Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.795725

52 (2014) 384–389
January

Taylor & Francis
Taylor & Francis Group

Phosphate removal through crystallization using hydrothermal modified steel slag-based material as seed crystal

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Received 25 February 2012; Accepted 6 March 2013

ABSTRACT

A novel steel slag-based material (SSM) was prepared, based on the powdered steel slag and modified by hydrothermal treatment to improve its activity for phosphate removal. The phosphate removal and recovery with the SSM and the modified steel slag-based material (MSSM) as seed crystal were evaluated, and the reuse performance of the MSSM was investigated. The results showed that the hydration activity of the MSSM could be improved by hydrothermal modification, which might be attributed to the releasing of OH^- and Ca^{2+} from MSSM after the hydrothermal treatment is in favor of the calcium phosphate crystallization. The MSSM as a seed crystal could be used repeatedly about 20 times in this experiment, and the residual phosphate concentrations were all below 0.5 mg/L with the initial concentration of 10 mg/L. The X-ray diffraction pattern of the reaction products revealed that the crystallinity of the products increased with increasing reaction time and the diffraction peaks well matched with that of hydroxyapatite (HAP). The scanning electron micrograph and energy dispersive X-ray spectroscopy analysis showed that the products existed in a globular form and had a Ca/P molar ratio of 1.66, close to the theoretical value (1.67) of HAP.

Keywords: Steel slag-based material (SSM); Hydrothermal modification; Phosphate removal and recovery; Seed crystal; Hydroxyapatite (HAP)

1. Introduction

As a limiting nutrient for alga growth, phosphorus is considered as a major cause for water eutrophication [1]. Therefore, phosphate removal from wastewater is an essential way to protect water from pollution. Moreover, phosphorus is also an important natural resource to modern agriculture and industry, which will run out in the coming 100 years [2], resulting in an urgent exploration for a new phosphorus source. Consequently, phosphorus recovery from wastewater by crystallization process has been widely investigated to realize the sustainable utilization of phosphorus resources recently [3–4].

The crystallization process is dependent on the supersaturation of the solution [5]. Seed-induced crystallization could happen at low supersaturation by addition of seed crystal, which lowers the interfacial energy and triggers the crystallization process [6]. In recent years, most studies focused on phosphorus recovery from highly concentrated phosphate wastewater, of which the crystallization could be obtained easier

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due to the highly supersaturation of the solution. However, investigations into the phosphorus recovery from low phosphate concentration wastewater are rarely reported in the literature. Theoretically, it is possible to recover phosphate from low phosphate concentration wastewater through the crystallization of calcium phosphate, because the solubility product of hydroxyapatite (HAP) is very low ($K_{sp} = 10^{-114}$) [7], which is suitable for crystallization with low supersaturation.

Several materials have been used as seed crystal for phosphate recovery, such as sand [8], mineral apatite [9], tobermorite [10], and converter steel slag [11]. It is well known that the physicochemical property of seed crystal is a crucial influence factor to induce crystallization. Therefore, it is very important to select an effective and economical seed material for the crystallization of calcium phosphate.

Recently, steel slag has attracted a great attention for the treatment of wastewater due to its favorable adsorption performance. The use of steel slag or modified steel slag with different methods in phosphate removal has been reported in several literatures [12–14]. However, most of these researches focused on the performance of phosphate adsorption by powdered steel slag, but ignored the phenomenon that a large amount of solid waste is produced in the adsorption process, which is not suitable for the engineering application. Therefore, it is necessary to develop a novel method to avoid the adverse effect in the application of steel slag.

Steel slag is an industrial waste derived from steelmaking process, which is a compound mixture of some main oxides such as CaO, Fe_2O_3, SiO_2, Al_2O_3, and MgO. Steel slag has the ability to release OH^- ions, porous structure, and large specific surface area [12], as well as the specified hydration activity, which could generate the high-alkalinity calcium silicate hydrates (C–S–H) [15], such as tobermorite and xonotlite [16,17]. These high-alkalinity calcium silicate hydrates (C–S–H) are in favor of calcium phosphate crystallization for phosphate removal and recovery.

In this paper, a steel slag-based material (SSM) was prepared, and modified by hydrothermal method to develop a suitable and effective seed crystal. The phosphate removal performance by crystallization with the hydrothermal modified steel slag-based material (MSSM) as a seed crystal was investigated. Finally, the surface structures of the SSM and MSSM and the physicochemical properties of the crystallization products were characterized by scanning electron microscopy (SEM), XRD, and energy dispersive X-ray spectroscopy (EDS), respectively, for the analysis of phosphate crystallization.

