struvite crystal growth rate following these theoretical principles is difficult to establish from experimental results, and is often correlated with practical parameters such as concentration and temperature using the following general power law:

$$G = \frac{dL \text{ (i.e. size variation)}}{dt \text{ (i.e. time variation)}} = k_g \sigma^g \quad (14)$$

where G represents the growth rate, k_g the growth constant and σ^g the relative supersaturation with $g=1$, for diffusion controlled growth, and $g=1-2$ or >2 for surface integration controlled growth.

Although nucleation seems to be the most important step in producing struvite crystals, it is obvious that mechanisms involved in crystal growth can not be neglected, as they are responsible for the final size and structure of the crystals, which are essential parameters in struvite recovery processes. For instance, Abbona and Boistelle (1979) demonstrated that for high growth kinetics crystals adopted a flat configuration while for low growth kinetics “*stick-like crystals*” were formed.

3.3 Parameters affecting struvite crystallisation

Predicting and controlling nucleation and crystal growth is all the more complex as it depends on a combination of factors such as the initial crystal states of the compounds, phenomena of matter transfer between solid and liquid phases, thermodynamics and kinetics of reaction, as well as several physico-chemical parameters including: pH, supersaturation level Ω , mixing energy, temperature and the presence of foreign ions in the precipitating solution.

3.3.1 pH

The pH at which struvite may precipitate is one of the main factors influencing the crystallisation process as it is linked to the notion of solubility and supersaturation. It can then control the rate of precipitation and, as seen previously, the induction period. In WWTPs, struvite scaling occurs partly because of a pH increase as a result of CO_2 stripping ($\text{HCO}_3^- \rightarrow \text{CO}_2 \uparrow + \text{OH}^-$) (Neethling and Benisch, 2004).

Several authors have studied the effects of pH on struvite crystallisation. For instance, Borgerding (1972) reported that struvite solubility could decrease from around 3000 mg.L^{-1} to less than 100 mg.L^{-1} for pH rising from 5 to 7.5, while Buchanan *et al.* (1994) identified pH 9 as the pH of minimum solubility for struvite.

Furthermore, Booker *et al.* (1999) and Stratful *et al.* (2001) proposed a specific pH range where the precipitation rate of struvite is optimum. By analysing the molar removal of NH_4^+ , Mg^{2+} and PO_4^{3-} by struvite crystallisation from initial solutions with an equimolar quantity of both N and P, and an excess of about 7% in Mg, Bouropoulos and Koutsoukos, 2000 confirmed this statement as the removal of the different species observed were maximum within the pH range 8.5 to about 9.5.

According to equation (1), as struvite precipitates, it triggers a release of protons in solution, thus lowering the pH. The rate of pH decrease reflects the speed at which struvite particles are forming and may influence the quality of the crystals formed. It can thus be used as an indicator of struvite nucleation (Bouropoulos and Koutsoukos, 2000; Kabdaşlı *et al.*, 2004; Le Corre *et al.*, 2005).

Solution pH is also important in the sense that it causes the transformation of NH_4^+ ions into gaseous ammonia, thus reducing the nitrogen concentration and affecting the molar ratio Mg:N:P (minimum value 1:1:1) necessary to form struvite.

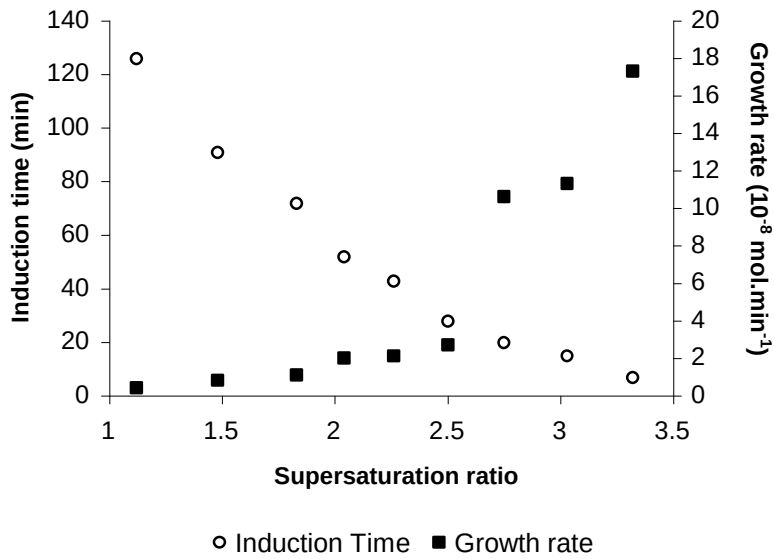
Solution pH also affects struvite crystal growth rate. Ohlinger *et al.* (1999) showed that the accumulation of struvite on stainless steel coupons in contact with supernatants of anaerobically digested sludge was influenced by the pH. An increase in pH caused an increase of supersaturation and a resultant increase in the growth rate. This was shown to be responsible for 30 % of the growth rate difference between no mixing (*i.e.* quiescent zone of a solid storage basin, SSB) and moderate mixing area (*i.e.* near a surface aerator of the SSB), and of 9 % of the growth rate between moderate and high mixing area (*i.e.* in the aerator splash zone of the SSB).

Finally, pH can affect struvite crystal characteristics. Matynia *et al.* (2006) demonstrated that an increase of pH from 8 to 11 could decrease 5 times the mean crystal size of struvite formed in synthetic solutions ($\text{NH}_4\text{H}_2\text{PO}_4$ / MgCl_2 / NaOH). Le Corre *et al.* (2007b) have also shown that pH was responsible for the change in struvite zeta-potential, hence influencing struvite agglomerative properties. They also indicated that in synthetic solutions ($\text{NH}_4\text{H}_2\text{PO}_4$ / MgCl_2 / NaOH) at a pH 10.5 a different phase, $\text{Mg}_3\text{PO}_4 \cdot 22\text{H}_2\text{O}$, may be stable rather than struvite. $\text{Mg}_3\text{PO}_4 \cdot 22\text{H}_2\text{O}$ usually precipitates at pH 9 and above, and depending on the conditions may interfere with struvite precipitation (Tünay *et al.*, 1997).

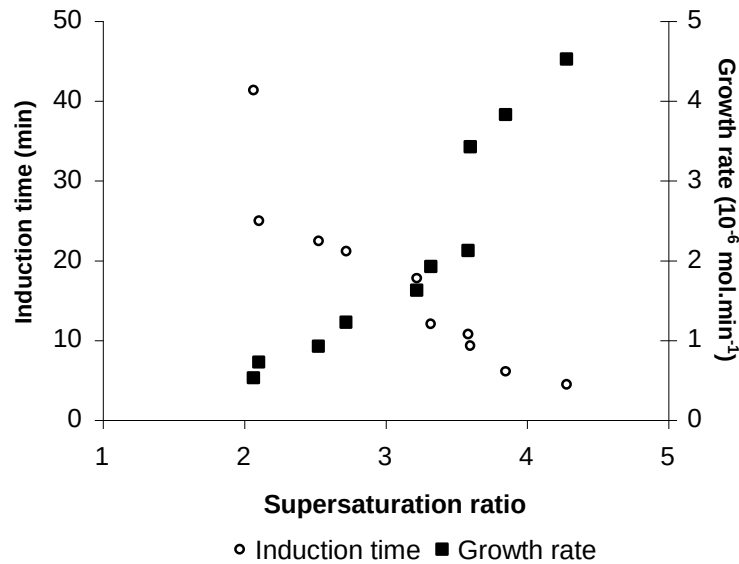
3.3.2 Supersaturation ratio

At a fixed pH, the supersaturation level of the solution affects the crystallisation process in terms of induction time and influences the rate at which the struvite crystals are produced. Bouropoulos and Koutsoukos (2000) demonstrated that at a fixed pH of 8.5 struvite spontaneous precipitation was dependant on the solution precipitation and struvite growth rate was following a power law $R_p = k_p \cdot \sigma^n$ where σ is the relative supersaturation ($\sigma = \Omega^{1/3} - 1$), n is the apparent order of the reaction, and k_p the constant of precipitation. They showed that an increase of Ω value from 1.13 to 3.33 shortened by around 20-fold the induction time and increased more than 55 times the crystal growth rate (Figure 4).

