Synthesis of Zeolite from Electrolytic Manganese Residue: Investigation on the Variation of the Property of Zeolite during the Conversion Process

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1. Introduction

By 2012, China’s electrolytic manganese production capacity has exceeded 2.11 million tons per year, which takes up 98% of global annual output. Electrolytic manganese residue (EMR) is a by-product derived from the production of electrolytic manganese metal (EMM) in the electrolytic manganese industry [1, 2]. With generation of every ton of EMM, roughly 10–12 tons of EMR is being released into the environment, which is a common practice in the EMM industry nowadays. Since there are toxic and hazardous materials in EMR, it is crucial that EMR is properly treated. At the moment, the reality in China is that nearly all EMRs are being dumped into a close-by landfill untreated after being generated in the plant. With ceaseless migration of pollutants in EMR, severe environmental pollution, such as soil contamination and river or groundwater pollution, is induced as a result [3–5]. Moreover, as a result of ever-increasing expense for continuing maintenance and newly established disposal sites, the financial burden for EMM manufacturers to process extensive amount of EMR from large-scale industrial activities becomes a growing one. In order to meet environmental protection, as well as to achieve sustainable development, it is a pressing necessity to study novel and state-of-the-art recycling techniques which facilitate EMR exploitation.

Through the recent studies, it came to our research group’s knowledge that Si and Al in EMR can be used for the synthesis of EMRZ (EMR based zeolite). Owing to their large specific surface area (SSA) and cation exchange capacity (CEC), zeolites are well accepted as useful adsorption materials. As a result, the study of contaminant removal by zeolites has been carried out widely in all types of zeolites including natural zeolite, commercial zeolite, and chemically synthesized zeolite [6–10]. Removing pollutants in wastewater using EMRZ not only serves as an effective means to
lower cost, but also, more importantly, achieves the purpose of fulfilling the requirement of green economy.

Generally, zeolite with lower Si/Al ratio shows higher CEC and adsorption capacity due to the presence of exchangeable cations. Therefore, the targeted type of framework/structure of zeolite is zeolite A (LTA), which inherently possesses lower Si/Al ratio and higher cation exchange ability. Although our previous studies revealed that EMRZ can be successfully prepared from EMR, the influence of synthesis conditions on the formation process and properties of EMRZ has not been clearly defined. The objective of the existing study was to understand the synthesis process and to lay out more information on improving the quality of EMRZ with regard to contaminant removal. To better understand the influence of synthesis conditions, the factors of the mineralogical composition, chemical composition, CEC (cation exchange capacity), PIC (phosphate immobilization capacity), and morphology in the conversion of EMR to EMRZ under different synthesis conditions were investigated.

2. Experimental Section

2.1. Materials. The EMR tested in this study was gathered from Xinxing Metallurgical Chemical Co., Ltd., located in western Hunan, China. The major chemical composition of the EMR used in this study is listed in Table 1. All the reagents used in this study were AR grade chemicals and were used without further purification.

2.2. Zeolite Synthesis. Before synthesis of EMRZ, the EMR was first activated and fully dissolved by 1.5 mol/L H2SO4 aqueous solution at 80°C for 2 h. Then, the leaching residue of EMR (LR-EMR) was collected by filtration and used as a raw material for zeolite synthesis so as to fully utilize chemical components of EMR.

Based on a previous relevant study [11], our research team here acquired the fusion method involving alkaline fusion followed by hydrothermal treatment. During the reaction process, various amounts of sodium aluminate (NaAlO2) were added to the reaction system to change the reaction process, various amounts of sodium aluminate fusion followed by hydrothermal treatment. During the team here acquired the fusion method involving alkaline chemical components of EMR. The raw material for zeolite synthesis so as to fully utilize of EMR (LR-EMR) was collected by filtration and used as raw material for zeolite synthesis so as to fully utilize chemical components of EMR.

