



Releasing characteristics of phosphorus and other substances during thermal treatment of excess sludge

XUE Tao, HUANG Xia*

Department of Environmental Science and Engineering, State Key Joint Laboratory of Environment Simulation and Pollution Control, Tsinghua University, Beijing 100084, China. E-mail: xuet03@mails.tsinghua.edu.cn

Received 26 January 2007; revised 15 February 2007; accepted 8 March 2007

Abstract

The releasing characteristics of phosphorus, nitrogen compounds, organics, and some metal cations during thermal treatment of excess sludge were investigated. It was found that during heating not only phosphorus, but also nitrogen compounds, organics, and some metal cations could be released in abundance. The maximum orthophosphate (*ortho*-P) release of about 90 mg/L in concentration was observed at 50°C in 1 h. Except for volatile fatty acids (VFAs), comparatively little total nitrogen (TN), total organic carbon (TOC), and metal cations were released at the same time. Such results might favor further process of phosphorus recovery. VFAs were considerably released only at 50°C. Acetic, butyric, and propionic acid were the most abundant components in turn and their releasing profiles exhibited good linear relationship with time ($R^2 = 0.9977, 0.9624, \text{ and } 0.8908$, respectively). The concentrations of Mg^{2+} and K^+ increased with time and temperature during thermal treatment, but Ca^{2+} decreased. The release of Mg^{2+} and K^+ agreed well with TP release ($R^2 = 0.9892 \text{ and } 0.9476$, respectively). Temperature in the experimental range had very little impact on the linear relationships, especially of Mg^{2+} . Moreover, the parameter of mixed liquor suspended solids (MLSS) was found to be an important factor for thermal sludge treatment as the released *ortho*-P and total phosphorus (TP) at 50°C increased more than one-fold when MLSS was increased from 4000 to 8000 mg/L.

Key words: phosphorus recovery; excess sludge; volatile fatty acids (VFAs); metal cations

Introduction

Phosphorus, indispensable component of DNA (deoxyribonucleic acid), RNA (ribonucleic acid), and ATP (adenosine triphosphate), is indeed the staff of life (Karl, 2000). No microbes, plants, or animals including human beings can exist without it. It is irreplaceable and nonrenewable. However, finite phosphate reserves on earth are being exploited and consumed expeditiously by anthropogenic activities. It has been estimated that the current economically exploitable phosphate reserves around the world would be exhausted in 60–130 years (Steen, 1998).

On the other hand, over input of phosphate to sensitive water bodies might trigger the undesirable aquatic disturbance in the form of eutrophication, giving rise to great environmental and health losses (Pretty *et al.*, 2003). Because of the considerable contribution of phosphate input, sewage in wastewater treatment plants (WWTPs) has been confirmed as the major point source (Bowes *et al.*, 2005), and has been treated by numerous enhanced biological phosphorus removal (EBPR) processes globally, which has resulted in the mass production of excess sludge with high phosphorus content. This sludge can thus be considered as a kind of potential resource for phosphorus

recovery and recycle.

However, owing to the copresence of impurities such as heavy metals and pathogens, there is a high risk for direct recycle of excess sludge without any further treatment. One feasible strategy is to release phosphate into the supernatant from the sludge and then get safe products such as struvite or calcium phosphate by precipitation or crystallization, which can be reused as industrial raw materials or fertilizers (CEEP, 2000). Therefore, to begin with, an efficient way to release phosphate from sludge is needed. Biological phosphate release by microorganisms as polyphosphate accumulating organisms (PAOs) is a common phenomenon in activated sludge processes, with alternating anaerobic-aerobic conditions (Fuhs and Chen, 1975). However, as it requires an adequate supply of organic substrates and relies fully on functions of special microorganisms, the biological approach shows an inherent instability. Then other techniques involving sludge disintegration mechanism, such as, thermal treatment (Kuroda *et al.*, 2002; Takiguchi *et al.*, 2003), ozonation treatment (Saktaywin *et al.*, 2005a, b; Suzuki *et al.*, 2006), and H_2O_2 /microwave treatment (Pan *et al.*, 2006), appear to be good alternatives to release phosphate from sludge. Among them, thermal treatment might be one of the most promising techniques. This is because the heat

