A case study targeting K fertilizer chemical synthesis with complete valorization of extraction by-products options

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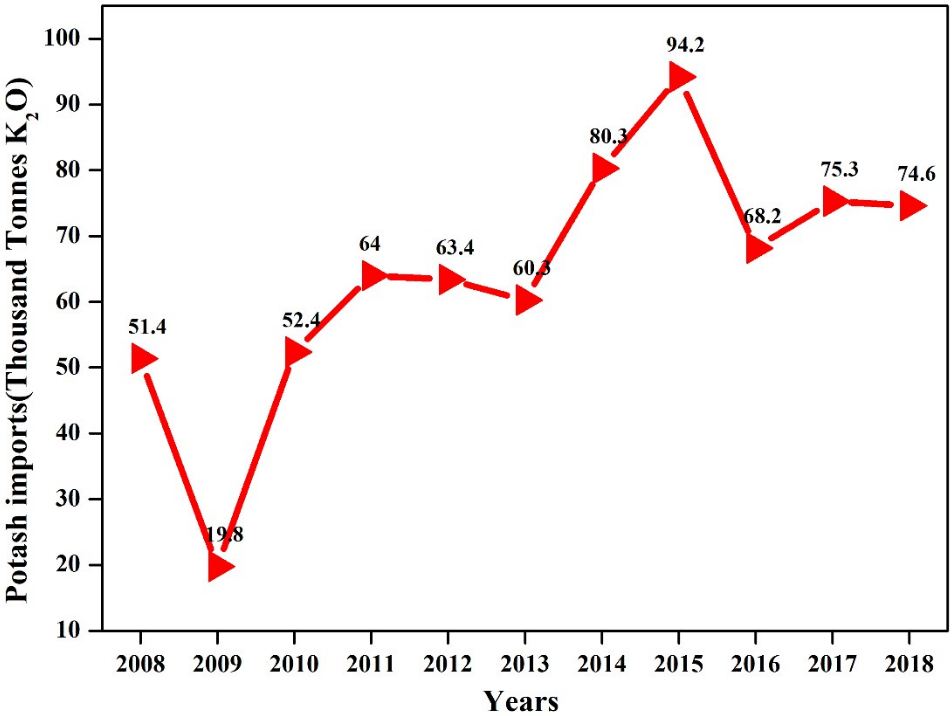

Figure S1. The changes of potash imports in China (Thousand Tonnes K_2O) from 2008 to 2018 in China.

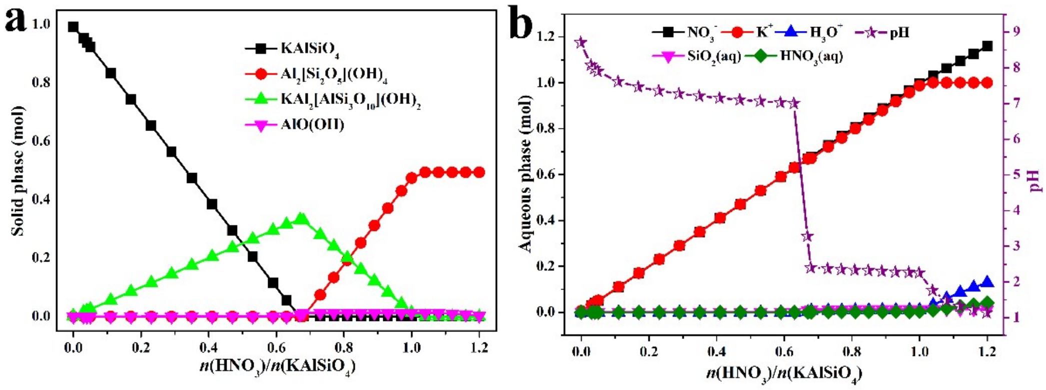

Figure S2. Thermodynamic calculation results of the relations of solid- aqueous phase and n(H^+/K^+) Using OLI Analyzer 9.6.

Some introduction about Figure S2:

The Figure S2 is the thermodynamic calculation results of the relations of solid-aqueous phase and $n(H^+/K^+)$ before experiments. It shows only the calculation when the $n(H^+/K^+)$ is 0.67 where pure muscovite can be obtained. At other conditions, there would be kalsilite and kaolinite. In addition, the pH value suddenly drops from 7 to 3.2 at the point where muscovite shows maximum value, indicating the pH value range of muscovite formation is close to 3.