2.3. Characterization. The X-ray (powder) diffraction (XRD) patterns of different samples were obtained using a D8 Discover X-ray diffractometer (D8 Discover, Bruker, Germany). The chemical analysis of the samples was conducted using XRF spectroscopy (Axios, PANalytical, Holland). The morphological structure of the synthesized zeolitic materials was obtained using field emission scanning electron microscopy (FE-SEM) (Mira3, TESCAN, Czech Republic). The specific surface area (SSA) was obtained via BET equation by N2 adsorption method on ASAP2020 (Micromeritics, USA). Cation exchange capacity (CEC) of EMRZ was evaluated based on the study of Zhang et al. [12] and the CECs were thus determined and represented as meq per gram of solids. The PIC value was determined according to the study of Wu et al. [13] and denoted as milligram per gram of solids.

3. Results and Discussion

3.1. Effect of Synthesis Conditions on EMRZ Mineralogical Composition. The changes of mineralogical composition of the EMRZ synthesized from EMR under various experimental conditions are summarized in Figures 1–3. Figure 1 shows the XRD patterns of EMRZ synthesized under various Si/Al ratios within a range from 1.5 to 3.0, together with LR-EMR. The XRD pattern of EMRZ shows some spiky diffraction peaks, which are inconsistent with those in LR-EMR. The several crystalline phases of quartz and muscovite were notable in the LR-EMR, while the original crystalline phases of LR-EMR were decomposed in the zeolitization process (see Figure 1). This is due to the fact that quartz and muscovite in the LR-EMR were transformed to amorphous alum inosilicates in the fusion process at 600°C. However, the resulting alum inosilicates are unstable in the hydrothermal environment and therefore contribute to the generation of zeolite crystals. Moreover, the synthesis products obtained under various initial Si/Al ratios in the reaction mixture contained both zeolite A and zeolite P in all tests, as indicated by XRD patterns (see Figure 1). The statistics in Figure 1 further points out that the crystal growth of zeolite A was intensified when initial Si/Al ratio decreased from 3.0 to 1.5. Comparable conclusions were drawn by several other authors regarding the formation of zeolite A at lower initial Si/Al ratio [14, 15]. Considering possible future uses in terms of contaminant removal, the three-dimensional parallel channel structure of zeolite A makes a high ion exchange capacity possible, and it is thus widely used in contaminant separation or collection processes [16, 17].

The synthesis temperature is a very key factor in determining structure of zeolite, and the results in Figure 2 show that the reaction temperature had a remarkable impact on the kind of zeolite and the crystallinity of zeolite. From Figure 2, at a relatively low hydrothermal temperature of 40°C, carnegieite is the main phase, while zeolite A forms at a relatively higher reaction temperature of 100°C. The characterization results disclose that, at the tested synthesis condition, zeolite A is stronger at higher reaction temperatures, and the formation of zeolite A was in terms of the dissolution of silicon. As seen from Figure 2, quartz in the reaction mixture would only be fully dissolved when the reaction temperature was above 90°C. Thus, it seems that, at reaction temperatures lower than 90°C, Si/Al ratio is low enough in the reaction system to facilitate the generation of zeolite A. That is to say, a higher temperature facilitates the Si ingredient getting dissolved from the LR-EMR and the crystallization of zeolite phase [13, 16].

Another parameter which can greatly affect the synthesis of zeolite is the reaction time. The impact of reaction time on the kind of the synthesized samples was investigated from 0.5 h to 2.0 h, and the results are presented in Figure 3. The
The figure shows that quartz, zeolite Na-ZK-4, and andalusite were synthesized at the reaction time of 0.5 h, whereas the Na-ZK-4 type zeolite and andalusite both disappear after 0.75 h treatment revealing a metastable behavior [16]. Meanwhile, when reaction time increases further to 0.75 h, quartz still can be detected while formation of zeolite A is insignificant. From the figure, it was also obvious that the crystallinity of the prepared EMRZ increased moderately with the increase in reaction time up to 1.5 h and zeolite A is the dominant phase; then no further development in the crystal growth was seen after 1.5 h. This observation is also consistent with the conclusion of Ojha et al. [18], because there is an incubation period for the nucleation of zeolites during zeolite synthesis. After nucleation process, zeolitization increases only slightly over time.

