Potassium-capture by Kaolin. Part 1: KOH

Supporting Information

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Appendix I. Detailed experimental information on the EFR experiments.

Table 1. Detailed experimental information on the EFR experiments.

Experimental series	**Additives**	**Temp./°C**	**Gas residence time/s**	**K in gas /ppmv**	**K/(Al+Si)**	**Slurry (wt. %)**			**Feeding rate g/min**	**Secondary gas flow rate/Nl/min**
						kaolin	KOH	Ethanol		
(A) KOH evaporation experiments	No additive	800	1.2	500	0.481	0	3.07	5.00	5.2	86
		900							4.7	74
		1100							4.0	58
		1300							3.5	46
		1450							3.3	40
(B) KOH-capture by kaolin (impact of **K-concentration**)	normal kaolin (D_{50} = 5.47 µm)	1100	1.2	50	0.048	7.64	0.31	5.00	4.0	58
				250	0.240	7.64	1.53	5.00		
				500	0.481	7.64	3.07	5.00		
				750	0.721	7.64	4.56	5.00		
				1000	0.961	7.64	6.12	5.00		
(C) KOH-capture by kaolin (impact of **temperature**)	normal kaolin (D_{50} = 5.47 µm)	800	1.2	50, 500	0.048, 0.481	7.64	0.31, 3.07	5.00	5.2	86
		900							4.7	74
		1100							4.0	58
		1300*							3.5	46
		1450							3.3	40
(D) KOH-capture by kaolin (impact of **residence time**)	normal kaolin (D_{50} = 5.47 µm)	800, 1100	0.7	500	0.481	7.64	3.07	5.00	7.0	127
			1.2						4.0	58
			1.5						4.1	60
			1.9						3.9	55
(E) KOH-capture by	fine kaolin (D_{50} = 3.51	900, 1100, 1300	1.2	500	0.481	7.64	3.07	5.00	4.0	58

kaolin (impact of **kaolin particle size**)	μm)									
	normal kaolin (D_{50} = 5.47 μm)	800, 900, 1100, 1300*, 1450								
	coarse kaolin (D_{50} = 13.48 μm)	900, 1100, 1300								
(F) KOH-capture by **mullite**	Mullite (D_{50} = 5.90 μm)	800, 900, 1100, 1300, 1450	1.2	500	0.471	7.62	3.09	5.00	4.0	58

Appendix II. Quantification method of K-conversion (X_K) and K-capture (C_K)

Two parameters were defined to quantify the amount of potassium captured by kaolin: the K-conversion (X_K), and the K-capture level (C_K). X_K is the percentage (%) of input KOH chemically captured by solid additives (kaolin/mullite) forming water-insoluble K-aluminosilicate. C_K is the mass of potassium captured by 1 g of additive (kaolin/mullite) (g K/g additive).

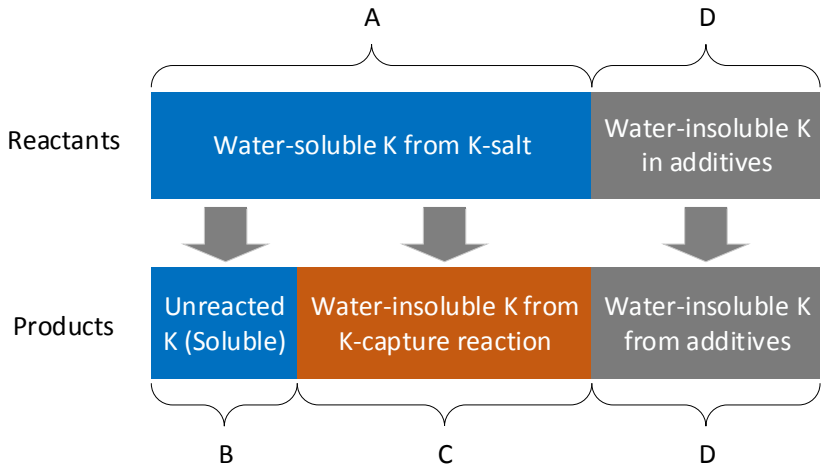


Figure 1. . Potassium transformations in the K-capture reaction.

