

Impact of calcium on struvite crystal size, shape and purity

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Abstract

Struvite precipitation occurs spontaneously in wastewater treatment plants under conditions that are influenced by many factors including concentration of Mg^{2+} , NH_4^+ and PO_4^{3-} ions, pH, temperature and mixing energy. These parameters are often difficult to control and as a result struvite generates problems of scale deposits in areas such as pipes and recirculation pumps. At the same time, struvite is considered as a potentially marketable product as an alternative fertiliser. For those two reasons, it has become important to study the principles of struvite precipitation, and to assess the parameters controlling struvite crystallisation. In the present work the influence of Ca^{2+} ions on the precipitation of struvite was investigated in aqueous solution containing Mg^{2+} , NH_4^+ and PO_4^{3-} ions in a molar ratio 1:2:2 at room temperature and constant pH. Different laboratory experiments have been used to assess the

effects of Ca^{2+} ions on size, shape, and purity of the crystals formed. Tools used include particle size analysis, X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDS). The experimental results showed that the presence of calcium in the media can affect significantly struvite crystal growth, and the characteristics of the crystal produced.

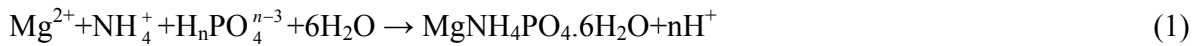
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1. Introduction

Struvite or magnesium ammonium phosphate hexahydrate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) scale deposits are causing considerable concern to wastewater treatment operators [1, 2]. The problem is not necessarily a new one as problems due to struvite spontaneous precipitation were first reported as *a crust of crystalline material* in 1937 in a multiple-stage sludge digestion system [3]. Often perceived as a nuisance affecting the efficiency of treatment processes and causing maintenance problems [4], the control of struvite deposition has been widely investigated, including the dilution of struvite crystals with water effluents [5]; preventive action by chemical dosing of iron salts [6] or addition of chemical inhibitors [1,7]. In the past 10 years struvite precipitation has gained interest as a route to phosphorus recovery [1]. Its composition (nitrogen (N), phosphorus (P) and magnesium (Mg) ions in equal molar concentrations) makes it a potentially marketable product for the fertiliser industry, if the properties of the final product can be controlled [8].

1.1. Struvite formation

Struvite usually precipitates as stable white orthorhombic crystals in a 1:1:1 molar ratio according to equation 1 (with $n = 0, 1$, and 2 , as a function of pH) [9]:



The occurrence and development of struvite crystals follows two chemical stages: nucleation (crystal birth) and crystal growth (enlargement of crystals until equilibrium) [10].

Predicting or controlling these stages is complex as it is controlled by a combination of factors including thermodynamic of liquid-solid equilibrium, phenomena of matter transfer between solid and liquid phases [10, 11], and kinetics of reaction [12] as well as several physico-chemical parameters such as: pH of the solution from which struvite may precipitate, supersaturation, mixing energy, temperature and presence of foreign ions.

The influence of pH and supersaturation on the precipitation rate and crystal characteristics of struvite has been demonstrated by a number of authors [12-16], but as yet little interest has been paid to the influence of foreign ions on struvite nucleation and crystallisation.

Theoretically speaking, impurities in solution from which a compound may precipitate can affect the growth rate of crystals due to blocking of active growth sites inhibiting the increase of crystal size, [10]. In the case of struvite crystallisation from wastewater sludge, foreign compounds are numerous (amongst them potassium, chloride, calcium, carbonates, zinc) and could perturb, be absorbed on crystal surfaces and retard struvite formation, hence phosphorus binding [17].

Indeed for a struvite precipitation process to be successful and economically valuable at full scale, particular attention has to be paid to the properties and quantity of the final product formed. That is to say purity and size of crystal recovered has to be controlled for a reuse as fertiliser: the strength of the granule formed has to be sufficient enough for practical reason (collection, transport and land filling) while purity is essential for environmental reasons.

