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Mineralogical controls on phosphorus recovery from wastewaters

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ABSTRACT

The removal of phosphorus from wastewaters is becoming very common, to meet water quality targets, and avoid environmental problems related to eutrophication. At the same time, agricultural application of P-rich sewage biosolids is diminishing for reasons of logistics and of public pressure. As a result P from wastewaters is ultimately disposed of in landfills. Over the long term, phosphate ore reserves will become depleted. Recycling of P from wastewaters may thus be a realistic prospect if scientific and technical issues can be resolved. At the centre of the scientific problems lie considerations about optimizing phosphate precipitation as Ca phosphates. A number of Ca phosphate minerals exist, although by far the most common of these is hydroxylapatite. Precipitation kinetic considerations, however, suggest that other Ca phosphates (such as brushite, octacalcium phosphate, whitlockite, monetite or amorphous Ca phosphate) may initially precipitate, and later recrystallize into the most stable hydroxylapatite. This article reviews the complex precipitation mineralogy, chemistry and kinetics of Ca phosphates.

KEYWORDS: phosphorus recovery, wastewater, landfill, hydroxylapatite, Ca phosphate.

Introduction

PHOSPHORUS is an essential nutrient for all life forms on Earth. It is therefore present in, or added to, both fertilizers and animal/human foodstuff. It is also used in a wide variety of industrial, detergent and pharmaceutical applications. Extensive use of phosphate, mainly due to increasing agricultural needs, has resulted in high P levels in surface waters (eutrophication), which contributes to environmental problems. For this reason, P removal from municipal wastewater is developing across Europe in response to water quality objectives, in particular the Urban Waste Water Treatment Directive (91/271/EEC) and the recent Water Framework Directive (2000/60/EC). In wastewater treatment plants, P is removed chemically or biologically from the waters and incorporated into a solid waste (sewage biosolids). For a while, P and other nutrients in biosolids were recycled via agricultural spreading. However this route is becoming increasingly impractical for logistical reasons (lack of farmland close to population centres) or unacceptable, due to concerns about heavy metals and pathogens contained in biosolids. Sewage biosolids are currently mainly disposed of in landfill, after thermal treatment. The lack of appropriate technology to recover P from the sludge means that this non-renewable resource is also lost to landfills.

At the same time, the need for raw phosphate is not expected to decline and the extraction and processing of phosphate rock (the only primary source of P) is becoming increasingly expensive. The remaining reserves of phosphate rock are also becoming limited: at the current usage rate, phosphate reserves are expected to be depleted in the next 75 to 100 years (Driver *et al.*, 1999). Unlike other resources that may become obsolete before world reserves run out (e.g. oil), there can be no alternative to the use of P; better controls of its utilization, and recovery rather than disposal, are therefore essential.

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Phosphorus recovery from wastewater can have significant operating benefits and economic incentives for the water industry through the potential reduction of biosolids for disposal, the prevention of uncontrollable precipitation of phosphates (scale formation) in wastewater works and the potential generation of a product for sale. A recycling pathway appropriate to the existing wastewater works infrastructure would be the development of a controlled precipitation process from liquid streams, of Ca phosphates (most likely amorphous or hydroxylapatite) or struvite (Mg ammonium phosphate) in a dedicated reactor. Calcium phosphate as the product of the recycling process will often be preferable to struvite, because it is the same substance as the current raw material, i.e. phosphate rock, used by industry. Despite a considerable volume of work, including laboratory, pilot and full-scale trials, P recycling from wastewaters has not yet been widely adopted.

Identifying the optimum conditions for P recycling is, to a large extent, a mineralogical problem. It is necessary to develop better understanding of processes such as nucleation and growth of Ca phosphate phases in an organic-rich solution matrix, to enable the design of an appropriate reactor configuration. The present article introduces the chemistry and mineralogy of wastewater treatment, discusses the chemistry and mineralogy of Ca phosphate precipitation and reviews existing work on precipitation kinetics. Finally, it considers the research challenges still remaining and proposes future directions.

