# Experimental Investigation and Kinetic Modeling of Potassium Alum Dodecahydrate Thermal Decomposition

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Potassium is an essential ion for plant nutrition, usually supplied in the form of chlorides and sulphates. According to Brazilian availability and demand of agriculture fertilizers, the importation of compounds carrying this chemical element is mandatory in order to fulfil the huge demand for this nutrient. Thus, initiatives looking for alternative sources of potassium become increasingly interesting and economically attractive. A potential route is associated with the sulfuric acid digestion of glauconite bearing greensands and sequential unit operations in order to recover aluminium, iron, magnesium and potassium compounds. In the context of this chemical process, the potassium alum ($KAl(SO_4)_2$) appears as a relevant intermediate product, which allows the selective recovery of potassium sulphate ($K_2SO_4$) and aluminum oxide ($Al_2O_3$) through thermal decomposition followed by solubilization in water and filtration. Based on what was said, the present work investigates the kinetics of potassium alum dodecahydrate ($KAl(SO_4)_2.12H_2O$) decomposition with and without the presence of charcoal, which acts as a reducing agent. Additionally, the current work proposes a novel mathematical model to describe the weight loss as a function of time for both processes (with and in absence of charcoal). Thermogravimetric analyses (TGA) were conducted under inert atmosphere (nitrogen) and using different heating rates (10, 15 and 20 ℃ min$^{-1}$). Given the low required computation time, less than 1 s simulates 160 min of reaction, the proposed model can be used to monitor and control mass compositions at industry.

## 1. Introduction

Agriculture is the key activity of world food production. The enormous population growth rate since the industrial revolution poses an always increasing annual demand. Therefore, farmers need to produce more, in a smaller area and in a more sustainable way, highlighting the need for fertilizers that, according to the definition of Cakmak (2002), offer a fast response of increase productivity and reduce deforestation and erosion.

The most important macronutrients needed for the plant are nitrogen (N), phosphorus (P), sulfur (S) and potassium (K). Nitrogen helps the vegetative development, phosphorus impacts on formation of roots and organic products and potassium acts mainly for improve disease resistance and durability, as described in Nor *et al.* (2018). The Brazilian fertilizer production represents only 15 % of its demand and, therefore, the country is still strongly dependent on fertilizer importation. The need for fertilization ends solving a crucial agriculture problem: the production of environmentally safe products without decreasing food production and assuring favourable soil characteristics to guarantee the proper plant nutrition. (Mingaleeva *et al.*, 2014).

The search for more efficient fertilizers with better competitive prices leads to the development of new chemical routes to produce fertilizers key components. Mining companies have been investigating the use of glauconite bearing ores as raw materials to obtain compounds rich in potassium (Souza *et al.*, 2018). Glauconite is a hydrated silicate mineral composed mainly of aluminum, potassium, magnesium, iron, silicon, oxygen and hydrogen. In general, glauconite has a potassium content ranging from 6 to 14 % $K_2O$, which promotes its use in processes of obtaining $K_2SO_4$, given its high amount of potassium (Prakash S. and Verma J.P., 2016). Brocchi *et al.* (2015) proposed a chemical route to obtain potassium sulphate and aluminum oxide from glauconite concentrate. Souza *et al.* (2018) investigated the kinetics to produce an intermediate product

from the glauconite thermal decomposition under non-reductive and reductive atmospheres through thermal gravimetric analyses and X-ray diffraction (XRD). The investigated compound is potassium alum dodecahydrate ($KAl(SO_4)_2 \cdot 12H_2O$) and, for its thermal decomposition, the authors proposed the existence of at least four reaction steps until the loss of all the 12 water molecules, and at least two reactions to obtain $K_2SO_4$ and $Al_2O_3$ from anhydrous alum. According to the authors, the presence of charcoal does not affect the alum dehydration step.The authors do not know any research reports published in the literature on the mathematical modelling of the potassium alum thermal degradation kinetics in the absence, or presence, of a reducing agent under inert atmosphere. Therefore, this work investigates both processes using distinct heating rates for TGA and proposes one mathematical model for each non-reductive and reductive experimental conditions capable to describe the mass loss as a function of time of the potassium alum dodecahydrate thermal decomposition. The present work improves the knowledge about this system and, consequently, stays one step closer to the scenario where this process is conducted at industrial scale.