Using the same methods but a different solvent (*i.e.* synthetic water composed of glucose, NaHCO_3 , NaCl , NaNO_2 and Na_2SO_4 instead of de-ionised water), Kofina and Koutsoukos (2005) confirmed these results by demonstrating a high order dependence of struvite crystallisation over the range of supersaturation (2.07 to 4.29) indicative of surface diffusion mechanisms. However, as demonstrated on Figure 4, growth rates over this range of supersaturation were higher, and induction time shorter than for comparable supersaturation levels measured by Bouropoulos and Koutsoukos (2000). This indicated an influence of the nature of solution in which struvite is precipitated as Kofina and Koutsoukos (2005) precipitated struvite by mixing $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solutions into synthetic water composed of glucose, NaHCO_3 , NaCl and NaNO_3 whereas Bouropoulos and Koutsoukos (2000) mixed solutions of $\text{MgCl}_2 \cdot 7\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ diluted in de-ionised water.



Adapted from Bouropoulos and Koutsoukos (2000)



Adapted from Kofina and Koutsoukos (2005)

Figure 4. Effect of supersaturation ratio on the induction time, and growth rate of struvite at pH 8.50, 25° C.

Doyle *et al.* (2002) illustrated the dependence of struvite growth rate on supersaturation level of centrate liquors derived from sludge digesters. The accumulation of struvite on stainless steel coupons during 40 hours (Table 7) showed that at constant supersaturation level the growth rate reached up to 7 times its initial value from 8 h to 40 h of precipitation.

Table 7. *Scaling struvite rates on stainless steel coupons submerged in centrate liquors.*

Doyle et al., (2002).

Ω	Scaling rate ($\text{gm}^{-2}.\text{h}^{-1}$)		
	0-8h	16-24h	32-40h
1.7	0.4	2.6	2.8
2.2	1.2	1.9	3.8
5.3	1.2	3.9	5.4

3.3.3 Temperature

Although temperature has a lower impact on struvite precipitation than other parameters such as pH and supersaturation (Durrant *et al.*, 1999), it can affect struvite solubility and crystal morphology. Aage *et al.* (1997) and Burns and Finlayson (1982) showed the influence of the temperature on the solubility product of struvite (Figure 5). Struvite solubility product, determined with a radiochemical method, increased from $0.3.10^{-14}$ to $3.73.10^{-14}$ between 10 °C and 50 °C in Aage *et al.*, (1997) study. Burns and Finlayson (1982) obtained a similar trend using pH and concentrations measurements, but here the increase in solubility was from $0.7.10^{-14}$ to $1.45.10^{-14}$ at 25 °C and 45 °C respectively. As the solubility product is linked to the supersaturation state of the solution in which crystals may occur, the precipitation of struvite is more difficult to obtain at high temperatures. This may explain why the temperature range between 25 and 35 °C, is usually used by authors to study struvite precipitation either from synthetic solutions or real anaerobic digested liquors.

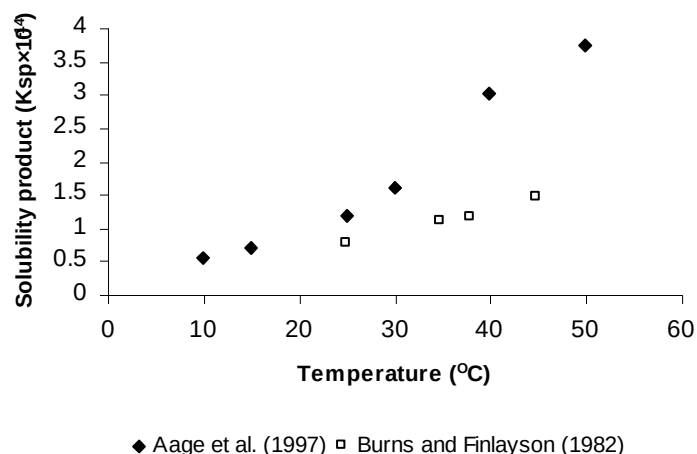


Figure 5. Evolution of struvite solubility product (pK_{sp}) on temperature (Aage et al., 1997; Burns and Finlayson, 1982).

Temperature is also known to affect crystal growth as it affects the relative rates of diffusion and surface integration. High temperature of crystallisation usually leads to diffusion controlled growths, while low temperature leads to surface integration controlled growths (Jones, 2002). Moreover the rate of crystal growth often increases at high temperature, and can affect crystal size shape and type. Boistelle *et al.* (1983) effectively noticed a change between struvite crystals obtained at 25° C and crystals obtained at 37° C. While at 25° C struvite crystals were found “*rectangular and prismatic*”, at 37° C they were mainly “*square and thick*”. This was later confirmed by Babić-Ivančić *et al.* (2002) who explained that for an identical range of concentrations, struvite crystals adopted a dendritic form in a wider zone at 37° C than at 25° C. They also indicated that for high magnesium concentrations, high temperature could affect the nature of crystal formed, with for example struvite transforming faster into newberyite ($MgHPO_4 \cdot 3H_2O$) than at lower temperature.

3.3.4 Mixing energy or turbulence

Mixing energy (or turbulence) can also influence the precipitation of struvite. In areas of high turbulence, CO₂ liberation can cause an increase of pH in the solution favouring thus the occurrence of struvite crystals.

For constant thermodynamics conditions, Ohlinger *et al.*, (1999) showed that different mixing energy could influence struvite crystal size and shape as in areas of low turbulence where struvite was precipitating crystals were more elongated than in areas of high mixing speeds suggesting transport limitation of struvite growth. He demonstrated that the lowest growth rates (*i.e.* 1.8 g.m⁻².d⁻¹) occurred in quiescent zone of the process where struvite was precipitating, while the highest rates (*i.e.* 22.4 g.m⁻².d⁻¹) were always found in high mixing environments.

In struvite crystallisation reactors, the mixing energy is known to affect size of crystals formed. Indeed, high mixing speeds can accelerate nucleation rate hence limit crystal growth, and is also known to increase crystal breakage (Durrant *et al.*, 1999).

3.3.5 Presence of foreign ions

Impurities in solution are also known to affect the growth rates of crystalline compounds due to blocking of sites where crystals could formed, inhibiting the increase of crystal size (Jones, 2002). Although few authors have studied the influence of foreign ions on struvite crystallisation, it is known that the presence of calcium or carbonates ions in the media affects negatively the growth rate and can lengthen the induction time preceding the first occurrence of crystals (Koutsoukos *et al.*, 2003). In sludge liquors where calcium levels can be relatively high (Table 8), calcium ions can interact with phosphate or carbonate ions to form calcium phosphates (usually as hydroxylapatite) or calcium carbonates (usually calcite) according to equation (15) and (16) (Le Corre *et al.*, 2005).



Table 8. Average levels of magnesium and calcium in settled sludge liquors of different WWTP in United Kingdom. (Adapted from Parsons *et al.*, 2001).