*Corresponding author. E-mail: xhuang@tsinghua.edu.cn.

www.jesc.ac.cn

energy needed for thermal treatment could be, to some extent, compensated from the combustion of the flammable gases collected from the digestion unit in WWTPs. And the digestive efficiency and methane productivity of sludge were still improved after thermal treatment (Takiguchi *et al.*, 2004). Then the idea of a systematic combination of thermal sludge treatment for phosphorus recovery and the following digestion system will be attractive from the practicable and sustainable point of view.

However, so far as the mechanism of thermal sludge treatment is concerned there is still a lack of understanding, especially with regard to the releasing characteristics of substances other than phosphorus. This is important because factors of some ions such as Mg^{2+} , Ca^{2+} , and NH_4^+ (Bouropoulos and Koutsoukos, 2000; Stratful *et al.*, 2001; Song *et al.*, 2002; Le-Corre *et al.*, 2005; Yi *et al.*, 2005), and some organic matters (van der Houwen *et al.*, 2001, 2003; Alvarez *et al.*, 2004; Rosmaninho and Melo, 2006) have proved to have close impact on the phosphate precipitation process, and it is highly possible that these substances can also be released into the supernatant from sludge, just like phosphorus, during the sludge disintegration process under heating. Consequently, for the effective coupling of thermal treatment and phosphorus recovery, detailed knowledge about the releasing characteristics of such substances during thermal treatment is to a certain extent necessary.

The purpose of this article then aims at the full investigation of the releasing characteristics of phosphorus, nitrogen, organic substances, and some metal cations during the thermal sludge treatment. Meanwhile, the accompanying changes of mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) of the sludge during heating were also examined.

1 Materials and methods

1.1 Operation of sequencing batch reactor

A sequencing batch reactor (SBR) with 10 L working volume was operated as a bench-scale EBPR system to offer the excess sludge for thermal treatment experiments. This SBR was operated in a 6-h cycle at $23 \pm 2^\circ C$: fill (15 min), anaerobic (90 min), aerobic (180 min), settle (45 min), and decant and idle (30 min). Between every two cycles, 5 L of treated supernatant was withdrawn and then replaced by an equal volume of synthetic wastewater containing glucose and acetate as the main organic substrates (COD 500 mg/L, TN 50 mg/L, TP 20 mg/L). To avoid nitrification in the reactor, 1 mg/L of allylthiourea was also added to the influent. The MLSS in the SBR was 3810 ± 460 mg/L. Average 0.5 L of mixed liquor was discharged at the end of the aerobic phase daily to maintain a designed sludge age of 20 d.

After a cultivation period of about two months, this SBR showed good and steady EBPR capability. Subsequently, the thermal treatment experiments were conducted.

1.2 Thermal treatment experiments

Batch experiments were undertaken to study the process of thermal treatment of excess sludge. The excess sludge sample (8200 ± 110 mg/L of MLSS, 3%–4% of TP content) was immediately prepared from the newly discharged mixed liquor by withdrawing a certain amount of supernatant after sedimentation. And the prepared sample was precisely dispensed into a series of 50 ml centrifuge tubes with 40 ml sample in each. These tubes were then firmly sealed and incubated for 3 h at the designed temperature ($40^\circ C$, $50^\circ C$, $60^\circ C$, $70^\circ C$) using a temperature controlled water bath. Every hour one of the tubes was taken out and immediately centrifuged for 5 min at 8000 r/min, at $4^\circ C$. Then the supernatant was subjected to TP, TN analyses directly, and *ortho*-P, NH_4^+ -N, NO_3^- -N, NO_2^- -N, TOC, volatile fatty acids (VFAs), and metal cation analyses after filtration through 0.45- μm membrane filters, even as the residual solid phase was taken for the determination of MLSS and MLVSS. For validation, all batch experiments were carried out in triplicate at each designed temperature.