The chemistry and mineralogy of wastewater treatment

Wastewater is treated to remove organic and inorganic components that may be detrimental to human health or the environment if released. The treatment of organic nutrients aims to reduce the biological oxygen demand (BOD) of the wastewater, firstly by removing suspended solids (primary treatment), and then usually by microbial degradation (secondary treatment) (Atlas and Bartha, 1997). The latter may be augmented to remove N and P from the wastewater; this treatment is called biological nutrient removal (BNR). Phosphorus may alternatively be removed chemically at the end of the process (tertiary treatment) by introduction of Fe, Al or, very rarely, Ca salts, and precipitation of insoluble phosphates. Either way, P is incorporated in the sewage biosolids, but in the case of tertiary treatment phosphate precipitation results in a significant volume increase of the biosolids (generally 30–50%, Woods *et al.*, 1999). Despite the volume increase, this method is still popular, as the sole or as additional treatment, because it can reduce P levels in the final effluent very reliably (e.g. Strickland, 1999), and involves little or no direct infrastructure investment.

Phosphate precipitation in wastewater can occur spontaneously; this is a common problem in many wastewater works, particularly after installation of biological nutrient removal, which results in high orthophosphate concentration in anaerobic effluents (e.g. Williams, 1999). Phosphate phases that may precipitate are struvite ($MgNH_4PO_4 \cdot 6H_2O$), if ammonia and Mg concentrations are elevated, and/or Ca phosphates, usually amorphous, if the effluent is high in Ca. Most wastewater precipitation problems reported are associated with struvite (e.g. Williams, 1999), although this may be an artefact of its high crystallinity, which makes it easy to identify by X-ray diffraction (XRD). Phosphate precipitation is reported to occur in pipes transporting the treated effluent, particularly at bends where pressure changes occur, and within anaerobic digesters (Loewenthal *et al.*, 1994; Maqueda *et al.*, 1994). In all instances the trigger mechanism appears to be a reduction in pressure, which results in CO_2 degassing, and, as a result, increase in pH.

The same mechanisms that result in the spontaneous precipitation of phosphates, can, in principle, under controlled conditions generate a reasonably pure precipitate, that may be removed from the system and potentially recycled. There have been several laboratory, pilot and full-scale trials to date, but P recycling has still not become a main stream process. Recovery trials to date involve the use of a dedicated reactor, usually fed by a side stream, rather than the main treatment line. The majority of reactors tested operate on a fluidized bed principle (Fig. 1). The process requires the use of seed particles to trigger precipitation, which remain suspended in the fluidized bed; the inflow rate controls the height of the bed. During operation, the suspended seeds grow up to a predetermined size, and are then replaced by fresh seeds. The role of the seed is to facilitate nucleation, which can be sluggish, particularly at low supersaturation. For some trials addition of either Mg, for struvite precipitation, or Ca, for Ca phosphates precipitation, has been necessary.

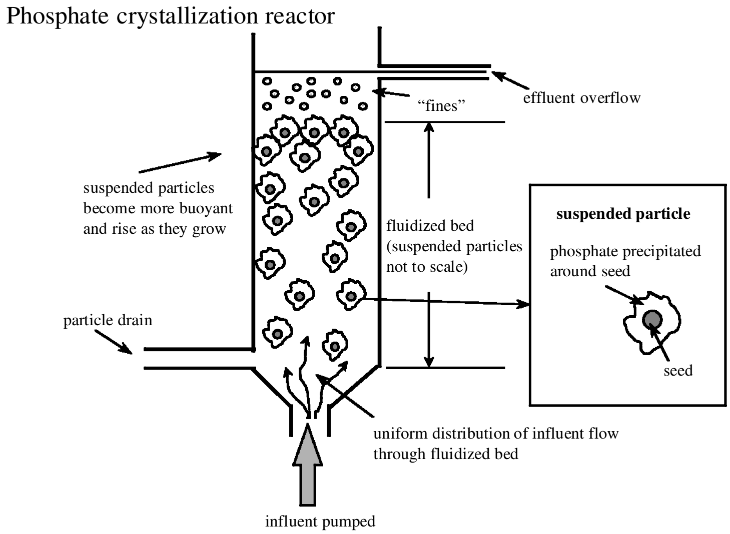

FIG. 1. Schematic representation of a fluidized bed reactor for phosphate crystallization. The influent flow rate controls the height of the fluidized bed. Phosphate precipitates around the seeds, which are drained and replenished after reaching a certain size. The effluent returns to the main wastewater line.