The transformation of potassium in the reaction system is illustrated in Figure 1. The water-insoluble K in the products originated from two different sources: Part C in Figure 1 was formed from the reaction between KOH and additives (kaolin or mullite), while part D in Figure 1 was from the solid additives (kaolin or mullite). The reacted solid samples collected from the Entrained Flow Reactor (EFR) experiments were subjected to ICP-OES analysis. The concentration of water soluble potassium (B of Figure 1) and total potassium (B+C+D in Figure 1) were analyzed. The concentration of water-insoluble potassium (C+D) was calculated consequently. However, C and D in Figure 1 need to be calculated based

on the composition of the reactants and the products. The calculation was based on the following assumptions:

1. The solid samples collected are representative, i.e., the samples collected and those not collected has the same constituents (the molar ratio of K/(Al+Si) in reactants and in products are almost identical, implying the collected products were representative);

2. Potassium that exists in solid feed additives are water-insoluble (Concentration in kaolin is low and it mainly stays in the form of K-aluminosilicates which is water-insoluble);

The K-conversion (X_K) was calculated according to Equation 1.

$$X_K = \frac{C}{A} = \frac{A-B}{A} = \frac{\frac{A}{A+D} - \frac{B}{A+D}}{\frac{A}{A+D}} = \frac{Y_F - Y_P}{Y_F} \times 100\ \% \tag{1}$$

Where Y_F and Y_P are the molar ratio of water soluble K to total K in fed reactants and collected products respectively. Y_F was calculated based on the constituents of slurry and potassium concentration in utilized additives, while Y_P was calculated based on the ICP-OES result of collected solid samples.

The K-capture level (C_K) was calculated according to Equation 2.

$$\mathrm{C}_K = \frac{n_{KOH}\, M_K X_K}{m_{ad.}} \tag{2}$$

Where n_{KOH} is the molar amount of KOH in reactants (mol). M_K is the molar mass of potassium (g/mol). X_K was the K-conversion (%); m_{ad} is the mass of additives (kaolin or mullite) in reactants (g).

Appendix III. Equilibrium calculation results of KOH capture by kaolin

To provide a theoretical analysis of the experimental results, global equilibrium calculations were carried out. The comparison of the results from equilibrium calculation and experiments may shed light

upon how far the EFR reaction system is from the prediction of equilibrium calculation and provide information for understanding the EFR experimental results.

The global equilibrium calculation was performed using the Equilibrium module of the thermochemical software FactSage 7.0. The Equilibrium module is the Gibbs energy minimization work horse of FactSage. It can calculate the concentration of different chemical species when specified elements or compounds react or partially react and reach a state of chemical equilibrium.[1, 2] In this study the databases of FactPS, FToxid, FTsalt and FTpulp were employed for the calculation. FactPS is the data base for pure substance, and it contains data for over 4777 compounds. FToxid is the oxide database for slags, glasses, minerals, ceramics and refractories, etc. FTsalt data base is the salt date base, which contains data for pure salt and salt solutions formed among various combinations of 20 common cations. FTpulp is the pulp and paper database, which contains data for the pulp and paper industry and data on corrosion and combustion in recovery boilers.[2] In the calculations, slag options in solution phases were not checked. Therefore no slag was included in the calculation.

Equilibrium calculations were conducted at 50, 250, 500, 750, and 1000 ppmv KOH in the flue gas. Molar K/(Al+Si) ratio in reactants varied from 0.048 to 0.961 correspondingly. The reaction temperature was changed from 500 °C to 1800 °C. Similar to the experimental results, the equilibrium K-conversion ($X_{Keq.}$) and equilibrium K-capture level ($C_{Keq.}$) were calculated basing on the equilibrium calculation data. Additionally, the equilibrium Al-conversion ($X_{Aleq.}$) and equilibrium Si-conversion ($X_{Aleq.}$) were calculated as well.

The K-containing products in the equilibrium calculations were categorized into two groups: K-aluminosilicates and other K-containing compounds. The total molar amount of K, Al and Si in the equilibrium calculation system was n_{Kt}, n_{Alt} and n_{Sit}, respectively. The molar amount of K, Al and Si in K-aluminosilicate products was n_{Kals}, n_{Alals} and n_{Sials}, respectively. The mass of additives in the equilibrium

calculation system was $m_{ad.eq}$. The equilibrium K-conversion ($X_{Keq.}$), Al-conversion ($X_{Aleq.}$), Si-conversion ($X_{Sieq.}$) and equilibrium K-capture level ($C_{Keq.}$) was calculated as shown in equation (3), (4), (5) and (6).

