

Article

The Alkaline Fusion-Hydrothermal Synthesis of Hydroxyapatite-Zeolite (HAP-ZE) from Blast Furnace Slag (BFS): Effects of Reaction Temperature

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Abstract: This study was performed to investigate the effects of reaction temperature on the alkaline fusion-hydrothermal preparation of hydroxyapatite-zeolite (HAP-ZE) using blast furnace slag (BFS) as raw material. Firstly, HAP-ZE samples were obtained under various reaction temperatures; then the analysis was carried out utilizing XRD, FT-IR, BET/BJH, XRF, FE-SEM and EDX. The results reflect that the optimum reaction temperature for preparing HAP-ZE from blast furnace slag (BFS) using alkaline fusion-hydrothermal treatment is around 100 °C. The HAP-ZE synthesized at 100 °C had the largest specific surface area (SSA) value. Under 100 °C aging, the main phases in HAP-ZE were zeolite and HAP with the average SSA is 44.22 m²·g^{−1}. Molar ratio of Ca/P, Si/Al and Na/Al is 1.61, 1.31, 1.75, respectively. Additionally, HAP-ZE crystals with a diameter of about 500 nm form an open frame structure with coral surface morphology could be clearly observed at 100 °C. The observed surface morphology feature agrees well with that for HAP-ZE previously reported, again elucidating the successful formation of HAP-ZE.

Keywords: blast furnace slag; alkaline fusion-hydrothermal; hydroxyapatite; zeolite; reaction temperature



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1. Introduction

According to the data of the National Bureau of Statistics, in 2020, the cumulative output of crude steel in China reached 105.2999 million tons, with a cumulative growth of 5.2%. Blast furnace slag (BFS) is an industrial by-product of iron and steel manufacturing industry. It is estimated that 290 kg blast furnace slag will be produced per ton of pig iron [1,2]. In China, a large number of BFS are usually landfilled due to the only about 80% resource recycling efficiency of BFS [3], which has aroused great attention about groundwater pollution by contaminants and particles. Therefore, we urgently stand in need of a new way to convert blast furnace gas into higher-value specialty materials in line with resource recycling and environmental protection.

Due to the chemical make-up of BFS, BFS is extensively used in civil engineering and in the environmental field [4–9]. Considering the increasingly stringent environmental legislations and potential environmental impacts, it is absolutely necessary to strive to convert BFS into valuable products. In addition, the preparation of other materials by taking BFS as ingredients is not only conducive to the consumption of blast furnace slag inventory, but also conducive to reducing production costs.

Recently, research on the preparation of zeolite using solid wastes and minerals rich in silicon and aluminum, including ash (fly ash, putty and shell ash) [10–14], clay and slag [15–18] and natural zeolite rock [19,20] has been widely carried out. However, the

high content of calcium has the tendency to react with silicate to form calcium silicate while inhibiting the formation of zeolite crystals. Therefore, it is not suitable to prepare zeolite directly from BFS [21,22]. As described above, in order to obtain zeolite without special pretreatment or synthesis method, a novel method for preparing hydroxyapatite-zeolite (HAP-ZE) composites from BFS is put forward according to the chemical properties of calcium in BFS. Due to the adsorption and catalysis features of hydroxyapatite and zeolites, our research group successfully prepared HAP-ZE using BFS as raw material via alkaline fusion-hydrothermal method. In our previous studies, we have systematically studied the effect of aging time and Ca/P ratio in the reaction system on product structure and characteristics [23]. Nevertheless, further work is needed in order to elucidate all factors controlling HAP-ZE composite material crystalline phases and formation. Moreover, we know that reaction temperature has remarkable impact on resulting crystalline phases as well as total crystallinity. For those reasons, study on the influences of the reaction temperature on the preparation of HAP-ZE is of practical significance. Hence, the goal of the present study is to gain more knowledge on the formation of HAP-ZE crystals under various reaction temperature during hydrothermal treatment and thus to reach a fine control of HAP-ZE crystals' crystallinity, content, microstructural characteristics and morphology. To characterize the synthesized HAP-ZE, the samples were obtained under various reaction temperatures and XRD, SEM, EDX, XRF, FT-IR spectroscopy and BET/BJH method were applied for analysis of these samples.

2. Materials and Methods

2.1. Materials

Table 1 displays XRF analysis results of the BFS employed in this research. The main components in the slag were CaO, Al₂O₃ and SiO₂. Moreover, those components are very suitable for hydroxyapatite and zeolites' synthesis. Other chemical reagents are purchased from Sinopharm Chemical Reagent Co., Ltd.

Table 1. Chemical components of blast furnace slag (BFS).