	Magnesium (mg.L ⁻¹)	Calcium (mg.L ⁻¹)	Molar ratio Mg:Ca
Barston	46	257	1:3.4
Coleshill	19	94	1:3
Mansfield	52	123	1:1.4
Milcote	34	165	1:3
Owestry	31	185	1:3.6
Spernal	53	321	1:3.7
Wanlip	41	188	1:2.8

Le Corre *et al.* (2005) demonstrated that for molar ratios Mg:Ca 1:1 and above, struvite formation was limited and even inhibited by the formation of an amorphous calcium phosphate. Kabdaşlı *et al.* (2006a) also showed that the presence of sodium, calcium, sulphate and carbonate-bicarbonates ions had an impact on either induction time or struvite crystal morphology and sizes. To illustrate, for identical supersaturation ratios, an increase of concentrations in sulphate from 12.5 mM to 25 mM, increased the induction time from 1 min 59 to 4 min 25s.

4. Phosphorus removal and recycling as struvite

4.1 Phosphorus removal from wastewater

4.1.1 Current treatments

Unlike nitrogen, phosphorus contained in wastewater effluents has to be transformed into a solid to be removed (Heinzmann, 2004). Traditional phosphorus removal processes work by fixing the phosphorus into the sludge:

- either chemically by precipitation of soluble phosphorus with aluminium or iron salts into insoluble phosphates compounds. Separation of the precipitates is then achieved by sedimentation, filtration or flotation. (Parsons and Berry, 2004)
- or biologically (*i.e.* BNR, EBPR) using the ability of some micro-organisms to accumulate phosphates as polyphosphates for their own metabolism (Mulkerrins *et al.*, 2004, Driver *et al.*, 1999),

These processes are efficient in the sense that they can reduce phosphorus concentrations in wastewater treated to less than 1 mg.L^{-1} (Booker *et al.*, 1999, Tebutt, 1998), but they have certain disadvantages, including:

- ⇒ the accumulation of P in the resulting sludge (Parsons and Doyle, 2004),
- ⇒ an increase of sludge volumes (Woods *et al.*, 1999)
- ⇒ the spontaneous accumulation of struvite in pipelines, and other parts of the treatment works. Previous studies have reported large increases of soluble Mg levels in effluents treated with iron metal salts, raised the potential for spontaneous struvite precipitation (Mamais *et al.*, 1994, Laridi *et al.*, 2005).

Finally the phosphorus precipitates generated by these methods are not directly recyclable (de-Bashan and Bashan, 2004).

4.1.2 The crystallisation solution

A promising technology to help removing phosphorus from concentrated wastewater streams consists in the crystallisation of reusable compounds such as calcium phosphate or struvite (Doyle and Parsons, 2002). This has gained particular interest since both struvite and calcium phosphates have been identified as marketable fertilisers (Gaterell *et al.*, 2000) although their recovery from wastewaters remains principally experimental due to problems linked to the economics of the process and the product formed as well as technical difficulties (Adnan *et al.*, 2003a/b).

Several laboratory and pilot scale studies have been carried out to assess the potential of such methods in removing and recovering phosphorus as a reusable product; there is also a couple of full scale trials in The Netherlands (Giesen, 1999) and Italy (Battistoni *et al.*, 2005a/b) (Table 9). However Japan is the only country where complete P removal and recovery from anaerobically digested sludge liquors as struvite has been implemented and the resulting product sold to fertiliser companies (Gaterell *et al.*, 2000, Ueno and Fujii, 2001)

The recovery technologies currently tested are based on the crystallisation of phosphorus as hydroxylapatite (HAP) or struvite (MAP) and the majority use sludge liquors generated from anaerobic digesters as their influent (Table 9). The technologies can be classified in three main categories:

- ⇒ Selective ion exchange (*i.e.* RIM NUT[®] process, Liberti *et al.*, 1986).
- ⇒ Precipitation in a stirred reactor (Laridi *et al.*, 2005; Stratful *et al.*, 2004; Mangin and Klein, 2004; Seco *et al.*, 2004)
- ⇒ Precipitation in fluidised bed reactors (FBRs) or air-agitated reactors, which is the most common of processes experimentally trialled (Von Münch and Barr, 2001, Ueno and Fujii, 2001, Battistoni *et al.*, 2005a/b)

FBRs are the most studied processes for struvite crystallisation. According to Mangin and Klein (2004), this is because solid and liquid retention times are not systematically similar. Their design can be integrated as an additional process step to most wastewater treatment works, as they can be continuously fed with liquors, while the solid product can be sequentially harvested.

Table 9. Crystallisation technologies for P recovery

References	Process/Technology	Scale	Source	P removal	P recovered form
Liberti <i>et al.</i> (1986)	Selective ion exchange, RIM-NUT Process®	Full scale	Chlorinated secondary effluents	≥ 90%	MAP
Fujimoto <i>et al.</i> (1991)	Aeration, stirring and crystallisation in a stirred reactor.	Bench and pilot	Supernatant from anaerobic digester	60 to 70%	MAP
Brett <i>et al.</i> (1997).	■ CSIR Fluidised bed crystallisation column seeded with quartz sand	Bench	Anaerobic digester supernatant, pond effluents, abattoir wastes	90%	MAP/HAP
	■ Kurita fixed bed seeded with phosphate rock grains (Kurita Water Industries Ltd, 1984)	Full scale	Secondary effluent of STW	Up to 90%	HAP
Giesen (1999).	DHV Crystalactor®	Full scale	Supernatant from anaerobic sludge	-	CaP
Battistoni <i>et al.</i> (2000)	FBR, seeded with sand.	Bench	Anaerobic supernatants after belt press.	62 to 81%	MAP, or mixed MAP/HAP
Jaffer (2000)	Aerated reactor	Bench	Centrifuge liquors	Up to 97%	MAP
Ohlinger <i>et al.</i> (2000)	FBR seeded with struvite crystals	Pilot scale	Sludge lagoon supernatant	> 80%	MAP
Ueno and Fujii (2001)	FBR	Full scale	Dewatered liquors from anaerobic sludge digestion	≥ 90%	MAP
Von Münch and Barr (2001)	Air agitated column reactor	Pilot scale	Centrate from anaerobically digested sludge	94%	MAP
Suzuki <i>et al.</i> (2002)	Aeration column	Pilot scale	Swine waste water	65%	MAP/HAP
Wu and Bishop (2003)	2L beakers seeded with sand or struvite	Bench	Centrate from sludge dewatering centrifuge	Between 65 and 70%	MAP
Adnan <i>et al.</i> (2003a/b)	FBR	Pilot scale	Synthetic liquors	90%	MAP
Cecchi <i>et al.</i> (2003)	FBR seeded with silica	Full scale	Anaerobic supernatant	Average of 62%	MAP/HAP
Jaffer and Pearce (2004)	Air-agitated reactor	Full scale	Centrifuge liquors	60-80%	MAP
Ishikawa <i>et al.</i> (2004)	FBR seeded with struvite crystals	Full scale	Centrate from dewatering system	≥ 90%	MAP
Seco <i>et al.</i> (2004)	Stirred reactor	Pilot	Supernatant from sludge digestion	90%	MAP/CaP
Mangin and Klein, (2004)	Stirred reactor	Pilot	Synthetic liquors	> 60%	MAP
Laridi <i>et al.</i> (2005)	Stirred reactor	Pilot	Pre treated swine wastewater	Up to 98%	MAP
Battistoni <i>et al.</i> (2005b)	FBR	Full scale	Anaerobic supernatants after belt press.	64-69%	MAP/HAP

*MAP: magnesium ammonium phosphate; HAP: Hydroxyapatite; CaP: Calcium phosphate

4.2 Design and description of processes used for struvite crystallisation

4.2.1 Selective ion exchange processes

4.2.1.1 The RIM-NUT[®] Technology

This type of process consists of a three stage combined ion exchange and precipitation set up. Secondary effluents from an activated sludge sedimentation tank enter a combined resin columns system made of 2 cationic and 2 anionic columns (Figure 6). The cationic resins (R_c), filled with natural zeolite, remove ammonium ions following the general equation:

$R_cNa + NH_4^+ \rightarrow R_cNH_4 + Na^+$ while the anionic resins (R_a), filled with a basic resin, remove

PO_4^{3-} ions according to the general equation: $2R_aCl + HPO_4^{2-} \rightarrow R_{a2}HPO_4 + 2Cl^-$.