$$X_{Keq.} = \frac{n_{Kals}}{n_{Kt}} \times 100\ \% \tag{3}$$

$$X_{Aleq.} = \frac{n_{Alals}}{n_{Alt}} \times 100\ \% \tag{4}$$

$$X_{Sieq.} = \frac{n_{Sials}}{n_{Sit}} \times 100\ \% \tag{5}$$

$$C_{Keq.} = \frac{n_{Kt} M_K X_{Keq.}}{m_{ad.eq.}} \tag{6}$$

Where,

$X_{Keq.}$, $X_{Aleq.}$ and $X_{Sieq.}$ - the equilibrium calculated K-conversion, Al-conversion and Si-conversion (%);

$C_{Keq.}$ - the equilibrium calculated K-capture level;

n_{Kals}, n_{Alals}, n_{Sials} - the molar amount of K, Al and Si contained in the equilibrium calculated product K-aluminosilicates;

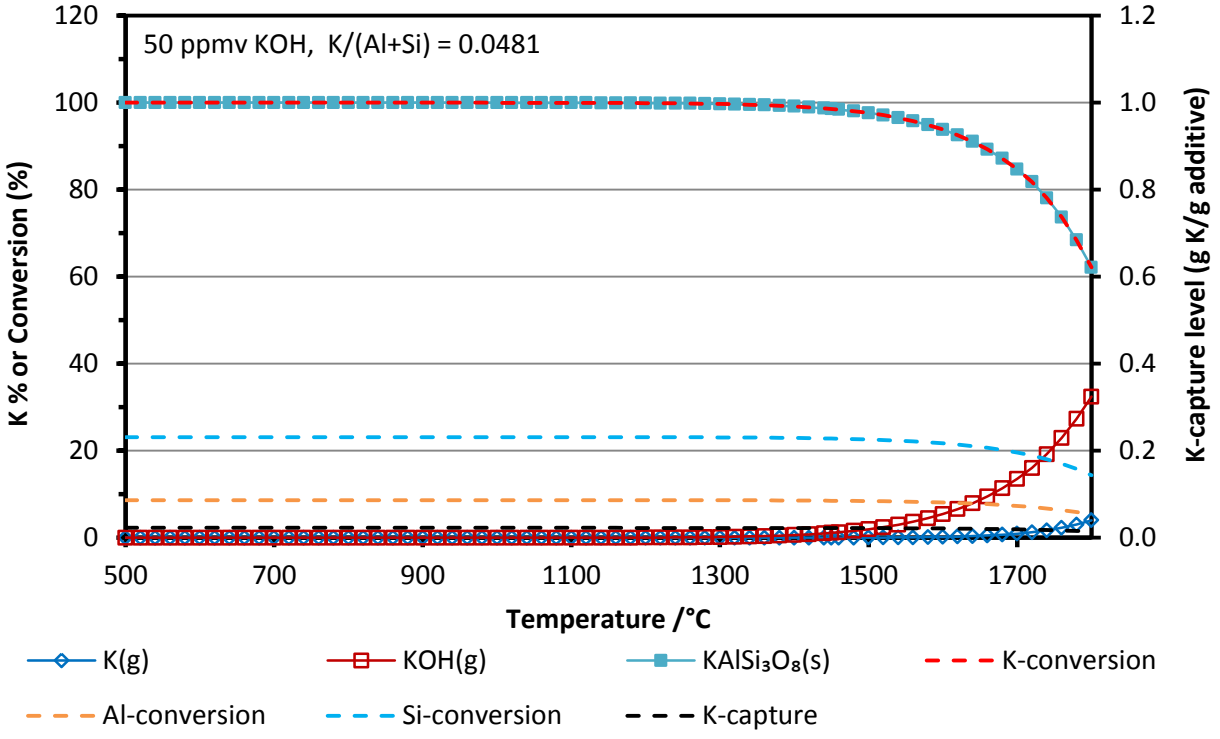
n_{Kt}, n_{Alt} and n_{Sit} - the total molar amount of K, Al and Si in the equilibrium calculation system;

M_K - the molar mass of K;