Component	wt.% ^a
CaO	47.08
SiO ₂	29.13
Al ₂ O ₃	20.59
MgO	1.11
Fe ₂ O ₃	1.58
Na ₂ O	0.27
Total	99.76 ^b

^a Determined by XRF analysis. ^b Sulfur oxides may exist in remaining components.

2.2. Synthesis of HAP-ZE

The BFS was first pulverized by a ball crusher at 650 rpm for 30 min and classified by screening a 100-mesh sieve to achieve higher dissolution performance. The alkaline fusion-hydrothermal synthesis was used for HAP-ZE preparation in this paper. Usually HAP-ZE preparation was carried out as follows: first, a mass ratio of sieved BFS to NaOH was blended at 1:1.3 (wt.%/wt.%) to certify a homogeneous mixture. Then the mixture was placed and roasted in a ceramic crucible in muffle furnace at 600 °C for 90 min. After that, the obtained roasted sample was cooled and crushed. Secondly, 5.0 g fusion products was added and dissolved in 30 mL 2.0 mol/L NaH₂PO₄ (aq) until homogenized. After homogenization, the addition of 50 mL 3.0 mol/L NaOH (aq) into the suspension was carried out dropwise. Afterwards, the obtained slurry was vigorously stirred at 100 °C for 1.0 h, then acquired through hydrothermal synthesis aging at the same temperature for 6.0 h until crystallization without agitation in the hydrodynamic reactor (storage volume 250 mL), internally coated with polytetrafluoroethylene (TEFLON). Finally, the obtained

solid product, namely HAP-ZE was taken out and gathered by filtration, washed with deionized water, and then stoving at 80 °C.

For further analysis, the impact of reaction temperature on HAP-ZE synthesis, multiple HAP-ZE samples were prepared under various reaction temperature (80 °C, 90 °C, 100 °C and 120 °C). The other process parameters during preparation of HAP-ZE were fixed as mentioned above.

2.3. Characterization

D8 Discover X-ray diffractometer (Bruker, Berlin, Germany), XRF spectroscopy (Axios, PANalytical, Eindhoven, Holland) and SU 8220 FE-SEM (Hitachi, Tokyo, Japan) were respectively used for crystalline phase, chemical analysis and micromorphology testing. ASAP2020 (Micromeritics, Norcross, GA, USA) and Nicolet 6700 (Thermo Fisher Scientific, Waltham, MA, USA) were used to get specific surface area (SSA) and FT-IR spectra, respectively. Moreover, CEC (cation exchange capacity) and PIC (phosphate immobilization capacity) value were determined via the study of Zhang et al. [24] and Wu et al. [25].

3. Results and Discussion

3.1. Crystalline Characteristics

The XRD patterns of raw BFS and HAP-ZE samples obtained at various reaction temperatures are displayed in Figure 1. The XRD pattern of the raw BFS demonstrated that the BFS is mainly composed of the crystalline of SiO_2 and Al_2O_3 (see Figure 1(a)). As Figure 1 presents, XRD profiles of the obtained HAP-ZE at different reaction temperatures from 80 °C to 120 °C display multiple diffraction peaks, and those are significantly different to the diffraction peaks list in the raw BFS. From Figure 1(b), the XRD patterns for 80 °C of reaction temperature revealed some diffraction peaks, which belong to HAP, sodalite type zeolite and aluminum oxide. Yet, the aluminum oxide existed, which means that the reaction process of zeolite formation was not complete. Comparing with HAP-ZE synthesized at 90 °C (see Figure 1(c)), the aluminum oxide phase disappeared, showing better developed crystals in HAP-ZE under higher reaction temperature. Meanwhile, as reaction temperature increased to 100 °C, except for the further increase of XRD intensity, the main phase has no obvious change (see Figure 1(d)). However, a further increase in the reaction temperature to 120 °C did not have a significant effect on the phase formation and phase intensity (see Figure 1(e)). That is to say, under 100 °C aging, both HAP and zeolites reached the maximum XRD intensity, indicating that 100 °C was sufficient to fully develop HAP-ZE samples.