1.2. Influence of calcium and carbonate ions

The way calcium and carbonate ions could affect struvite nucleation and growth is particularly of interest as their levels in wastewater effluent are relatively high. The study published by Parsons *et al.*, 2001 mentioned magnesium to calcium ratio (Mg:Ca) ranging from 1:1.4 to 1:3.7 in settled sludge liquors from various wastewater treatment plant in the UK [18]. While it is also not unusual to find carbonates (CO_3^{2-}) concentrations, (measured in terms of alkalinity, i.e. mg/L as CaCO_3) above 200 mg/L in various streams of sewage treatment works [19].

Although few authors have studied the influence of calcium and carbonates on struvite crystallisation, it has been showed previously that the presence of calcium (Ca^{2+}) or carbonates ions (CO_3^{2-}) in the media where struvite precipitates can lengthen the induction time preceding the first occurrence of crystals and affect negatively the growth rate [16, 17, 20]. Ca^{2+} ions interact effectively with phosphate or carbonate ions to form calcium phosphates (in wastewater systems commonly a poorly crystallised hydroxylapatite) or calcium carbonate according to the following equations:



The presence of Ca ions can influence struvite formation, either by competing for phosphate ions or by interfering with the crystallisation of struvite. In the latter case, the characteristics of struvite crystals formed are likely to be affected; but this has never been assessed. The main objective of this paper is thus to explore how Ca ions can affect struvite crystals nucleation and growth, and discuss the impact this has on the quality of the recovered product.

2. Materials and methods

A series of experiments have been undertaken to assess the impact of Ca ions on struvite crystallisation using absorbance measurements, particle size analysis and the characterisation of struvite crystals formed through X-ray diffraction (XRD) and scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDS).

For all the experiments reported here struvite was precipitated from mixed solutions of magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$). Stock solutions of magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ / BDH AnalaR) 0.05 M and ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$ / Sigma ACS Reagent) 0.2 M were prepared by dissolving the corresponding crystalline compounds in ultra-pure water (Purelab Ultra, Elga). Each stock solution was then filtered through a 0.22 μm paper filter to eliminate the presence of impurities, and stored at room temperature. All the experiments mentioned in the present paper have been undertaken at room temperature.

2.1. pH and absorbance experiments

Initial experiments used changes in solution pH to indicate the start and rate of nucleation. Experiments at various initial Mg concentrations were carried out to determine an initial Mg concentration for which the induction period is reasonable and the nature of the crystal formed acceptable.

Struvite was precipitated from volumes of stock solutions $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ diluted in 250 mL flasks so that the final concentration of Mg after mixing ranged from 1.2 mM to 3.5 mM and the molar ratio of magnesium, nitrogen and phosphorus (Mg:N:P) always equal 1:2:2. Prior to mixing, the diluted solutions were adjusted to pH 9, by addition of sodium hydroxide (analytical reagent grade) 0.01 N and 2 N and then the two solutions were simultaneously mixed together in a 600 mL beaker, and the pH was measured periodically over 25 minutes. At the end of each test, the precipitate was filtered through a 0.22 μm , dried at room temperature and then characterised via XRD (Powder X-Ray Diffractometer D5005 Siemens) and SEM-EDS (Philips XL 30 SFEG).

The influence of Ca ions on absorbance during struvite crystallisation was investigated at constant initial Mg concentration ($[\text{Mg}^{2+}] = 1.64 \text{ mM}$) and at a wavelength of 385 nm.

Ca ions were added in the Mg chloride solution as Ca chloride dihydrate 0.4M ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ / Fisher Chemicals) and carbonates ions were added in the ammonium phosphate solution as sodium hydrogen carbonate 0.4M (NaHCO_3 / AnalaR Fisher Chemicals) to provide alkalinity so that the solutions were better analogues to real media (i.e.: wastewater effluents/sludge liquors). The molar ratios Mg:Ca: CO_3 investigated were 2:1:1, 1:1:1 and 1:2:2.