## 2. Materials and Methods

The following chemical materials were used in the current work: nitrogen (99.999 % from Linde GA), charcoal and synthetic potassium alum dodecahydrate (98.0 % from Isofar Indústria e Comércio de Produtos Químicos). Netzsch thermogravimetric analyzer, model STA 449 F3 Jupiter®, was employed. The samples of synthetic hydrate potassium alum were submitted to thermogravimetric analyses according to Table 1. For all samples, after reaching 1000 °C, they were kept at this temperature for 1 hour. S15Ch refers to a charcoal sample. Nitrogen was used as an inert carrier gas with 0.2 L/min flow rate. For reactions with charcoal, the speciation was carried out for 1 mol of $KAl(SO_4)_2 \cdot 12H_2O$ in association with 1 mol of carbon (Souza *et al.*, 2018).

*Table 1: Experimental conditions used for thermogravimetric analyses.*

| Sample Identification | Presence of charcoal | Sample weight (mg) | Heating Rate (K min$^{-1}$) |
|:---:|:---:|:---:|:---:|
| S10 | No | 30.2 | 10 |
| S15 | No | 30.6 | 15 |
| S20 | No | 30.6 | 20 |
| S15Ch | Yes | 34.4 | 15 |
| S10C | Yes | 30.9 | 10 |
| S15C1 | Yes | 31.4 | 15 |
| S15C2 | Yes | 31.8 | 15 |
| S20C | Yes | 30.4 | 20 |

## 3. Mathematical Modeling

Based on experimental analysis on the TGA and DTG curves (shown in the next section), the following mechanisms are proposed to represent the thermal decomposition of $KAl(SO_4)_2 \cdot 12H_2O$ under inert atmosphere with the absence and the presence of charcoal as reducing agent respectively.
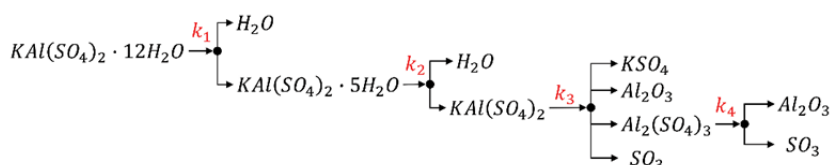


*Figure 1: Kinetic mechanism for $KAl(SO_4)_2 \cdot 12H_2O$ thermal decomposition in an inert atmosphere*
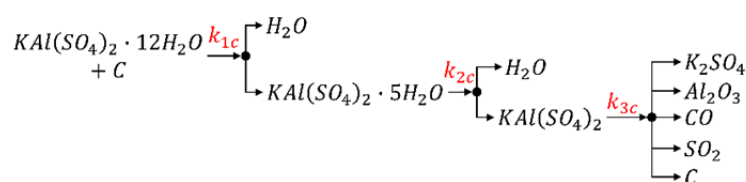


*Figure 2: Kinetic mechanism for $KAl(SO_4)_2 \cdot 12H_2O$ and charcoal thermal decomposition in an inert atmosphere*

where $k_i$ (from $i$ = 1 to 4) is the kinetic reaction constant from the mechanism of $KAl(SO_4)_2 \cdot 12H_2O$ thermal decomposition in inert atmosphere, and $k_{ic}$ (from $i$ = 1 to 3) is the kinetic reaction constant from the mechanism of $KAl(SO_4)_2 \cdot 12H_2O$ and charcoal thermal decomposition in inert atmosphere. All reaction constants follow Arrhenius equation and they can be represented according to Eq.(1).

$$k_i = exp\left[A_i + B_i\left(\frac{T(K) - T_{ref_i}(K)}{T(K)}\right)\right]$$ (1)

Where $T$ and $T_{ref_i}$ are reaction and reference temperatures for reaction $i$ in $K$. The reference temperature is usually defined as a suitable average for the evaluated experimental data (Schwaab et al., 2008). In this work, the values set for $T_{ref}$ are shown in Table 2.

Table 2: Experimental conditions used for thermogravimetric analyses.

| Kinetic reaction constant | $T_{ref}$ (°C), 10 °C min$^{-1}$ | $T_{ref}$ (°C), 15 °C min$^{-1}$ | $T_{ref}$ (°C), 20 °C min$^{-1}$ |
|---|---|---|---|
| $k_1$ | 115.0 | 115.0 | 115.0 |
| $k_2$ | 220.0 | 220.0 | 220.0 |
| $k_3$ | 800.0 | 849.5 | 855.0 |
| $k_4$ | 800.0 | 849.5 | 855.0 |
| $k_{1c}$ | 115.0 | 115.0 | 115.0 |
| $k_{2c}$ | 220.0 | 220.0 | 220.0 |
| $k_{3c}$ | 748.0 | 748.0 | 755.0 |

The pre-exponential factor $k_{0i}$ and the activation energy $E_i$ for each reaction can be recovered from parameters $A_i$ and $B_i$ through the following equations.

$$k_{0i} = e^{(A_i + B_i)}$$ (2)

$$E_i = B_i R T_{ref_i}(K)$$ (3)

where $R$ is the universal gas constant.