Meanwhile, Table 2 illustrates the crystallinity, phase contents and indicator parameters of HAP-ZE obtained at various reaction temperatures. Additionally, the phase contents were determined by the Rietveld refinement using Jade 9.0. The Rietveld refinement generally includes the following steps: add phase data to refinement, global parameters for refinement, phase parameters for refinement, global refinement controls, phase refinement controls and refinement displays and results. Table 2 shows that the crystallinity of HAP-ZE tended to improve along with the enhancement of reaction temperature. It was observed that the crystallinity of HAP-ZE obtained at 80 °C was only 48.12%, and the crystallinity of HAP-ZE obtained a 1.49-fold increase when the reaction temperature increased to 100 °C, compared to that of HAP-ZE obtained at 80 °C. Moreover, with a further increase in the reaction temperature to 120 °C, the crystallinity of obtained HAP-ZE also displayed a slight increase and reached to 75.82%. The change trend of crystallinity with temperature can be attributed to the improvement of reactivity caused by higher reaction temperature. On the other hand, compared to the zeolite content in HAP-ZE, HAP content always increases with the increase of temperature. However, with the increase of reaction temperature, the zeolite content in HAP-ZE first increases and then decreases. This phenomenon can be attributed to the competitive growth between zeolite and HAP. According to our previous research, although the nucleation of HAP and zeolite occurs simultaneously, the formation of HAP crystal is dominant. This can be due to the fact that

HAP can be generated under lower activation energy and the nucleation of zeolite can be restrained by high Ca content in the reaction system [7,26]. From Table 2, the reaction temperature has a significant effect on the CEC and PIC value of HAP-ZE. The change trend on CEC and PIC value is the same as that of the zeolite and HAP content with the increase of reaction temperature. This phenomenon should be attributed to the fact that the CEC and PIC value extremely depends on the zeolite and HAP content in the HAP-ZE. In terms of CEC value, the CEC value of HAP-ZE increases rapidly in the temperature range of 80~100 °C and then decreases. The increase of CEC along with reaction temperature (80~100 °C) is clearly due to the enhancement of zeolite formation (see Table 2). Moreover, the drop of CEC value at 120 °C was mainly attributed to the unfavorable formation of zeolite at high temperature caused by the restraint of Ca ions in the reaction system. On the other hand, it also can be seen from Table 2 that the PIC value increased continuously with the increase of reaction temperature. The reason can be attributed to the fact that PIC value was very dependent on the content of calcium and iron in the HAP-ZE, and the total consumption of calcium and iron for synthesized HAP-ZE was more under higher reaction temperature [27,28]. Given above, the lower CEC and PIC value of HAP-ZE is possibly due to the discrepancy in most favorable crystallization temperature and phase composition in HAP-ZE.

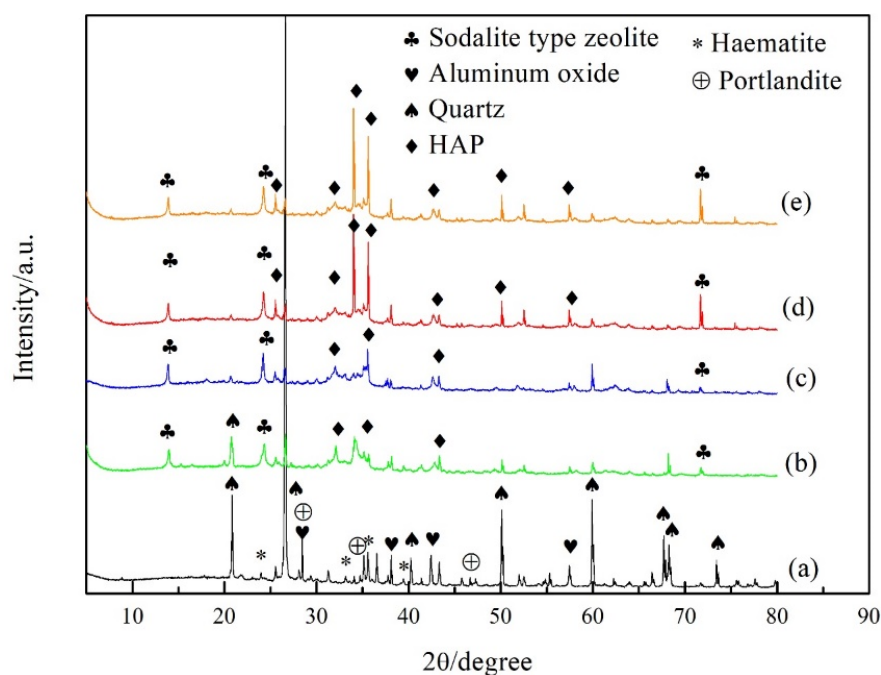


Figure 1. XRD patterns of (a) BFS; the HAP-ZE samples obtained at reaction temperature of (b) 80 °C; (c) 90 °C; (d) 100 °C and (e) 120 °C.

Table 2. The crystallinity, phase contents and indicator parameters of HAP-ZE synthesized at the various reaction temperatures.

