

中温分解钾长石的热力学分析与实验

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摘 要: 综合介绍了利用助剂分解钾长石的研究现状。通过热力学计算预测以碳酸钠、碳酸钾为助剂分解钾长石的分解反应温度在 800 ~ 890 之间。分解反应机理的分析表明: 随着焙烧温度的升高, 钾长石由单一的焙烧分解状态进入分解和烧结同时进行的状况。实验表明: 钾长石矿的分解率达 98 % 以上, 以碳酸钠、碳酸钾为助剂在 820 ~ 850 即可使钾长石分解。

关键词: 钾长石; 分解率; 碳酸钠; 碳酸钾; 助剂

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THERMODYNAMIC ANALYSIS AND EXPERIMENTS OF THERMAL DECOMPOSITION
FOR POTASSIUM FELDSPAR AT INTERMEDIATE TEMPERATURES

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Abstract: Advances on thermal decomposition of potassium feldspar with flux agents are reviewed. Thermodynamic calculation shows that the temperature range of the thermal decomposition of potassium feldspar is 800—890 with stoichiometric additive of sodium carbonate or potassium carbonate. Analysis on the mechanism of thermal decomposition reaction shows that with increasing the calcination temperature, potassium feldspar passes through a stage predominated by single decomposition entering that predominated by decomposition and sinter simultaneously. Decomposition proportions of various potassium feldspar powder materials determined are over 98 %. This shows that with stoichiometric additive of sodium carbonate or potassium carbonate, the potassium feldspar can be decomposed at 820—850.

Key words: potassium feldspar; decomposition rate; sodium carbonate; potassium carbonate; flux agent

In China, soluble hoevellite resource is extremely bare, but insoluble potassium resource, the principal mineral of which is potassium feldspar (KAlSi_3O_8), has a large amount of reserve besides its extensive distribution. Therefore, extraction of various potassium compounds from insoluble potassium ores has become a strategy need, which could bring on enormous potentially economic value and social benefit.^[1] Decomposition of KAlSi_3O_8 , by which converting insoluble

potassium in the framework of KAlSi_3O_8 to soluble species, is the first assignment for preparation of various potassium compounds from insoluble potassium ore. Potassium feldspar has a stable three dimensional $[\text{AlSi}_3\text{O}_8]^-$ framework that it does not react with various acid or alkali except hydrofluoric acid at normal temperature and pressure. At the temperature of $(1\ 150 \pm 20)$, potassium feldspar begins to incongruent melt, broken down into leucite and fused

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mass phase rich in silica; whereas when the temperature of reaction drops, the leucite tends to react with silica to form KAlSi_3O_8 again. It is therefore not feasible to decompose KAlSi_3O_8 merely by calcination at high temperature. It is thus necessary to decompose KAlSi_3O_8 completely by adding flux agents, which could substantially lower the temperature of the decomposing reaction of KAlSi_3O_8 .

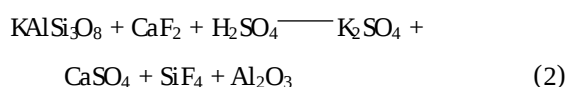
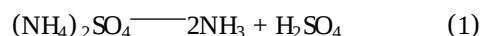
Recently there are many research^[2-43] on decomposition of KAlSi_3O_8 at home and abroad, mainly concentrating on the control of processing condition, seldom dealing with thermodynamic analysis on decomposition reaction of KAlSi_3O_8 . This research is mainly concentrated on the thermodynamic analysis, which hopefully provides the theoretical basis for decomposition of KAlSi_3O_8 at intermediate temperature, and is proved accurate and valid by the current experiments in laboratory. Research on decomposition of KAlSi_3O_8 with sodium carbonate or potassium carbonate as flux agent is not reported in literature up to now. This research is thus a new effort to explore decomposition of KAlSi_3O_8 in both of thermodynamics and laboratory experiments.

1 REVIEW OF DECOMPOSITION OF KAlSi_3O_8

Currently, methods of decomposition of KAlSi_3O_8 mainly include decomposition of KAlSi_3O_8 at normal pressure and low temperature, leaching of potassium at high pressure by hydrochemistry, decomposition of KAlSi_3O_8 at intermediate temperature and fusion of KAlSi_3O_8 with alkali at high temperature.