1.3 Analytical methods

Analyses of *ortho*-P, TP, NH_4^+ -N, NO_3^- -N, NO_2^- -N, TN, MLSS, and MLVSS were performed according to the Chinese Standard Methods (EPA of China, 2002). Total organic carbon (TOC) was measured by a TOC analyzer (TOC-5000, Shimadzu). Metal cations including Mg^{2+} , K^+ , Ca^{2+} , Na^+ , Fe^{3+} , Mn^{2+} , Cu^{2+} , and Zn^{2+} were determined using an ICP emission spectrophotometer (IRIS Intrepid II XSP Thermo Electron Corporation). In addition, for VFA determination, a gas chromatograph (GC122, Shanghai Precision and Scientific Instrument Co. Ltd., China) with flame ionization detector was used.

2 Results and discussion

2.1 Phosphorus release

The results of phosphorus release during thermal treatment process at different temperature are shown in Fig.1. *ortho*-P and TP were both released quickly as expected. But at $40^\circ C$ the releasing rate was comparatively moderate, whereas, at 50 – $70^\circ C$ the releasing rates were much higher in the first hour and then gradually slowed down later. *ortho*-P was the major form of the phosphate released. However, as temperature increased from 40 to $70^\circ C$, the ratio of *ortho*-P/TP kept dropping.

Figure 1 indicates that a temperature of no less than $50^\circ C$ is needed for efficient phosphorus release from

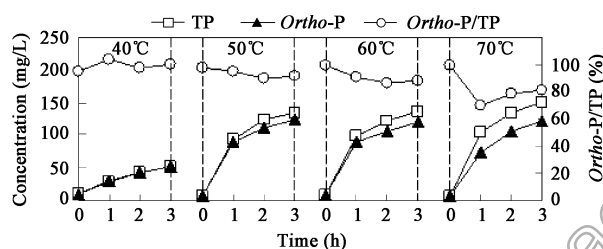


Fig. 1 Phosphorus release during thermal treatment process.

sludge. And a maximum *ortho*-P release of approximately 90 mg/L (about 95% of TP released) is observed in the first hour at 50°C. For phosphorus recovery, the concentration of *ortho*-P is more significant than that of TP. One hour and 50°C were thus concluded as the optimal parameters for phosphorus release in these experiments. However, such a result does not agree with that of Kuroda *et al.* (2002). In their work, only a small amount of phosphorus (approximately 10 mg/L of poly-P and 25 mg/L of TP) could be released in 1 h at 50°C. The optimal parameters acquired in their work were 70°C and 1 h, and polyphosphate (poly-P) was the most abundant component (around 85–90 mg/L, or 87% of TP released).

The MLSS is about 8200 mg/L in these experiments and 3100 mg/L in Kuroda's work, whereas, the content of TP in the sludge is 3%–4% and 4.3% in each. The difference in MLSS is supposed to account for the different performance of phosphorus release in each work. Higher MLSS means more solid substance, which is the storage medium of phosphorus, will exist in the fixed volume of sludge. And for higher MLSS, the water content in the sludge will be reduced correspondingly, and this can contribute to the enrichment of the phosphorus released in the supernatant. Meanwhile, the heating efficiency will also improve when water content decreases, because most of the heat energy is actually simply dispended on water heating in the thermal sludge treatment process. Therefore, at the same temperature, more phosphorus is expected to be released at higher MLSS in the thermal treatment.