Focusing on Ca phosphates, a previous laboratory study identified the precipitating phase as hydroxylapatite (e.g. Kaneko and Nakajima, 1988). However, two large-scale trials published recently, one in Holland, at Geestmerambacht (Giesen, 1999) and the other in Sydney, Australia (Angel, 1999) reported an apparently amorphous Ca phosphate. The seed material used in the former was silica sand and in the latter Mg oxide. Several other types of seed have been tested in laboratory studies, including calcite (House and Donaldson, 1986), dolomite (Roques *et al.*, 1991) and phosphate rock, bone char, magnesia clinker, zirconium hydroxide and pumice (Kaneko and Nakajima, 1988). To demonstrate the product of seeded precipitation, scanning electron microscope (SEM) images of precipitates from Geestmerambacht are shown (Fig. 2*a–d*). The figures show a general view of a recovered seed following precipitation (Fig. 2*a*), and contrast the seed surface (Fig. 2*b*) with that of the newly precipitated phosphate (Fig. 2*c,d*).

The studies mentioned above, and others, report a number of operational problems associated with inducing Ca phosphate precipitation. These can be summarized as follows: for precipitation to occur it was found that chemically induced high pH, and CO_2 stripping prior to entering the precipitation reactor were necessary. Problems with fines and non-recyclable quality precipitates have been reported. These correspond to scientific/mineralogical problems related to sluggish or unpredictable nucleation and interference from other ions, such as organic species and carbonate. Current understanding of heterogeneous nucleation and growth kinetics of Ca phosphates is generally poor, particularly under conditions that would apply to wastewater works. The following sections explain how thermodynamics and kinetics of the dissolution and precipitation of Ca phosphates can contribute to a better understanding of precipitation processes at wastewater works, and describe current knowledge.

Calcium phosphates: solubility and occurrence

Solubility is a measure of the maximum concentration in solution for the free ionic components of a phase, before saturation occurs, and precipitation begins. In environments such as wastewater, significant apparent supersaturation is necessary for precipitation to occur. This is due to a number of factors but mainly to the effects of ion association (resulting from the high concentration of dissolved species). The net result is that the free ion concentration contributing to saturation is