2.2. Particle sizing experiments and crystal characterisation

The effects of Ca ions on struvite crystal size, shape and purity were then investigated using particle size analysis, SEM, and XRD. Here a Mastersizer 2000 combined with a Hydro 2000MU (Malvern instruments) was used to follow changes in particle size distribution during struvite crystallisation in presence of Ca ions. Struvite was precipitated in a 1L beaker from equal volumes (400 mL) of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ so that the Mg concentration in the final solution was 1.64 mM and the ratio of Mg:N:P was 1:2:2. Prior to mixing, various volumes of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ 0.4 M were added to the Mg chloride solution, and equal volumes of NaHCO_3 0.4 M were added in the ammonium phosphate solution. Then each solution was pH adjusted to 9 by addition of NaOH. Ratios Mg:Ca: CO_3 experimented were 2:1:1, 1:1:1 and 1:2:2. The particle size distribution was automatically recorded as the experiment progressed. At the end of each experiment, the samples were filtered through 0.22 μm filter, dried at room temperature and analysed with XRD and SEM-EDS.

3. Results and discussion

3.1 pH

Struvite crystallisation is governed by the combination of key parameters amongst which are the pH, the initial concentration of the ionic species in solution, the mixing speed and the presence of foreign ions. In order to assess the impact of Ca ions on the quality, that is to say here size, morphology and purity, of struvite crystals, it was necessary to limit the impact of the other parameters on crystal formation. Experiments were undertaken at room temperature and

at a constant mixing speed. Solutions were made to a standard recipe with the molar ratio Mg:N:P (1:2:2) leaving the concentration of Mg as the limiting parameter.

The initial experiments undertaken used pH as an indicator of struvite nucleation. As struvite precipitates, it triggers a release of protons ions in solution and hence a change in pH occurs during the nucleation process. The drop in pH is characteristic of the speed at which the first crystals of struvite occurs, and is linked to the rate of struvite formation which can influence the quality of the crystals formed.

The first series of tests measured changes of pH with time for a range of Mg concentrations. It was seen that as expected increasing the concentration of the limiting Mg ions lead to an increase in the change in pH and a reduction in induction time (Figure 1). XRD and SEM were used to characterise the purity and morphology of the produced crystals. Little difference in purity was observed but the morphology of the crystals was influenced by the initial concentration of Mg in solution. When the Mg concentration increases, the characteristics of struvite crystals is better, that is to say that the typical orthorhombic shape of struvite is more frequent and their size is bigger. From these experiments the Mg concentration of 1.64 mM was chosen as a good compromise between induction period and quality of the resulting product.

3.2. Effects of Ca ions on absorbance during struvite crystallisation

In addition to pH, absorbance measurements have often been used to follow nucleation and growth [21]. The absorbance measurement corresponds to the quantity of energy absorbed (or transmitted) by the matter, and hence following the evolution of the absorbance of a

solution at a specific wavelength, we can see the advancement of the crystallisation process and hence the evolution of the particle growth.

Here we have investigated the effect that Mg:Ca ratio has on struvite nucleation and growth. Without any Ca the absorbance increases quickly (less than 2 minutes) due to the nucleation of struvite particles, before reaching a maximum stable value (around 0.170) corresponding to crystal growth and sedimentation stages (Figure 2). By adding Ca at a molar ratio of Mg:Ca 2:1, we observe an increase in absorbance values, probably due to the formation of Ca carbonate or phosphate but we also notice an increase in the induction time from 2 minutes to more than 3 minutes. At the higher molar ratios Mg:Ca 1:1, and 1:2, the turbidity of the solution just after mixing is high due to the preferential reaction of Ca ions with carbonate or phosphate ions making it difficult to extract data on the formation of struvite crystals.

At a molar ratio Mg:Ca 2:1, it appears that an instantaneous precipitation occurs in the early stage of the reaction causing the initial turbidity of the solution, but the time taken to reach constant absorbance values is not as quick as it was during the first experiment without Ca. Despite this first reaction, some particles continue thus to nucleate. As phosphate ions are present in this case in large excess comparing to calcium, even if the totality of Ca ions react preferentially with phosphates to form calcium phosphate, the minimum 1:1:1 Mg:N:P ratio necessary for struvite to occur is still available, this would explain that struvite nucleation is possible. At this level, calcium ions could thus affect the rate of growth and the induction time as Koutsoukos *et al.*, 2003 mentioned it in their work [17]. At higher molar ratios Mg:Ca 1:1, and 1:2, the results are more difficult to interpret as although the turbidity of the solution just after mixing is high due to the preferential reaction of Ca ions with carbonate or phosphate ions, making it difficult to extract data from absorbance measure on the formation of struvite crystals. To understand what happens in those cases in terms of crystal formation and/or

characteristics of the compound generated, analysis of the recovered product was necessary. To clarify these first statements the following experiments concerning particle sizing and crystal characterisation were carried out.