1.1 Decomposing KAlSi_3O_8 at low temperature^[3,4]

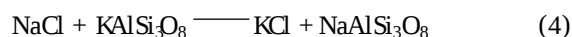
Potassium feldspar can be decomposed by low temperature calcinations at normal pressure with the existence of $(\text{NH}_4)_2\text{SO}_4$, H_2SO_4 and CaF_2 . Chemical reactions are as follows:



Experiments show that fluoride and sulfate play a significant role in the decomposition of KAlSi_3O_8 by low temperature calcination. As heated to the temperature of 200, the admixture of fluorite (CaF_2) and sulfuric acid (H_2SO_4), which functions similarly with that of hydrogen fluoride in decomposition of KAlSi_3O_8 . Fluorine ion (F^-) released in the process of adding fluorite to H_2SO_4 at the temperature of 200 can also destroy the structural framework of KAlSi_3O_8 and leach the potassium ion (K^+) into the solution.^[3] By this method, it is likely to decomposing KAlSi_3O_8 at low temperature, but it will produce a great amount of ammonia gas, accompanied by the overflow of hydrogen fluoride, which will be harmful to the operators and the surrounding environment.

1.2 Leaching potassium with sodium chloride (NaCl)^[5,6]

The process of melt-leaching potassium from KAlSi_3O_8 with NaCl is a reversible reaction, which is expressed as follows:

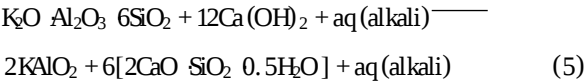


During the reaction, K^+ within the solid phase is replaced by sodium ion (Na^+), and then dissolved into the solution. As reaction goes further, concentration of K^+ in the solid phase gradually decreases, whereas that in the liquid phase increases correspondingly. At last a dynamic equilibrium occurs, and the leaching ratio of potassium reaches maximum. The reaction takes place between the liquid and solid phases, and only as NaCl is melted thoroughly, the leaching ratio of potassium reaches higher value. If the reaction temperature is too high, the leaching ratio will be lowered due to calcination of KAlSi_3O_8 . The appropriately temperature is 890 - 950 with mass ratio of NaCl to KAlSi_3O_8 as 1:1.^[5] The leaching ratio of potassium in the reaction is restricted by the equilibrium constant, and hard to reach a higher value. Moreover the reaction will take a rather long period to reach equilibrium, and consume lots of energy.

1.3 Leaching potassium at high pressure by hydrochemistry^[7,8]

This technique was put forward by the Soviet Union

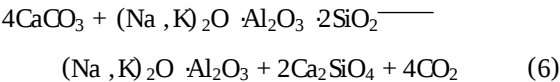
scientists in fifties. However, it has not yet industrialized because of some technical difficulties. In this method, the powder of KAlSi_3O_8 was mixed with lime and alkali lye, and then transferred to high-pressure reaction kettle to proceed hydrochemical reaction.^[7] The principle of reaction is as follows:



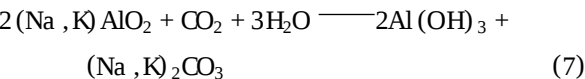
The leaching ratio of kali (K_2O) can reach 80 % and that of alumina is over 75 %. This technique is promising, especially with the perfection of the technique of leaching potassium through pipeline at high pressure, it is hopefully to be industrialized in the near future. However, it still demands improvement in certain key techniques, especially the choice of flux agent.

1.4 Decomposition of KAlSi_3O_8 by calcination with limestone^[9]

Russian, poor in alumyite resource, began to produce alumina, alkali carbonate and Portland cement from nepheline syenite in early fifties. The main process is that the vaned powder of nepheline syenite is mixed thoroughly with that of limestone and then calcinated at 1 300 . Beta β -dicalcium silicate and aluminate (potassium aluminate and sodium aluminate) generate in the process. The chemical reaction is as follows:



As soon as the resultant (solid phase) of the above reaction enters in sodium hydroxide solution, the alkali aluminate dissolves into the liquid phase, while the dicalcium silicate is still insoluble. When the aluminate solution reacts with CO_2 by virtue of Eq. (7), the aluminum hydroxide precipitates, while the alkali carbonate is still in solution. In this way, the different solid phases are separated from the alkali aluminate solution through selective crystallization.

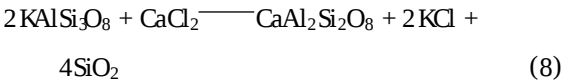


Mixed materials of β -dicalcium silicate with limestone, low grade bauxite and slag of pyrite are calcinated at 1 600

, and Portland cement is produced by mixing the calcinated chamotte with β -dicalcium silicate (15 %, in mass, the same below) and gypsum (5 %), and grinding by ball mill.^[9] The Institute of Aluminum Industry Inc. of Shandong adopts a similar technique to prepare potassium carbonate, aluminum hydroxide, silicon fertilizer from potassium-rich slate. This reaction requires a higher temperature to decompose KAlSi_3O_8 , and thus a higher consumption of energy, and moreover a large amount of limestone, accompanied by serious discharge of carbon dioxide.