To further investigate the effect of MLSS on phosphorus release in the thermal sludge treatment, comparative experiments with MLSS of 4000 and 8000 mg/L were performed at 50°C. As shown in Fig.2, the result confirmed the effect of MLSS as the concentrations of released *ortho*-P and TP were increased, actually more than one-fold, when MLSS was doubled from 4000 to 8000 mg/L. Hence MLSS had proved to be an important factor for thermal treatment of sludge. High MLSS could mean a save in energy and costs by allowing the reduction of operational temperature for substantial phosphate release in thermal sludge treatment.

For unknown reasons, the main form of phosphate released was *ortho*-P in this work, but poly-P in Kuroda's. Though the released poly-P could be easily precipitated

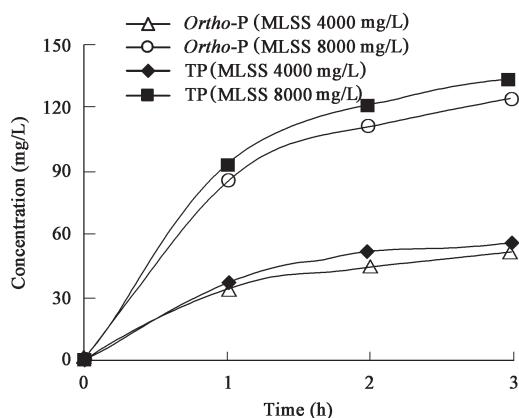


Fig. 2 Effect of MLSS (mg/L) on phosphorus release at 50°C.

by the addition of CaCl_2 at room temperature without pH adjustment (Kuroda *et al.*, 2002), the form of *ortho*-P might have a wider application currently, as we know that nearly all the related works on phosphorus recovery were based on *ortho*-P precipitation products, such as, struvite, calcium, phosphate, iron phosphate, and so on.

2.2 Nitrogen release

Figure 3 shows the releasing characteristics of nitrogen compounds during the thermal treatment process. TN was also released quickly during heating, but the concentrations of NH_4^+ -N, NO_3^- -N, and NO_2^- -N were very low all along. Hence, organic nitrogen was supposed to be the major component of the released TN.

As for phosphorus recovery, the nitrogen form as NH_4^+ -N could be utilized. This is because the precipitation process of struvite, namely, magnesium ammonium phosphate hexahydrate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) needs the participation of NH_4^+ -N. Then to recover phosphorus as struvite would have the advantage of simultaneous removal and recovery of phosphorus and nitrogen from wastewater. But as shown in Fig.3, the concentration of NH_4^+ -N released here was too low. Therefore, calcium phosphate was probably more appropriate as a target product for phosphorus recovery in the authors' future work.

A substantial release of nitrogen, however, may lead to an excessive input of nitrogen load in the wastewater treatment system, where the supernatant is supposed to be returned after recovery. Thus, the problem of nitrogen must be taken into account in the application of thermal sludge treatment in WWTPs. From this point of view, high heating temperature must be avoided. In that case the optimal temperature of 50°C for phosphorus release will also be an acceptable choice.

2.3 Organic substances release

For the investigation of organic substances, the releasing characteristics of TOC and VFAs were examined.

During the thermal treatment process, the concentration of TOC in the supernatant is observed to increase remarkably as shown in Fig.4. More TOC could be released at higher temperature. Compared to the biological way of releasing phosphate by PAOs, thermal treatment then has the advantage, in that, it demands no carbon source supply at all, and on the contrary is able to produce plenty of soluble organic substances, which can be subsequently utilized by the wastewater treatment process.

VFAs investigated included acetic, propionic, butyric,

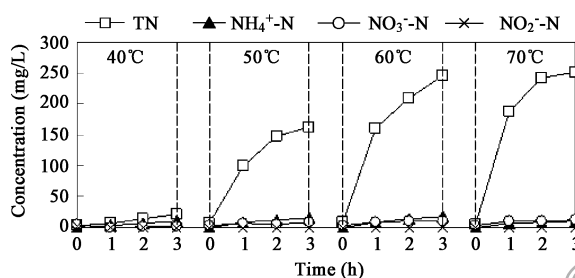


Fig. 3 Nitrogen release during the thermal treatment process.