3.3 Particle sizing experiments and crystals characterisation

To determine the influence of Ca ions at higher concentrations, and to investigate their effect on the struvite crystal properties, it was decided to undertake a series of experiments using particle sizing, XRD and SEM-EDS. Particle size measurements were performed continuously at constant speed ($V_r = 2500$ rpm) during the precipitation process and the particle size was recorded over periodic intervals. Again changes in particle size were followed for a range of Mg:Ca ratios. As a reference the change in particle size in a solution without added Ca was measured and the data obtained showed a monomodal particle size distribution for all the distributions, with a mean size rising to constant values comprised between 13.416 and 15.157 μm after 5 minutes of experiment (Figure 3, Figure 4).

The effects of Ca concentration on the evolution of struvite particle size are showed here by plotting the particle size distribution at the beginning ($T = 5$ min) and the end ($T = 20$ min) of the experiment. An increase of the Ca concentration in relation to the Mg concentration results in a decrease of the mean size measured after 5 minutes run: maximum peaks are recorded between 2.15 μm to 2.429 μm for the ratio 2:1, 2.745 μm to 3.101 μm for the ratio 1:1 and 3.958 μm to 4.472 μm for the ratio 1:2. After 20 minutes run, the results are different. The distribution in presence of Ca ions at low concentration (ratio Mg:Ca 2:1) appears with a maximum peak corresponding to a mean size of particle lower than for the run without Ca. At higher Ca concentrations (ratios 1:1, and 1:2), the data showed a rise in the population of

particles with higher mean size (Figure 4) than for the results without Ca addition. This may indicate an agglomeration of the particles so that the percentage of individual particles decreases compared to the agglomerates. SEM pictures taken of dried samples recovered at the end of each trial helped to explain this supposition.

Firstly, the XRD pattern generated from the sample without Ca matched with the database model for struvite (i.e. position and intensity of the peaks, figure 5, sample 1), identifying the precipitate to be struvite [19]. But as Ca concentration increases (Mg:Ca 2:1, figure 5, sample 2), XRD results showed a more noisy pattern with reduction in peak size and definition. At higher Ca concentrations the analysis revealed only background noise, indicating that there was no macro crystalline compound present in the samples (Figure 5, XRDs of samples 3 and 4). SEM confirmed the results of the particle size experiments and XRD analysis in that the formation of struvite crystals (Figure 5, picture sample 1) is affected by the presence of Ca ions. At a low calcium concentration in solution, we can still distinguish the shape of struvite particle but covered by a precipitate (Figure 5, picture sample 2) whilst a rise to higher Ca concentration inhibits the occurrence of struvite crystals and leads to the formation an amorphous matter (Figure 5, pictures sample 3 and 4), probably a calcium phosphate compound. To identify the elemental composition of this amorphous matter, energy dispersive spectrometry has been used on specific area localised on the SEM pictures.

As expected for samples without Ca, EDS spectrum (Figure 6, Sample1) showed highest peaks were obtained for Mg, P and O (i.e.: major elements composing struvite in mass percentage), confirming the purity of the crystal formed as no traces of other compounds have been found. At a Mg:Ca ratio of 2:1, EDS performed on struvite like crystals covered with an amorphous substance, showed the presence of a distinctive peak for Ca while peaks for Mg and P were quasi unchanged (Figure 6, Sample2 A). We can say that at this level another phase precipitates

on struvite crystal surfaces and around, hence starting to interact with its formation. It is more than just calcium which is absorbed on the surface of struvite crystals. An EDS analysis performed on an amorphous part next to the crystal like shape in the same sample (Figure 6, Sample2 B) revealed a higher peak for Ca and an important peak for phosphorus when compared to the magnesium. The formation of this precipitate at the surface of crystals would thus explain the multitude of background noises observed previously on the XRD patterns (Figure 5, sample2) while struvite peaks are still identifiable.