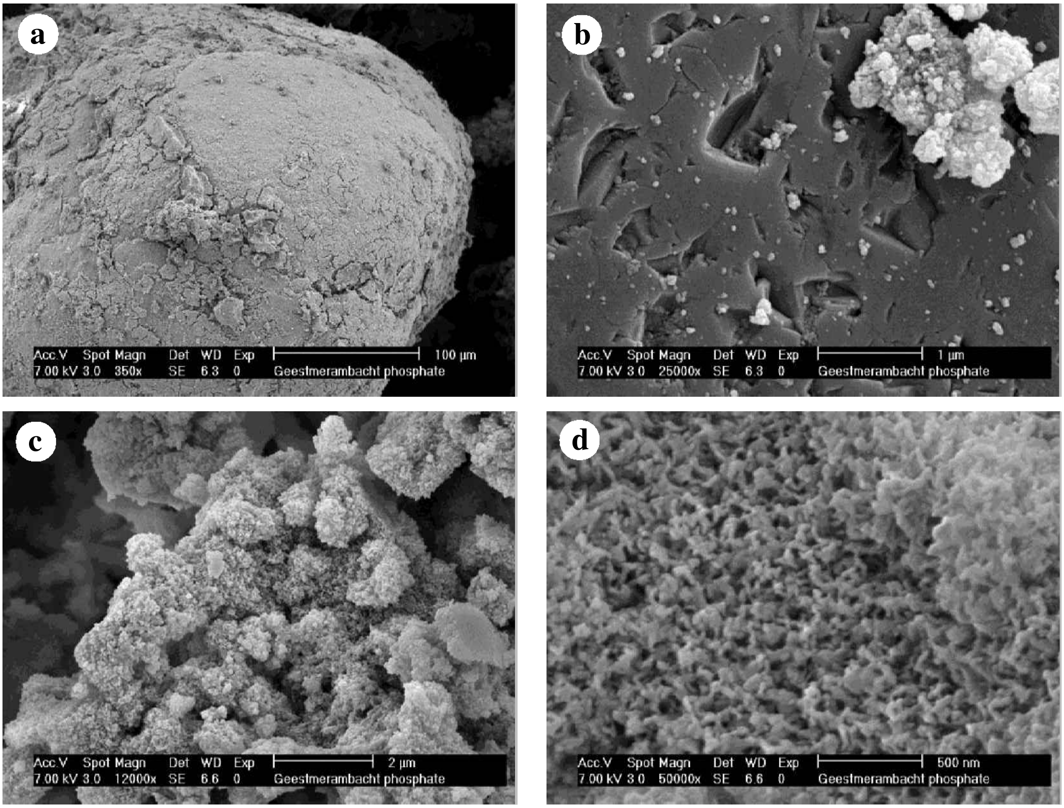

FIG. 2. Calcium phosphates recovered from the wastewater works at Geestmerambacht: (*a*) a seed covered with precipitated Ca phosphate; (*b*) the surface of a quartz sand seed with virtually no phosphate precipitated, except for the top right corner; (*c*) the precipitated Ca phosphate shows no apparent crystallinity at this scale (scale bar: 2 µm); (*d*) crystallites, perhaps a few tens of nanometres in size, are apparent at this scale (scale bar: 500 nm).

substantially lower than the total ion concentration. The degree of supersaturation required can be predicted theoretically, or assessed experimentally.

In solutions containing Ca and phosphate, a number of Ca phosphate phases may form (Table 1), depending on the pH and solution composition. Which Ca phosphate precipitates will depend on which phase(s) may be above saturation at the prevailing solution conditions (Fig. 3), but also kinetic factors (see below). If thermodynamic factors were the only control, Fig. 3 suggests that the most stable Ca phosphate is hydroxylapatite, except at low pH where brushite becomes more stable. There is also evidence that ultimately, any Ca phosphate precipitated will probably transform into the thermodynamically more stable hydroxylapatite (e.g. Kibalczyc, 1989).

Hydroxylapatite (HAP, $[Ca_5(PO_4)_3OH]$), is the prevalent form of Ca phosphate in the environment and in bio-minerals (bone and teeth) (e.g. Dowker *et al.*, 2000; Skinner, 2000). For that reason, the majority of published experimental solubility studies regarding Ca phosphates focus on HAP, although basic equilibrium solubility data are available in the literature for most Ca phosphates (see Table 1). The mechanism of HAP dissolution is most likely a process controlled by the mineral surface (Christoffersen *et al.*, 1978; Valsami-Jones *et al.*, 1998).

Brushite (also known as dicalcium phosphate dihydrate, DCPD $[CaHPO_4´2H_2O]$) is often found in phosphate deposits (Nriagu, 1984) and other P-rich environments, such as fertilized soils (e.g. Fixen *et al.*, 1983). There is evidence that brushite, along with other Ca phosphates such as

TABLE 1. Calcium phosphates, their molar ratios and solubilities.

Name, abbreviation and formula	MR	SP
Brushite or dicalcium phosphate dihydrate (DCPD): $CaHPO_4 \cdot 2H_2O$	1.0	2.49×10^{-7} $(\text{mol l}^{-1})^2$
Monetite or dicalcium phosphate anhydrous (DCPA): $CaHPO_4$	1.0	1.26×10^{-7} $(\text{mol l}^{-1})^2$
Octacalcium phosphate (OCP): $Ca_4H(PO_4)_3 \cdot 2.5H_2O$	1.33	1.25×10^{-47} $(\text{mol l}^{-1})^8$
Tricalcium phosphate (TCP): $Ca_3(PO_4)_2$ (calcium end-member of whitlockite group)	1.5	1.20×10^{-29} $(\text{mol l}^{-1})^5$
Hydroxylapatite (HAP): $Ca_5(PO_4)_3OH$	1.67	4.7×10^{-59} $(\text{mol l}^{-1})^9$
Amorphous Ca phosphate (ACP): $Ca_3(HPO_4)_2$	~1.5	variable, more soluble than crystalline phosphates

MR = molar ratio of calcium:phosphate
SP = thermodynamic solubility product: brushite – Patel *et al.* (1974); monetite – McDowell (1968); octacalcium phosphate – Moreno *et al.* (1960); tricalcium phosphate – Gregory *et al.* (1974); hydroxylapatite – McDowell *et al.* (1977)

octacalcium phosphate, tricalcium phosphate and monetite (see below) play a crucial, albeit transient, role in many natural environments, as precursors to HAP. They may also act as intermediate to HAP phases in biological and engineered systems (Frèche *et al.*, 1992, Koutsoukos and Nancollas, 1981, Nancollas and Wu, 2000), and they have all been identified in sewage sludges (Frossard *et al.*, 1994). Brushite has been documented as a precursor of HAP in a number of experimental studies, in the neutral to acidic pH range (e.g. Johnsson and Nancollas, 1992; Heughebaert *et al.*, 1986). It has been found to form soon after soluble fertilizers have been applied, and to persist in soils for many years in a range of conditions (Fixen *et al.*, 1983). At pH <5.5, equilibrium thermodynamic considerations indicate that brushite is the most stable Ca phosphate (see Fig. 3).