1.5 Decomposition of KAlSi_3O_8 with calcium chloride (CaCl_2)^[10,11]

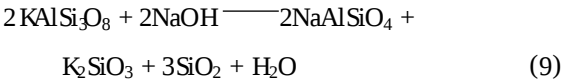
While KAlSi_3O_8 reacts with CaCl_2 at high temperature, K^+ in KAlSi_3O_8 is substituted by calcium ion (Ca^{2+}) in CaCl_2 , resulting in the generation of anorthite and dissolvable potassium. The chemical reaction is as follows:



When the amount of calcium chloride exceeds the stoichiometric value, the leaching ratio of potassium is up to 85 %, then remains constant.^[10,11] Waste residues, i. e., anorthite produced in this reaction is difficult to be comprehensively utilized.

1.6 Decomposition of KAlSi_3O_8 with sodium hydroxide (NaOH)^[10]

While KAlSi_3O_8 , mixed with NaOH , is calcinated at about 500 , the resultant after leaching has the structure of nepheline, as indicated by XRD analysis. The chemical reaction is as follows:

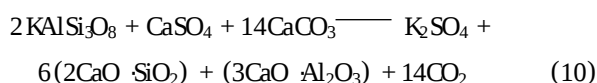


Equation(9) indicates that the structure of KAlSi_3O_8 must be transferred into that of nepheline by NaOH , accompanied by the increase of the leaching ratio of potassium.^[10] As the ratio of KAlSi_3O_8 to NaOH is taken as 1 : 1 by mass, the leaching ratio of potassium reaches 98.06 %. This technique will generate a mass of waste residues, similar to that with CaCl_2 as flux agent, the principal solid

phase is nepheline, of which with a small amount of total iron could be raw materials of silicate glasses and ceramics.

1.7 Decomposing KAlSi_3O_8 to prepare potassium sulfate (K_2SO_4)^[12]

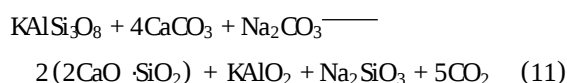
Potassium feldspar can be thermally decomposed, with gypsum and calcium carbonate (CaCO_3) as additives, to prepare K_2SO_4 . The chemical reaction is as follows:



The conditions at which Eq. (10) takes place are that the mass mixture with proportions of $\text{KAl} \cdot \text{Si}_3\text{O}_8$ to gypsum to CaCO_3 as 1 : 1 : 3.4 is calcinated at 1 050 °C for 2.0—3.0 h. The decomposition ratio of KAlSi_3O_8 reaches 92.8 % - 93.6 %.^[12] Potassium feldspar is decomposed at a higher temperature in this system. Meanwhile a mass of CaCO_3 is consumed, accompanied by discharge of a large amount of carbon dioxide. Combining the procedure to prepare K_2SO_4 with that to produce cement makes this technique promising.

1.8 Decomposition of KAlSi_3O_8 with sodalime^[13]

Potassium feldspar can be decomposed at high temperature, with lime, CaF_2 and Na_2CO_3 as composite additives. The chemical reaction is as follows:

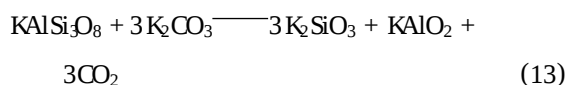
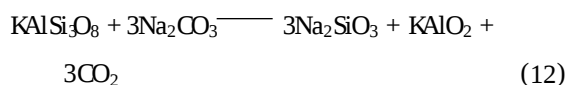


Both of potassium and aluminum in KAlSi_3O_8 are transferred into soluble potassium metaaluminate and sodium metasilicate. Residues after leaching and separated from alkali solution, can be used as cement raw material.^[13]

The optimal decomposition temperature is at 1 280 - 1 330 °C, and during calcinations the average volatilization rate of potassium oxide is up to 24.22 %, but most of volatile potassium oxide can be reclaimed through chimney neck. This technique requires more energy consumption, as the higher calcinations temperature, resulting in severe volatilization of potassium oxide, which is difficult to be dealt with in practice.

1.9 Decomposition of KAlSi_3O_8 at intermediate temperature^[14,15]

Potassium feldspar, with sodium carbonate (Na_2CO_3) or potassium carbonate (K_2CO_3) as additives, can be decomposed by calcination at intermediate temperature (820—860 °C). Chemical reactions are as follows:



Potassium and aluminum in KAlSi_3O_8 are transferred into soluble potassium metaaluminate and sodium metasilicate during the process. While K_2CO_3 is only used as flux agent, a pure solution consisted mainly of potassium metaaluminate and potassium metasilicate will be obtained. After the process of acidification by entrance of CO_2 and leaching, a liquid solution of K_2CO_3 - Na_2CO_3 and colloid precipitant mainly composed of metasilicate and metaaluminate are obtained respectively by filtration. After further separation and purification, high-grade K_2CO_3 can be prepared, meanwhile high-profit by products such as 13X zeolite and white carbon black, or mineral polymer can also synthesized or manufactured.^[14—17] High profits of products offset the disadvantage of higher price of the flux agent (K_2CO_3 and Na_2CO_3). The decomposition rate of KAlSi_3O_8 is up to more than 98 %. As the relatively low decomposition temperature and energy consumption, there is almost no volatilization loss of K_2O during the process. This technique is hopeful to be industrialized in the near future, considering both of economic benefits and completely clean-processing with kindness to the local environment.