At Mg:Ca 1:1 and above (Figure 6, samples 3 and 4), the EDS spectrum of this amorphous matter reinforce the first hypothesis that the precipitate formed at this stage is due to the formation of an amorphous calcium phosphate. Indeed both spectra show prominent peaks for phosphorus and calcium when compared to magnesium. From a first point of view, we could have identified it as either an amorphous calcium phosphate or another calcium phase (i.e. calcium carbonate or calcium hydroxide), but in the latter case XRD pattern for samples 2 to 4 would have showed them on Figure 5, as they are crystalline substances. This confirms thus that the chemical nature of this matter is easily assimilated as an amorphous calcium phosphate.

4. Conclusion

The impact of Mg and Ca solution concentrations on struvite crystallisation has been investigated using a range of analytical tools including pH, absorbance, particle size, XRD and SEM-EDS.

It has been shown that the presence of Ca ions in solution has a significant impact on struvite crystallisation in terms of size shape and purity of the product recovered. In the present study, it has been found that increasing the calcium concentration reduces the crystal size and inhibits

the struvite growth, or affects struvite crystallisation and leads to the formation of an amorphous substance rather than crystalline struvite.

At molar ratios Mg:Ca~1:1 and above, no more crystalline compound is formed but a substance identified as an amorphous calcium phosphate.

As Ca ions levels in sludge liquors are high in relation with Mg levels, Ca impact on struvite crystal morphology will have to be considered in the future in order to improve the recovery and reuse as a fertiliser.

Further works will thus focus on the extrapolation of these laboratory results using a reactor which has been designed and is currently being used to study struvite nucleation and growth at larger scale.

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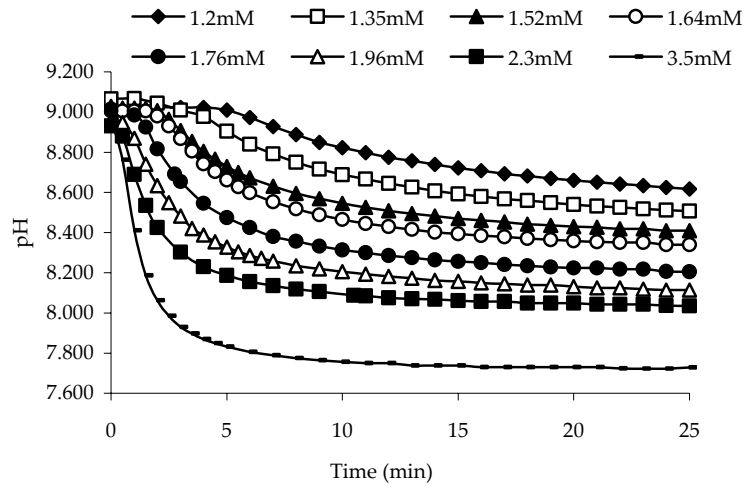


Fig. 1. Evolution of pH during struvite crystallisation for different initial Mg concentration