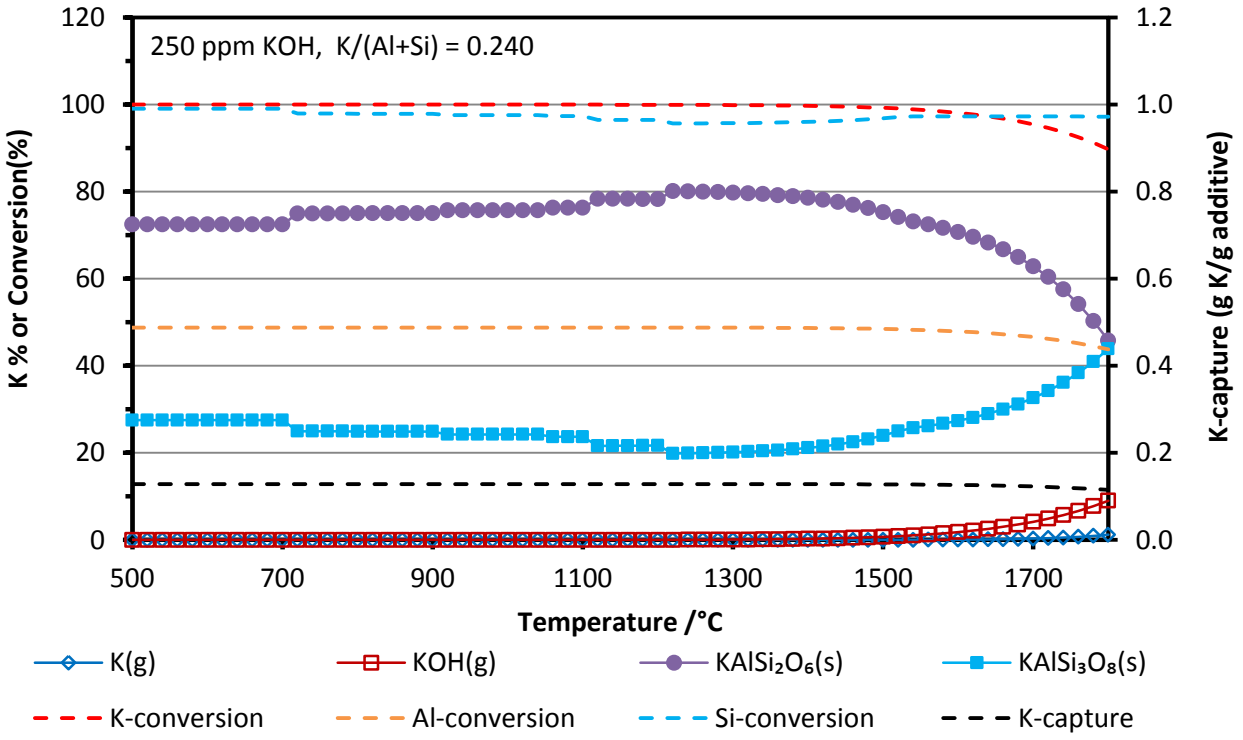
$m_{ad.eq.}$ - the mass of additives entered into the equilibrium calculation system;

The equilibrium calculation results of KOH capture by kaolin are summarized in Figure 2 (A-E). The primary axis of each figure (left Y-axis) is the percentage of different K-containing compounds or the percentage of conversion of K, Al or Si to K-aluminosilicates. The secondary axis (right Y-axis) is the K-capture level (C_K - the mass of K captured by 1 g of kaolin). In all the figures, gaseous K-containing compounds are represented with no filled markers; liquid compounds are represented with pattern filled

