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Thermodynamic simulation of α-spodumene calcination with Na_2SO_4
Simulación termodinámica de la calcinación de α-espodumena con Na_2SO_4

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Abstract

In this research work, the calcination reaction of α-spodumene (LiAlSi2O6) with Na2SO4 through thermodynamic simulation using the Equilib module included in the Fact Sage 8.2 software was studied. The LiAlSi2O6:Na2SO4 molar ratios (RM) analyzed were: 1:0.5, 1:0.6, 1:0.7, 1:0.8, 1:0.85, 1:1, and 1:1.5 in the temperature range from 50°C to 1200°C and 1 atmosphere of pressure determining the chemical species in equilibrium every 50 °C through Gibbs energy minimization. The most stable chemical species formed in all RMs were: Li2SO4, NaAlSi3O8, NaAlSiO4 and LiNaSO4. The maximum % percentage yield (% PY) for the Li2SO4 specie was 50% in the solid state starting at 500°C and in the liquid state at temperature ≥ 900°C for the 1:1 RM with an excess of Na2SO4 of 15%. The results obtained from the present study allowed us to propose the reaction mechanism of the calcination process of α-spodumene with Na_2SO_4.

Keywords: α-spodumene, Calcination, Lithium, Simulation, Thermodynamics.

Resumen

En este trabajo de investigación se estudió la reacción de calcinación de α-espodumena ($LiAlSi_2O_6$) con Na_2SO_4 mediante simulación termodinámica utilizando el módulo Equilib incluido en el software Fact Sage 8.2. Las relaciones molares (RMs) $LiAlSi_2O_6$:Na_2SO_4 analizadas fueron: 1:0.5, 1:0.6, 1:0.7, 1:0.8, 1:0.85, 1:1, y 1:1.5 en el rango de temperatura de 50°C a 1200°C y 1 atmosfera de presión determinando las especies químicas en equilibrio cada 50 °C a través de la minimización de energía de Gibbs. Las especies químicas más estables formadas en todas las RMs fueron: Li_2SO_4, $NaAlSi_3O_8$, $NaAlSiO_4$ y $LiNaSO_4$. El máximo % de rendimiento porcentual (% PY) para la especie Li_2SO_4 fue de 50% en estado sólido a partir de 500°C y en estado líquido a temperatura ≥ 900°C para la RM 1:1 con un exceso de Na_2SO_4 de 15%. Los resultados obtenidos del presente estudio permitieron proponer el mecanismo de reacción del proceso de calcinación de α-espodumena con Na_2SO_4.

Palabras Clave: α-espodumena, Calcinación, Litio, Simulación, Termodinámica.

1. Introduction

α-spodumene is an anhydrous alumino-silicate mineral with the formula $LiAlSi_2O_6$ belonging to the group of inosilicates/pyroxenes, it has a monoclinic system and can appear as prismatic crystals or with acicular habits, associated with lithium-rich pegmatites, along with quartz, albite, potassium feldspar, lepidolite, tourmaline and other lithium minerals (Garrett, 2004). Its physical appearance can vary from green, yellow, purple, gray or white depending on the amount and presence of other metals such as sodium, manganese, magnesium, iron, or titanium (Garrett, 2004). α podumene contains lithium as LiO_2 at approximately 8 wt% in pure mineral samples (Garrett, 2004), (Choubey et al., 2016) and is transformed to the β phase with a tetragonal structure by calcination at 900°C, which has a greater crystal volume, increasing the mobility of lithium atoms that then become easily accessible to acidic or alkaline aqueous leaching

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solutions. The type of monoclinic highly packed crystal structure type α, which consists of SiO_3 chains linked through Al^{+3} ions, and its high density (3.27 g cm^{-3}) makes the mineral spodumene hard, abrasive and refractory to attack by liquid or gaseous chemical agents (Peltosaari et al., 2015), (Abdullah et al., 2019). The greatest use of lithium is due to its use as a component of rechargeable batteries used in electronic devices, in the manufacture of high-temperature lubricants, pharmaceutical products, chemical products and psychopharmacological agents (Champion, 2019), (Nguyen and BOHLE 2004). The most common method to obtain a lithium oxide as a soluble aluminate ($LiAlO_2$) is the alkaline method (calcination) of $LiAlSi_2O_6$ with limestone ($CaCO_3$) in a 1:4 ratio from which Li can be recovered by leaching with water with a maximum Li recovery percentage of 64% (Choubey et al., 2016). Looking for alternatives, various investigations have been carried out on calcination of spodumene with salts such as $CaSO_4$, Na_2CO_3, and NaCl and its subsequent leaching in an autoclave at a temperature around 250°C (Chen et al., 2011), (Yan et al., 2012), (Yan et al., 2012). The objective of this work is to evaluate, by using the FactSage 8.2 thermodynamic software, the calcination of pure α spodumene with Na_2SO_4 analyzing different molar ratios between $LiAlSi_2O_6$ and Na_2SO_4 in order to determine the optimal amount of Na_2SO_4 and obtain the water-soluble lithium mineral specie (Li_2SO_4) that facilitates the posterior recovery of the metal of interest. Computational thermodynamics is an important tool that will allow us to better understand the equilibrium phase relationships present during the calcination of the mineral spodumene with Na_2SO_4 in addition to optimizing the process.