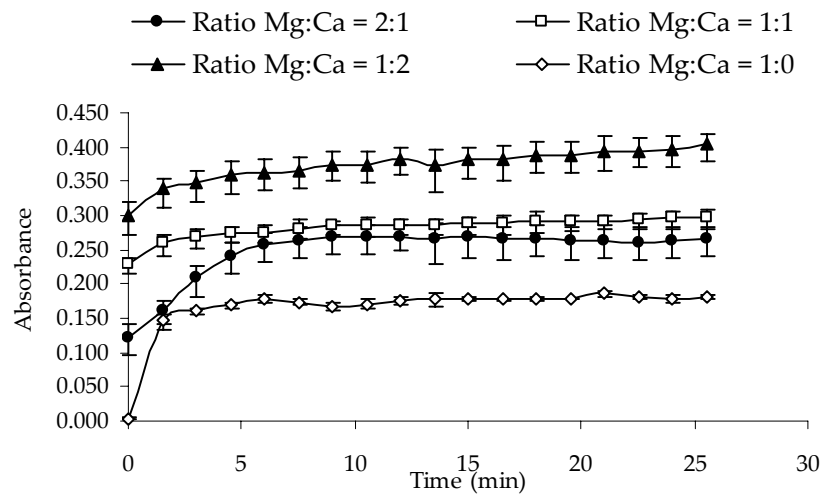


Fig. 2. Influence of increasing addition of Ca on absorbance measurements during struvite crystallisation

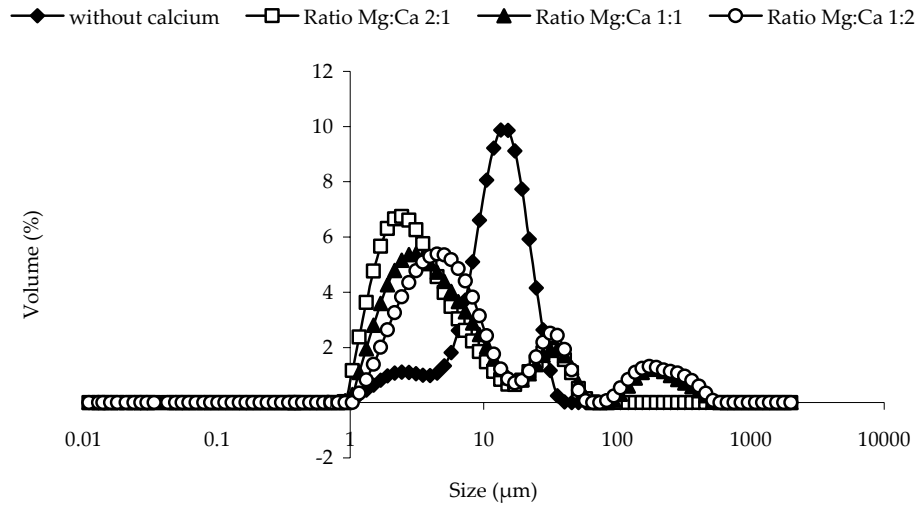


Fig. 3. Particle size distribution five minutes after the mix of the solutions for different molar ratio Mg:Ca. ($V_{\text{mixing}}=2500$ rpm)

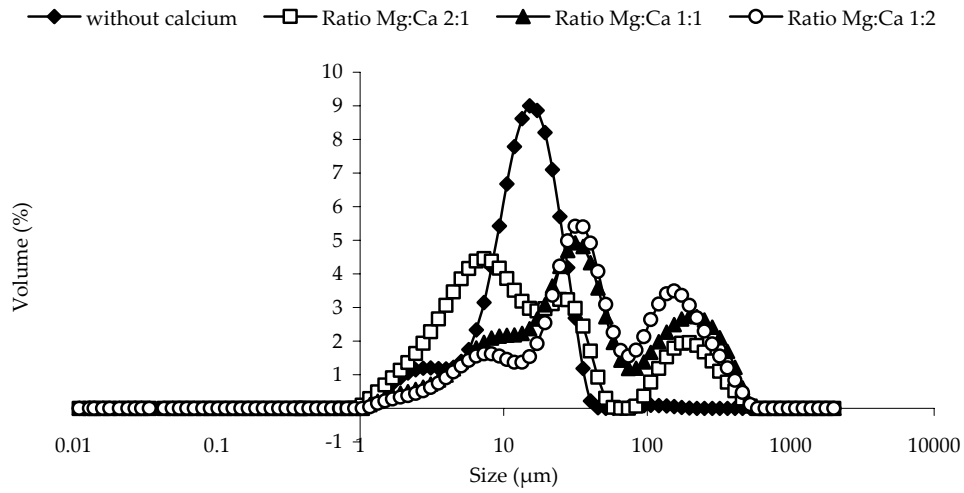
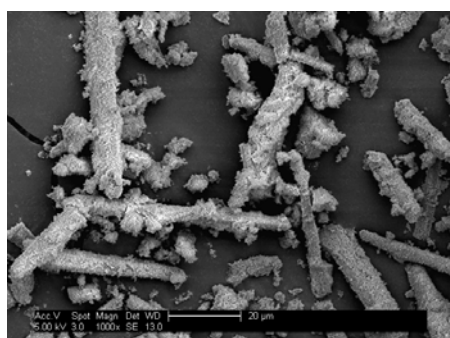
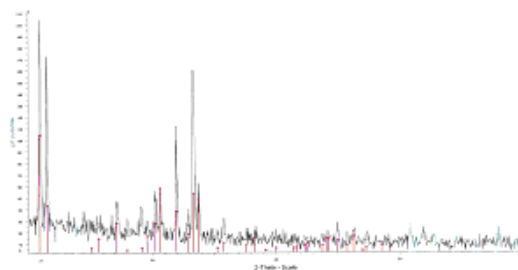


