Journal of Wuhan University of Technology-Mater. Sci. Ed. www.jwutms.net Dec.2016

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Extraction and Reaction Mechanism of Potassium from Associated Phosphorus and Potassium Ore

LI Liang[1,2], LEI Shaomin[1*], LIU Yuanyuan[1], LUO Huihua[2]

(1.School of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan, 430070, China; 2.School of Chemistry and Environmental Engineering, Wuhan Institute of Technology, Wuhan, 430073, China)

Abstract: Potassium and phosphate were extracted at low temperature by acid hydrolysis process to decompose a new type of associated phosphorus and potassium ore. The main factors affecting the dissolution rate were investigated, such as grinding fineness, the amount of sulfuric acid and fluoride salt, reaction time and temperature, etc. Meanwhile, the effects of various factors on the formation of soluble potassium and phosphate were also discussed. The reaction products and residues were determined by X-ray diffraction (XRD), scanning electron microscopic (SEM) analysis and other means. The results showed that the dissolution rates of potassium and phosphorus were 70wt% and 93.7wt%, respectively, under the conditions of a grain size of 95.64wt% lessthan 0.074 mm, 9.78 g•g^{-1} sulfuric acid, 0.5 g•g^{-1} ammonium fluoride, 160 ℃ and a reaction time of 2 h. The thermodynamic and chemical reaction mechanism was revealed that the primary reaction could be completed spontaneously in a temperature range of 298-433 K. The increase of reaction temperature had an important influence on ion exchange reaction, which was more conducive to the spontaneous process. The research will open up a new way for efficient use of potassium ore resources.

Key words: associated phosphorus and potassium ore; extraction; soluble potassium salt; reaction mechanism

1 Introduction

More than 180 kinds of processed potassium materials come from the raw potassium salts. The potassium salts are commonly used in the field of industries due to their physical and chemical properties. For example, they are employed in the manufacturing of glass, ceramic glaze, dye, kinescope, photographic agent and fertilizers[1-3].

The potassium resources can be simply divided into two types, the soluble and the insoluble. The soluble potassium resources are very scarce in China, whereas the insoluble ones are very abundant. So taking full advantage of insoluble potassium mineral is absolutely essential to reduce the usage of soluble resources and protect the environment. Various potassium-rich rocks, as the insoluble potassium materials, mainly include potassium feldspar, nephelite, muscovite and hydromica clay minerals.

In recent years, a deposit containing collophanite and potash feldspar minerals was found in Yichang, Hubei province, China. The major components of the associated phosphorus potassium ore comprise phosphate rock, potassium mineral and quartz with P_2O_5 (6wt%-12wt%) and K_2O (4wt%-9wt%). The prospective reserves of the ore are approximately 800 million ton[4,5].

However, the associated phosphorus and potassium ore is only used as phosphate resources, the potassium is not effectively utilized. Hence the conversion of K-feldspar into water-soluble potassium materials at lower cost with high efficiency is of great importance.

In China, methods for the potassium extraction were adopted by dry and wet processes[6-9]. The dry processes refer mainly to the calcination of K-feldspar with various additives that are sodium-containing and calcium-containing to convert K-feldspar into water-soluble potassium salts at high temperature. Then water

dissolution is adopted for the extraction of potassium. Potassium feldspar is decomposed by thermal decomposition system. Hu Tianxi[10] used the acid mixed with $CaCl_2$ and NaCl, and the rate of potassium extraction was 93.65wt% by mixed additives at 800 ℃ for 60 min. Ding Sheng Chen[11] used 2.94 g•g^{-1} Na_2SO_4 as the additive and roasted for 2 h with the potassium leaching rate ranging from 92wt% to 94wt%.

The wet processes use the hydrofluoric acid-sulfuric acid method. Zhongbing Wang[12] used the pressure alkali leaching method, the K-feldspar containing about 11.4% hydroxide was prepared as potassium fertilizer and the K_2O dissolution rate was up to 90wt%. Wang Yuguo[13] used the method of pressure acid leaching to produce potassium fertilizer, $Al_2(SO_4)_3$, $Al(OH)_3$, silica filler and other products. Ding Yu[14], Han Xiaozhao[7] and Guo Deyue[15] found that extracting potassium could get high yield of soluble potash under atmospheric pressure and lower temperature conditions by acid and additive from potash feldspar.