2. Experimental

2.1. Preparation of SSM

The steel slag used in this study was generated from the Jinan Iron and steel Co. Ltd., Jinan, China. The materials were first crushed to homogeneous size to satisfy the milling requirement, and then ground to powdered steel slag by a ball miller and sifted through a 200-mesh sieve. The SSM was obtained first by mixing the powdered steel slag with Portland cement in a volume ratio of 4:1, and then these mixtures were pelleted with water and cured in standard condition to achieve enough intensity [18]. The chemical composition of powdered steel slag and cement is given in Table 1.

The novel MSSM was procured from SSM through hydrothermal modification with 6 M NaOH solutions for 6 h. The proportion of liquid-to-solid was 1:1, and the temperature for hydrothermal treatment was 105℃. The treated products were washed with distilled water and dried at 80℃ for 12 h before experiments.

The phosphate stock solution containing 100-mg P/L was prepared by dissolving potassium dihydrogen orthophosphate (KH_2PO_4) in distilled water. All the desired experimental concentrations were prepared by diluting the phosphate stock solution with distilled water. The different pH of the experimental phosphate solutions were adjusted with 0.1 M HCl and 0.1 M NaOH.

2.2. Experimental methods

The phosphate removal performance of SSM and MSSM was studied using phosphate solution with a concentration of 10 mg/L. A defined volume of phosphate stock solution was diluted to 100-mL phosphate solutions with distilled water for different experiment concentrations. The pH of the solution was then adjusted to the desired value, and a defined amount

Table 1
Chemical composition of steel slag and cement

Chemical composition	Steel slag (SS)	Cement
Calcium (as CaO)	40.9	20.8
Silica (as SiO_2)	15.3	62.7
Alumina (as Al_2O_3)	3.6	6.6
Iron (as Fe_2O_3 and FeO)	30.1	
Magnesium (as MgO)	5.6	1.3
Phosphorus (as P_2O_5)	1.5	

of SSM was added. The mixtures were stirred at 120 rpm for a certain time and kept at a constant temperature (20℃). After the stirring process, the solution was filtered through 0.45-μm membrane filter, and then the phosphate concentrations and effluent pH were analyzed.

The sustaining phosphate removal ability of the MSSM was investigated by using 1 g MSSM as seed crystal in 100 mL phosphate solutions repeatedly, until the residual phosphate concentration in the solution was greater than 0.5 mg/L. The 100-mL phosphate solutions were prepared with initial phosphate concentration of 10 mg/L, solution pH of 8.50, and initial Ca/P of 2.0, and the reaction time was fixed at 2 h in every repetition. At the end of each reaction, the added MSSM in the reaction solution was removed by filtration initially, and then the residual phosphate and pH in the filtrate were analyzed. The filtrated MSSM was washed slightly for several times to wipe off the residual phosphate, and then reused sequentially in the next run.

2.3. Analytical methods

The solution pH was measured with a pH meter (Sartorius Co., PB-10, Germany). An UV spectrophotometer (752s, China) was used to analyze the phosphate concentration according to ammonium phosphomolybdate volumetric method [19]. The microstructures of SSM, MSSM, and the products generated from the phosphate removal were examined by SEM equipped with EDS (SEM–EDS, Hitachi Co., S-2500C, Japan) and the X-ray diffraction (XRD, BRUKER-AXS Co., D8 Advance, Germany).

3. Results and discussion

3.1. Characteristics of SSM and MSSM

The SSM prepared in this experiment has a bulk density of 1.0975 g/cm^3 with a grain size of 3–5 mm. The surface properties of SSM and MSSM were characterized with XRD. The XRD patterns are shown in Fig. 1.

Fig. 1 indicates that the main phases of SSM are dicalcium silicate (C_2S), tricalcium silicate (C_3S), and CaO–FeO–MgO solid solution (RO phase), of which C_2S and C_3S have potential hydration activity. After the hydrothermal treatment (the MSSM), the peaks of C_2S and C_3S turn weak, with the formation of calcium hydroxide ($Ca(OH)_2$) and amorphous calcium silicate hydrate gel (C–S–H) [20] which make the peaks to become wide and inconspicuous. It was reported that the C–S–H could stimulate the aggregation of calcium phosphate on its surface [21] and improve the phosphate removal. At the same time, the $Ca(OH)_2$ released from MSSM could supply the Ca^{2+} and OH^- for the formation of calcium phosphate [22]. Therefore, the hydrothermal treatment of SSM might be more effective for the crystallization of calcium phosphate when compared with MSSM, and this will be discussed in the following paragraphs.