Reaction Temperature/°C	Crystallinity ^a (%)	Zeolite Content ^b /wt. %	HAP Content ^c /wt. %	CEC / (meq/g)	PIC / (mg/g)
80	48.12	56.36	41.21	2.56	8.89
90	56.61	60.13	39.87	3.66	11.12
100	71.78	69.24	30.76	4.26	15.12
120	75.82	62.07	37.93	3.35	15.68

^a Crystallinity of HAP-ZE. ^b Determined by the Rietveld refinement using Jade 9.0. ^c Determined by the Rietveld refinement using Jade 9.0.

3.2. Chemical Analysis

Table 3 presents alteration of chemical components and Ca/P, Si/Al and Na/Al molar ratio with reaction temperature. As shown in Table 3, a small amount of impurity metals was commonly measured in the HAP-ZE product, such as Mg and Fe. However, no Fe and Mg compounds were detected in the XRD patterns (see Figure 1); hypothetically, those impurity metals' ions are distributed evenly into the structure of HAP-ZE by replacement of Ca^{2+} and Na^+ sites in HAP and zeolite, respectively [29–31]. The Ca/P ratios were measured to be 1.85, 1.79, 1.61 and 1.72 at reaction temperature of 80 °C, 90 °C, 100 °C and 120 °C, respectively. The Ca/P ratios of HAP-ZE samples generally indicate that higher temperature is favorable for phosphorus to incorporate into HAP-ZE in the reaction system. The Ca/P molar ratio approached a value near 1.67 (stoichiometric composition of pure HAP) under the reaction temperature of 100 °C. However, at 120 °C, Ca/P ratios was 1.72, indicating that more Ca ions or Fe and Mg ions are involved in the synthesis of HAP than those of lower reaction temperature. Meanwhile, by comparing the Na_2O content in raw BFS, the Na_2O content in the obtained HAP-ZE tended to be increased significantly. Moreover, the remarkable changes in Na_2O content were also an evidence of successful conversion of zeolite material [31]. Moreover, the Na_2O content in the obtained HAP-ZE increased as the reaction temperature increased from 80 °C to 100 °C. However, a further increase in the reaction temperature did not promote the increase of Na_2O content. This phenomenon can be attributed to the fact that at higher temperature, such as 120 °C, more calcium ions are dissolved in the reaction system, which can hinder the formation of zeolite [7,26]. Moreover, the change trend on Na_2O content in HAP-ZE was consistent with the variation trend of zeolite content listed in Table 2. Additionally, Si/Al and Na/Al molar ratio both decrease with the increase of reaction temperature. That is to say, after nucleation of zeolite, consumption of Al was much faster than that of Si in the solution [32,33]. It is commonly known that Al ions was the governing species in zeolite synthesis; during zeolite synthesis process, nearly all Al was consumed. Meanwhile, Si/Al molar ratio asymptotically approached 1.30 with the increase in reaction temperature. Yet, as the reaction temperature increased from 80 °C to 120 °C, the Na/Al molar ratio fell from 1.91 to 1.45. The comparison on the change trend of Si/Al and Na/Al molar ratio shows that part of silicon compounds can be embedded in the structure of HAP at higher temperature.

Table 3. Change of chemical components and molar ratio of Ca/P, Si/Al and Na/Al as a function of reaction temperature.

Reaction Temperature /°C	Chemical Component/wt.%							Molar Ratio		
	CaO	SiO ₂	P ₂ O ₅	Al ₂ O ₃	Na ₂ O	Fe ₂ O ₃	MgO	Ca/P	Si/Al	Na/Al
80	12.26	22.02	8.41	12.40	14.39	0.89	1.32	1.85	1.51	1.91
90	11.12	23.89	7.86	14.01	16.13	1.12	0.89	1.79	1.45	1.89
100	9.55	25.15	7.52	16.33	17.32	1.16	1.05	1.61	1.31	1.75
120	10.65	26.64	7.86	17.35	15.32	1.06	1.02	1.72	1.30	1.45

3.3. FT-IR Analysis

Figure 2 illustrates FT-IR spectroscopy of the HAP-ZE synthesized at different reaction temperatures which intends to study the details of HAP and zeolite crystallization development. Clear absorption peaks can be observed at 1030, 958, 839 and 558 cm^{-1} in the spectra of the synthesized specimens, those are normally due to the vibration of the PO_4^{3-} groups [1,34]. Due to SiO_4^{4-} and PO_4^{3-} tetrahedral units sharing great resemblance, zeolite and HAP share plenty of similar vibration modes, such as 424 cm^{-1} (Si-O-Si stretch/P-O bending) and 1030 cm^{-1} (Si-OH deformation vibration/vibration mode of PO_4^{3-} group) [1,34]. The peaks at 1440 cm^{-1} are owing to the CO_3^{2-} exchanging the PO_4^{3-} in the HAP. The peaks of the CO_3^{2-} are a common product in every HAP obtained in the air [35]. The bands at 839 and 558 cm^{-1} are distinctly indicative of hydroxyapatite, which can serve as a solid proof for hydroxyapatite formation [1]. Meanwhile, the peak at 558 cm^{-1} was also attributed to the double ring that is a characteristic peak for