In summary, high energy consumption is the greatest problem restricting the industrialization of the dry processes. So the wet processes with the associated phosphorus and potassium ore were investigated in this paper. This research provided a better technique path way for extracting potassium salts from associated phosphorus potassium ore.

2 Experimental

2.1 Associated phosphorus and potassium ore

The samples of associated phosphorus and potassium ore of middle-low grade used in the experiments were obtained from Yichang, Hubei Province, China. The major chemical components of the associated ore are shown in Table 1 and Fig.1.
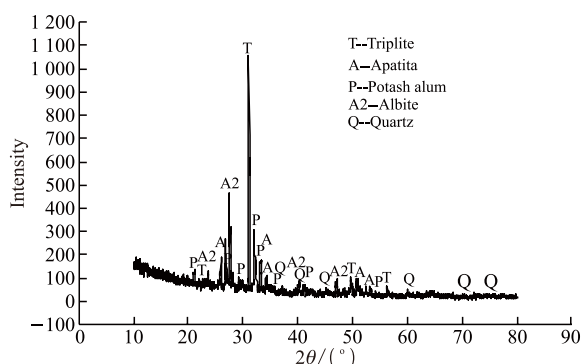

Fig.1 XRD pattern of the associated phosphorus and potassium ore

Both results of Table 1 and Fig.1 indicate that the major mineral phases of the associated phosphorus and potassium ore are collophanite, potash feldspar and albite, and the gangue minerals are dolomite, quartz and calcite, *etc*[16,17].

Table 1 Chemical composition of the associated phosphorus and potassium ore/wt%

Component	Mass fraction	Component	Mass fraction
P_2O_5	21.36	Fe_2O_3	2.45
K_2O	4.70	MgO	1.37
SiO_2	26.46	CO_2	1.46
CaO	29.18	F	2.30
Al_2O_3	7.74	Na_2O	0.56

2.2 Reagents and equipments

Reagents (analytically pure): sulfuric acid (H_2SO_4), and ammonium fluoride (NH_4F).

Equipments: (XMB-67, 200×240) rod mill, (2XZ2) vacuum filter, (101-4) electrothermal drying oven, (FA2104N) electronic balance and (TAS990) atomic absorption spectrophotometer.

2.3 Methods

To obtain optimal technological conditions, first of all, the associated phosphorus and potassium ore was ground to the particle size of 0.074 mm by rod mill. Then the ore, sulfuric acid and ammonium fluoride were mixed in the teflon crucible proportionally and reacted for some time at fixed temperature. Finally, the samples were cooled to room temperature. The materials in teflon crucible were transferred to a volumetric flask and diluted to 50 mL with water.

The content of K^+ in the filtrate was analyzed by using the atomic absorption spectroscopic (AAS) method. The content of P_2O_5 was measured by the gravimetric method[18].

The dissolution rate of potassium (wt%)=Amount of K_2O in leaching solution×100/Amount of K_2O in phosphorus and potassium

The dissolution rate of phosphorus (wt%)= Amount of P_2O_5 in leaching solution×100/Amount of P_2O_5 in phosphorus and potassium

3 Results and discussion

Several affecting factors were studied in this work, such as the mineral particle size, the dosage of sulfuric acid and ammonium fluoride, reaction temperature and the heating time.

3.1 Grinding time

The associated ore was ground for 6, 8, 10 and 12 min respectively. The grinding products of different grain sizes were produced with the less than 74 mm

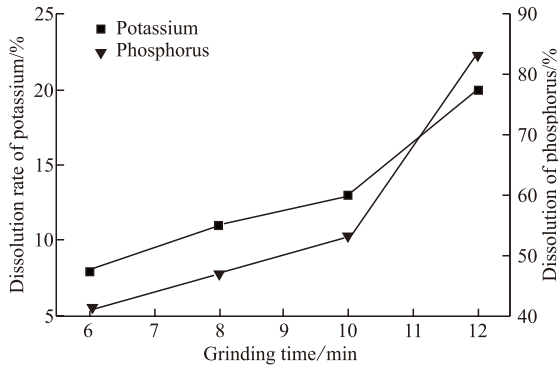fractions of 77.13wt%, 85.6wt%, 92.97wt%, and 95.64wt%, respectively.