Whitlockite (Mg-Ca phosphate; the Ca end-member of the whitlockite group is referred to as tricalcium phosphate, TCP or β-tricalcium phosphate β-TCP, [$Ca_3(PO_4)_2$]) is commonly found in biological systems, particularly pathological calcifications, in lunar materials and meteorites (Tung, 1998) and may crystallize after amorphous Ca phosphate at high temperatures (e.g. Angel, 1999). It should be noted that the name whitlockite is appropriate only for a mixed Mg-Ca phosphate; for the pure Ca end-member the term β-tricalcium phosphate is more correct (Tung, 1998).

Monetite (also known as dicalcium phosphate, anhydrous, DCPA [$CaHPO_4$]) has been identified in natural phosphate rock occurrences (Nriagu, 1984), in addition to biological and engineered systems. Octacalcium phosphate (OCP [$Ca_4H(PO_4)_3 \cdot 2.5H_2O$]) is only associated with biological precipitation (LeGeros and LeGeros, 1984) and anthropogenic environments, and does not appear to have natural occurrences. It has been shown to precipitate as a precursor of HAP in experimental systems under a range of conditions (Feenstra and de Bruyn, 1979; Heughebaert *et al.*, 1986).

A number of workers have established that the rate of dissolution of hydroxylapatite is influenced by solution saturation, as batch experiments approach equilibrium, and this has compromised several early dissolution kinetic studies. Further difficulties in assessing rates are due to the non-stoichiometric dissolution of hydroxylapatite and preparation and handling of the mineral (Budz and Nancollas, 1988; Margolis and Moreno, 1992; Smith *et al.*, 1977). There is evidence that hydroxylapatite dissolution rates increase in the presence of acetic, lactic and phosphoric acid (Margolis and Moreno, 1992) and octacalcium

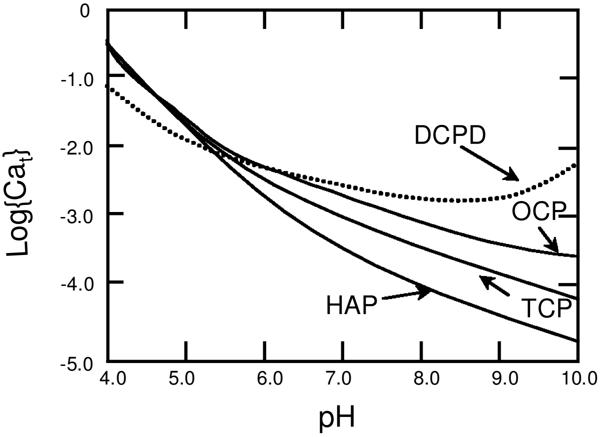

FIG. 3. Solubility isotherms for some Ca phosphates, calculated at 25°C and 0.15 M NaCl and shown on a plot of total Ca concentration against pH (modified after Koutsoukos, 1998). HAP – hydroxylapatite; TCP – tricalcium phosphate; OCP – octacalcium phosphate; DCPD – brushite (dicalcium phosphate dihydrate).

phosphate dissolution rates are influenced by the Ca/P ratio and the degree of saturation (Verbeeck and Devenyns, 1992).

Kinetics of calcium phosphate precipitation

Precipitation kinetics provide a measure of the rate of formation of new phases, and thus can assist reactor design by defining optimum residence time and precipitation conditions. Two steps control formation by precipitation from solution: nucleation and growth.

Nucleation can take place in several different ways: spontaneous formation of individual crystallites in solution, a process known as homogeneous nucleation, or growth on existing surfaces (e.g. seed crystals), known as heterogeneous nucleation. Heterogeneous nucleation is less energetically demanding, and a better analogue for wastewater environments where a multitude of surfaces exists (suspended particles, pipe surfaces). Following nucleation, crystal growth takes place in a number of steps: transport from the bulk solution to the nuclei surface, followed by adsorption to the surface and a number of steps through which the location of the newly adsorbed species changes on the surface to gain an energetically favourable position (Nancollas, 1984).