zeolite [26,36]. Moreover, the peak at 504 cm^{-1} and 709 cm^{-1} were due to the internal linkage vibrations and asymmetric stretching of the TO_4 tetrahedra in zeolite, respectively. Therefore, the FT-IR analysis again clarified the fact that the zeolite crystal was successfully prepared in HAP-ZE materials. In addition, the bands at 3291 cm^{-1} (stretching mode) and 1640 cm^{-1} (bending mode) are due to the existence of water molecules in HAP-ZE structure [37].

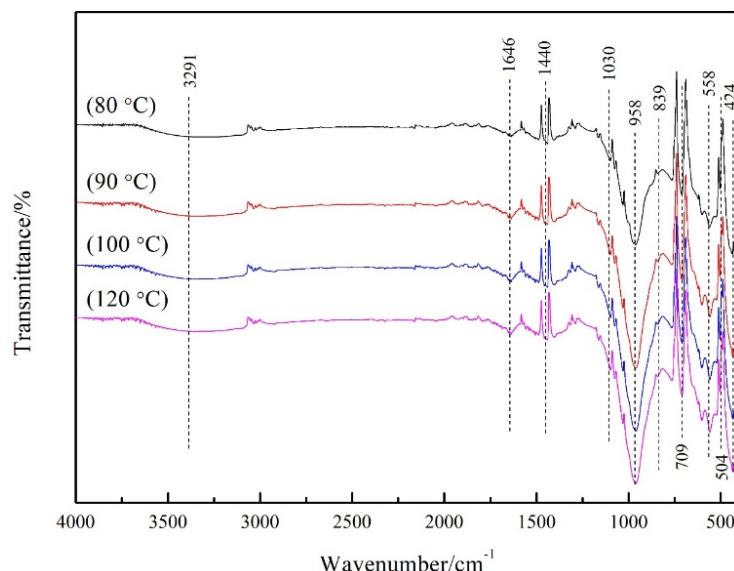


Figure 2. FT-IR spectroscopy of the HAP-ZE synthesized at the different reaction temperature.

3.4. Microstructural Characteristics

To analyze specific surface area (SSA), pore volume and average pore diameter of the HAP-ZE obtained under various reaction temperature in this study, BET/BJH test was carried out. The SSA, pore volume and average pore diameter of the HAP-ZE are demonstrated in Table 4. Results show that the SSA of the HAP-ZE became greater with the reaction temperature rise from $80\text{ }^{\circ}\text{C}$ to $100\text{ }^{\circ}\text{C}$. Additionally, the HAP-ZE synthesized at $100\text{ }^{\circ}\text{C}$ had the largest SSA value, while the SSA of the HAP-ZE synthesized at $120\text{ }^{\circ}\text{C}$ decreased continuously. This change trend on the SSA of the synthesized HAP-ZE was perhaps due to the changes in content among HAP and zeolite in the synthesized HAP-ZE (see Table 2). As zeolite phases generally have a higher SSA than that of HAP, this tendency is comparable with the cumulative pores' volume from BJH desorption data. On the other hand, the crystal agglomeration can be intensified with the increasing of reaction temperature (indicated in Figure 3), and the morphology of HAP-ZE crystals will be discussed below. This agglomeration could cause a disconnection of the pore in HAP-ZE crystals, which resulted in a decrease in both the SSA and pores' volume value at $120\text{ }^{\circ}\text{C}$ compared with $100\text{ }^{\circ}\text{C}$. Meanwhile, the BJH desorption average pore diameter generally preferred to decrease along with the increase of reaction temperature. These results seem to be due to the different pore distribution of HAP-ZE obtained under different reaction temperatures. Moreover, the average pore diameter generally tended to be inversely proportional to the SSA value of the HAP-ZE. Namely, the reduction of pore diameter is also instrumental in enhancement of SSA. This can be due to the fact that the relatively small pores can establish a hierarchical connection system of pores in HAP-ZE, which can lead to a high SSA value for the obtained HAP-ZE samples.

Table 4. BET/BJH results of the materials synthesized at the different reaction temperature.

Reaction Temperature (°C)	SSA (m ² /g) ^a	Pore Volume (cm ³ /g) ^b	Average Pore Diameter (nm) ^c
80	38.28	0.081	12.24
90	42.08	0.092	10.13
100	44.22	0.11	9.67
120	38.19	0.073	9.98

^a BET surface area. ^b Determined by BJH desorption data. ^c Determined by BJH desorption data.