Fig.2 Effects of grinding time on the dissolution rates

In Fig.2, the contents of soluble potassium and phosphorus show an upward trend. At the grinding time of 12 min, the dissolution rates of potassium and phosphorus reached 20.1wt% and 84.6wt% respectively. The finer the particle size, the more separated the useful minerals and gangue minerals, which contributed to mutual contact between the substances and increased the speed of reaction.

The 12-minute-grinding of the associated phosphorus and potassium ore was ground for the subsequent tests. The particle size was 95.64wt% less than 0.074 mm.

3.2 Dosage of sulfuric acid

The effect of the sulfuric acid dosage on the dissolution rates of potassium and phosphorus is shown in Fig.3.
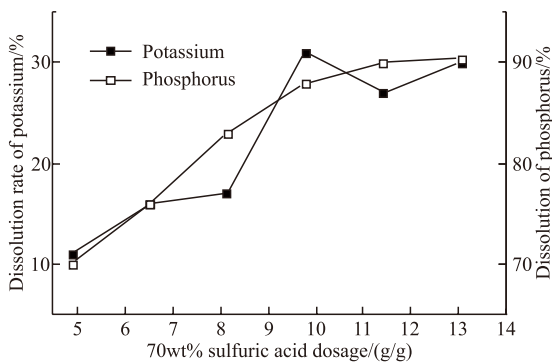

Fig.3 Effects of sulfuric acid dosage on the dissolution rates

The content of soluble potassium increased firstly and then decreased. When the sulfuric acid dosage was 9.78 $g \cdot g^{-1}$, the dissolution rate of potassium reached 30.51wt%. With the continuous reaction between the associated phosphorus and potassium ore and sulfuric acid, the soluble Ca^{2+} released was used to displace K^+ in the feldspar.

With the increase of the sulfuric acid dosage, the residual sulfuric acid that was not involved in the reaction reduced the pH of the solution, which

changed the nature of the ion exchange system[7,19]. At the same time, the excess sulfate ion and Ca^{2+} ion released from potash feldspar combined and generated $CaSO_4$, which then adsorbed on the surface of the associated phosphorus and potassium ore and hindered further reaction between the minerals and sulfuric acid. The above is the reason why the dissolution rate of potassium increased firstly and then decreased.

The dissolution rate of phosphorus was increased firstly. When the sulfuric acid dosage was over 11.41 $g \cdot g^{-1}$, the dissolution rate of phosphorus kept stable and reached 90wt%. The slope of the curve was large at the beginning, and the decomposition rate of phosphorus increased rapidly, indicating that in the presence of sulfuric acid, the conversion of calcium phosphate to phosphorus was effective. The slope of the curve became smaller later on, and the decomposition rate increased slowly and was close to 100%, which indicated that the phosphorus element was gradually and completely decomposed.

The associated ore was decomposed into phosphoric acid and half water calcium sulfate by sulfuric acid, which was a fast reaction that can be completed in half an hour. After sulfuric acid completely reacted, the associated ore was decomposed into calcium phosphate monobasic by phosphoric acid[20,21].

Potassium dissolution was on the basis of ion exchange reaction. Under the strong acid condition, the radius of Ca^{2+} was less than that of K^+, so the electrostatic potential between Ca^{2+} and O^{2-} was greater than that between K^+ and O^{2-}. Therefore, when Ca^{2+} replaced K^+, the dissolution was achieved[22]. Considering the potassium and phosphorus dissolution rate, 9.78 $g \cdot g^{-1}$(6 mL of 70wt% sulfuric acid) sulfuric acid dosage was selected.

3.3 Dosage of ammonium fluoride

The effect of the ammonium fluoride dosage on the dissolution rate of potassium and phosphorus is
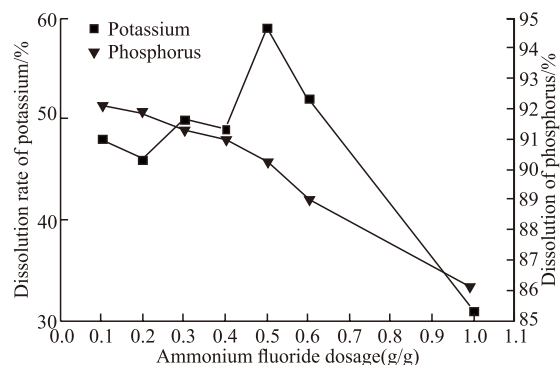

Fig.4 Effects of ammonium fluoride dosage on the dissolution rates

shown in Fig.4.