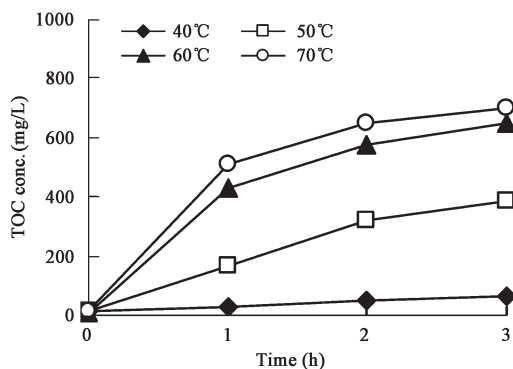


Fig. 4 TOC release during the thermal treatment process.

iso-butyric, valeric, and *iso*-valeric acid. Different from the releasing patterns of phosphorus, nitrogen, and TOC, VFAs release did not coincide with the change of temperature. Only at 50°C, considerable VFA release was observed as shown in Fig.5a. Acetic, butyric, and propionic acid were the most abundant components in turn and their releasing profiles exhibited good linear relationships with time ($R^2 = 0.9977$, 0.9624 , and 0.8908 respectively). But at 40°C, no VFAs were released in 3 h. At 60 and 70°C, only a small amount of VFAs (less than 8 mg/L in total) was detected, and nearly all of it was acetic acid (data

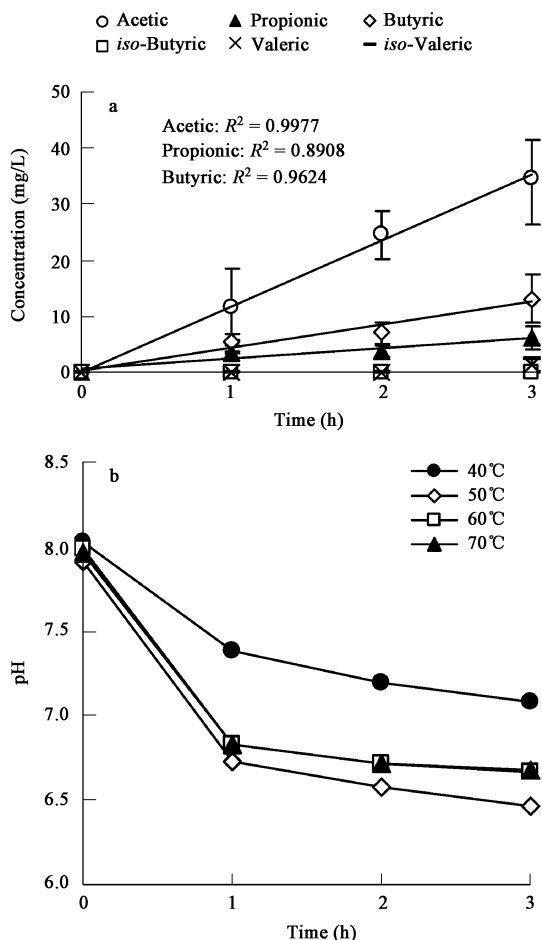


Fig. 5 VFA release during the thermal treatment process at 50°C (a) and pH change during thermal treatment process from 40 to 70°C (b).

not shown). The reason for this unexpected phenomenon is not clear yet, but the record of pH in thermal treatment processes from 40 to 70°C shown in Fig.5b demonstrated a similar trend, which shows that pH decreased most rapidly at 50°C.

There is evidence that some organic substances can inhibit the phosphate precipitation process. Then there comes an interesting question of, which one will be the more decisive inhibitor, TOC or VFAs? If it is TOC, then lower temperature is preferable. If it is VFAs, then the temperature of 50°C, in particular, must be avoided. Although citrate has proved to have a bigger influence than acetate on precipitation of calcium phosphate (van der Houwen *et al.*, 2001, 2003), the answer to this question still remains unclear because the composition of VFAs and TOC are both complicated and related knowledge is lacking.