The resultant enriched phosphate and ammonium effluents are mixed and enter a reactor where struvite is precipitated by addition of NaOH, $MgCl_2$, H_3PO_4 to reach the required molar ratio Mg:P:N of 1:1:1, (Liberti *et al.*, 1986).

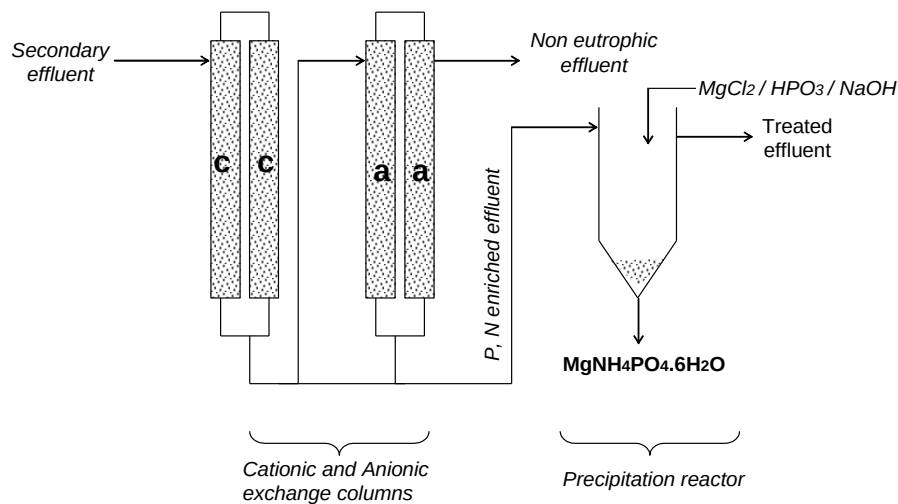


Figure 6. The RIM-NUT process (adapted from Liberti *et al.*, 1995)

4.2.1.2 Advantages and drawbacks

The RIM NUT[®] process uses chemical dosing to precipitate struvite from enriched P and N effluents. No additional sludge is produced and P removal of 90 % can be achieved.

The downside of this process is the competition by NO_3^- , HCO_3^- and SO_4^{2-} . Indeed, according to Petruzzelli *et al.* (2004), the efficiency of the process used by Liberti *et al.* (2001) was limited by the lack of phosphate ion selectivity of the anion resin and further work is under way on new phosphate sorbents, to remedy this problem.

Furthermore, monitoring of P and N concentration in the enriched effluent is also required to dose the chemicals in the precipitation reactor. And finally the ions exchange process requires extra time to recover the struvite and needs regular regenerations of the resin (*i.e.* a regeneration cycle with NaCl is required every 3 hours, Brett *et al.*, 1997) due to the fouling by solids present in regenerated effluents. The combination of all this factors is known to affect the economics of the process (Petruzzelli *et al.*, 2004).

4.2.2 Stirred reactors

4.2.2.1 Operation principles

In these types of processes, struvite is crystallised in the reactor by addition of chemicals, usually MgCl_2 , to reach the minimum molar ratio Mg:P 1:1. The pH required to set off the nucleation is typically adjusted by NaOH addition, while a propeller is used to mix the solutions and favour the occurrence of struvite crystals. A settling zone has to be integrated to the reactor to allow for the accumulation of particles (Mangin and Klein, 2004).

To date only a few studies have considered the efficiency of mechanically stirred reactors for struvite crystallisation (Regy *et al.*, 2002; Yoshino *et al.*; 2003, Stratful *et al.*, 2004). One pilot scale process and a laboratory scale one are illustrated in Figure 7.

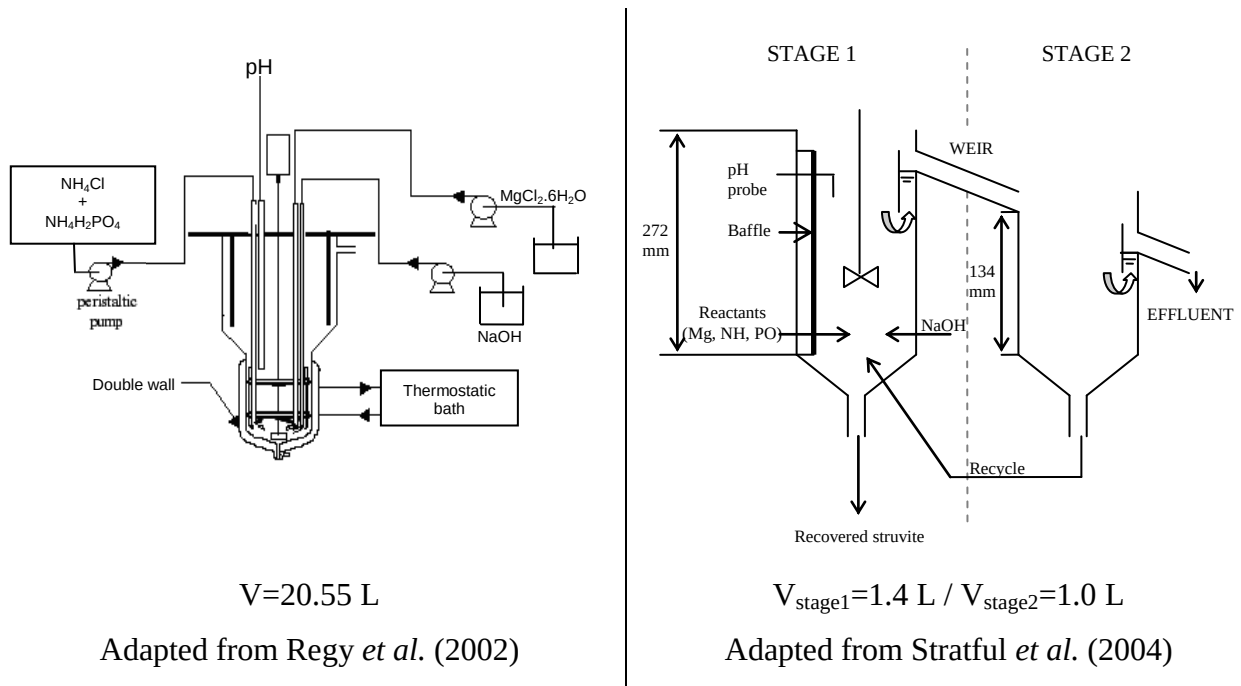


Figure 7. Pilot stirred reactor for struvite crystallisation.

The first stirred reactor presented here (Figure 7) has been designed and developed at pilot scale at the “Laboratoire d'Automatique et de Génie des procédés” in Lyon (Regy *et al.*, 2002). Its capacity in removing phosphorus from synthetic liquors as struvite has been assessed with and without seed material (sand or struvite pellets). Seco *et al.* (2004) used a similar reactor to precipitate struvite from supernatants of digested sludge.

In this reactor type, the crystallisation takes place in the lower part of the reactor. The reacting solutions, a phosphate solution made by dilution of NH_4Cl , $\text{NH}_4\text{H}_2\text{PO}_4$ and NaOH in drinking water, MgCl_2 and NaOH for the experiments on synthetic liquors (Regy *et al.*, 2002), or digested sludge supernatant (Seco *et al.*, 2004) were mechanically agitated and the pH adjusted with sodium hydroxide to values around 9. The upper part of the reactor, or settling zone, was enlarged to keep the solid particles in the reactor.