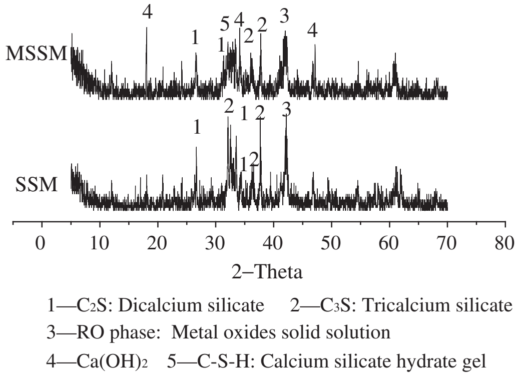

Fig. 1. X-ray diffraction diagram SSM and MSSM (SSM: steel slag-based material; MSSM: modified steel slag-based material).

3.2. Phosphate removal of SSM and MSSM

The phosphate removal capacity of SSM and MSSM as seed crystal in 1000 mL phosphate solutions was examined in this study. The solution supplied with an enough phosphate for removing, as well as a compared test without seed crystal was conducted synchronously. The dosage of SSM and MSSM was 1 g/L, the initial phosphate concentration was 10 mg/L, and the solution pH was adjusted to 6.80, which was approximate to that of domestic wastewater. The residual phosphate and effluent pH were analyzed at regular intervals. The results are shown in Fig. 2(a) and (b).

Fig. 2(a) shows that the residual phosphate concentration decreases with the increasing of reaction time. The residual phosphate concentration in the solution with the SSM as a seed crystal is lower than that of the compared test, but greater than that of solution with the MSSM as a seed crystal. This result indicates that the existence of seed crystal could promote the reaction rate of phosphate precipitation, and the crystal-inducing ability could be highly improved by the hydrothermal modification. The residual phosphate concentration tends to stabilise after 48 h. The effluent pH of different reaction times in Fig. 2(b) could explain this phenomenon. The effluent pH remaining stable in the solution without seed crystal was lower

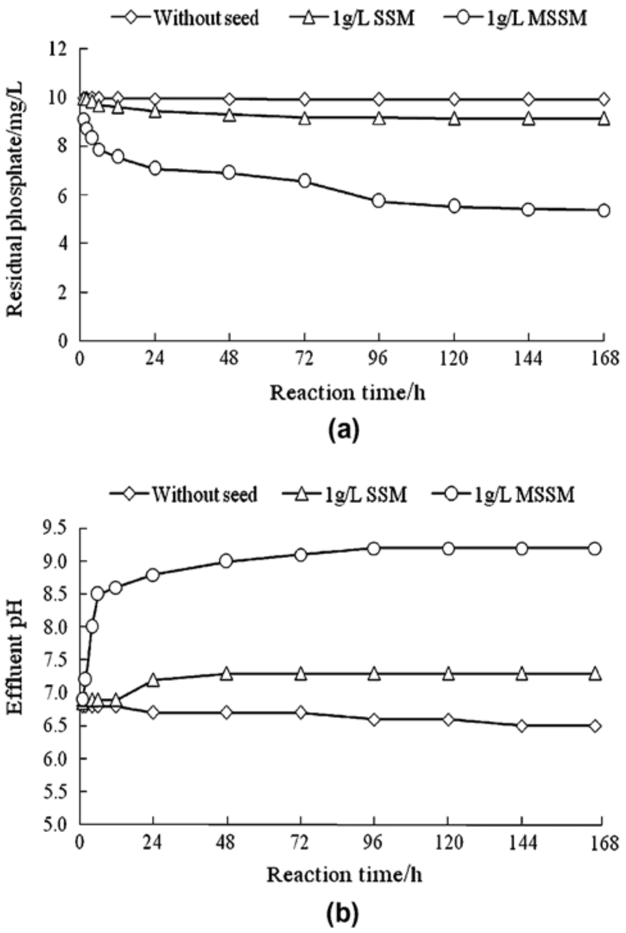

Fig. 2. Phosphate concentration (a) and pH value (b) in the reaction solution with or without seed crystal (Initial *P*: 10 mg/L, initial solution pH = 6.80).