3.2. Effect of Synthesis Conditions on the Chemical Composition of EMRZ. Table 2 shows a summary of chemical composition of LR-EMR and synthetic EMRZ under
different experimental conditions. From Table 2, the data reveals that the LR-EMR with Si/Al = 3.60 was reduced to 1.01∼1.36 by increasing of the Al₂O₃ content from 15.8% to 24.8∼29.5% in the final product. Moreover, the change of Si/Al ratio in the EMRZ samples is not in proportion to the applied change of Si/Al ratio in the reaction mixture. As we all known, during the process of zeolite synthesis, Al acts as the controlling substance, and the consumption rate of Al is much higher than that of Si in the reaction [19]. Therefore, the drop in the Si/Al ratio after the synthesis process was generally caused by the loss of dissolved Si during the synthesis process. As to why the dissolved Si is lost, the reasonable explanation would be the formation of Al rich zeolite (mainly zeolite A), and the generation of zeolite A would cause excessive soluble Si when compared with dissolved Al. Instead of being consumed in the zeolite formation, the extra soluble silicates got lost. That is to say, an excess amount of water-soluble silicates ions did not take part in EMRZ formation (mainly zeolite A, LTA), while almost all of the Al was depleted during the synthesis of EMRZ. As for the Mg²⁺, Fe²⁺, and Ca²⁺ (n = 2 or 3), it is believed that those cations in the solution can be incorporated into the interlayer or aggregated species on the crystallite surface during the zeolitization process. Due to the mechanisms of zeolite growth, the amounts of Mg²⁺, Fe²⁺, and Ca²⁺ (n = 2 or 3) incorporated into the zeolite are very sensitive to the synthesis conditions. Namely, the amounts of Mg²⁺, Fe²⁺, and Ca²⁺ (n = 2 or 3) incorporated into the zeolite are different under various synthesis conditions, thus causing significant differences in molar ratio of components in the as-synthesized zeolites. As no detectable peaks attributable to Fe, Mg, and Ca compounds

![Figure 3: XRD patterns of the synthesized zeolites under various reaction periods (synthesis conditions: initial Si/Al ratio, 1.5; reaction temperature, 100°C).](image-url)
were observed in the XRD patterns, it is speculated that the minor metal ions such as Fe, Mg, and Ca are likely to be uniformly incorporated within the structure without forming any crystalline phases. On the other hand, the remarkable increase of Na$_2$O content in the as-obtained EMRZ was also observed in Table 2. The rise in Na$_2$O content in EMRZ during the use of NaOH in the synthesis process can be explained by the initial saturation of the EMRZ samples by Na$^+$ [20]. The remarkable changes in Na$_2$O content before and after the synthesis process can be also considered as another evidence of successful preparation of EMRZ from EMR.

3.3. Effect of Synthesis Conditions on the CEC of EMRZ. The CEC value was analyzed by the ammonium acetate method to evaluate the ion exchange capability of the synthesized EMRZ, and the outcomes are illustrated in Figure 4. From Figure 4, the CEC of the synthesized EMRZ is much greater than that of LR-EMR (0.015 meq/g). Besides, within the initial Si/Al ratio used, the CEC value of EMRZ enhanced with the increase of initial Si/Al ratio (Figure 4(a)). The reason for this is that raising the initial Si/Al ratio facilitated the transformation of synthesized product from zeolite A to zeolite P (see Figure 1). In addition, the CEC value of zeolite P tested by the ammonium acetate method is lower than that of zeolite A. Meanwhile, the reaction temperature also notably influenced the CEC value of EMRZ. The CEC value increased by a considerable amount along with the increase of reaction temperature. The increase of CEC along with reaction temperature is clearly due to the enhancement of zeolite formation (see Figure 2). That is to say, higher reaction temperature is instrumental in promoting the level of zeolitization and, as a result, a higher capacity to exchange cations. As for the reaction time, the CEC value of EMRZ increased rapidly within the first 1.5 h and then remained stable. The prolonged reaction time leading to the increase in CEC can be explained by both the increase in zeolite content and the phase change from quartz and andalusite to high CEC zeolite A (see Figure 3). Table 3 also shows the comparison of CEC value of prepared zeolite and other related zeolites in literature [12, 21–24]. The CEC of the final zeolite product that we determined in this work (i.e., 3.45 meq/g) is much higher than the related zeolites mentioned in the literature. This is an indicator that the EMRZ is a suitable cation exchange material in multiple applications such as water softener and contaminant adsorption.