2.4 Metal cations release

Metal cations including Mg^{2+} , K^+ , Ca^{2+} , Na^+ , Fe^{3+} , Mn^{2+} , Cu^{2+} , and Zn^{2+} were investigated in this work. Among them, Mg^{2+} , K^+ , and Ca^{2+} were generally considered as playing important roles in the EBPR process, in that, besides phosphorus, they were the most frequently detected components of polyphosphate granules (Schönborn *et al.*, 2001). The releasing profiles of Mg^{2+} , K^+ , and Ca^{2+} in these experiments are given in Fig.6a, where the concentrations of Mg^{2+} and K^+ increased with time and temperature, but Ca^{2+} decreased.

The decrease of Ca^{2+} might reflect that the spontaneous precipitation process happened during thermal treatment.

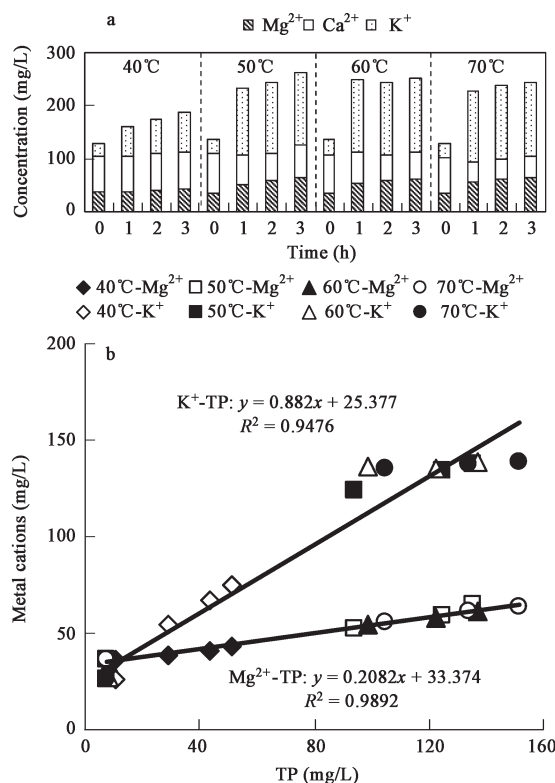


Fig. 6 Metal cations release (a) and linear relationships between Mg^{2+} or K^+ release and TP release (b) during the thermal treatment process.

This could probably explain why less *ortho*-P was detected at higher temperature as mentioned in Section 2.1, because Ca^{2+} also decreased obviously as the temperature increased. Ca^{2+} and *ortho*-P could form the precipitation product as calcium phosphate, which had a lower solubility product constant than magnesium phosphate did.

As shown in Fig.6b, the release of Mg^{2+} and K^+ agreed well with TP release, and it seemed that the parameter of temperature in the experimental range had very little impact on the linear relationships, especially for Mg^{2+} . As the temperature rose, the concentrations of both $\text{Mg}^{2+}/\text{K}^+$ and TP released increased, but the correlated relationships between them remained comparatively steady. This phenomenon might suggest the specific composition of the polyphosphate in the tested sludge.

The precipitation of struvite and calcium phosphate needed the participation of Mg^{2+} and Ca^{2+} , respectively. But their high concentrations in the supernatant, before the recovery step, might result in unwanted precipitation as discussed earlier, which would consume the phosphate released. Additionally, Mg^{2+} would interfere with the precipitation of calcium phosphate and Ca^{2+} would influence the precipitation of struvite. Therefore, in general, it is safer to choose a lower temperature to avoid excessive release of such metal cations in the thermal sludge treatment.