It is well established that kinetic factors may be more important in determining the nature, and hence the characteristics, of the solid deposits formed during the precipitation process than equilibrium considerations. In other words, what is thermodynamically the most stable phase, may not precipitate, because its precipitation kinetics are slow; an alternative less stable phase, able to nucleate faster, may precipitate instead, or precipitation may not happen at all, or not until an appropriate ‘trigger’ (e.g. seeding) becomes available. Complications may also arise from the simultaneous precipitation and overgrowth of one crystalline phase onto another. For Ca phosphates in particular, the possibility of more than one phase being at or above saturation, makes predictions more complex.

Current understanding of Ca phosphate kinetics suggests that any Ca phosphate from Table 1 may precipitate from supersaturated solutions first, as a precursor phase, but this will eventually crystallize to form hydroxylapatite (Kibalczyc, 1989; Meyer, 1983; Nancollas, 1984).

The specific conditions and order of formation of the precursor phases have been the subject of a number of kinetic studies. Early work showed that the optimum experimental environment is achieved using the constant composition method (Tomson and Nancollas, 1978). This method relies on automatic addition of reactants (via an autotitrator) during a precipitation experiment, so as to retain the solution concentration constant. It can thus provide reproducible experimental conditions and reliable precipitation rates, and a fixed degree of supersaturation, unlike previous experiments, which would commence with supersaturation and end with undersaturation with respect to transient phases, with experimental conditions varying through the run.

Previous studies of heterogeneous and epitaxial growth of Ca phosphates have produced disparate results. For example, by using the constant composition method Zawacki *et al.* (1990) observed a nucleation of Ca deficient HAP on HAP seeds, while Barone *et al.* (1976), observed a precipitation of DCPD onto HAP seeding crystals, under similar conditions. Frèche and Heughebaert (1989) and Heughebaert *et al.* (1986) reported the precipitation of OCP and DCPD onto seed crystals of OCP and DCPD, but not hydroxylapatite.

It is generally understood, that at pH >7 and high supersaturation, the likely precursor phase is an amorphous Ca phosphate (ACP), as observed experimentally, and also in some pilot/field studies (see above). In experiments, the ACP may dissolve again to form HAP nuclei (Boskey and Posner, 1973). A three-stage formation of hydroxylapatite, starting with the formation of ACP, followed by OCP has been proposed by Meyer (1983). Kibalczyc (1989), under pH-drift conditions, and within the pH range 7–9, observed a transformation of one type of ACP into another ACP, followed by recrystallization into HAP. It was concluded that under the conditions of that experiment, OCP was not a possible precursor phase to HAP. Precipitation of non-stoichiometric apatites has also been observed (Heughebaert *et al.*, 1990, Zawacki *et al.* 1990).

Calcium phosphate precipitation may be inhibited by other ions present in solution, which may attach to the newly forming surfaces and block nucleation. The influence of inhibitor ions, such as carbonate and Mg, on Ca phosphate precipitation has been discussed by many authors (e.g. Abbona and Franchini-Angela, 1990; House, 1999). Co-precipitation of Mg, with the Ca phosphates, for example, may induce firstly the formation of ACP rather than HAP, which will later transform into the more stable HAP. It is possible for HAP to incorporate a small percentage of Mg into its structure, but this causes structural changes and has an inhibiting effect on further HAP formation (Kibalczyc *et al.*, 1990). Salimi *et al.* (1985) studied the crystal growth of DCPD and OCP in the presence of Mg and carbonate using constant composition and pH stating methods. They found that the crystal growth of DCPD was not affected while the OCP crystal growth rate decreased considerably. The presence of CO_2 may also affect precipitation of HAP, either by blocking phosphate nucleation sites, or, at higher concentration, by inducing Ca carbonate precipitation instead (e.g. House, 1999). A recent study showed that the effect of carbonate can vary depending on the solution supersaturation and carbonate concentration; at relatively high supersaturation, carbonate ions had an accelerating effect, while at lower supersaturation they inhibited the seeded crystal growth of HAP (Kapolos and Koutsoukos, 1999). In the latter case, carbonate ions are incorporated into the apatite lattice replacing up to ~5% of the phosphate groups.