than the solution with SSM and MSSM as seed crystal, which could not meet the requirement for crystallization. However, both SSM and MSSM can release OH^- ions and the solution pH will be increased, which could promote the phosphate crystallization. Moreover, the ability to release OH^- and Ca^{2+} ions of MSSM was significantly improved by hydrothermal treatment, resulting in a promising phosphate removal performance in the solution, with the MSSM as seed crystal. It was reported that the solution pH had a great influence on the specification of the participants and the base uptake in the crystallization reaction for phosphate recovery [6]. It is concluded that the phosphate removal rate is closely related to the solution pH.

Furthermore, it was also observed in the experiment that the amount of the reaction products increased with the increasing of reaction time. The appearance of the MSSM had good sphericity and uniform grain sizes distribution. In the course of the reaction, there were huge amounts of white precipitates generated on the surface of the MSSM and increased with the reaction time.

3.3. The sustaining phosphate removal by MSSM

The results of investigation of sustaining phosphate removal ability are shown in Fig. 3.

It can be observed in Fig. 3 that the MSSM cycling can be used about 20 times until the effluent phosphate concentration exceeds 0.5 mg/L, which meets the requirement of national criterion of wastewater discharge of China. It is also observed that the effluent pH is high at the initial phase, but appears to declin with the increase of reuse time. The residual phosphate concentration increases rapidly when the effluent pH is close to 8.0, indicating that the solution alkalinity does not meet the requirement of the calcium phosphate crystallization.

3.4. Characteristics of the crystallization products

As mentioned above, large amounts of precipitates generated in the aqueous solution, X-ray diffraction (XRD), and SEM and EDS (SEM–EDS) were used to analyze the characteristics of the precipitates. The results are shown in Figs. 4 and 5.

3.4.1. XRD analysis

Fig. 4 shows the XRD patterns of the reaction products produced at the reaction time of 2 h, 12 h, 24 h, and 48 h, respectively. It is considered that the characteristic diffraction peaks of pure HAP are $2\theta = 25.8^\circ$, 32.1°, and 49.6° [15]. It can be observed in Fig. 4 that the crystallinity of the products increases with the increasing of reaction time. At the initial phase, a number of crystal nucleuses generate in the

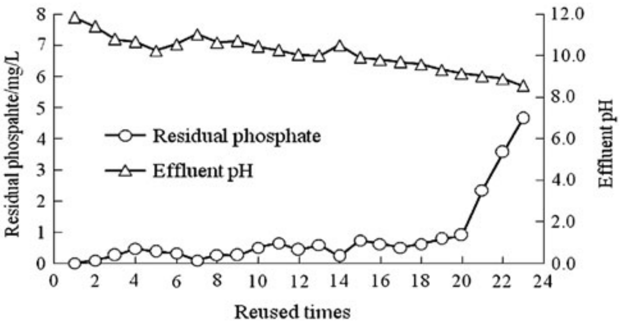

Fig. 3. Sustaining phosphate removal ability of the MSSM and variation of effluent pH (Initial *P*: 10 mg/L, initial solution pH = 8.50, initial Ca/p = 2.0).

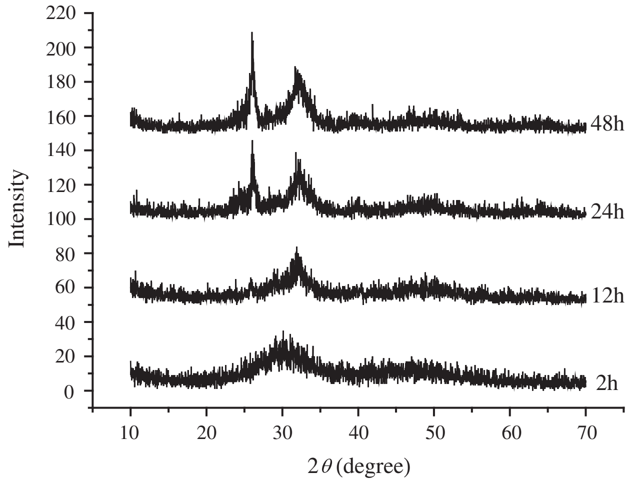

Fig. 4. XRD patterns of crystallization products at different reaction times with MSSM as seed crystal.

solution and form the precursor of HAP. Then, the growing up of nucleation and the transformation of other forms calcium phosphate enhance the diffraction peaks gradually. The diffraction peaks become remarkable when the reaction time is 48 h and match with the special diffraction peaks of pure HAP.