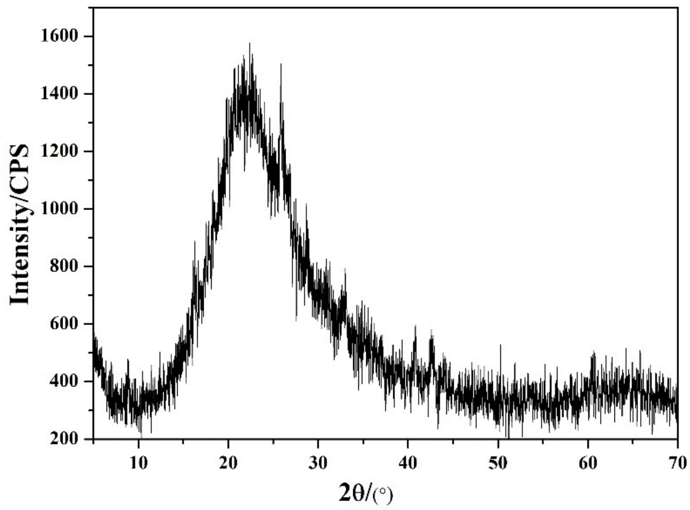

Figure S3. The XRD pattern of Calcined kaolin.

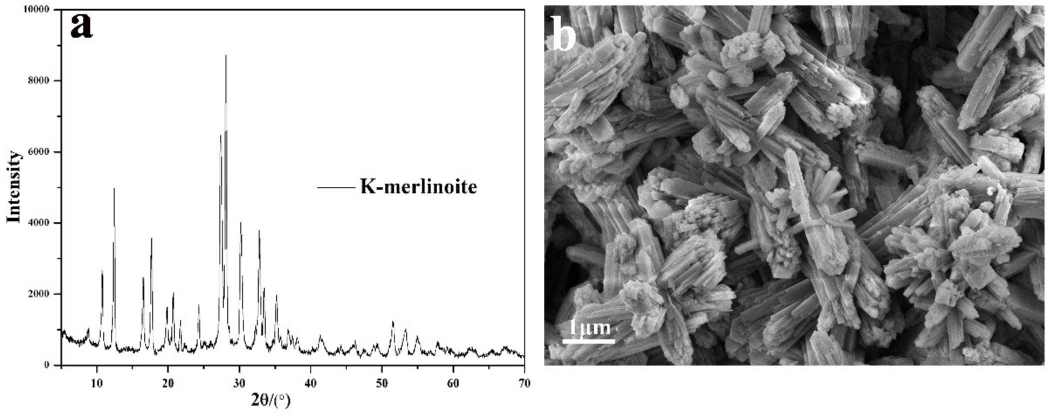

Figure S4. The XRD pattern [ICDD-PDF No. 00-02-0989 (2020)] and SEM image of K-merlinoite as synthesized from AS.