3.5. SEM and EDX Test

FE-SEM and EDX spectrometry were used to analyze the morphology and element distribution, respectively. The SEM image of HAP-ZE and EDX results are displayed in Figures 3 and 4, respectively. As seen from Figure 3, compared with the raw BFS, the morphology of the prepared HAP-ZE has changed greatly. The HAP-ZE crystals generated at 80 °C implied nice development compared to those from BFS (see Figure 3B). It is speculated that the circular-shaped crystals and lumpy crystals are attributable to HAP and zeolite, respectively, based on the crystallographic features [38,39]. For the HAP-ZE crystals produced at 90 °C, HAP-ZE crystals also had asymmetrical circular shapes and lumpy crystals, which is smaller than the shape of the samples generated at 80 °C. At 100 °C, HAP-ZE crystals with a diameter of about 500 nm form an open frame structure with coral surface morphology (see Figure 3D). As the reaction temperature increased to 120 °C, it was found that the size and crystallinity of the HAP-ZE both increased. The observed morphological feature stays consistent with that for HAP-ZE previously reported [38,39], again proving the successful formation of HAP-ZE. Moreover, via the morphology displayed in the Figure 3, the lumpy crystal zeolite can be found to be most in the HAP-ZE obtained at 100 °C, which is consistent with zeolite content in Table 2. In addition, a certain degree of crystal agglomeration can be seen in HAP-ZE obtained at 120 °C (Figure 3E). This phenomenon could be attributed to the fact that the higher reaction temperature led to a higher surface energy of HAP-ZE crystals, and then led to the agglomeration of HAP-ZE crystals. The agglomeration of HAP-ZE crystals can significantly reduce both SSA and adsorption capacity. This is why the SSA of obtained HAP-ZE decreases when the reaction temperature increases over 100 °C. Therefore, HAP-ZE obtained at 100 °C with an open frame structure signifies that it has a large surface area and pore volume for adsorbates to access. Moreover, most zeolite crystals are evenly dispersed on the HAP crystals. Generally, before the EDX test, we use aluminum and copper standard sample for calibration. Meanwhile, the Ca/P molar ratios measured by EDX spectrometry were 1.96, 1.85, 1.69 and 1.79 at 80 °C, 90 °C, 100 °C and 120 °C, respectively. The Si/Al molar ratios measured by EDX spectrometry were 1.70, 1.65, 1.41 and 1.42 at 80 °C, 90 °C, 100 °C and 120 °C, respectively. The Ca/P and Si/Al molar ratios measured by EDX spectrometry were consistent with the XRF spectra analysis results (see Table 3). This phenomenon may be due to the uniform dispersion during the growth process of HAP-ZE.