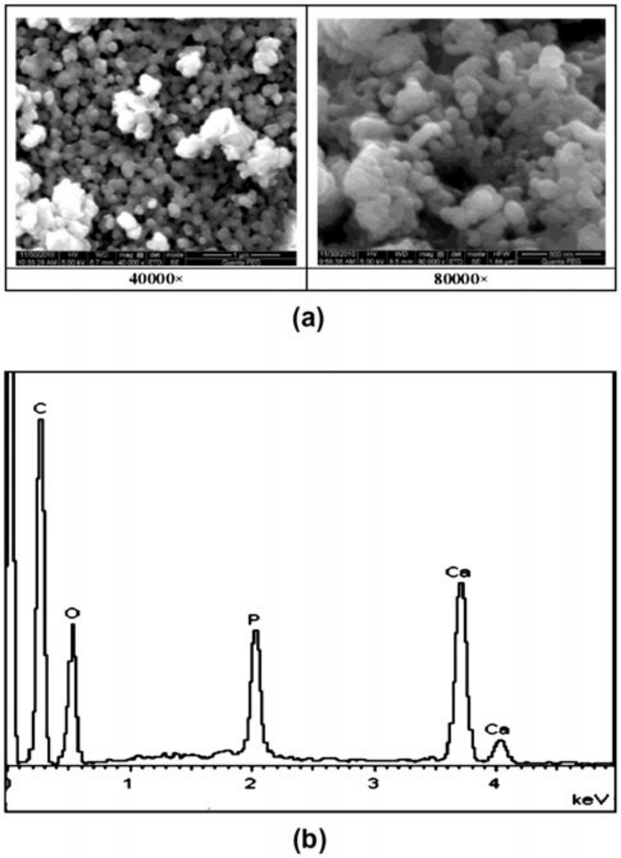

Fig. 5. SEM (a) and EDS analysis and (b) of crystallization products at 48 h with MSSM as seed.

Montastruc et al. [23] reported that the calcium phosphate crystallization was a quite complex subject involving various parameters. There are several different forms of crystallized calcium phosphate, such as DCPD($CaHPO_4{\cdot}2H_2O$), DCPA($CaHPO_4$), TCP($Ca_3(PO_4)_2$), ACP($Ca_3(PO_4)_2$), and HAP($Ca_{10}(PO_4)_6(OH)_2$). The result in Fig. 4 illustrates that the HAP does not form directly in the calcium phosphate crystallization, in which other forms of precursors should be formed first, and then transform into HAP at about 24 h.

3.4.2. SEM–EDS analysis

The reaction products obtained at 48 h were analyzed by SEM–EDS (Fig. 5). As shows in Fig. 5, the samples exist in a globular form with small particle size. In addition, the EDS spectrum reveals that the precipitates mainly consist of Ca and P, with a Ca/P molar ratio of 1.66, which is very close to the theoretical value of Ca/P (1.67) of HAP, indicating that the crystal is HAP.

4. Conclusions

The prepared SSM served as a seed crystal that could carry out a little higher phosphate removal rate than that of the compared test without seed addition. The hydration activity of the SSM can be improved as the $Ca(OH)_2$ and C–S–H gel formed by using hydrothermal modification, which are effective to promote the calcium phosphate crystallization. The MSSM, which can release more OH^- and Ca^{2+} after the hydrothermal modification, has an effective and sustaining phosphate removal ability, indicating that this novel material has the potential to be employed as an efficient seed crystal in the process of phosphate removal and recovery from wastewater. The XRD and SEM–EDS analysis reveals that the phosphate removed from the reaction solution with the MSSM as seed crystal mainly generates into the globular HAP with Ca/P molar ratio of 1.66, and crystallinity of the products increases with the increasing of reaction time.

Acknowledgments

This study was supported by National Natural Science Foundation of China (50978121,51278225), Natural Science Foundation of Shandong Province, China (ZR2011EEM018).

References

[1] J.B. Xiong, Z.L. He, Q. Mahmood, D. Liu, X.E. Yang, E. Islam, Phosphate removal from solution using steel slag through magnetic separation, J. Hazard. Mater. 152 (2008) 211–215.