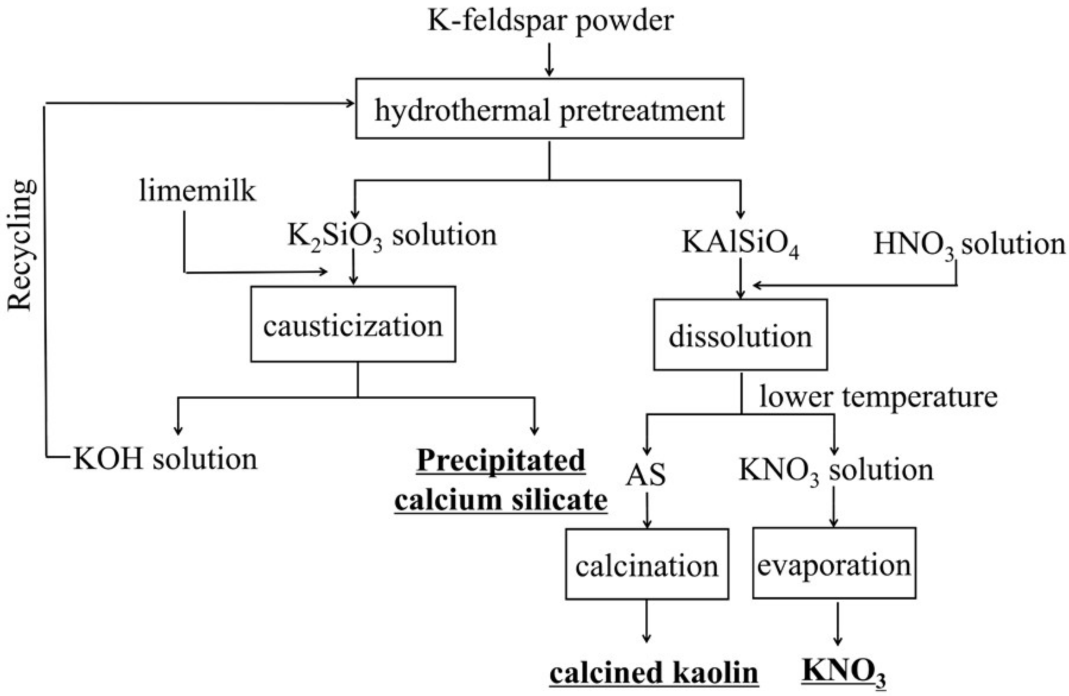

Figure S5. Flow sheet of whole technique to obtain KNO_3 and calcined kaolin.

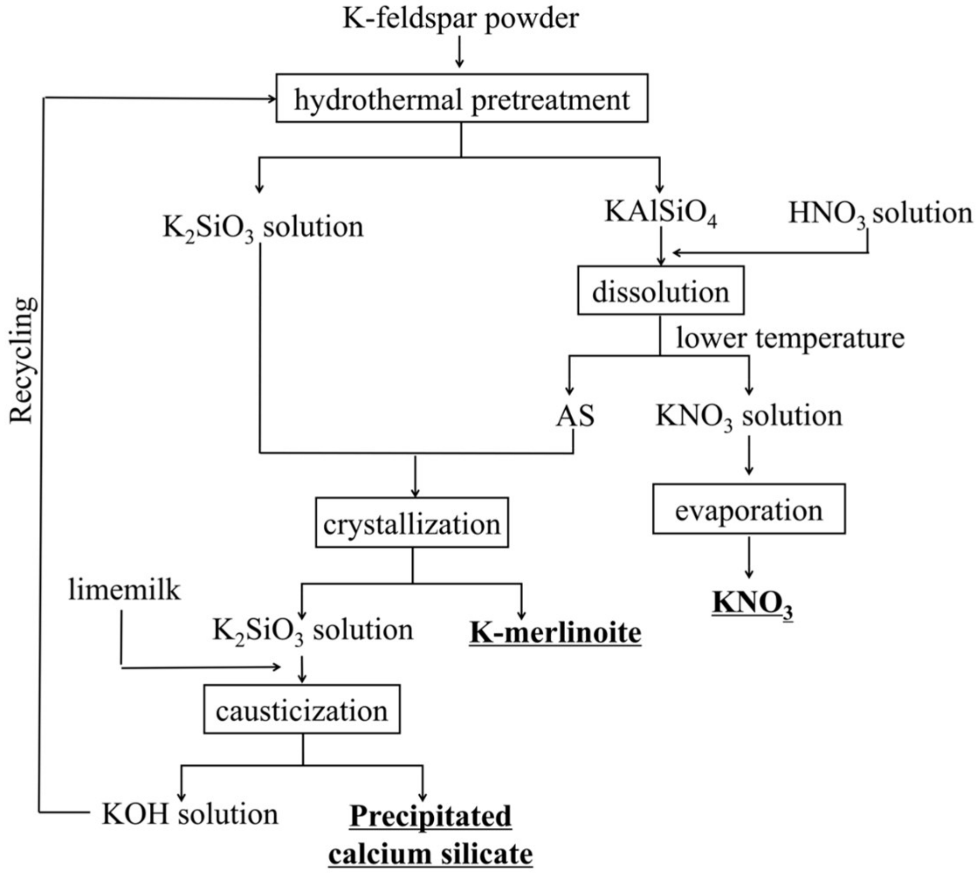

Figure S6. Flow sheet of whole technique to obtain KNO_3 and K-merlinoite.