2. Experimental method

The experimental method used consisted of using the equilib module included in FactSage 8.2 computational thermodynamic software (Bale et al., 2002), (Bale et al., 2009) to calculate the chemical species and their concentrations generated when the reactants $LiAlSi_2O_6$ and $NaSO_4$ reacted at different RMs (1:0.5, 1:0.6, 1:0.7, 1:0.8, 1:0.85, 1:1 and 1:1.5), temperatura range 50 to 1200°C with step of 50°C and 1 atm. of pressure totally or partially to reach a state of chemical equilibrium by minimizing Gibbs energy as a function of temperature according to the equation (1).

$$G = \sum_{Ideal\ gas} n_i(g_i^o RTlnP_i) + \sum_{\substack{Pure\ condensed \\ phases}} n_i g_i^o \sum_{Solution-1} n_i\left(g_i^o + RTlnx_i + RTln_{\gamma i}\right) \sum_{Solution-2} n_i\left(g_i^o + RTlnx_i + RTln_{\gamma i}\right) + \cdots \quad (1)$$

Where: n = moles, Pi = partial pressure of gas, xi = mole fraction, γi = activity coefficient, $gi°$ = standard Gibbs molar energy. The thermodynamic properties of the $LiAlSi_2O_6$, such as heat capacity (Cp), absolute entropy at 298.15 K (S298.15) and relative enthalpy of formation at 298.15 K (ΔH298.15), were taken from fitting the recommended experimental data performed by Barin (Barin, 1995), (Konar et al., 2018), see Table 1.

Table 1: Thermodinamic properties of α-spodumene.

Function			Reference
C_p J mol^{-1} K^{-1}	$S_{298.15}$ J mol^{-1} K^{-1}	$\Delta H_{298.15}$ J mol^{-1}	
(298 to 800 K) 312.1 + 0.02604T – $2759T^{-0.5}$	129.29	-3,054,701	Barin, 1995
(800 to 1200 K) 354.717 – $3375T^{-0.5}$			
(>1200 K) 354.717 – 3375 $T^{-0.5}$	131	-3,060,000	Konar et al., 2018

The program considered 1127 possible pure species from the databases FTmisc 8.2, FToxid 8.2, and FactPS 8.2 (Bale et al., 2002), (Bale et al., 2009) and only reported those that showed an activity coefficient of 1. The results were analyzed and processed to establish the mechanism of the calcination reaction of $LiAlSi_2O_6$ with $NaSO_4$.

3. Results and discussion

The species generated for each simulation were expressed in % percentage yield (% PY) calculated according to equation 2 (Mosher and Kelter, 2023):

$$Percentage\ yiel\ (\%) = \frac{Simulated\ yield}{Theoretical\ yield}\ x\ 100 \quad (2)$$

Where the *simulated yield* is the amount of the species obtained during the simulation and the *theoretical yield* is the amount of the species obtained theoretically. Additionally, the initial percentages of the molar concentrations of the reactant species were included in the graphs.

Figure 1 presents the % PY for the molar ratio $1LiAlSi_2O_6$:$0.5Na_2SO_4$, showing that the species of interest, Li_2SO_4, is stable above 500°C with a % PY of 25%. This indicates that the thermal decomposition of $LiAlSi_2O_6$ with Na_2SO_4 generates $LiNaSO_4$ at 350°C, which is stable from 400°C to 450°C, and then forms Li_2SO_4, $NaAlSiO_4$ (Nepheline) and $NaAlSi_3O_8$ (albite) which are stable from 500°C to 1200°C. Also, 50% of $LiAlSi_2O_6$ remains unreacted up to 450°C. Luong et al. (Loung et al., 2013) reported that experimentally, 1000°C was required to achieve a 90.4% conversion of $LiAlSi_2O_6$ to Li_2SO_4 but thermodynamically temperatures greater than 900°C generate Li_2SO_4 in a liquid state, considering chemically pure reactants, see Figure 1.