As for other metal cations investigated, it was found that the concentration of Na^+ kept relatively constant during heating, but Fe^{3+} , Mn^{2+} , Cu^{2+} , and Zn^{2+} could also be released at very small rates (data not shown). For safety, the investigation of the content of heavy metals in the supernatant during heating and in the final recovered products is of great importance. But in these experiments the sludge is from a bench-scale reactor treating synthetic wastewater containing few heavy metals, hence, further work using sludge from full-scale WWTPs is needed for this reason.

2.5 Sludge reduction

Reduction of MLSS and MLVSS were observed during the thermal treatment process as illustrated in Fig.7. But at 40°C, the reduction rate was very slow. When temperature reached 50°C, a clear reduction was experienced, as the MLSS reduction ratio rose rapidly, and more sludge would be reduced at higher temperature. This result agreed with the releasing profiles of phosphorus, nitrogen, TOC, and some metal cations. And such results could prove that the mechanism of sludge disintegration was responsible for the substantial release of various substances during thermal treatment.

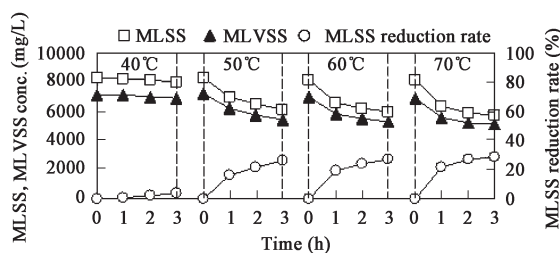


Fig. 7 Sludge reduction during the thermal treatment process.

3 Conclusions

The main conclusions obtained in this article are as follows:

During thermal treatment of excess sludge, not only phosphorus, but also nitrogen compounds, organics, and some metal cations like Mg^{2+} and K^+ could be released in abundance. And in the experimental temperature range of 40–70°C, more TP, TN, and TOC would be released from sludge at higher temperature.

The maximum *ortho*-P release of about 90 mg/L (95% of TP) was observed at 50°C in 1 h. And except for VFAs, comparatively few TN, TOC, and metal cations were released at the same time. Such results might favor the further process of phosphorus recovery. VFAs were only considerably released at 50°C. Acetic, butyric, and propionic acid were the most abundant components in turn and their releasing profiles exhibited good linear relationships with time ($R^2 = 0.9977, 0.9624, \text{ and } 0.8908$, respectively).

As for metal cations, the concentrations of Mg^{2+} and K^+ increased with time and temperature during thermal treatment, but Ca^{2+} decreased. The release of Mg^{2+} and K^+ agreed well with TP release ($R^2 = 0.9892 \text{ and } 0.9476$, respectively). The temperature in the experimental range had very little impact on the linear relationships, especially for Mg^{2+} .

MLSS was found to be an important factor for thermal treatment of excess sludge. By increasing the MLSS from 4000 to 8000 mg/L, the released *ortho*-P and TP at 50°C increased more than one fold. And the phenomenon of sludge reduction showed that the mechanism of sludge disintegration was responsible for the substantial release of various substances during thermal treatment.

References

- Alvarez R, Evans L A, Milham P J *et al.*, 2004. Effects of humic material on the precipitation of calcium phosphate[J]. *Geoderma*, 118: 245–260.
- Bouropoulos N C, Koutsoukos P G, 2000. Spontaneous precipitation of struvite from aqueous solutions[J]. *J Cryst Growth*, 213: 381–388.
- Bowes M J, Hilton J, Irons G P *et al.*, 2005. The relative contribution of sewage and diffuse phosphorus sources in the River Avon catchment, southern England: implications for nutrient management[J]. *Sci Total Environ*, 344: 67–81.
- CEEP, 2000. Phosphate precipitation from waste waters—recent scientific and technical developments[J]. *Scope Newsletter*, 41: 8–24.
- EPA of China, 2002. The methods for the monitoring and analysis of water and wastewater[M]. 4th ed. Beijing: Environment Science Press of China.
- Fuhs G W, Chen M, 1975. Microbiological basis of phosphate removal in the activated sludge process for the treatment of wastewater[J]. *Microb Ecol*, 2: 119–138.
- Karl D M, 2000. Phosphorus, the staff of life[J]. *Nature*, 406: 31–33.
- Kuroda A, Takiguchi N, Gotanda T *et al.*, 2002. A simple method to release polyphosphate from activated sludge for