Fig.4 indicates that the dissolution rate of potassium reached the peak value of 58.97wt% when the dosage of ammonium fluoride was 0.5 g•g^{-1}. The phosphorus in associated phosphorus and potassium ore dissolved completely, and the dissolution rate showed a downward trend. The addition of ammonium fluoride resulted in consumption of H$^+$ and incomplete dissolution of the phosphorus in the associated ore. The addition of excess fluoride made soluble potassium transfer into K$_2$SiF$_6$ again. K$_2$SiF$_6$ is water-insoluble and leads to the losses of energy and material.

Fluoride which was associated in the associated ore and ammonium fluoride reacted with H$^+$ and generated HF. HF deeply damaged the lattice structure of the Si-O, which promoted the dissolution of K$^+$. The mechanism of decomposition reaction in feldspar-hydrofluoric acid system completely destroyed the feldspar silicon oxygen tetrahedron structure, which turned water-insoluble potassium in the feldspar into soluble potassium[23-25]. Therefore, the suitable dosage of ammonium fluoride was 0.5 g•g^{-1}.

3.4 Reaction temperature

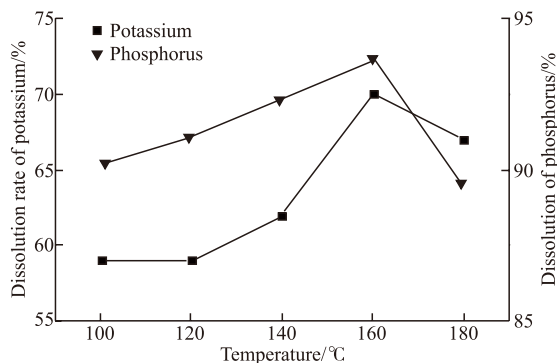The effect of temperature on the dissolution rate of potassium and phosphorus is shown in Fig.5.

Fig.5 Effects of temperature on the dissolution rates

In Fig.5, the dissolution rates of potassium and phosphorus rapidly increased and reached 70.30wt% and 93.70wt%, respectively. The phenomenon showed that the material in the teflon crucible became dry at 180 ℃. At a constant volume, the heat release was obvious, and the reaction of sulfuric acid was incomplete. So 160 ℃ was chosen as the suitable dissolution temperature.

3.5 Heating time

The effect of the heating time on the dissolution rates of potassium and phosphorus is shown in Fig.6.

Fig.6 indicates that the dissolution rates of potassium and phosphorus increased with extremely slow rates. It can be concluded that with increasing heating time, the reactants can fully contact with each other, which was beneficial for ion exchange. However, this effect is limited for the dissolution of potassium and phosphorus.

Because of the comprehensive cost and other factors, the optimal heating time was set to 2 h.
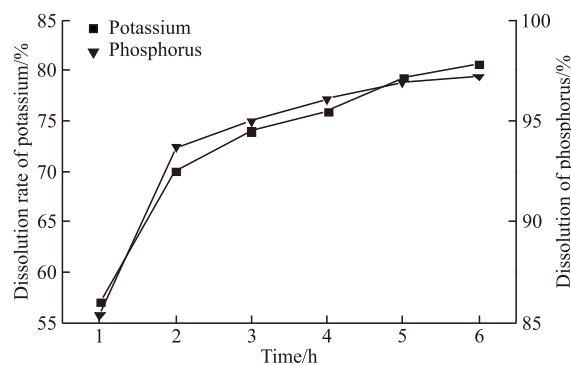

Fig.6 Effects of heating time on the dissolution rates

Combining the results of Figs.2-6, the highest dissolution rates of the associated phosphorus and potassium ore were 93.7wt% and 70wt%, respectively under the optimized conditions. The extraction technique of potassium material not only avoided a substantial waste of phosphorus resources, but also provided a new way for the effective use of potassium associated ore resources.

4 Thermodynamic analysis of the ore decomposition

The main decomposition reactions of the associated ore are shown in Table 2.