The kinetics of the potassium alum dodecahydrate thermal decomposition, with and without the presence of charcoal under $N_2$ atmosphere, was assumed to follow a first-order rate model except for the reaction where the charcoal takes part of it, for this unique case the order rate model was assumed equal to 2.5 as the can be seen in Table 3.

Table 3: Reaction rate expressions

| Reaction | Reaction rate expression | Reaction | Reaction rate expression |
|---|---|---|---|
| R1 | $k_1 n_{KAl(SO_4)_2 \cdot 12H_2O}$ | R1C | $k_{1C} n_{KAl(SO_4)_2 \cdot 12H_2O}$ |
| R2 | $k_2 n_{KAl(SO_4)_2 \cdot 5H_2O}$ | R2C | $k_{2C} n_{KAl(SO_4)_2 \cdot 5H_2O}$ |
| R3 | $k_3 n_{Al(SO_4)_2}$ | R3C | $k_{3C} n_{Al(SO_4)_2} n_C^{1.5}$ |
| R4 | $k_4 n_{Al_2(SO_4)_3}$ | | |

where $n_i$ is the number of moles of specie $i$.

Finally, to calculate the weight loss, only the formed solid components were computed. At each time interval, the total weight of all solid components present was counted and compared to the initial potassium alum dodecahydrate weight. From this approach, the weight loss represents the formation of gaseous products (water vapor and $SO_3$) according to Eq(4).

$$WL = \frac{\sum_{i=1}^{N} w_{i(t=t)}}{w_{sample(t=0)}} \cdot 100$$ (4)

where $WL$ is the weight loss in %, $N$ is the total number of solid components present in the system and $w_{sample(t=0)}$ is the initial sample weight shown in Table 1.

From the kinetic mechanisms proposed in Figures 1 and 2, molar balances for all components were done, resulting in an ODE (ordinary differential equation) system that were solved numerically using implicit BDF (backward differentiation formula) programmed in Python (Petzold, 1983).

## 4. Results and Discussion

The thermogravimetric results, TGA curves are presented in Figure 1.



*(a)*        *(b)*        *(c)*
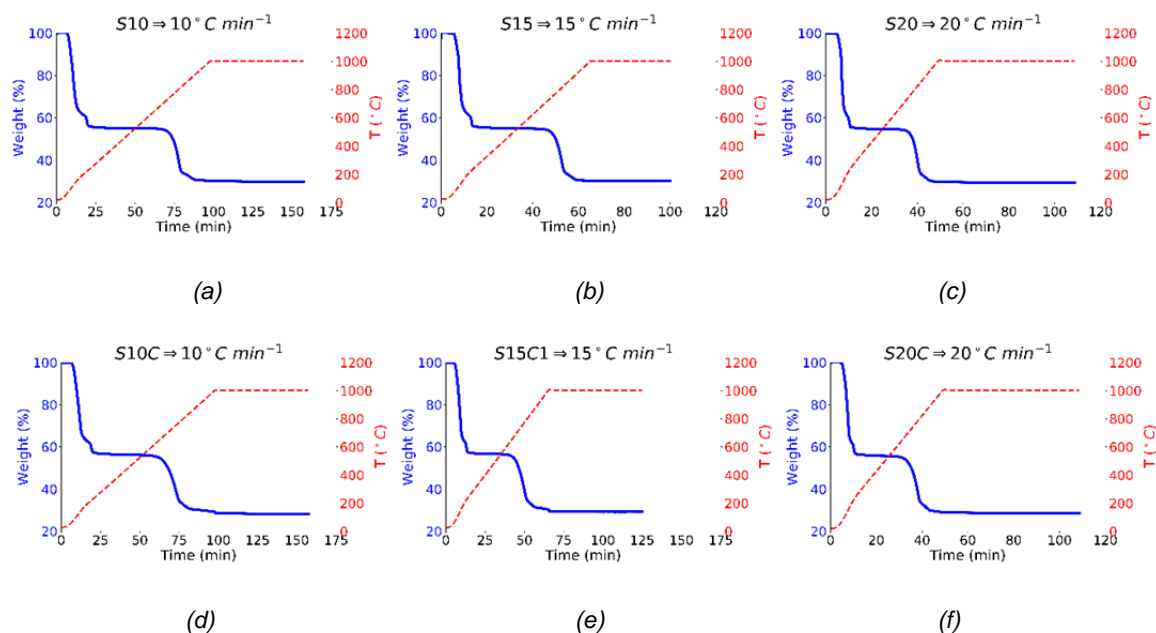
*(d)*        *(e)*        *(f)*