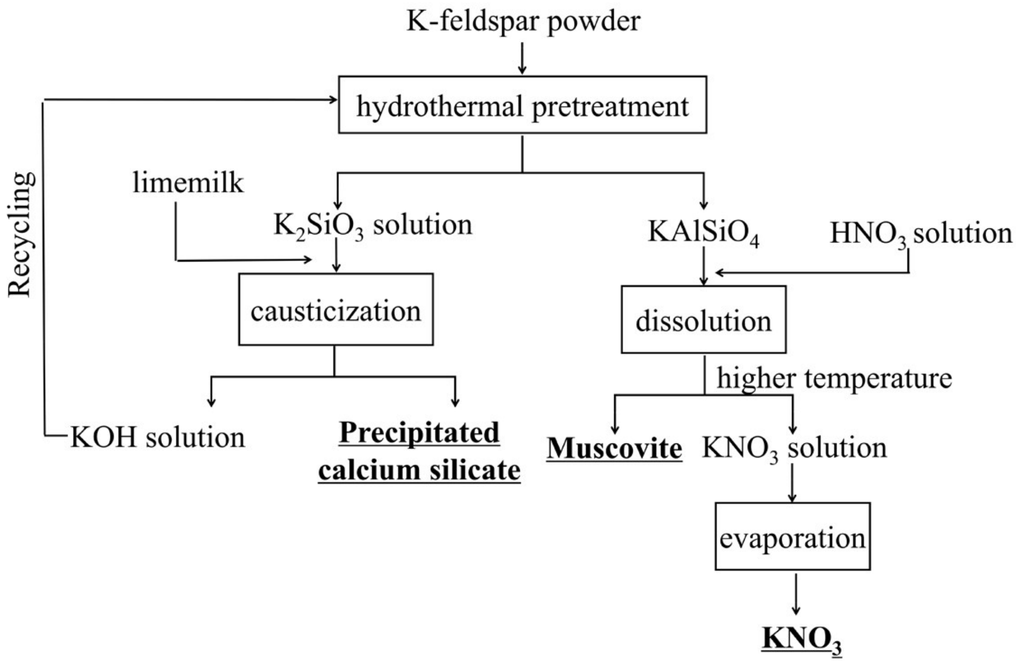

Figure S7. Flow sheet of whole technique to obtain KNO_3 and muscovite.

Table S 1. Summary of raw sources and reaction conditions for the synthesis of kaolinite in previous studies.

Synthesis method	Raw materials	Reaction time	Temperature	Ref.
Sol-gel method	Na_2CO_3, K_2CO_3, $Al(OH)_3$, SiO_2	-	850~990 ºC	[1]
	SiO_2, $Al(NO_3)_3.9H_2O$, CH_3COOK	6 days	750 ºC	[2]
	TEOS, KNO_3, $Al(NO_3)_3$	12h	862 ºC	[3]
Melting method	Muscovite, 70% KOH	1-3 weeks	410 °C	[4]
	$RbAlSiO_4$, KNO_3	16h	450 °C	[5]
Sintering method	LTA zeolite, KCl	1~2h	900~1000 °C	[6]
	Kaolinite, K_2CO_3	1~2h	700~900 °C	[7]
	K-feldspar, K_2CO_3	1~2h	800 °C	[8]
Hydrothermal method	Kaolinite, KOH solution	6h	300 °C	[9]
	Kaolinite, KOH solution	12h	300 ºC	[10]
	Microcline, KOH solution	2~8h	240 °C	[11]

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Table S2. Comparison between calculated cell parameters of synthetic kalsilite, KA-16 and standard crystal cell parameters of kalsilite

Sample names	a_0=b_0/Å	c_0/Å	α=β/°	γ/°
Synthetic kalsilite, KA-16	5.165	8.709	90	120
ICDD-PDF standard	5.159	8.703	90	120

Table S3. Chemical composition of AS (w_t%).

Sample	Al_2O_3	CaO	TFe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SiO_2	TiO_2	LOSS	SUM
AS2-01	29.86	0.14	3.13	0.85	0.05	0.00	0.04	0.02	40.58	0.04	26.76	101.47

* TFe_2O_3 = Total iron oxides as FeO and Fe_2O_3.

Table S4. Fitting results of ^{27}Al MAS-NMR spectra for the hydrothermal products as a function of hydrothermal treatment time at 250°C.

Reaction time (h)	coordination	Chemical shift	Relative area	Proportion (%)
6	Al^{IV}	51.0	14.02	55.2
	Al^{V}	22.6	3.13	12.3
	Al^{VI}	-0.07	8.27	32.5
12	Al^{IV}	58.4	10.60	44.1
	Al^{VI}	-0.07	13.43	55.9
24	Al^{IV}	61.9	6.36	31.4
	Al^{VI}	-0.07	13.90	68.6
60	Al^{IV}	61.9	14.88	50.1
	Al^{VI}	0.65	14.80	49.9

Table S5. The solid and aqueous phase composition obtained after hydrothermal reaction at 250°C for various reaction times.