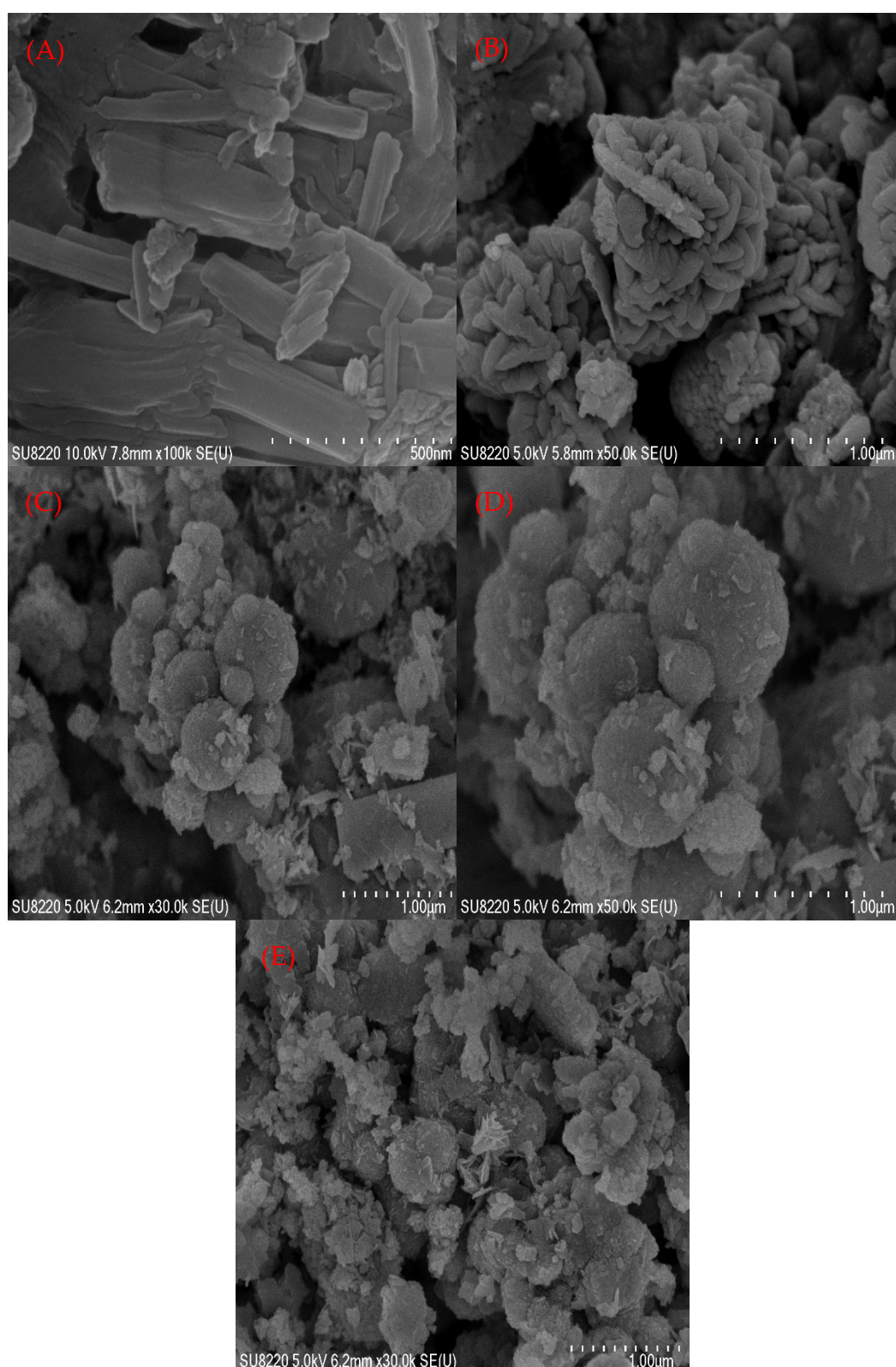


Figure 3. SEM images of (A) BFS; the product samples obtained at reaction temperature of (B) 80 °C; (C) 90 °C; (D) 100 °C and (E) 120 °C.