*Figure 1: Weight loss and temperature as a function of time for potassium alumen dodecahydrate in the absence of charcoal (a to c) and with the presence of charcoal (d to f) under inert atmosphere.*

Table 4 shows the final weights achieved at the end of each thermogravimetric analysis. Figure 1a clearly shows the influence of increasing the heating rate on reducing the decomposition time. For the lowest heating rate used (10 $°C$ $min^{-1}$), reactions R3 and R4 only take place after 65 min approximately while for 20 $°C$ $min^{-1}$ these reactions occur before the first 50 min. The presence of charcoal does not affect the dehydration step, since the curves for reactions R1 and R2 (first 30 min) did not shift with the charcoal addition. On the other hand, the charcoal addition accelerated the anhydrous alum thermal decomposition as shown in Fig. 2b for the reactions R3 and R4 that occurred between 600°C and 900°C. The anhydrous alum thermal decomposition occurs at lower temperatures when charcoal is present in the reaction system.

*Table 4: Heating rates and their respective final weights for thermal decomposition of potassium alumen dodecahydrate with and without the presence of charcoal under inert atmosphere*

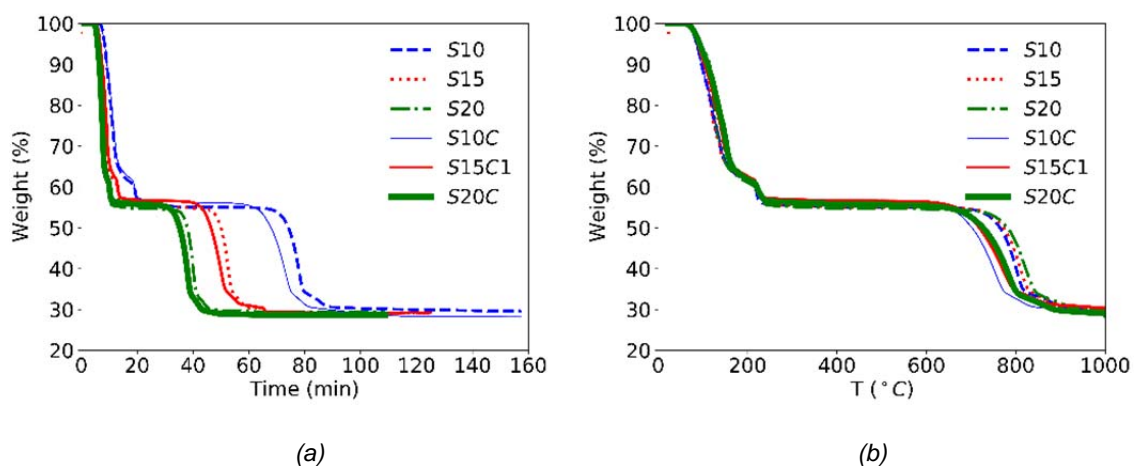| Sample Identification | Heating rate ($°C$ $min^{-1}$) | Final weight (%) |
|---|---|---|
| S10 | 10 | 30.324 |
| S15 | 15 | 30.262 |
| S20 | 20 | 29.304 |
| S10C | 10 | 28.179 |
| S15C1 | 15 | 29.214 |
| S15C2 | 15 | 29.909 |
| S20C | 20 | 28.697 |

(a)
(b)