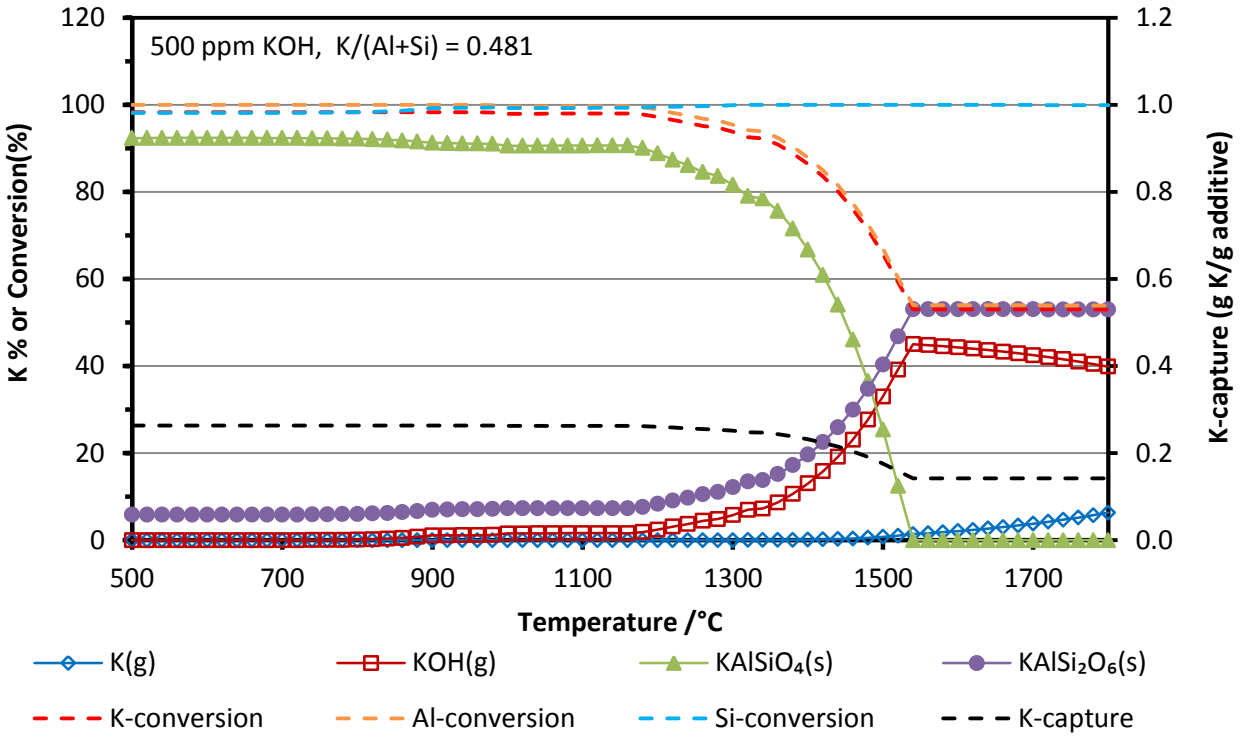
markers; solid compounds are represented with solid filled markers. The percentage of K, Al and Si conversion were represented with dash lines. The K-capture level was represented with black dash line.