The second process, a continuously stirred tank reactor (CSTR) (Figure 7), tested at laboratory-scale by Stratful *et al.* (2004) combined a CSTR and a second tank used for recycling of fines. Struvite was precipitated from solutions of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, NH_4Cl and NH_2HPO_4 . pH was adjusted in the CSTR to values between 8 and 9 by addition of NaOH. The second reactor was used to test the influence on crystal growth of recycling fine struvite particles issued from the main reactor.

4.2.2.2. Advantages and drawbacks

Mechanically stirred reactors are simple and P removal efficiencies are relatively high. Regy *et al.* (2002) achieved P removals over 60 % for precipitation from synthetic liquors, whereas Seco *et al.* (2004) reached up to 90% from anaerobic digestion supernatant. However, in the Seco *et al.* (2004) example the removal percentage was higher due to the presence of calcium in the liquors leading to the co-precipitation of P as struvite (76.9%) and calcium phosphate (23.1%). In their laboratory scale CSTR, Stratful *et al.* (2004) achieved magnesium removals ranging from 76 % to 88 % at a constant pH of 8.5 but for stirring speed increasing from 200 rpm to 500 rpm, while at a constant stirring speed of 500 rpm but pH ranging from 8 to 9, magnesium removals varied from 64% to 88%. Both processes achieved reasonable struvite mean crystal size of 300 μm and 425 μm for respectively Regy *et al.* (2002) and Stratful *et al.* (2004). Improvement of crystal growth by seeding with sand or struvite in this type of reactor is difficult due to the high mixing speed necessary to fluidise the seed (Regy *et al.*, 2002).

The main advantage of this type of processes is their simplicity of operation when compared to other processes such as ion exchange and fluidised bed reactors (Stratful *et al.*, 2004). One of the main problems of their application at full scale would be the fouling of the impeller when used in continuous mode. Furthermore, growth limitation and production of large

quantities of fines can be observed due to high mixing speed (600 rpm) necessary to homogenise the solution and keep particles in suspension (Regy *et al.*, 2002).

4.2.3 Fluidised bed reactors and air agitated reactor

4.2.3.1 Process principles

Processes most commonly used to crystallise struvite from wastewater are fluidized bed reactors FBR or air agitated reactors. In such processes, struvite particles can precipitate spontaneously from supernatants following the addition of chemicals to reach the molar ratio Mg:P:N 1:1:1. Once the nucleation of the first particle starts, the growth takes place either by interaction of small struvite particles together that is to say agglomeration (air agitated reactors), or by contact on seed materials (*e.g.* sand or struvite) constituting the initial bed of particles (FBR). Suspension of particle is controlled by either liquid flowrates (Cecchi *et al.*, 2003) or an up-flow circulation of air (Suzuki *et al.*, 2002; Jaffer, 2000), so that the particles in the reactor are in continuous motion, and behave like a dense fluid.

Methods using air agitated or fluidized bed reactor to recover phosphorus as struvite crystals have been widely investigated and a selection of them is presented in table 10a and 10b. Feed solutions, typically centrate liquors and anaerobic digested sludge liquors, enter in the reacting zone from the bottom of the reactor. Depending on the reactors configuration, influent flowrates can vary from 0.004 to 0.3 m³·h⁻¹ (Table 10a and 10b). When used, upward airflows allow a uniform fluidisation of particles to avoid growing struvite particles from settling down. Airflows can also help to reach the pH value (*i.e.* 8-9) necessary for struvite crystallization (Battistoni *et al.*, 2004 and 2005a). However pH is often adjusted by NaOH addition (Table 10a and 10b). The velocity of the flow (as well as the pressure in the reactor) decreases from the column to the upper section allowing the evacuation of the treated effluent at the top of the reactor, while struvite particles (and seed) are fluidized and grow in the

column section. Removal of phosphorus achieved by these types of processes can vary from 60 % up to 94 % mainly depending on the type of effluent and the nature of the crystallisation process used (Table 9). The solid phase is partly or totally recovered from the reactor when particles reached a reasonable size for reuse, this mean that such reactors work in batch for the solids phase and continuously for the liquid phase (Mangin and Klein, 2004). Solid retention times are usually in the order of days with for example 3 to 14 days for Shimamura *et al.* (2003) to achieve particle size between 0.41 and 1.43 mM or 6 to 17 days for Adnan *et al.* (2003a/b) to reach size of struvite crystals up to 3.5 mm. In that latter case, size of particles was enhanced by agglomeration phenomena. But size of struvite particles is also strongly dependant on the utilisation of seed materials. To illustrate, Von Münch and Barr (2001) (Table 10a) who initially used 500 g (i.e. $\sim 3.5 \text{ g.L}^{-1}$) of crushed struvite crystal to seed their agitated reactor achieved an average size of particles of 110 μm whereas Battistoni, (2004) observed an increase of sand grains from 0.9 mm to 0.14-0.18 mm (depending on the volume of supernatant treated) by struvite (and hydroxylaptite) growth onto them.

Table 10a. Struvite crystallisation in fluidised bed or air agitated reactors.

References	Process	Method	Shape	Influent	Seed material	Dimensions			Bed height, volume or mass	Flow rates	pH adjustment	Size (mm) of recovered product	Fines	Solid RT (days)
						*H (m)	*D (m) *	V (m ³)						
Battistoni, <i>et al.</i> (1997)	Bench scale FBR	Batch	Glass column	Anaerobic supernatants	quartz	0.42	0.058	1.1.10 ⁻³	*H _c =0.15 m *H _x =0.30 m	0.11<Up flowrate <0.3 m ³ .h ⁻¹	Air aeration 8.3-8.6	-	Yes (8.7 up to 24.5%)	
	Stripper		Tank					5.10 ⁻³		Air flow rate=0.9 m ³ .h ⁻¹				
Battistoni <i>et al.</i> (2000)	FBR	Batch	Column connected to an expansion tank	Anaerobic supernatants	quartz sand (0.21 to 0.35mm)	1	0.09	6.36.10 ⁻³	*H _c =0.4m *H _x =1 m	4 to 19 L.h ⁻¹	Air aeration 8.1-8.9	0.4	yes	
	Stripping tank+stripping device		Tank +column			-	-	18.10 ⁻³ + 3.10 ⁻³		15<Airflow rate< 19 L.h ⁻¹				
Ohlinger <i>et al.</i> (2000)	Pilot scale	Batch and continuous	Acrylic plastic column	Sludge lagoon supernatant	struvite (1.7mm)	1	0.0635	3.17.10 ⁻³	*H _c =0.31 m 100% expanded	Influent flowrate= 3.2 to 20 L.h ⁻¹ upflow velocity =11 cm.s ⁻¹	Medium bubble aeration (+0.1N NaOH when necessary)	-	-	
	Stripping tank+stripping device pH adjustment tank		high density polyethylene plastic			0.30 x 0.30		9.10 ⁻³ or 19.10 ⁻³						
Ueno and Fujii (2001)	FBR	continuous	Column	Dewatering filtrate from anaerobic sludge digestion	granulated struvite	9	1.43	-	-	filtrate flow rate= 650 m ³ .d ⁻¹	Mg(OH) ₂ 8.2-8.8	0.5 to 1.0	Yes	10
	(full scale)		+ precipitation portion				3.6							
Von Münch and Barr (2001)	Air agitated reactor	continuous	Reaction zone + Settling zone	Anaerobic digested liquors	crushed struvite		0.3	143L	-	Air~7L.min ⁻¹ Feed=0.3-2L.min ⁻¹	8.5-9 with Alkali	Range from 0.025-0.215 D _{0.5} = 0.11	loss of fines	5
							0.6							
Shimamura <i>et al.</i> (2003)	Air agitated tank coupled with fines recycle tank	continuous	Column with enlarged section	Anaerobic wastewaters	struvite fines	-	-	-	-	Raw water in main tank = 1.1 to 6.7 m ³ .d ⁻¹ Raw water in sub tank = 0.11-0.32 m ³ .d ⁻¹	NaOH	0.41-1.43	Yes	3-14 days

*H_c: High of the compressed bed, H_x: High of the expanded bed, RT: solids retention time, calc: calculated, H: height, D: diameter, V: volume, D_{0.5}: mean crystal size, calc: calculated, NM: not mentioned

Table 10b. Review of struvite crystallisation in fluidised bed reactors.