2 THERMODYNAMIC ANALYSIS ON DECOMPOSITION OF KAlSi_3O_8

2.1 Analysis of phase diagram containing KAlSi_3O_8 ^[18]

In phase diagram of the leucite - SiO_2 system (Fig. 1), it is indicated that KAlSi_3O_8 can be thermally decomposed with no flux agent. When calcination temperature

risers to $(1\,150 \pm 20)$, KAlSi_3O_8 , an incongruent melting mineral in the system , begins to incongruent melt and form a solid phase of leucite and a fused liquid phase rich in silica. The reaction goes further at the constant temperature until KAlSi_3O_8 is fully decomposed. With temperature increased again , resultant leucite continues to melt. While the system is cooling , the fused liquid phase equilibrated with leucite , starts to crystallize leucite again. As soon as the temperature drops to the peritectic point , such a peritectic process as granite + fused phase — potassium feldspar occurs. In other words , leucite originally precipitated melts into the fused phase to form KAlSi_3O_8 . Figure. 1 shows that structural transformation of KAlSi_3O_8 completes a circulation , *i. e.* , potassium feldspar — leucite + fused phase — potassium feldspar , with the increase and the drop of temperature correspondingly. Therefore , under conditions of decomposition of KAlSi_3O_8 with no flux agent , while calcination temperature exceeds $(1\,150 \pm 20)$ and maintained for enough time , KAlSi_3O_8 will change into leucite and silica glass at high temperature , whereas KAlSi_3O_8 is precipitated once again when the temperature declines. If the content of silica in the liquid phase can be reduced during the process of calcination , reactions as follows will take place in the system :

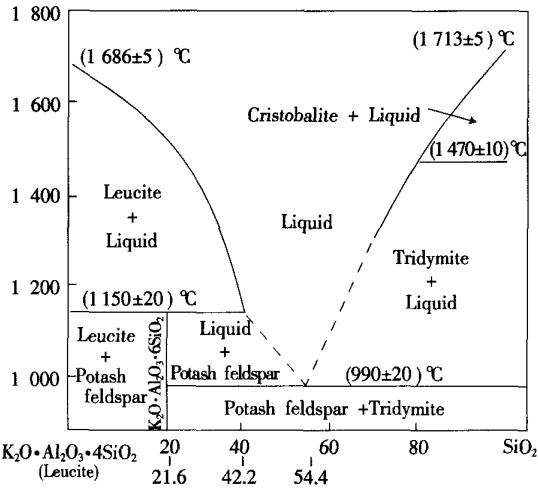
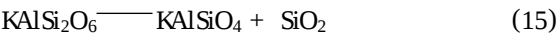
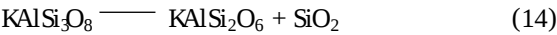


Fig. 1 Phase diagram of leucite — SiO_2 system^[18]



If appropriately flux agents are added to the system to react with SiO_2 , reactions depicted above will proceed towards the right direction , resulting in complete decomposition of KAlSi_3O_8 . This is the theoretic basis of decomposition of KAlSi_3O_8 with flux agent.

2. 2 Calculation of Δr_{G_m} for decomposition of KAlSi_3O_8 ^[19]

The Gibbs free energy (Δr_{G_m}) of chemical reactions is a criterion of direction of thermochemical reaction. Gibbs put forward that : Δr_{G_m} is a criterion of spontaneous thermochemical reaction process , at the premise of no non-volume work , in a closed system at constant temperature and pressure. Namely : $\Delta r_{G_m} < 0$ spontaneous process , reaction of chemistry can spontaneously proceeds ; Here $\Delta r_{G_m} = 0$ equilibrium state ; And $\Delta r_{G_m} > 0$ non-spontaneous process , reaction of chemistry can reversely proceeds. During the process of decomposition of KAlSi_3O_8 at intermediate temperature , using Na_2CO_3 and K_2CO_3 as additives , the chemical reactions are given in Eqs. (12) and (13) respectively.

Δr_{G_m} of Eqs. (12) and (13) at the temperature of 900 , 1 000 , 1 100 , 1 200 K are calculated according to the thermodynamic method in literature [19]. Owing to lack of thermodynamic data of potassium metaaluminate , Δr_{G_m} of Eq. (12) is taken as the sum of that of Eqs. (17) and (19) , Δr_{G_m} of Eq. (13) as the sum of that of Eqs. (18) and (19) , and the average value of Δr_{G_m} of Eqs. (20) and (21) as the value of Δr_{G_m} of Eq. (19) . All of the thermodynamic data are taken from literature [19 — 21]. Calculation results are referred in Tab. 1.