3.4. PIC of EMRZ Prepared under Different Conditions. As reported in the literature, both CEC and PIC value in zeolite prepared from fly ash turned out to be high. In this study, the PIC of the EMRZ also proved to be suitable for the removal of contaminant in the wastewater, especially for phosphate. The PIC of the EMRZ obtained at different initial Si/Al ratios is displayed in Figure 5. It can be seen that as initial Si/Al ratio increased, the PIC value dropped quickly. As also shown in Figure 5, the changes of SSA (specific surface area) with initial Si/Al ratio and PIC shared a quite similar model. The reason can be attributed to the fact that the SSA of EMRZ correlates significantly with PIC, and higher initial Si/Al ratio results in formation of zeolite P which might reduce the specific surface area of EMRZ in comparison with formation of zeolite A. Although, the zeolitization process caused a great increase in SSA over the starting material (the SSA of LR-EMR was only 0.28 m$^2$·g$^{-1}$), the values of SSA of EMRZ were relatively lower than those of other artificial zeolites mentioned in the literature according to expectation. And the relatively lower SSA of the as-synthesized EMRZ compared with the commercial or traditional zeolite was due to the following reasons. On the one hand, the crystallinity of the EMRZ was lower than those of commercial or traditional zeolite reported in the literature. On the other hand, Mg$^{2+}$, Fe$^{3+}$, and Ca$^{2+}$ ($n = 2$ or $3$) cations in the solution can be incorporated into the interlayer or aggregated species on the crystallite surface during the zeolitization process (see Table 2). In addition, those cations led to a lower surface area than alkali metals (K, Na) did. Moreover, Figure 6 shows the N$_2$ adsorption-desorption isotherms and pore size distribution of EMRZ synthesized under reaction temperature of 100°C, reaction time of 1.5 h, and initial Si/Al ratio of 1.5. The N$_2$ adsorption-desorption isotherm of EMRZ shows an obvious hysteresis loop in the range of $P/P_0 > 0.4$ (see Figure 6(a)), reflecting the intra- and intercrystalline mesoporosity. Meanwhile, a gradual increase in the range of $P/P_0 > 0.8$ corresponds to the presence of macroporous structure in EMRZ. And the pore size distributions calculated using the BJH adsorption data (see Figure 6(b)) again confirm that EMRZ has both mesoporous and macroporous size pores with average pore diameter of ca. 10–80 nm. And the existence of macroporous structure in EMRZ can also lead to the relatively lower SSA of the as-synthesized EMRZ. The low PIC of EMRZ was attributed to the fact that the total consumption of iron and calcium for synthesized EMRZ was low and the immobilization of phosphate by synthesized zeolite was mainly due to calcium and iron components [25, 26]. Since the PIC of EMRZ can be further enhanced by saturation with Ca$^{2+}$ solution, EMRZ was modified through a previous Ca$^{2+}$ and Fe$^{3+}$ solution treatment [26]; thus it is possible that it can serve as a favorable material for removing both ammonium and phosphate in wastewater.