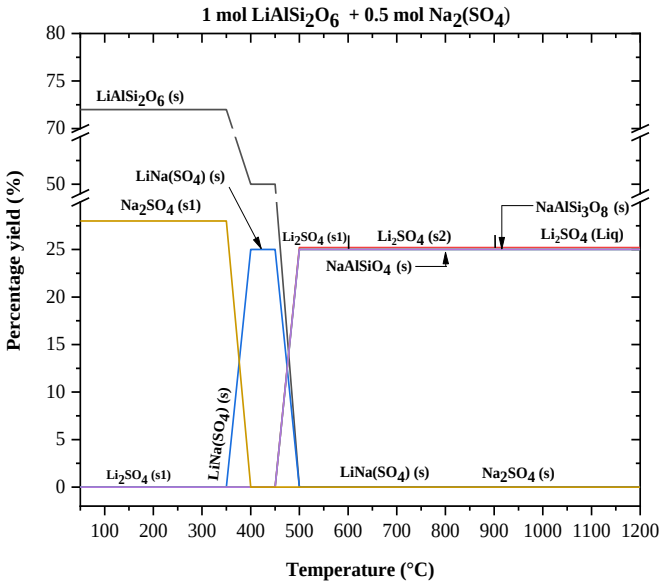

Figure 1: Percentage yield (%) for calcination of 1 mol $LiAlSi_2O_6$ with 0.5 mol Na_2SO_4.

Figure 2 presents the results for the molar ratio $1LiAlSi_2O_6$:$0.6Na_2SO_4$ showing that Li_2SO_4 is stable from 500°C with a % PY of 30%. Has been reported (Loung et al., 2014) that calcination of α-spodumene with Na_2SO_4 (melting point of 884 ºC), in mass ratios of α-spodumene:Na_2SO_4 low, results in low extraction of lithium which is consistent with the results obtained thermodynamically in this study.

In Figure 2 also an increase in the formation temperature (400°C) of $LiNaSO_4$ was also observed with a % PY of 30% at 450°C that remained stable for 50°C. Setoudeh et al., 2020, reported the $LiNaSO_4$ and β-spodumene phases from 500°C in the produced calcine after roasting at 1000 °C in air, in a study carried out experimentally for α-spodumene:Na_2SO_4 mixtures mechanically activated with a mass ratio of 1:0.5.

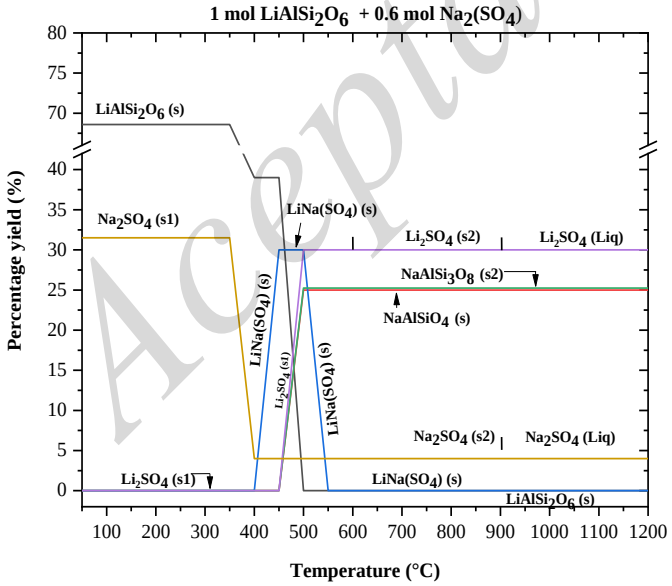

Figure 2: Percentage yield (%) for calcination of 1 mol $LiAlSi_2O_6$ with 0.6 mol Na_2SO_4.

$NaAlSiO_4$ (Nepheline) and $NaAlSi_3O_8$ (High albite) formed from 450°C and remained stable from 500°C. It was also observed that 39% of $LiAlSi_2O_6$ remained unreacted from 400°C to 450°C, with 4% of unreacted Na_2SO_4 observed from 450°C in the solid state and ≥900°C in the liquid state. It is important to mention that the nepheline phase ($NaAlSiO_4$) is valued for use in glass manufacturing in place of feldspar and is decomposed by hydrochloric acid, with separation of gelatinous silica and cubes of salt (Esposito et al., 2005)

The %PY of the species of interest, Li_2SO_4, increased 35% at 550°C where it remained stable in the solid state up to 900°C at a molar ratio of 1:0.7 $LiAlSi_2O_6$:Na_2SO_4, see Figure 3. A decrease to 30% of the unreacted $LiAlSi_2O_6$ species was also observed, which remained stable from 400°C to 450°C. Also, 25% of $NaAlSiO_4$ formed at 400°C and $NaAlSi_3O_8$ remained stable at 500°C with an increase to 6.5% of unreacted Na_2SO_4. Mineralogically, the $NaAlSi_3O_8$ phase is an impurity feldspars common associated with α-spodumene that is considered gangue minerals and are not included in elemental substitution reactions that occur with α-spodumene. However, in this study, thermodynamic functions determine the formation of this species during the thermal decomposition of the mineral with Na_2SO_4 (Edgar et al., 1967).