Reaction time (h)	Aqueous / mol							Solid / mol				
	$SiO_{2(aq)}$	Al^{3+}	Ca^{2+}	Na^{+}	K^{+}	η (K_2O)%	pH	SiO_2	Al_2O_3	CaO	Na_2O	K_2O
6	0.0002	0.0036	0.0002	0.0002	0.037	99.3	4.29	0.0385	0.0160	0.0000	0.0001	0.0001
12	0.0008	0.0038	0.0002	0.0002	0.0318	85.2	3.56	0.0379	0.0159	0.0000	0.0001	0.0028
18	0.0003	0.0028	0.0002	0.0002	0.0306	81.8	3.39	0.0384	0.0164	0.0000	0.0000	0.0034
24	0.0006	0.0044	0.0002	0.0002	0.0256	68.5	3.61	0.0381	0.0156	0.0000	0.0000	0.0059
36	0.0009	0.004	0.0002	0.0002	0.0256	68.7	4.12	0.0378	0.0158	0.0000	0.0001	0.0058
48	0.0006	0.0038	0.0002	0.0002	0.0262	70.4	4.45	0.0381	0.0159	0.0000	0.0000	0.0055
60	0.0001	0.0038	0.0002	0.0002	0.0262	70.4	4.29	0.0386	0.0159	0.0000	0.0001	0.0055

Table S6. Chemical composition of KNO_3 products (concentration, g/L).

samples	SiO_2	Al_2O_3	CaO	K_2O	MgO	Na_2O
KN-01	1.55	0.02	0.73	35.46	0.34	0.91
KN-02	1.25	0.03	0.47	34.79	0.27	0.37

Table S7 Chemical composition of K-merlinoite (w_t%)

samples	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Loss	Total
K-merlinoite	43.85	0.05	20.40	1.66	0.00	0.02	0.10	0.18	21.22	0.01	13.02	100.51

Some descriptions about Table S8, S9, S10 and S11

A Material comsumption were calculated to assess the input and output of different whole process flows based on using 1 ton K-feldspar.

1、Reaction condition:

1) Hydrothermal pretreatment: Concentration of KOH solution= 5mol/kg, water/solid (w/w)=3.
2) The synthesis of muscovite: $n(HNO_3)/n(KAlSiO_4)$=0.71,water/solid=10.
3) The generation of AS: $n(HNO_3)/n(KAlSiO_4)$=1.1, water/solid=10

2、The washing water usage was calculated using the moisture content of filter cake and combing the usage used in experiments.

3、There are also some hypotheses:

1) Whole water in the drying process was collected for recycling
2) The filter liquid I just contains K_2O, Na_2O and SiO_2. Other contents enter into solid part.
3) In the preparation of $CaSiO_3$, the KOH solution was collected completely without other loss.

Table S8. Whole process material balance result of KNO_3 preparation and calcined kaolin synthesis (/t-potash feldspar)

Stage	Inputs	kg	Outputs	kg
Hydrothermal pretreatment	K-feldspar powder	1000.0	Kalsilite Filter cake	834.9
	Recycled KOH	815.7	Filter liquor I (Potassium Silicate solution)	4851.7
	New added KOH (90%)	28.9		
	Washing water	751.4		
Causticization	Filter liquor I	4851.7	Precipitated $CaSiO_3$ (Dried)	840.4
	lime	403.0	Water collected from the dried process (for recycling)	2521.1
	Water for preparation of limemilk	2015.0	KOH solution (for recycling)	11471.6
	Washing water	7563.4		
AS preparation	Kalsilite Filter cake	834.9	AS Filter cake	1547.5
	HNO_3 (68%)	352.9	KNO_3 solution	10896.0
	Water for HNO_3 dilution	8349.4		
	Washing water	2906.1		
Calcined kaolin prepartion	AS Filter cake	1547.5	Calcined kaolin	426.1
			Water from drying (for recycling)	1121.3
KNO_3 preperation	KNO_3 solution	10896.0	KNO_3	359.3
			Water from evaporation (for recycling)	10536.7

Table S9. Whole process material balance result of KNO_3 preparation and K-merlinoite synthesis (/t-potash feldspar)