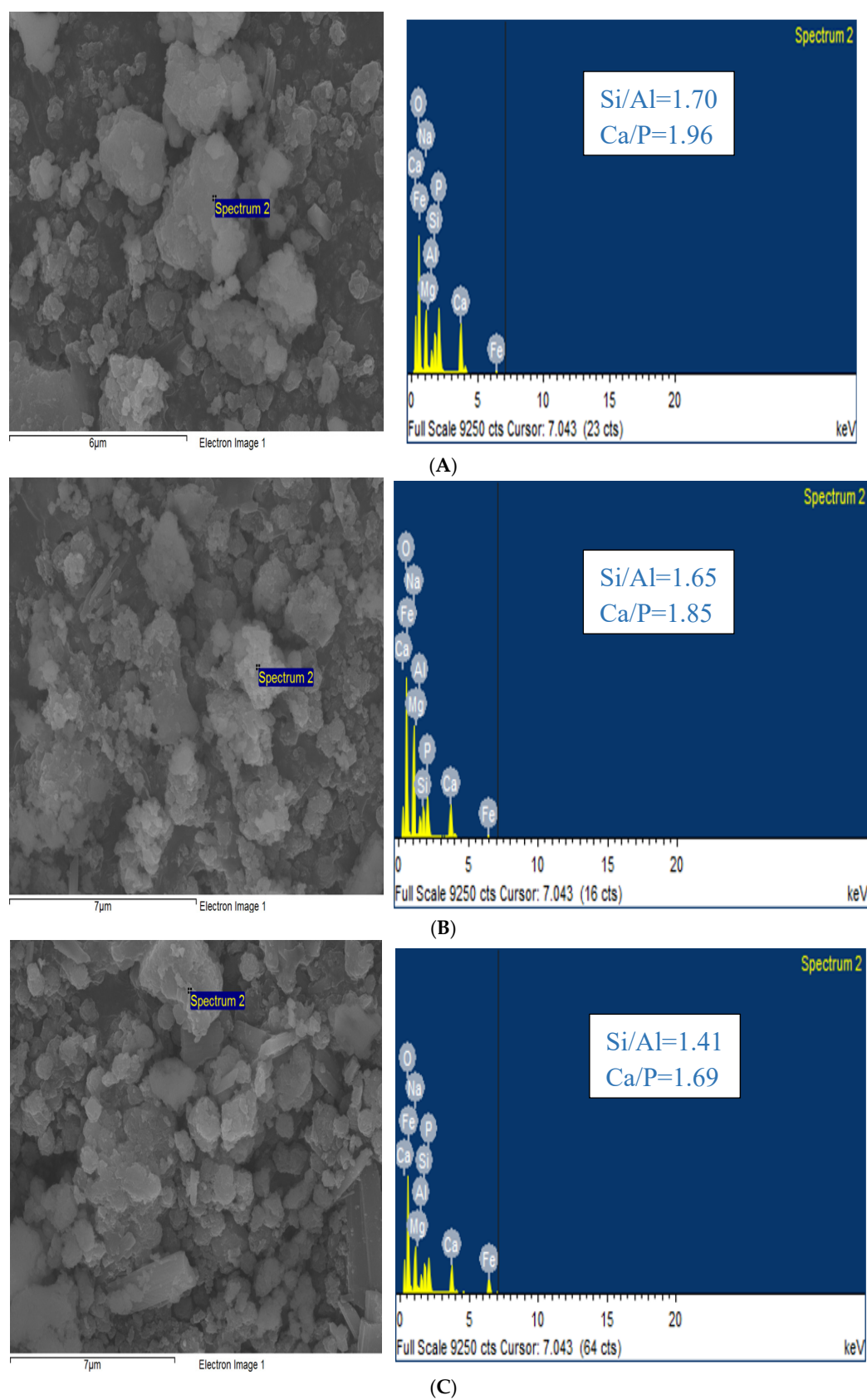


Figure 4. Cont.

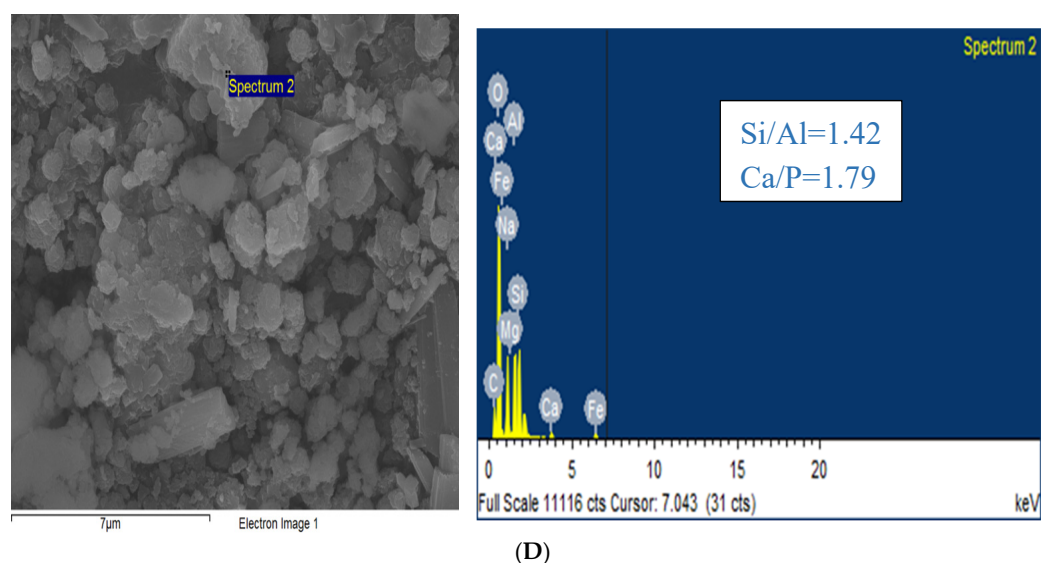


Figure 4. EDX spectroscopy of the HAP-ZE samples obtained at reaction temperature of (A) 80 °C; (B) 90 °C; (C) 100 °C and (D) 120 °C.

4. Conclusions

The effects of reaction temperature on the alkaline fusion-hydrothermal synthesis of HAP-ZE from BFS were investigated in this study. The HAP-ZE were synthesized under different reaction temperatures and then measured by XRD, FT-IR, BET/BJH, XRF, FE-SEM and EDX analysis. It was found that the crystallinity, phase contents, CEC and PIC of HAP-ZE was highly affected by reaction temperature. The optimum reaction temperature for preparing HAP-ZE from blast furnace slag (BFS) using alkaline fusion-hydrothermal treatment is around 100 °C. The HAP-ZE synthesized at 100 °C had the largest SSA value. Under 100 °C aging, the main phases in HAP-ZE were zeolite and HAP with the average SSA of 44.22 m²·g^{−1}. Moreover, molar ratio of Ca/P, Si/Al and Na/Al is 1.61, 1.31, 1.75, respectively. Additionally, HAP-ZE crystals with a diameter of about 500 nm form an open frame structure with coral surface morphology and could be clearly observed at 100 °C.

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