Other dissolved cations in solution may block Ca phosphate formation, or even cause HAP dissolution. Examples include the dissolution of HAP to form the less soluble fluorapatite in the presence of fluoride ions (Brown, 1981) or to form metal phosphates in the presence of lead or cadmium (Valsami-Jones *et al.*, 1998). The influence of temperature and pH on HAP precipitation was investigated by Zoltek (1974), who demonstrated that supersaturation may be achieved by a simple increase in pH.

Organic species are reported to have a mostly inhibiting effect on the precipitation of Ca phosphates. Humic, fulvic, tannic and several other low-molecular-weight acids were shown to inhibit the rate of precipitation of DCPD and OCP, and it was hypothesized that this inhibition is due to the obstruction of active crystal growth sites by the adsorbed ligands (Grossl and Inskeep, 1991; 1992; Frèche and Lacout, 1993). Natural amino acids with hydrophobic non-polar groups were found to inhibit HAP growth; this was interpreted as being the result of the amino acids blocking active growth sites and being related to the adsorption affinity of each amino acid to the crystal surface (Koutsopoulos and Dalas, 2000). On the other hand, enhanced nucleation of Ca phosphate crystals was observed on poly-electrolyte multi-layers compared to silica; the type of precipitated phosphate also varied, HAP and OCP being the phases precipitating on the polyelectrolyte and DCPD on silica (Ngankam *et al.*, 2000).

Studies on nucleation of Ca phosphates on polymer substrates have shown that the presence of carboxyl or phosphonic groups in the substrate promotes the nucleation of HAP. The initiation of the formation of a mineral phase on the polymer is attributed to the formation of surface ion-pairs between the dissociated groups and the Ca ions.

Increase of the P containing dissociable groups increased the Ca phosphate promoting capability (Dalas *et al.*, 1991). Most important from the P recovery point of view is the finding, by Paraskeva *et al.* (2000), that sand grains promote the formation of Ca phosphates. Those authors reported formation of DCPD, OCP or HAP on sand grains, depending on the solution supersaturation.

It is apparent that a substantial body of work exists on Ca phosphate precipitation kinetics. However this work cannot be directly applied to wastewater systems. This is because the majority of the above studies were performed in low-ionic strength solutions, and have not been tested in wastewater analogues, where the presence of organic and other species may inhibit or alter the stability of Ca phosphates. If we were to apply the above studies to wastewater conditions, we would, almost certainly, overestimate the Ca phosphate potential to precipitate, and this may have been the reason why previous trials have had poor results. Furthermore, a large number of early studies relied on chemical composition to identify the forming Ca phosphate phase. It is now known that HAP often precipitates in a non-stoichiometric form (e.g. Heughebaert *et al.*, 1990, Zawacki *et al.*, 1990), and therefore some previous work requires further validation.

Conclusions

The above discussion shows that although fundamental understanding of the behaviour of Ca phosphates exists, further mineralogical and geochemical studies are necessary to develop sufficient understanding to assist with a universally accepted technology. This section aims to point towards the less well studied or understood issues relevant to phosphate recovery for recycling from wastewater.

Firstly, the precise influence of all ions present in wastewater on phosphate nucleation and/or growth requires full investigation. This is to allow more realistic and reliable predictions of precipitation using geochemical codes. The competitive formation of Ca phosphates in the presence of other phases likely to be saturated (struvite, calcite) has not been considered: it may be that selective precipitation has to be triggered, for example by appropriate seeds, with a crystal lattice match.

Regarding precipitation inhibitors, it is necessary to consider the effect of species likely to be found in wastewaters, particularly organic species, with a view to assess their effect on nucleation onset and kinetics. Regarding inorganic inhibitors, although there is evidence that Mg and carbonate inhibit crystallization of Ca phosphate, this has not been tested in wastewater-type solutions. Finally, the partitioning of trace metals from solution into the phosphate phases needs to be considered.

Further studies on nucleation are also important. It is now understood that initial phosphate precipitation can be enhanced if an appropriate substrate is present, which will act as a template for nucleation. After formation of the first monolayer on the seed, further influence by the seed will depend on whether it becomes completely armoured by the precipitate, and also by compatibility between the seed and the precipitate. Phosphate seeds would have the added advantage of producing a more P-rich and hence more recyclable product. Other variables such as particle size and volume of seeds would need to be considered.

Phosphorus recycling from wastewaters is certainly the sustainable way forward, but further mineralogical work is needed before this can become reality.

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