References	Process	Method	Shape	Influent	Seed material	Dimensions			Bed height, volume or mass	Flow rates	pH adjustment	Size (mm) of recovered product	Fines	Solid RT (days)
						*H (m)	*D (m) *	V (m ³)						
Adnan <i>et al.</i> (2003a/b)	FBR (pilot scale)	continuous	4 sections plastic polyvinyl reactor:	synthetic water MgCl ₂ .6H ₂ O + (NH ₄)H ₂ PO ₄ +NH ₄ Cl	-	5	0.04-0.20	28.3.10 ⁻³		up flow rate=0.162 to 0.240 m ³ .h ⁻¹	NaOH	3.5		6 to 17
Ishikawa <i>et al.</i> (2004)	2-tank FBR (full scale), main reactor	continuous	Reaction zone+settling portion	Centrate from dewatering system	Struvite fines (0.3mm)	2.2+1.8	0.35 (reaction zone) 0.80 (settling portion)	0.85+3.62 (calc. as cylinder)	*H _x ~2	circulated water (+ MgOH ₂) = 0.5 to 2.5 m ³ .h ⁻¹ raw water = 0.5-0.8 m ³ .h ⁻¹	8	0.4	Yes D _{0.5} = 0.1mM	3-4
	Sub reaction Tank		Air lift pump Reaction portion (including settling zone) Air lift pipe	Centrate from dewatering system	Struvite fines (0.1mm)	2.4	0.25	0.117 (calc.)	-	Upward Air flow raw water flowrate=0.06 to 0.15 m ³ .h ⁻¹		0.3	yes	
							0.4			circulated water = 0.06 to 0.18 m ³ .h ⁻¹				
Cecchi <i>et al.</i> (2003)	FBR (full scale)	continuous	column enlarged at the top: column section enlarged section	anaerobic supernatants	Silica pellets	4.4		1.41		feed flow rate= 1 or 1.5 m ³ .h ⁻¹	air stripping	> 0.1 to 0.5	-	-
						4	0.6				8.3 or higher			
						0.4	1.2							
Jaffer and Pierce (2004)	Aerated reactor	continuous	Reaction zone + Settling zone	Centrate liquors	Recycled struvite	NM*	NM*	5.8 + 6.8 or 13.6	-	Influent= 5.4 to 7.2 m ³ .h ⁻¹ Air= 60-140 L.s ⁻¹	7.5-9 with air and NaOH	0.3 maximum	NM*	NM*
Battistoni, 2004,	Full scale FBR	Continuous	Column coupled to a Dortmund apparatus to avoid wash out of fines	Anaerobic supernatants	Sand seeded (0.09mm)	-	-	1	475 kg	Influent flow rate =1.3 m ³ .h ⁻¹ (long term performances)	Air stripping	0.14-0.18	yes	-
Battistoni <i>et al.</i> (2005a)	Stripping tank+ stripping device				Or auto-nucleated									
Suzuki <i>et al.</i> (2005)	Aerated reactor	continuous	Aeration column in a reaction tank	Swine wastewaters	None or Metallic surface	3.64	1.50	4.32	-	Swine wastewater = 4.0 m ³ .d ⁻¹ Air=15.6 m ³ .h ⁻¹	Air stripping	-	NM*	30

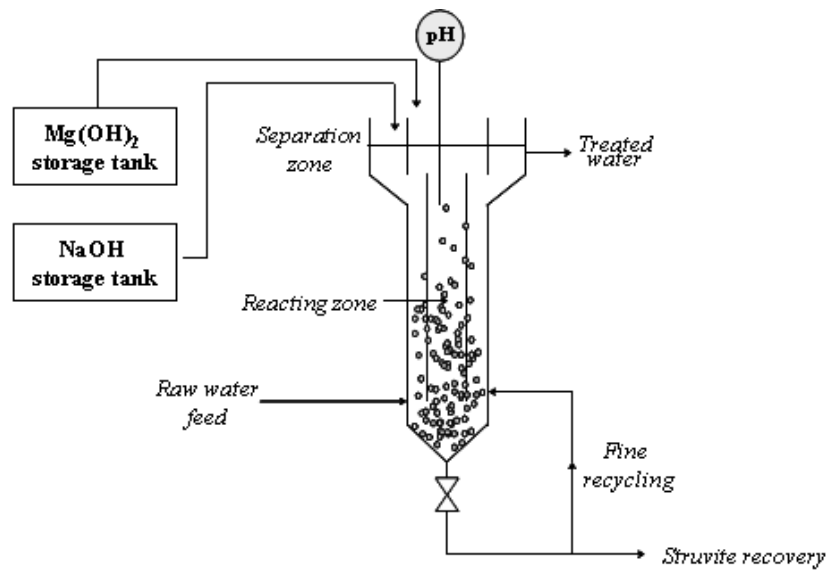
*H_c: High of the compressed bed, H_x: High of the expanded bed, RT: solids retention time, calc: calculated, H: height, D: diameter, V: volume, D_{0.5}: mean crystal size, calc: calculated, NM: not mentioned

4.2.3.2 Examples of two typical FBR and Air agitated designs

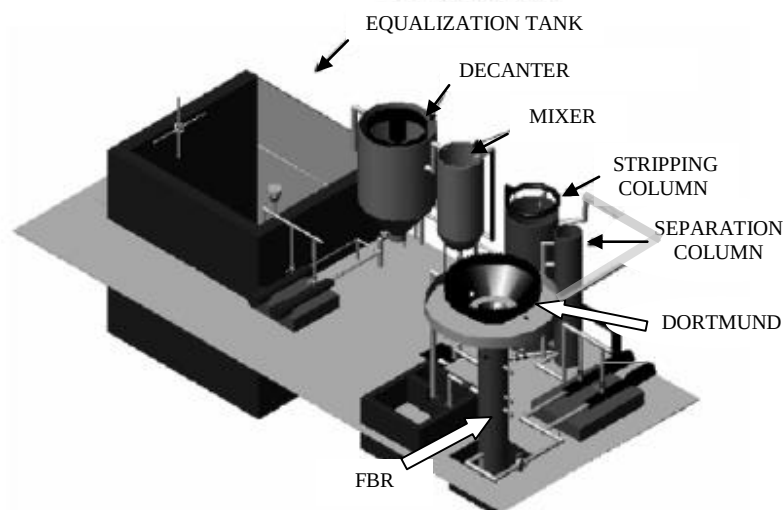
Good illustrations of this type of reactors are the processes used at full scale by Ueno and Fujii (2001) for Unitika Ltd, Japan and by Battistoni (2004) (Figure 8).

The process reported by Ueno and Fujii (2001) (Figure 8-A-) consists of an air agitated column. Digested sludge liquors enter at the bottom of the reactor. $\text{Mg}(\text{OH})_2$ and NaOH are respectively added in the reactor to reach a minimum 1:1 Mg:P molar ratio and adjust the pH to values ranging from 8.2 to 8.8. Struvite particles are kept in suspension by an upward airflow and grow up to sizes between 0.5 and 1.0 mm in 10 days. They are periodically separated from fines. Fines particles are recycled and returned to the reactor to act as seed material, while the larger particles are dried before being sold as a raw material for the fertiliser industry. Minimum P removals of 90 % obtained, and the good quality of the struvite generated make of this process the only full scale process economically reliable.