3.5. Effect of Synthesis Conditions on the Morphology of EMRZ. In this study, FE-SEM was used to observe the morphology and particle size of EMRZ synthesized under various initial ratios of Si/Al (Figure 7). Different crystalline shapes of synthesized EMRZ are caused by different types of zeolites. As demonstrated in the literature, typical shapes of synthesized zeolite are cubic and round, which matches zeolite A and zeolite P, respectively [27–29]. At initial Si/Al ratio of 1.5, zeolite A in its well-developed cubic shape as well as zeolite P in the shape of round crystals with a small amount of was presented (see...
Figure 4: Effects of initial Si/Al ratio on the CEC of the synthesized EMRZ (synthesis conditions: (a) reaction temperature, 100°C; reaction time, 1 h; (b) initial Si/Al ratio, 1.5; reaction time, 1 h; (c) initial Si/Al ratio, 1.5; reaction temperature, 100°C).

Table 3: Comparison of CEC value of the as-synthesized EMRZ and related typical zeolites.

| Sample                       | CEC (meq/g) | Reference   |
|------------------------------|-------------|-------------|
| EMRZ<sup>a</sup>            | 3.45        | This work   |
| Zeolite X                    | 2.79        | [12]        |
| Zeolite A (Na)               | 0.87~1.05   | [21]        |
| Na-P1                        | 0.99~1.31   | [22]        |
| Natural Turkish clinoptilolite | 0.95~1.40   | [23]        |
| Natural Chinese (Chende) zeolite | 0.82        | [24]        |

<sup>a</sup>EMRZ obtained in this work under the following synthesis conditions: reaction temperature, 100°C; reaction time, 1.5 h; initial Si/Al ratio, 1.5.
Besides, the particle size of this zeolite is around 1 μm. With the initial ratio of Si/Al being raised to 2.0, zeolite A cubes grew at the cost of these plates leaving some zeolite P coexisting with larger-sized well-formed zeolite A crystals (see Figure 7(b)). Additionally, the sample with initial Si/Al ratio of 2.5 has a morphology similar to the one with initial Si/Al ratio of 3.0 with the characteristic cube of zeolite A and round shape of zeolite P. Moreover, in the EMRZ synthesized at initial Si/Al ratio of 2.5 or 3.0, more round particles of zeolite P with a size of around 2 μm were generated in addition to the cubic particles (see Figures 7(c) and 7(d)), which once again was corroborated by the XRD data in Figure 1. These results also suggest that there is a sort of competition in zeolite P and zeolite A during the EMRZ synthesis that seems to be regulated by initial Si/Al ratio adopted in the experimental conditions. On top of that, it is worth noticing that no aggregates were observed in the SEM pictures, which can guarantee the higher dispersion of EMRZ with tiny pores. A large number of tiny pores which may exist inside the pellets help increase the specific surface area, which has been confirmed by SSA measurements.
4. Conclusion

EMRZ (mainly zeolite A, LTA), which can be used to treat polluted water for purification, was successfully produced. The CEC, PIC; and chemical, mineralogical, and morphological characteristics of the synthesized EMRZ were systematically investigated under various experimental conditions. The result proves that the experimental parameters including initial Si/Al ratio, reaction temperature, and reaction time are crucial for the type and chemical composition of zeolite generated. Depending on the experimental conditions, zeolite A (LTA) begins to form initially during hydrothermal treatment of fused LR-EMR, which can be transferred to zeolite P. Because of the formation of Al rich zeolite, the synthesis process caused decrease in Si/Al ratio and rise of Na2O content in the EMRZ samples. It was noticed that CEC, PIC, and SSA of the synthesized EMRZ were improved with respect to the original LR-EMR. In addition, the discrepancy of CEC and PIC of EMRZ supports the fact that various controlling factors/components in EMRZ are accountable for CEC (Na2O content and type of zeolite) and PIC (calcium and iron components). In terms of CEC, SSA, and crystallinity, the optimal synthesis conditions for EMRZ were an initial Si/Al ratio of 1.5, a reaction temperature of 100°C, and a reaction time of 1.5 h, respectively. The EMRZ synthesized under the optimum conditions was found to be primarily composed of Na-A zeolite (LTA) with a Si/Al ratio of 1.02 and a CEC of 3.45 meq/g. The present result is, therefore, very much practical in opening the way to the use of EMR to synthesize zeolite.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest regarding the publication of this paper.

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