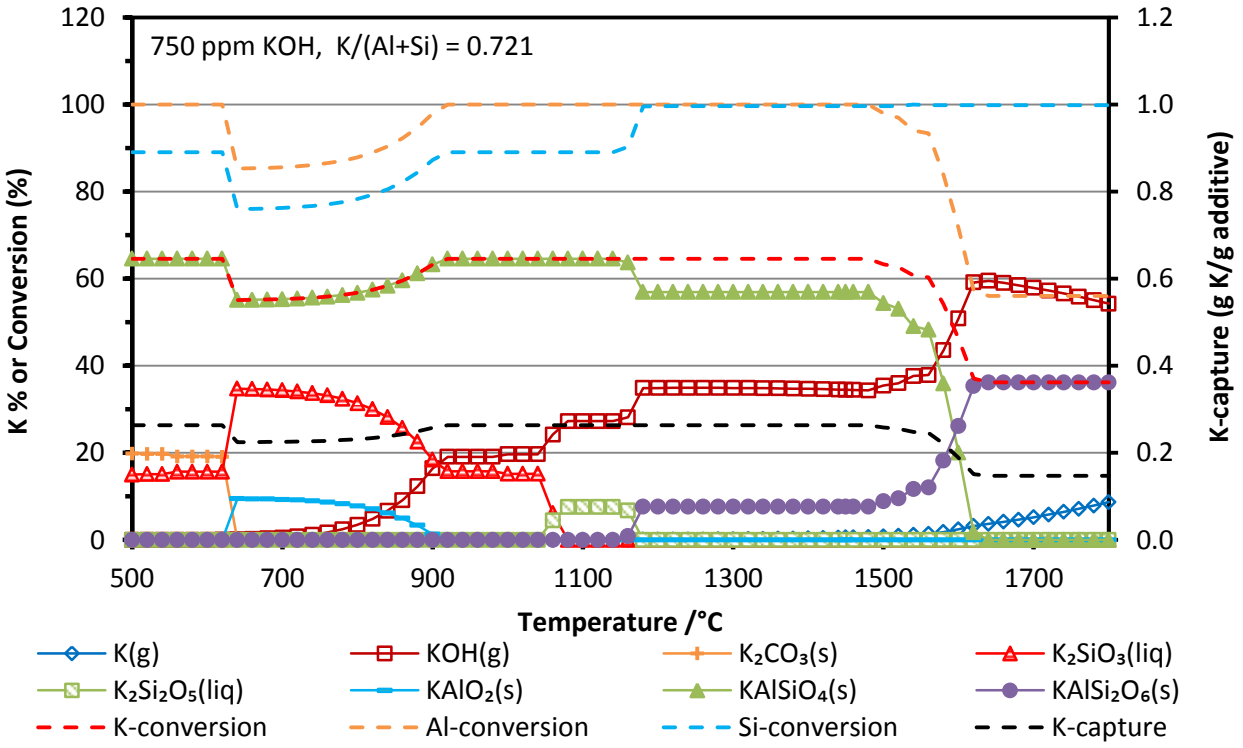
(A) 50 ppmv KOH, K/(Al+Si) =0.048



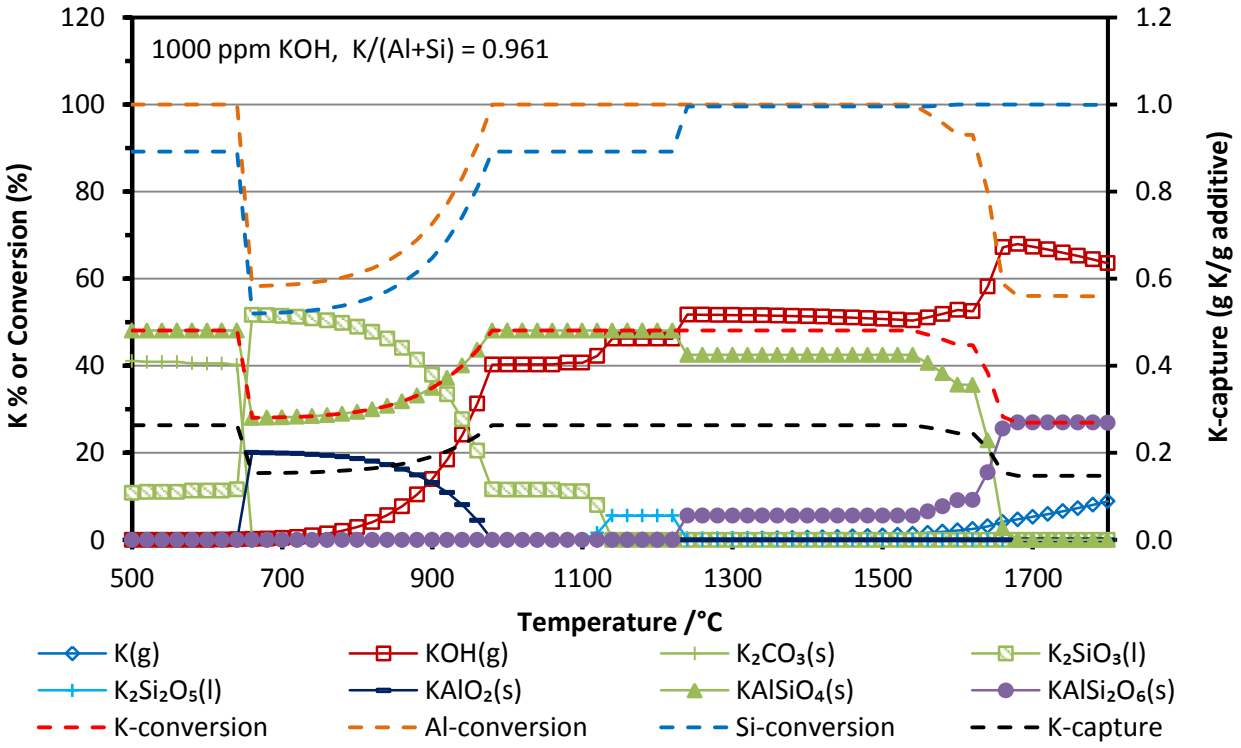
(B) 250 ppmv KOH, K/(Al+Si) =0.240



(C) 500 ppmv KOH, K/(Al+Si) =0.481



(D) 750 ppmv KOH, K/(Al+Si) =0.721



(E) 1000 ppmv KOH, K/(Al+Si) =0.961

Figure 2. Equilibrium calculation results of KOH capture by kaolin.

References

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