The process experimented at full scale by Battistoni (2004) (Figure 8-B-) used anaerobic supernatant from Treviso WWTP (Italy). Before entering the FBR, supernatants are pre-treated to remove suspended solids and stored in an equalisation tank to insure continuous feeding of the FBR. The influent is stripped with air then transferred into a de-aeration column before entering the FBR filled with sand grains (Battistoni, 2004). pHs of operation vary from 8.3 to 8.7. P removals achieved were of 61 % average in this configuration and sand particles increased in size from 0.09 mm to 1.4 mm. This process has also been recently tested without application of seed material by auto-nucleation of struvite, achieving in that configuration removals of up to 86 % and particles of up to 0.20 to 0.30 mm (Battistoni *et al.*, 2005a).



-A- Air agitated reactor
Adapted from Ueno and Fujii (2001)



-B- FBR seeded with sand
Courtesy of Battistoni (2004)

Figure 8. Example of full scale Fluidised Bed type reactors

4.2.3.3 Limitation of FBR and air agitated processes, areas of improvement

The size of particle is an essential parameter to control for practical reasons and its implications for any future reuse of struvite as a fertiliser. One of the solutions to produce larger struvite particles in a FBR is the utilisation of a seed material so that struvite can form agglomerates with seeds. This method has proved to be efficient with particle sizes ranging

from 0.1mm (Cecchi *et al.*, 2003) up to 1.0 mm (Ueno and Fujii, 2001). However, the operation of such processes requires high flow rates and/or significant mixing energy to insure the bed of seeds is continuously fluidised. This energy consideration, as well as raw material costs, could become a limit to their application by wastewater companies (Battistoni *et al.*, 2005a). The utilisation of a metallic support as a seed material to capture struvite crystals could be one of the solution to remedy this energy consideration while facilitating struvite recovery (Suzuki *et al.*, 2005). Furthermore, as seen in table 10a and 10b, processes often encountered problems due to the production of fines. Excess fine production is undesired as it usually leads to loss of particles in treated effluent due to the high mixing energy needed to maintain the growing particles in suspension (Mangin and Klein 2004, Battistoni *et al.*, 2005b). A few studies which have looked at problems of fines production have partly limited the problem by recycling fines as a fresh seed material to grow struvite on (Ueno and Fujii, 2001; Shimamura *et al.*, 2003).

For an effective and continuous P recovery as struvite, the characteristics of the influent used have to be monitored and adjusted when necessary. Indeed, to date the purity of the product precipitated is not always guaranteed, due to competition between calcite, struvite and hydroxylapatite crystallisation (Battistoni, 2004). Selectivity of the process toward struvite will depend on the levels of components known to interfere with the nucleation and growth of struvite crystals, thus on quantity of chemicals needed to reach the minimum ratio Mg:N:P 1:1:1 necessary for struvite to occur and/or counterbalance levels of foreign ions. To illustrate, as seen in table 8 ratios magnesium to calcium in the UK can vary from 1:1.4 to 1:3.7 depending on the location, which according to Le Corre *et al.* (2005) would mean that the utilisation of this kind of liquors for P recovery by crystallisation would favour calcium phosphates precipitation if no magnesium dosing was applied.

5. Interests in controlling and recovering phosphorus as struvite

5.1 Environmental impact

5.1.1 Potential pollution reduction

Eutrophication typically occurs in aquatic environments when levels of nutrients (P and N) increase significantly and lead to an excessive growth of algae that can cause the death of fish and other living organisms and reduce the availability of water resources. In their study on removing phosphorus from wastewater effluent, Pretty *et al.* (2003) mentioned that the costs generated by this form of pollution to the water industry in the UK is estimated to \$ 77 million per annum. As described above, most experimental methods on P removal from wastewater sludge by struvite crystallisation showed relatively high efficiencies (never less than 60 %) and would therefore limit problems linked to eutrophication if applied. Struvite crystallisation in particular offers the additional advantage of being able to remove nitrogen simultaneously to P (Table 11).

Table 11. Example of nitrogen removal by struvite precipitation.

References	Source	Ammonium removal (ratio 1:1:1)
Maekawa <i>et al.</i> (1995)	Swine wastewater	More than 90%
Priestley <i>et al.</i> (1997)	BPR anaerobic digested effluents	98%
Altınbaş <i>et al.</i> (2002)	Anaerobically pre-treated wastewater	from 68 to 72%
Kim <i>et al.</i> (2004)	Slurry type swine wastewater	Up to 99% depending on the ratios
Tünay <i>et al.</i> (1997)	Synthetic samples	Over 85%
	Industrial wastewater	Never less than 50%, mostly above 75%
Miles and Ellis, (1998)	Anaerobically treated swine waste	93%
	Waste activated sludge	51%
Uludag-Demirer <i>et al.</i> 2005	Anaerobically digested dairy manure	>95%
Kabdaşlı <i>et al.</i> (2006b)	Human urine	Up to 95%

5.1.2 Sludge reduction

Sludge disposal and production is effectively a major problem for water companies, especially since the application of the 91/271/EEC directive (UWWTD, 1991). It was effectively predicted in 2002 that the application of the directive would cause an increase in sewage sludge production from 7 to 9.4 million tonnes per year by 2005 in the European Union (Steén, 2004), and from 1.1 to 1.5 million tonnes in the UK by 2005/2006 (Bruce and Evans, 2002). Using computer modelling to assess the economical viability of implementing P recovery processes in municipal WWTP, Woods *et al.* (1999) and Woods *et al.* (2000) showed that sludge mass could be reduced by 8 to 31% by implementing phosphorus recovery by crystallisation.

5.1.3 Use as a fertiliser

The agronomic properties of struvite as a fertiliser have been widely discussed. It represents a highly effective source of nutrients (P, N and Mg) for plants (Li and Zhao, 2003) and was found to be as efficient as mono calcium phosphates (MCP) (Johnston and Richards, 2003). Its low solubility in water (0.018g/100ml at 25°C-Bridger *et al.*, 1961), also presents the advantage of prolonging the release of nutrients during the growing season (Gatterell *et al.*, 2000) without danger of burning roots of crops treated (Ries *et al.*, 1969). To date, struvite has only been commercialised in Japan as a fertiliser for growing rice and vegetables (Ueno and Fujii, 2001). Shu *et al.* (2006) gave the reasons as to why struvite is not widely applied as a fertiliser to its limited availability to farmers, and the lack of communication on its applicability and benefits.

5.2 Economics

As seen previously phosphorus recovery from wastewater effluent as struvite presents a number of advantages: it can help to solve and prevent scaling problems in WWTPs, it reduces pollution linked to excess discharge of nutrient (N and P) in wastewater effluents, while its potential reuse as a fertiliser could benefit the wastewater companies (Doyle and Parsons, 2002). However, the success of the implementation of struvite crystallisation processes to WWTPs depends on their economical sustainability. For this reasons the main challenge is to make P recovery as struvite cost effective by taking into account costs of production (*i.e.* chemicals, maintenance, and energy) and assessing the value of struvite on the market of fertilising products.