[2] N.C. Woods, S.M. Sock, G.T. Daigger, Phosphorus recovery technology modeling and feasibility evaluation for municipal wastewater treatment plants, Environ. Technol. 20 (1999) 663–679.

[3] L.E. Bashan, Y. Bashan, Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003), Water Res. 38 (2004) 4222–4246.

[4] H. Jang, S.H. Kang, Phosphorus removal using cow bone in hydroxyapatite crystallization, Water Res. 36 (2002) 1324–1330.

[5] Y.H. Song, P.G. Weidler, U. Berg, R. Nüesch, D. Donnert, Calcite-seeded crystallization of calcium phosphate for phosphorus recovery, Chemosphere 63 (2006) 236–243.

[6] Y.H. Song, H.H. Hahn, E. Hoffmann, Effects of solution conditions on the precipitation of phosphate for recovery. A thermodynamic evaluation, Chemosphere 48 (2002) 1029–1034.

[7] V.A. Jones, Calcium phosphate precipitation, in: Conference of Second International Conference on the Recovery of Phosphorus from Sewage and Animal Wastes, Noordwijkerhout, the Netherlands, March 12–13, (2001) 8–15.

[8] M.M. Seckler, O.S. Bruinsma, G. Van Rosmalen, Phosphate removal in a fluidized bed-I. Identification of physical processes, Water Res. 30 (1996) 1585–1588.

[9] N. Bellier, F. Chazarenc, Y. Comeau, Phosphorus removal from wastewater by mineral apatite, Water Res. 40 (2006) 2965–2971.

[10] K. Moriyama, T. Kojima, Y. Minawa, S. Matsumoto, K. Nakamachi, Development of artificial seed crystal for crystallization of calcium phosphate, Environ. Technol. 22 (2001) 1245–1252.

[11] E.H. Kim, S.B. Yim, H.C. Jung, E.J. Lee, Hydroxyapatite crystallization from a highly concentrated phosphate solution using powdereded converter slag as a seed material, J. Hazard. Mater. 136b (2006) 690–697.

[12] B. Kostura, H. Kulveitová, J. Leško, Blast furnace slags as sorbents of phosphate from water solutions, Water Res. 39 (2005) 1795–1802.

[13] Y.J. Xue, H.B. Hou, S.J. Zhu, Characteristics and mechanisms of phosphate adsorption onto basic oxygen furnace slag, J. Hazard. Mater. 162 (2009) 973–980.

[14] G.Z. Gong, S.F. Ye, Y.J. Tian, Q. Wang, J.D. Ni, Y.F. Chen, Preparation of a new sorbent with hydrated lime and blast furnace slag for phosphorus removal from aqueous solution, J. Hazard. Mater. 166 (2009) 714–719.

[15] P.E. Tsakiridis, G.D. Papadimitriou, S.T. Tsivilis, C. Koroneos, Utilization of steel slag for Portland cement clinker production, J. Hazard. Mater. 152 (2008) 805–811.

[16] U. Berg, D. Donnert, P.G. Weidler, E. Kaschka, G. Knoll, R. Nüesch, Phosphorus removal and recovery from wastewater by tobermorite-seeded crystallization of calcium phosphate, Water Sci. Technol. 53 (2006) 131–138.

[17] X.C. Chen, H.N. Kong, D.Y. Wu, X.Z. Wu, Y.Y. Lin, Phosphate removal and recovery through crystallization of hydroxyaptite using xonotlite as seed crystal, J. Environ. Sci. 21 (2009) 575–580.

[18] J.Y. Sun, Study of effects of ground steel slag on mechanical performance and soundness of concrete, Coal Ash China 5 (2003) 7–9.

[19] K. Moriyama, T. Kojima, K. Koga, S. Takino, Y. Minawa, Crystallization process using calcium silicate hydrate for phosphorus removal, Environ. Eng. Res. 40 (2003) 389–394.

[20] K. Moriyama, Crystallization process using calcium silicate as seed crystal material, Environ. Cons. Eng. 27 (1998) 412–417.

[21] C.S. Liu, Y. Huang, W. Shen, J.H. Cui, Kinetics of hydroxyapatite precipitation at pH 10 to 11, Biomaterials 22 (2001) 301–306.

[22] L. Montastruc, C. Azzaro, B. Biscans, B. CabaSSMud, A thermochemical approach for calcium phosphate precipitation modeling in a pellet reactor, Chem. Eng. J. 194 (2003) 41–50.