- phosphorus reuse and recycling[J]. *Biotechnol Bioeng*, 78: 333–338.
- Le-Corre K S, Valsami-Jones E, Hobbs P *et al.*, 2005. Impact of calcium on struvite crystal size, shape and purity[J]. *J Cryst Growth*, 283: 514–522.
- Pan S H, Lo K V, Liao P H *et al.*, 2006. Microwave pretreatment for enhancement of phosphorus release from dairy manure[J]. *J Environ Sci Heal B*, 41: 451–458.
- Pretty J N, Mason C F, Nedwell D B *et al.*, 2003. Environmental costs of freshwater eutrophication in England and Wales[J]. *Environ Sci Technol*, 37: 201–208.
- Rosmaninho R, Melo L F, 2006. The effect of citrate on calcium phosphate deposition from simulated milk ultrafiltrate (SMUF) solution[J]. *J Food Eng*, 73: 379–387.
- Saktaywin W, Tsuno H, Nagare H *et al.*, 2005a. Advanced sewage treatment process with excess sludge reduction and phosphorus recovery[J]. *Water Res*, 39: 902–910.
- Saktaywin W, Tsuno H, Nagare H *et al.*, 2005b. Operation of a new sewage treatment process with technologies of excess sludge reduction and phosphorus recovery[C]. The 9th–10th joint seminar of JSPS-MOE core university program on urban environment, Kunming, P. R. China. 157–168.
- Schönborn C, Bauer H D, Röske I, 2001. Stability of enhanced biological phosphorus removal and composition of polyphosphate granules[J]. *Water Res*, 35: 3190–3196.
- Song Y, Hahn H H, Hoffmann E, 2002. Effects of solution conditions on the precipitation of phosphate for recovery a thermodynamic evaluation[J]. *Chemosphere*, 48: 1029–1034.
- Steen I, 1998. Phosphorus availability in the 21st century: management of a non-renewable resource[J]. *Phosphorus and Potassium*, 217: 25–31.
- Stratful I, Scrimshaw M D, Lester J N, 2001. Conditions influencing the precipitation of magnesium ammonium phosphate[J]. *Water Res*, 35: 4191–4199.
- Suzuki Y, Kondo T, Nakagawa K *et al.*, 2006. Evaluation of sludge reduction and phosphorus recovery efficiencies in a new advanced wastewater treatment system using denitrifying polyphosphate accumulating organisms[J]. *Water Sci Technol*, 53: 107–113.
- Tagiguchi N, Kuroda A, Kato J *et al.*, 2003. Pilot plant tests on the novel process for phosphorus recovery from municipal wastewater[J]. *J Chem Eng Jpn*, 36: 1143–1146.
- Tagiguchi N, Kishino M, Kuroda A *et al.*, 2004. A laboratory-scale test of anaerobic digestion and methane production after phosphorus recovery from waste activated sludge[J]. *J Biosci Bioeng*, 97: 365–368.
- van der Houwen J A M, Vaisami J E, 2001. The application of calcium phosphate precipitation chemistry to phosphorus recovery: the influence of organic ligands[J]. *Environ Technol*, 22: 1325–1335.
- van der Houwen J A M, Cressey G, Cressey B A *et al.*, 2003. The effect of organic ligands on the crystallinity of calcium phosphate[J]. *J Cryst Growth*, 249: 572–583.
- Yi W, Lo K V, Mavinic D S *et al.*, 2005. The effects of magnesium and ammonium additions on phosphate recovery from greenhouse wastewater[J]. *J Environ Sci Heal B*, 40: 363–374.