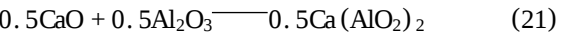
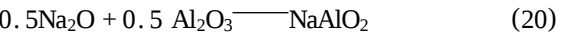
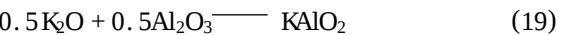
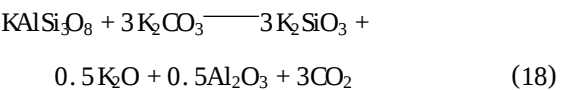
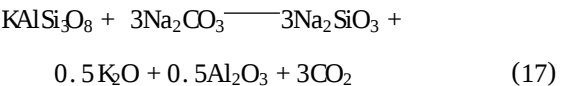


Table 1 Calculated ΔrG_m for thermal decomposition reactions of $KAlSi_3O_8$ at intermediate temperature

T/ K	900	1 000	1 100	1 200
$\Delta rG_m(18)/(kJ \cdot mol^{-1})$	49.24	8.74	31.14	- 71.14
$\Delta rG_m(19)/(kJ \cdot mol^{-1})$	58.11	8.49	- 38.05	- 72.28

Considering that ionic radius of potassium lies between those of sodium and calcium , resulting in that the chemical activity of potassium also lies between sodium and calcium , here ΔrG_m of Eq. (19) is taken as the average value of those of Eqs. (20) and (21) . It can be seen from Tab. 1 that at the temperature of 1 100 K (827) , and ΔrG_m is notable negative , indicating that reactions will take place. Taking principal factors which possibly influence the reactions substantially into consideration , decomposition temperatures of $KAlSi_3O_8$ with K_2CO_3 or Na_2CO_3 as flux agent should be above 800 and below the melting point of flux agent , which is 851 for anhydrous Na_2CO_3 , and 891 for K_2CO_3 respectively , *i. e.* , potassium feldspar must be decomposed at a temperature ranging from 800 to 890 . The decomposition reaction must take place at a higher temperature while using K_2CO_3 as additive than using Na_2CO_3 , due to a higher melting point of K_2CO_3 .

3 EXPERIMENTS AND DISCUSSION

3.1 Materials

Potassium feldspar powder materials used in present work are prepared from $KAlSi_3O_8$ ores as follows : potash slate from Baiyunebo of inner Mongolia (BYEB - 1) , potassium feldspar powder from Shaxian of Fujian province (FSX - 1) , potassium feldspar powder from Chicheng of Hebei province , which is a tailing waste of gold deposit hosted in syenite (HBCC - 1) , pseudoleucite phonolite from Zijinshan of Shanxi province (SXLX - 1) , and potash shale from Fengxian of Jiangshu province (JSFX - 1) . On the basis of wet bulk chemical analyses and XRD analysis data , according to the mass balance rule ,^[22] contents of principal minerals of the potassium ore are calculated by LINPRO ,^[23] a FORTRAN77 program with the simple linear programming algorithm , and listed in Tab.2. Chemical analysis results of $KAlSi_3O_8$ ores are referred in Tab. 3. Potassium carbonate and sodium carbonate used in the experiments are both analytically pure chemical reagents.

Table 2 Calculated mineral contents of $KAlSi_3O_8$ ores w/ %

Sample	Micro-cline	Quartz	Biotite	Sericile	Illite	Dolomite	Pyrite	Hemanite	Ilmenite	Magr-ite	G�ethite	H�rnbr-hende	Augite	Apatite	Rutile
BYEB - 1	73.6		14.4			3.6	5.1					1.0		0.4	
FSX - 1	84.2	9.8	3.1							0.2					
HBCC - 1	86.2	7.5					0.5			0.6			5.2		
SXLX - 1	83.0			10.0				5.8	0.8	0.1					
JSFX - 1	78.5				10.2	1.7					8.5			0.3	0.7

Table 3 Chemical analysis of $KAlSi_3O_8$ powder w/ %

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	H ₂ O ⁺	LI	�
BYEB - 1	56.00	0.32	14.65	2.92	5.69	0.14	1.72	2.17	1.23	13.00	0.05	0.48	1.17	99.54
FSX - 1	66.00	0.12	17.46	0.28	0.24	0.01	0.52	0.80	2.48	12.03	0.03	0.05		100.02
HBCC - 1	63.43	0.20	15.80	1.33	1.02	0.06	0.87	2.09	2.95	9.12	0.09	0.99	1.94	99.98
SXLX - 1	56.16	0.40	20.82	5.64	0.43	0.17	0.06	0.73	0.34	12.82	0.17	1.62	0.37	99.73
JSFX - 1	54.86	0.72	17.57	8.31	0.16	0.08	0.39	0.78	0.37	13.82	0.29	2.00	0.09	99.64