Table 2 Reaction equations[26-28]

No.	Reaction equation
1	Ca$_5$(PO$_4$)$_3$F + 5H$_2$SO$_4$ = HF↑ + 3H$_3$PO$_4$ + 5CaSO$_4$
2	Ca$_5$(PO$_4$)$_3$F+ 7H$_3$PO$_4$+ 5H$_2$O=5Ca(H$_2$PO$_4$)$_2$•H$_2$O+ HF↑
3	2KAlSi$_3$O$_8$ + Ca^{2+}= CaAl$_2$Si$_2$O$_8$ + 2K$^+$+ 4SiO$_2$↓
4	24HF + 2KAlSi$_3$O$_8$ + 8H$^+$= 2K$^+$+ 2Al^{3+}+6SiF$_4$↑ + 16H$_2$O
5	3SiF$_4$+2H$_2$O=2H$_2$SiF$_6$+SiO$_2$↓
6	2K$^+$+H$_2$SiF$_6$=K$_2$SiF$_6$+2H$^+$
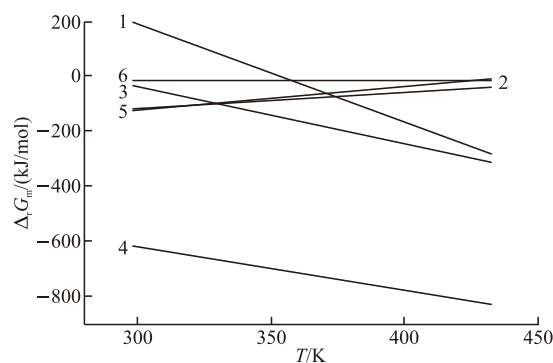
Note: Numbers corresponding to the reaction equations in Table 2
Fig.7 Relationship between $\Delta_r G_m$ and reaction temperature[29-31]

In Fig.7, when the temperature ranged from 298 K to 433 K, the main reaction $\Delta_r G_m$ was negative, which indicated that the main reaction can occur spontaneously. According to the values of $\Delta_r G_m$ in reaction Eqs.(3) and (4), we can see that with increasing temperature, water-insoluble potassium turned into soluble potassium and $\Delta_r G_m$ decreased. With the same substance concentration, the decreasing rate of reaction (3) was much faster than that of reaction (4). This meant that the increasing temperature had a great influence on the ion exchange reaction and was beneficial for the reactions in the process to occur spontaneously, but had little impact on the decomposition reaction.

5 Reaction mechanism

5.1 XRD analysis

The XRD patterns for extracted soluble and insoluble substances from the potassium salt are shown in Fig.8 and Fig.9, respectively.
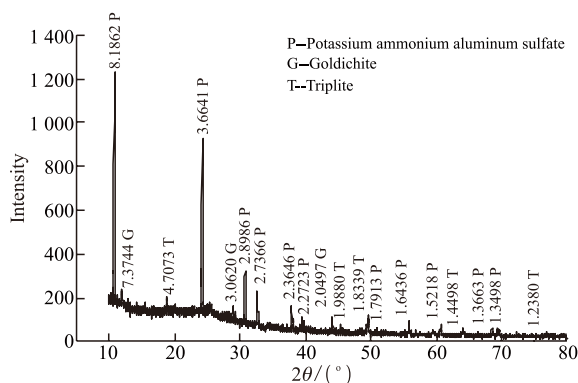

Fig.8   XRD pattern of soluble substances under the optimized reaction conditions
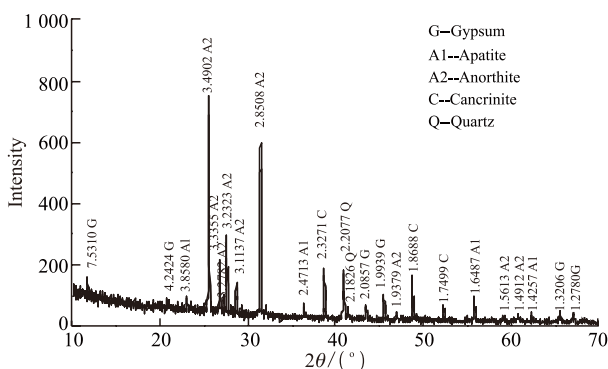

Fig.9   XRD pattern of insoluble substances under the optimized reaction conditions

The soluble substances were potassium ammonium aluminum sulfate, goldichite and triplite and the insoluble substances are anorthite, cancrinite and unchanged apatite. The XRD analysis demonstrated that the majority of potassium in the associated

phosphorus and potassium ore can be transformed into soluble forms.