Stage	Inputs	kg	Outputs	kg
Hydrothermal pretreatment	K-feldspar powder	1000.0	Kalsilite Filter cake	834.9
	Recycled KOH	604.9	Filter liquor I (Potassium Silicate solution)	4851.7
	Newly added KOH (90%)	263.1		
	Washing water	751.4		
AS preparation	Kalsilite Filter cake	834.9	AS Filter cake	1547.5
	HNO_3 (68%)	352.9	KNO_3 solution	10896.0
	Water for HNO_3 dilution	8349.4		
	Washing water	2906.1		
K-merlinoite preperation	AS Filter cake	1547.5	K-merlinoite	892.7
	Filter liquor I (Potassium Silicate solution)	4851.7	Filter liquor II (Potassium Silicate solution)	5348.9
			Water collected from the dried process (for recycling)	157.5
Causticization	Filter liquor II	5348.9	Precipitated $CaSiO_3$ (Dried)	506.8
	Lime	244.7	Water collected from the dried process (for recycling)	1520.4
	Water for preparation of limemilk	1223.3	KOH solution (for recycling)	9350.8
	Washing water	4561.1		
KNO_3 preperation	KNO_3 solution	10896.0	KNO_3	359.3
			Water from evaporation (for recycling)	10536.7

Table S10. Whole process material balance result of KNO_3 preparation and muscovite synthesis (/t-potash feldspar)

Stage	Inputs	kg	Outputs	kg
Hydrothermal pretreatment	K-feldspar powder	1000.0	Kalsilite Filter cake	834.9
	Recycled KOH	815.7	Filter liquor I (Potassium Silicate solution)	4851.7
	New added KOH (90%)	28.9		
	Washing water	751.4		
Causticization	Filter liquor I	4851.7	Precipitated $CaSiO_3$ (Dried)	840.4
	Lime	403.0	Water collected from the dried process (for recycling)	2521.1
	Water for preparation of limemilk	2015.0	KOH solution (for recycling)	11471.6
	Washing water	7563.4		
Muscovite synthesis	Kalsilite Filter cake	834.9	Muscovite (Dried)	502.8
	HNO_3 (68%)	227.8	KNO_3 solution	6339.8
	Water for HNO_3 dilution	5594.0	Water collected from the dried process (for recycling)	92.9
	Washing water	278.8		
KNO_3 preperation	KNO_3 solution	6339.8	KNO_3	241.5
			Water from evaporation (for recycling)	6098.3

Table S11. Overview of the inputs and outputs of the whole process in three routes with potash feldspar

Production types	Inputs	kg	Outputs	kg
KNO_3 calcined kaolin	K-feldspar	1000.0	calcined kaolin	426.1
	KOH (90%)	935.2	KNO_3	359.3
	HNO_3 (68%)	352.9	Precipitated $CaSiO_3$	840.4
	Lime (CaO)	403.0	KOH (90%)	906.3
	Water Usage	24585.4	Recyclable water	24835.0
KNO_3 K-merlinoite	K-feldspar	1000.0	K-merlinoite	892.7
	KOH (90%)	935.2	KNO_3	359.3
	HNO_3 (68%)	352.9	Precipitated $CaSiO_3$	506.8
	Lime (CaO)	244.7	KOH (90%)	672.1
	Water Usage	20791.3	Recyclable water	20960.4
KNO_3 muscovite	K-feldspar	1000.0	muscovite	502.8
	KOH (90%)	935.2	KNO_3	241.5
	HNO_3 (68%)	227.8	Precipitated $CaSiO_3$	840.4
	Lime (CaO)	403.0	KOH (90%)	906.3
	Water Usage	19202.7	Recyclable water	19363.0

Nomenclature

Description	Abbreviation
Solid to water ratios	S/L
Aluminosilicate gel	AS
X-Ray Powder Diffraction	XRD
Field Emission Scanning Electron Microscopy	SEM
transmission electron microscopy	TEM
Fourier Transform Infrared Spectroscopy	FTIR
X-ray Fluorescence Spectroscopy	XRF
Inductively Coupled Plasma-Atomic Emission Spectrometry	ICP-AES
Magic-Angle-Spinning Nuclear Magnetic Resonance Spectroscopy	MAS NMR
United States Geological Survey	USGS
Kalsilite	Kls
KNO_3 product at lower temperature	KN-01
KNO_3 product at higher temperature	KN-02
4-coordinated Al	Al (IV)
5-coordinated Al	Al (V)
6-coordinated Al	Al (VI)
Leaching ratio of K_2O from kalsilite	η (K_2O)
Concentration of K_2O in the aqueous solution obtained from the hydrothermal reaction	C (K_2O)
The K_2O contents in kalsilite	$M_{kalsilite}(K_2O)$
n is the number of bridging oxygens present in each[AlO_4] or [SiO_4] tetrahedron, and m is the substitution number of Si atoms by Al atoms	$Q^n(m\text{Al})$