Costs of struvite production mainly depend on amounts, hence costs, of chemicals to be injected in the process (Jaffer *et al.*, 2002; Von Münch and Barr, 2001), and on the energy required to ensure mixing during the crystallisation (Battistoni *et al.*, 2005a). Most studies use relatively high amounts of MgCl_2 to reach the appropriate Mg:N:P molar ratio, and NaOH to adjust the pH of precipitation. To illustrate, in their pilot scale study, Jaffer *et al.* (2002) identified the addition of sodium hydroxide needed to reach an appropriate pH for struvite crystallisation from centrate liquors (Slough Sewage Treatment Works, UK), as one of the principal sources of struvite production costs. Indeed, if reported to a full scale pilot plant that could treat $400 \text{ m}^3 \cdot \text{d}^{-1}$ of the same liquors, Jaffer *et al.* (2002) estimated that the sodium hydroxide addition would be responsible of 97 % of the chemical expenses corresponding to daily costs ranging from 0.0014 to 0.51 €/m^3 . In their pilot scale investigations, Battistoni (2004) used air stripping as a way to adjust the pH of struvite precipitation. This could be an option to reduce costs linked to NaOH additions. Moreover, some studies have looked at alternative ways to reduce costs associated with Mg dosing by for example using $\text{Mg}(\text{OH})_2$, which is cheaper than MgCl_2 and simultaneously helps to increase the pH (Von Münch and Barr, 2001). Shin and Lee (1997) also indicated that brine or seawater could be used as an alternative source of magnesium and managed to reach 95 % of P removal with seawater compared to 97 % removal with MgCl_2 . However, transporting seawater or brine would incur further costs and this solution could be only of interest to WWTPs located near the sea.

Another way of reducing costs of struvite production would be to limit the energy consumption needed for pumping and mixing of solutions. One option would be to favour auto-nucleation of struvite over seeded crystallisation with materials such as sand. Indeed, Battistoni *et al.* (2005a) indicated that operative costs of struvite production could be reduced from 0.28 €/m^3 to 0.19 €/m^3 when using the auto-nucleation method rather than seeded

crystallisation. Indeed, costs of seeded crystallisation are higher due to purchase costs of the raw seed material and mainly to greater airflows needed to fluidise the particles.

The profitability of a struvite crystallisation process will ultimately depend on profits generated from struvite sales. As the application of struvite at full scale is still limited, the estimation of its economical value as a fertiliser is difficult to assess as it should be influenced by rates of production and the regional demand for such a product (Gaterell *et al.*, 2000). However, in Japan struvite has already been sold as a fertiliser at a cost of nearly 250€·t⁻¹ (Köhler, 2004). Based on this value, Jaffer *et al.* (2002) estimated that for a process treating 400 m³·d⁻¹ of centrate liquors issued from a sewage treatment work including a conventional activated sludge system and a BNR, the potential income generation from the sell of their struvite production would be around 25000€ under optimum dosing regime (i.e. 90% P removal). In that specific case, the incomes would then only cover a third of the costs of chemicals used for struvite crystallisation (i.e. ~ 76000€·year⁻¹), hence generating no profits. Von Münch and Barr (2001) estimated that the selling price of struvite achievable in Australia could range from 180€ to 300€ per tonne, which for Oxley Creek WWTP (Australia) would result in profits ranging from -7800€ to +89400€ a year, equivalent to profits between -0.05€ to 1.72€ per cubic meter of centrate from the dewatering sludge centrifuge of the WWTP treated by a full scale reactor of 27m³.

The fertiliser industry currently uses phosphate rock, valued at 31 to 39€ per tonne in 1999, to generate phosphate fertilisers (Driver *et al.*, 1999). Compared to the economical value of struvite demonstrated above and to costs of struvite production which can range from 109€·t⁻¹ in Australia to 359€·t⁻¹ in Japan (Doyle and Parsons, 2002), fertiliser production from phosphate rock seems to be still more economical. However if the recovery of P as a fertiliser does not seem to be yet of direct economic interest, it could still be significant as a way of

improving handling costs of sludge disposal as it can reduce significantly sludge volumes. To illustrate, Shu *et al.* (2006) estimated that for WWTPs treating $100 \text{ m}^3 \cdot \text{d}^{-1}$, $1000 \text{ m}^3 \cdot \text{d}^{-1}$ and $55000 \text{ m}^3 \cdot \text{d}^{-1}$ of wastewaters, the savings per day generated on sludge handling and disposal by struvite crystallisation could reach respectively 0.68 €, 6.92 € and 374€. Furthermore, savings on costs due to struvite scaling in WWTPs would be reduced significantly. Indeed, Neethling and Benisch (2004) reported that annual costs due to struvite scaling including chemical addition, manpower, and maintenance costs could range from 1470€ to 7350€ per MGD depending on the size of the treatment plant.

Finally the implementation of a sustainable process for P reuse and recycling and the profitability of struvite recovery as a fertiliser will rely on the way potential customers will perceive struvite as a new fertiliser (Von Sothen, 2004).

6. Summary

- Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) crystallisation occurs spontaneously in WWTPs as stable white orthorhombic crystals. Struvite forms in a Mg:N:P molar ratio 1:1:1 under specific conditions (including supersaturation, pH, temperature, mixing energy and presence of foreign ions) and because of these generates problems of scale deposits in specific areas such as pipes and recirculation pumps.
- The formation of struvite is governed by two mechanisms: nucleation and crystal growth. The majority of published works on the principles of struvite formation has focused on the influence of supersaturation ratio and pH on the crystallisation, as these parameters were found to be the most influent on struvite crystallisation. Indeed they control the induction

period preceding the first release of struvite crystals, and also reduce crystal growth rate, while other parameters such as presence of foreign ions, mixing energy, and temperature mainly affect struvite crystal growth and crystal quality.

- The control or prevention of scaling by chemical dosing was the original incentive for the study of struvite formation in WWTPs. Nevertheless, the opportunity to deliberately form struvite before it occurs in WWTP and thus prevent maintenance problems became of interest more recently as struvite can help to remove phosphorus from wastewater effluents and recover it as a fertiliser.
- This paper has reviewed the techniques and processes experimented to date by researchers at laboratory, pilot and full scale to maximise phosphorus removal and reuse as struvite. Struvite crystallisation from digested sludge liquors by means of fluidised bed reactors directly integrated in WWTP lines are the most common processes studied with success. However, if good phosphorus removal has to be insured, the technique still needs improvements with regards to quality and quantity of the product formed to be applicable as an economically viable route to recover phosphorus.

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Appendix of main acronyms and notations

BNR – Biological Nutrient Removal

CEEP – Centre Européen des Polyphosphates

CSTR – Continuously Stirred Tank Reactor

EBPR – Enhanced Biological Phosphorus Removal

FBR – Fluidised Bed Reactor

HAP – Hydroxylapatite

MAP – Magnesium Ammonium Phosphate

MGD – Million Gallons Day

p.e. – Population equivalents

rpm – Revolutions per minute

SSB – Solid storage basin

UWWTD – Urban Waste Water Treatment Directive

WWTP – Waste Water Treatment Plant

A – kinetic factor

a_i – Ionic activity

C – Concentration of a reactant

c^* – Equilibrium solubility

C_0 – Initial concentration of a reactant

C_{eq} – Concentration of a reactant at equilibrium

C_{sp} – Conditional solubility product

G – Crystal growth rate

I – Ionic strength

J – rate of nucleation

k – Kinetic constant

$K_{d, Mg}$ – Dissociation constant for Mg^{2+}

k_g – Growth constant

k_H – rate of appearance of H^+ ions

k_{Mg} – rate of disappearance of Mg^{2+} ions

K_{so} – Activities solubility product

K_{sp} – Constant solubility product

pK_{so} - Negative log of K_{so}

pK_{sp} – Negative log of K_{sp}

T – absolute temperature

t_G – Growth time

t_{ind} – Induction time

t_N – Nucleation time

z^+, z^- – Valencies of the considered ions

γ – Interfacial tension

γ_i – Coefficient of ionic activity

ζ – Zeta-potential

λ - Wavelength

ρ – density

σ_g – Relative supersaturation

v – Molecular volume

Ω – Supersaturation ratio



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