3.2 Methods

Potassium feldspar powder mixed with flux agent is ground by vibrating mill to a grain size less than $74\ \mu\text{m}$. The mixture material is laid into a corundum porcelain crucible, and calcinated in the muffle. Then the crucible is cooled in air. The decomposition rate of KAlSi_3O_8 is measured by the following procedure: put the calcinated chamotte into a nitric acid solution with concentration around 15 % in volume; after stirred up fully, the solution is filtrated to separate out insoluble substance; the mass of which after dried at 105°C for 12 h is postulated as m_2 , and the mass of KAlSi_3O_8 powder in the mixture material as m_1 ; the decomposition rate is calculated from an expression as: $(m_1 - m_2) / m_1 \times 100\%$.

3.3 Results and discussions

3.3.1 Flux agents As for the choice of flux agents, taken into consideration should be the following major elements:^[24] The flux agent should contain such ingredient that could efficiently break down the stable Si—Al—O structural framework of KAlSi_3O_8 ; The flux agent should contain such a cation, the radius of which is less than that of K^+ , possibly a substitute for K^+ in the framework of KAlSi_3O_8 ; The melting point of the flux agent should be as low as possible, which makes it possible to decompose KAlSi_3O_8 at such a temperature that the flux agent comes near to fusion.

Anhydrous Na_2CO_3 , with melting point 851°C , is widely used as fusing agent in analytical chemistry. Generally, silicate rock, clay, kaolinite, oxide, carbonate, and fluoride are usually decomposed with Na_2CO_3 as flux agent. Potassium carbonate, with melting point 891°C , is prone to deliquesce, and less used as flux agent alone. The mixture of Na_2CO_3 and K_2CO_3 , with a lowest melting point of 712°C at 46 % (in mole) K_2CO_3 . While using this mixture material as flux agent to decompose silicate, the decomposi-

tion temperature can be substantially lowered.

Although the cost of either Na_2CO_3 or K_2CO_3 is higher than that of limestone, the decomposition temperature of KAlSi_3O_8 is much lower than that with the latter as flux agent. As a result, the energy consumption in the latter case is lowered correspondingly. Meanwhile the comprehensive utilization of KAlSi_3O_8 , with high profits of by-products in addition to high-grade K_2CO_3 product, could also compensate for the shortage of higher cost of sodium carbonate or K_2CO_3 as flux agent. In recent years, Ma *et al.* have developed several techniques to prepare such high profit products as electronic grade K_2CO_3 , 13X zeolite molecular sieve, white carbon black, and various mineral polymer *etc.* from insoluble potassium ores.^[14–17] Therefore, it is important to advance the technique of decomposition of KAlSi_3O_8 with Na_2CO_3 or K_2CO_3 as flux agent.

3.3.2 TG—DTA analysis Given in Fig. 2 is TG—DTA curves for decomposition of the mixture material of KAlSi_3O_8 powder with Na_2CO_3 and K_2CO_3 as flux agents.

Both curves in Fig. 2 show a broad, demulcent and smooth exothermic peak at a temperature around 300°C , indicating a weak exothermic effect of microcline at temperature of 380°C and the oxidation and burnout of other impurities. Owing to lost the absorbed water of K_2CO_3 in the mixture materials, curve of TG—KS shows distinct mass loss before 100°C . Curve of TG—NS shows distinct mass loss from 600°C to 850°C , and also the TG—KS curve, from 700°C to 900°C , accompanied by the occurrence of endothermal valleys at the curves of DTA. Obviously during the process of decomposition for KAlSi_3O_8 , the two terminals of temperature range correspond respectively to initiative and terminated temperatures of decomposition for KAlSi_3O_8 with two different additives. The decomposition temperature range obtained by TG—DTA analysis basically corresponds to that deduced through $\Delta_r G_m$ calculation.

Thermogravimetry curves show that ultimate mass loss of admixture for KAlSi_3O_8 and Na_2CO_3 is 22.63 %, that of admixture of KAlSi_3O_8 and K_2CO_3 is 18.45 %, basically equivalent to theoretical mass losses calculated from Eqs. (12) and (13), indicating that those two equations to describe the process of decomposition of KAlSi_3O_8 are credible.