Figure 2: Weight loss as a function of (a) time and (b) temperature for potassium alumen dodecahydrate in the absence of charcoal and with the presence of charcoal under inert atmosphere.
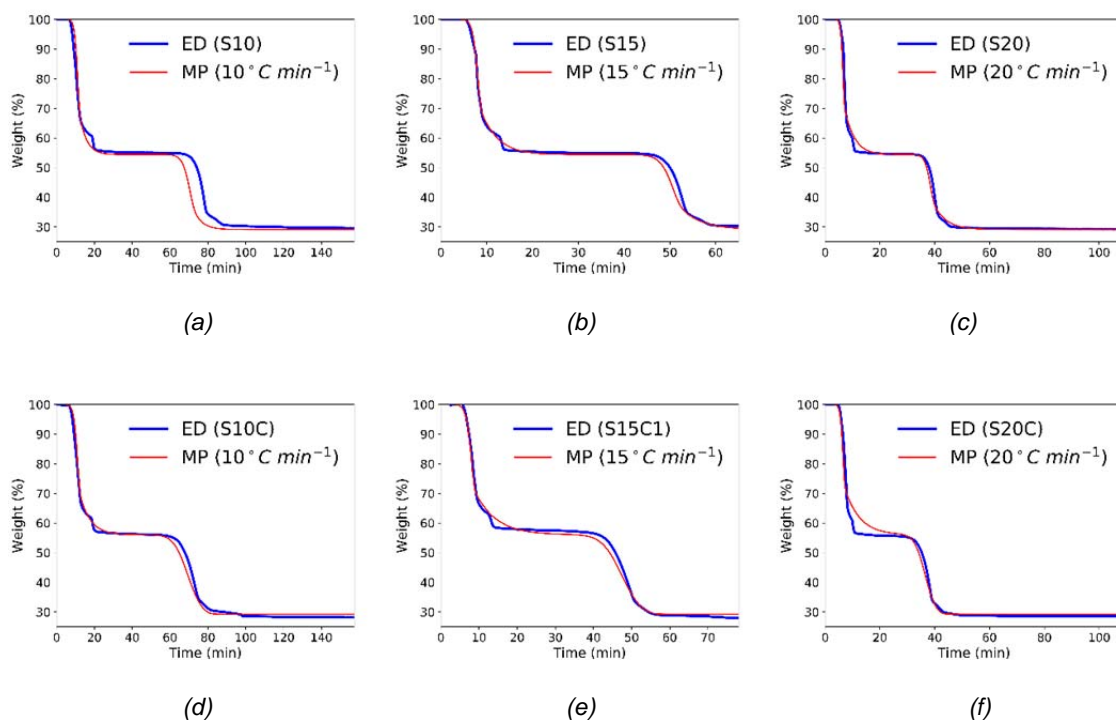


(a)
(b)
(c)

(d)
(e)
(f)

Figure 3: Comparison between experimental data (ED) and model prediction (MP) for potassium alumen dodecahydrate weight loss as a function of time with and without charcoal under inert atmosphere for different experimental conditions.

Observing the results shown in Table 4, the heating rate and the use of charcoal do not affect the final weight achieved. All experiments resulted in approximately the same final weight around 30 %.

After an exhaustive search, the best model parameters $A_i$ and $B_i$ are shown in Table 5. With these values, both models (one with the absence and the other with the presence of charcoal) were capable to predict weight loss data close to the ones measured experimentally. Finally, Figure 3 presents the comparison among the experimental data and model responses for some of the experimental conditions from Table 1 for weight loss during reaction time. For all conditions considered, both models could represent well the experimental data and they are ready to be submitted for the next step: parameters estimation. The parameters presented

in Table 5 are not the final ones, they are going to be used as initial guess in the estimation procedure. After this optimization step, the model predictions certainly will get even closer to the experimental data.

*Table 5: Parameter values used in the simulations*

| Kinetic reaction constant | S10, S15 and S20 $A_i$ | S10, S15 and S20 $B_i$ | S10C, S15C1 and S20C $A_i$ | S10C, S15C1 and S20C $B_i$ |
|:---:|:---:|:---:|:---:|:---:|
| $k_1$ | -1.30 | 39.81 | | |
| $k_2$ | -1.40 | 0.71 | | |
| $k_3$ | 0.60 | 38.02 | | |
| $k_4$ | -1.50 | 0.002 | | |
| $k_{1c}$ | | | -1.17 | 32.54 |
| $k_{2c}$ | | | -1.68 | 1.87 |
| $k_{3c}$ | | | -1.30 | 22.39 |

## 5. Conclusions

Potassium alumen dodecahydrate thermal decomposition in inert atmosphere was successfully conducted in the current work. The use of charcoal as reducing agent, although does not affect the dehydration step, proved efficient in reducing the initial decomposition of the anhydrous alum. A sequence of reactions is proposed to describe the kinetic mechanism of the potassium alumen dodecahydrate thermal decomposition in inert atmosphere and using charcoal as a reducing agent. The next step is to estimate the model parameters through an optimization model.

### Acknowledgments

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