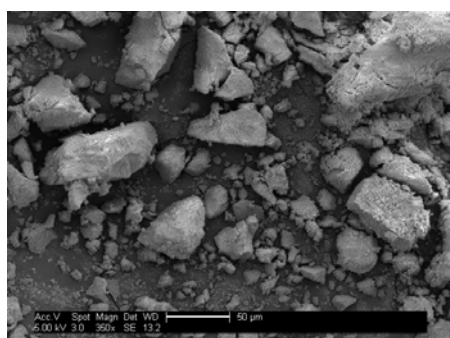
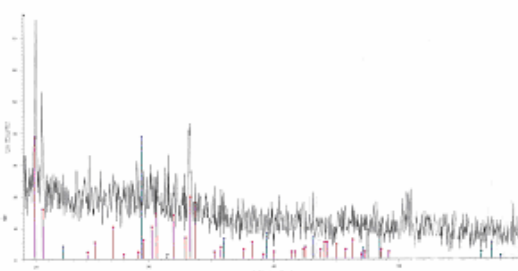
Fig. 4. Particle size distribution 20 minutes after the mix of the solutions for different molar ratio Mg:Ca. ($V_{\text{mixing}}=2500$ rpm)



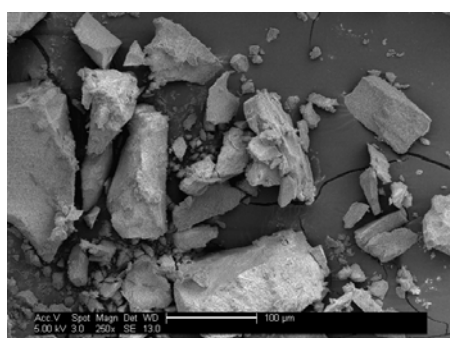
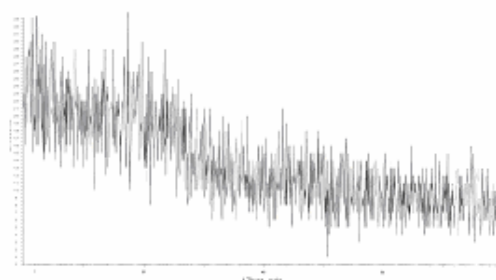
Sample 1:
[Mg]= 1.64mM
Ratio Mg:Ca=1:0



Sample 2:
[Mg]= 1.64mM
Ratio Mg:Ca=2:1



Sample 3:
[Mg]= 1.64mM
Ratio Mg:Ca=1:1



Sample 4:
[Mg]= 1.64mM
Ratio Mg:Ca=1:2

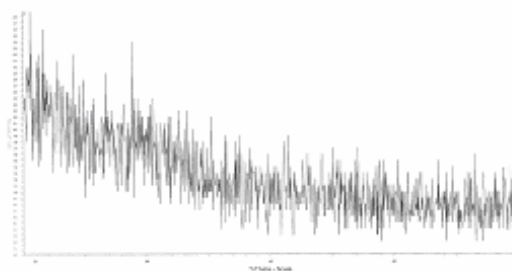


Fig. 5. Impact of growing amounts of Ca ions on struvite crystal morphology and purity. SEM pictures and their respective X-ray diffractograms