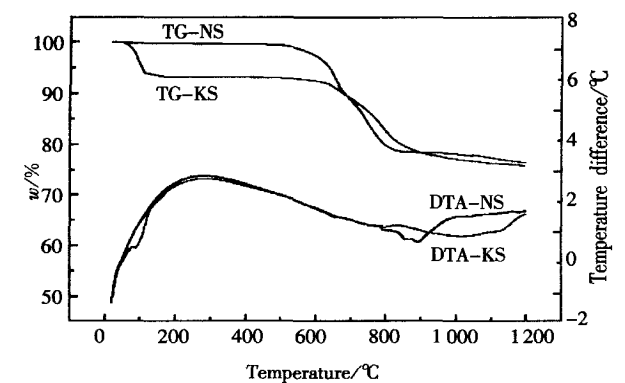


Fig. 2 TG- DTA curves of decomposition for KAlSi_3O_8 ore powder
NS —With Na_2CO_3 as addition agent ; KS —With K_2CO_3 as addition agent

3.3.3 Experiment discussions Table 4 shows that with different additives as flux agents, calcination results are as follows: The decomposition rate with Na_2CO_3 as flux agent is the best, but at a relatively higher decomposition temperature of 830. The decomposition rate with the mixture of Na_2CO_3 and K_2CO_3 as flux agent is inferior to the former, but at a decomposition temperature as low as 740, as the lower decomposition temperature of KAlSi_3O_8 with admixture as flux agent. Potassium carborate is used as flux agent, the chamotte is already over-calcined at temperature of 740, and sintered at above 800. Therefore, the decomposition reaction with K_2CO_3 is different from that with Na_2CO_3 as flux agent. It could be explained that K_2CO_3 is easy to deliquesce, resulting in beforehand appearance of liquid in calcinating, enhancing the chamotte easy to sinter. The compact-sin-

tered chamotte is quite soluble in water, so the sintered status of chamotte does not affect the leaching process. X-ray diffraction analysis (Fig. 3) indicates that the calcination chamotte is mainly composed of sodium (potassium) metasilicate and potassium (sodium) metalluminate.

Table 4 Experimental results for calcination of KAlSi_3O_8 with different additives

$m(\text{Na}_2\text{CO}_3)/\text{g}$	Calcination temperature/	Calcination time/ h	Decomposition rate/ %	State of calcined KAlSi_3O_8
9.8	830 —825 *	1.5 —1.0	98.4	Loosen
9.8	830	2.0	96.1	Loosen
$m(\text{Na}_2\text{CO}_3)/\text{g}$	Calcination temperature/	Calcination time/ h	Decomposition rate/ %	State of calcined KAlSi_3O_8
3.0/ 8.8	740	2.5	98.0	Rigid
4.0/ 7.6	740	1.5	94.2	Rigid
$m(\text{K}_2\text{CO}_3)/\text{g}$	Calcination temperature/	Calcination temperature/	Decomposition rate/ %	State of calcined KAlSi_3O_8
11	860	1.5	98.6	Sinter
11	740	2.5	59.0	Very rigid
10	710	2.5	35.7	Rigid

Note :10 g KAlSi_3O_8 powder was used for each calcination experiment. * Quadri-calcine

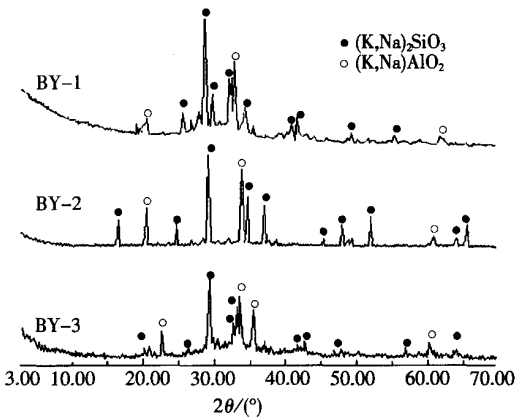


Fig. 3 XRD patterns of the calcined KAlSi_3O_8
BY- 1 —Addition agent : Na_2CO_3 ; BY- 2 —Addition agent : K_2CO_3 ; BY- 3 —Addition agent : $\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$

This technique of decomposition of KAlSi_3O_8 at moderate temperature is suitable for various types of KAlSi_3O_8 ores. Listed in Tab. 5 are optimal conditions for thermal decomposition of different types of KAlSi_3O_8 ores with

Na₂CO₃ as flux agent. Processing conditions of decomposition for KAlSi₃O₈ at moderate temperature less vary for different types of KAlSi₃O₈ ores, with various bulk chemical compositions and mineral concentrations, from different localities. The decomposition rate is up to over 98 % for KAlSi₃O₈ powders calcinated at temperature of 820 —850 for 1.5 —2.5 h. The optimal decomposition temperature obtained from experiments is in the range of that predicted by thermodynamic calculation, indicating that it is believable to evaluate the decomposition temperature of KAlSi₃O₈ by thermodynamic method.