5.2 SEM analysis of micromorphology

The SEM images of associated phosphorus and potassium ore, soluble substances and insoluble substances are shown in Fig.10.
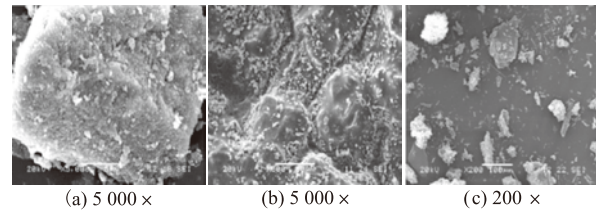

(a) 5 000 ×   (b) 5 000 ×   (c) 200 ×
Fig.10 Micromorphology images of SEM: (a)associated phosphorus and potassium ore; (b)soluble substances; (c) insoluble substances

In Fig.10 (a), the main components were potash feldspar and collophanite and they were mutually inclusive. Dolomite, quartz, calcite and some gangue minerals were attached on the mixture material. The dotted material distributed on the surface of sylvite in Fig.10(b) was the resultant goldichite and triplite. It is noteworthy that the insoluble substances which were gypsum, apatite and anorthite attached to the ore had obvious differences in morphology and size in Fig.10(c). Such remarkable differences in morphology and size of soluble and insoluble substances products can be attributed to the separation-recrystallization process.

5.3 Reaction mechanism

Feldspar is a kind of silicate mineral with special structure in which part of the oxygen-silicon tetrahedra ($[SiO_4]^{4-}$) have been replaced by oxygen-aluminum tetrahedra($[AlO_4]^{5-}$)[32,33]. There are excess negative charges in the structure which lead to lattice defect. The addition of cation with high coordination number and less electrovalence is a supplement to the lattice defect.

In the early stage of the reaction, the decomposition only occurred on the surface of the particles. External fluorine source (ammonium fluoride) and fluoride associated phosphorus potassium ore reacted with sulfuric acid and thus generated HF(gas). The hydrolytic reaction resultants were extremely active and strongly polar. They reacted on the surface of feldspar. The hydrogen bond of $(HF)_2$ and HF_2^- played an important role and the covalent bonds of Si-O, Al-O and Si-Si were broken easily[34-37]. The oxygen-silicon tetrahedra and oxygen-aluminum tetrahedra structures were broken, and the potassium ion was released, and SiF_4 and AlF_3 were generated.

In the medium stage of the reaction, the activation point of the reaction increased exponentially at a

dramatic rate. All kinds of anions and cations in the ore presented in ionic form in the solution. When the reaction system reached a certain temperature, the activation energy increased, the vibration of potassium ions intensified, and the amplitude of covalent bonds of Si-Si, Al-O, Si-O aggravated. Potassium feldspar crystal changed from the monoclinic system to anorthic system. The skeleton expansion of the feldspar structure led to the break of the K-O bond and the radius of the free calcium ion was less than that of potassium ion[30]. Then it was easy to extrude activated potassium ion and produce anorthite[20]. During the dissolution in silicate structure, neither oxygen-silicon tetrahedra nor oxygen-aluminum tetrahedra was destroyed, which was consistent with the XRD analysis results.

6 Conclusions

a) The extractive technique of potassium salt results in a high-efficient utilization of the associated phosphorus and potassium ore. Extracted soluble potassium salts are widely used industrial materials.

b) The optimized extraction conditions for soluble potassium salt from associated phosphorus and potassium ore are a grain size of 95.64wt% less-than 0.074 mm, 6 mL of 70wt% sulfuric acid, 0.5 g•g^{-1} ammonium fluoride, 160 ℃ and a reaction time of 2h. The dissolution rates of potassium and phosphorus are 70.3wt% and 93.7wt%, respectively.

c) In the early stage of the reaction, the decomposition occurs only on the surface of the particles and the ion exchange reaction plays an important role. In the medium stage of the reaction, the dissolution rate of decomposition reaction has greater impact than that of ion exchange reaction.

d) The thermodynamic studies demonstrate that the primary response can be completed spontaneously in a temperature range of 298 to 433 K, and the increase of reaction temperature has an important influence on the ion exchange reaction, but little impact on the decomposition reaction.

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