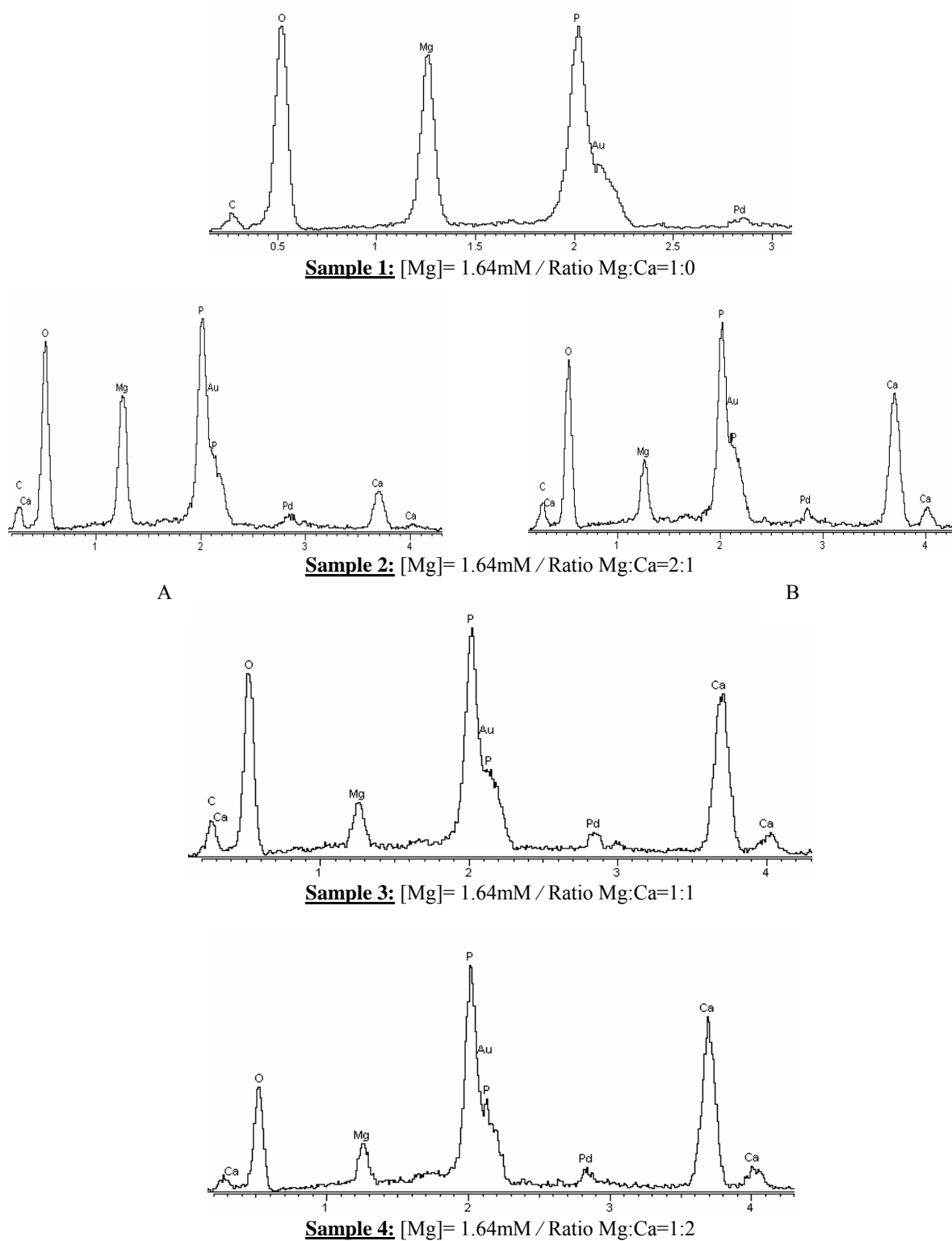


Fig. 6. Impact of growing amounts of Ca ions on struvite crystallisation. Elemental surface analysis by EDS.

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