Table 5 Optimal conditions for thermal decomposition of various types of KAlSi₃O₈ ores

Sample	<i>m</i> (Na ₂ CO ₃)/g	Calcination temperature/	Calcination time/h	Decomposition rate/ %
BYEB - 1	8.9	820 —830	2.0	98.4
FSX - 1	8.1	840 —850	2.5	99.2
HBCC - 1	7.4	800 —830	1.5 —2.0	98.6
JSFX - 1	7.9	820 —825	2.5	98.6

Note :10 g KAlSi₃O₈ powder was used for each calcination experiment.

In conclusion, decomposition of KAlSi₃O₈ with Na₂CO₃ or K₂CO₃ as flux agent is feasible. The present work demonstrates that the decomposition rate is over 98 % for various types of insoluble KAlSi₃O₈ ores from several localities. Appearance of the calcination chamotte varies along with the adapted flux agent. If Na₂CO₃ is used, the chamotte is loosen, and KAlSi₃O₈ is decomposed completely before the occurrence of sinter; whereas if K₂CO₃ is used, the chamotte is often rigid, and KAlSi₃O₈ is only decomposed completely after the occurrence of sinter.

3.3.3 Analysis of mechanism for decomposition reaction

Decomposition of KAlSi₃O₈ with additive as flux agent is a complicated physicochemical process. At the beginning of the reaction, solid reaction depends on diffusion between particles of KAlSi₃O₈ and the additive. Factors which influence the diffusion process involve the crystal structure of solid, imperfection inside the solid, superficial structure of solid, average size of solid particles, and reaction

temperature etc. in addition to general rules of chemical reactions. Usually, temperature has a great influence on the occurrence of a reaction and the reaction rate. Atoms and ions inside oxides and silicates are combined by covalent bond or ionic link, resulting in stable structures and low diffusion rates. Therefore, a solid reaction between silicates and oxides usually can only proceed at high temperatures. For majority of chemical reactions, the reaction rate increases with increasing temperature. Equation Arrhenius ($\ln K = \ln A - E_a/RT$) shows the influences of temperature and the activation energy on reaction rate.^[25] Here, E_a , is the activation energy of the process, A , a pre-exponential factor, are both constants; K is a constant of reaction rate; R is the gas constant; T is absolute temperature. Besides temperature, the state of solid materials also has important influence on solid reaction rate.^[13] For example, the exhaust of carbon dioxide, which changes the contact state between solid particles, affects the solid reaction rate. At the temperature of lowest congruent melting point, liquid phase appears. Under action of the high temperature liquid, materials starts to sinter, the appearance of which changes from loosen to compact, accompanied by the decrease of volume, and KAlSi₃O₈ passes through the stage predominated by single decomposition entering that by simultaneously decomposition and sinter. During the course of sinter, contents of the liquid gradually increase correspondingly with increasing temperature and prorogating time, accompanied by dissolution and diffusion of the solid phase and occurrences of new substances, and finally KAlSi₃O₈ is fully decomposed.

The process of decomposition for KAlSi₃O₈ will become complicated due to existence of secondly phases and organic matters. Follows will take place during the process of decomposition: (1) The dehydration and decomposition of clay minerals to eliminate the constituting water. *e. g.*, kaolinite is dehydrated at 500 —700, and montmorillonite and illite, at 600 —750 and 400 —600 respectively. (2) The decomposition of carbonate. *e. g.*, $MgCa(CO_3)_2 \longrightarrow CaO + MgO + 2CO_2$, at 730 —900 (3) The oxidation of organic substances. $C_{organic} + O_2$

—CO₂, at more than 350 (4) The decomposition and oxidation of ferrous sulfide. *e. g.*, FeS₂ + O₂ — FeS + SO₂, at 350—450 ; and 4FeS + 7O₂ — 2Fe₂O₃ + 4SO₂, at 500—800

4 CONCLUSIONS

The thermodynamic calculation indicates that the decomposition temperature of KAlSi₃O₈ with alkaline carbonates as additives is at 800—890 , optimal decomposition temperatures for various types of KAlSi₃O₈ ores from several localities determined by experiments are in consistent with those predicted by thermodynamic calculations, which proves the validity of thermodynamic approach. Experiments show that it is feasible to decompose KAlSi₃O₈, with Na₂CO₃ or K₂CO₃ as flux agent, at moderate temperature ranging from 820 to 850 , and the decomposition rate is over 98 %. Compared with decomposition of KAlSi₃O₈ with limestone as flux agent, this technique requires much less energy consumption, and still with little amount of K₂O volatilization wastage during the process. It is possible to design such a process based on this technique that the whole procedure is clean and environmental kindness, and high profits products produced thereby could compensate the disadvantage of higher cost of alkaline carbonate additives. The comprehensive exploitation and utilization of insoluble KAlSi₃O₈ resources in China based on the technique developed in this research is therefore prospective to be industrialized in the near future.

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