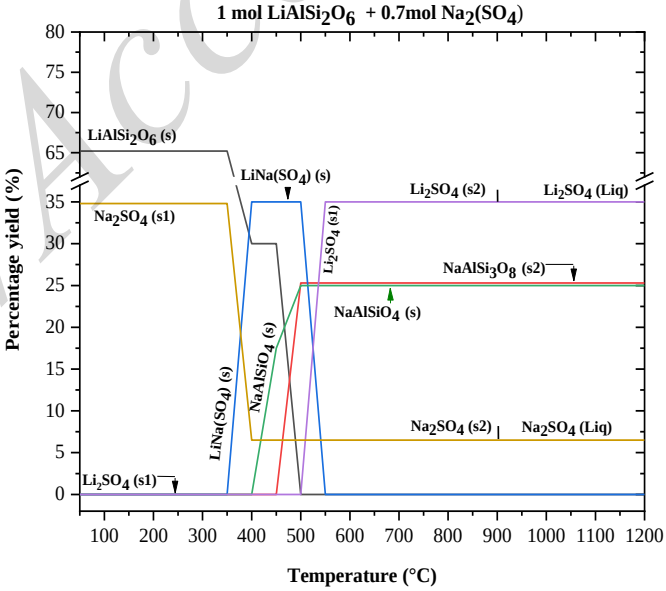

Figure 3: Percentage yield (%) for calcination of 1 mol $LiAlSi_2O_6$ with 0.7 mol Na_2SO_4.

With the increase in the molar amount of Na_2SO_4 to 0.8 and 0.85 mol, see Figure 4 and Figure 5, there was an increase in the % PY of Li_2SO_4 to 40% and 42% respectively, with 25% of $NaALSi_3O_8$ and $NaAlSiO_4$ remaining in equilibrium from 500°C. $LiNaSO_4$ increased to 40% with 0.8 mol of Na_2SO_4 and to 42.5% with 0.85 mol of Na_2SO_4 and was maintained in equilibrium from 550°C to 600°C and 400°C to 450°C respectively. Also, 9.6% and 12% unreacted Na_2SO_4 were observed for 0.8 and 0.85 mol Na_2SO_4.

Finally, 50% Li_2SO_4 was obtained for the molar amounts of 1 and 1.5 of Na_2SO_4, see Figure 6 and Figures **7**, the highest % PY for this species, and $LiNaSO_4$ remained stable at 50% from 600°C to 650°C and 650°C to 700°C respectively. $NaALSi_3O_8$ and $NaAlSiO_4$ remained constant at 25% in equilibrium from 450°C, indicating that the increase in the molar amount of

$NaSO_4$ during the calcination of α-spodumene tends to decrease the equilibrium temperature. The excess unreacted Na_2SO_4 was 15.7% and 26.5% for 1 and 1.5 mol of Na_2SO_4 respectively. A summary of the evolution of Li_2SO_4 as a function of the molar amount of Na_2SO_4 is shown in Figure 8, with the maximum % PY of 50% at a molar ratio of 1:1 $LiAlSi_2O_6$:Na_2SO_4.

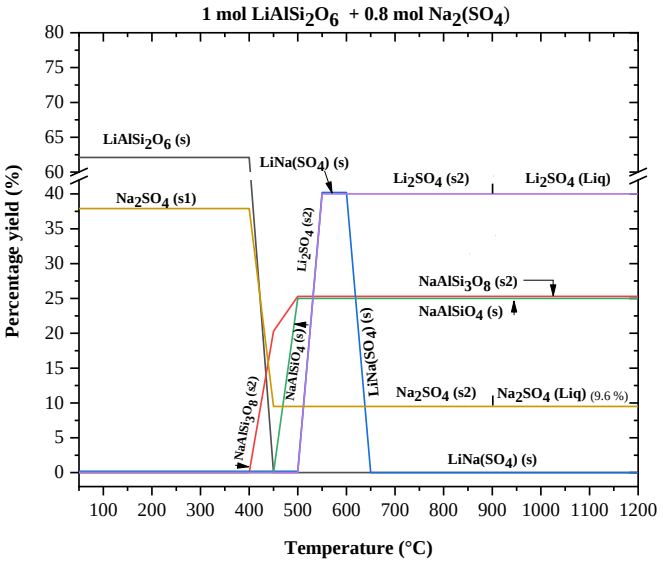

Figure 4: Percentage yield (%) for calcination of 1 mol $LiAlSi_2O_6$ with 0.8 mol Na_2SO_4.

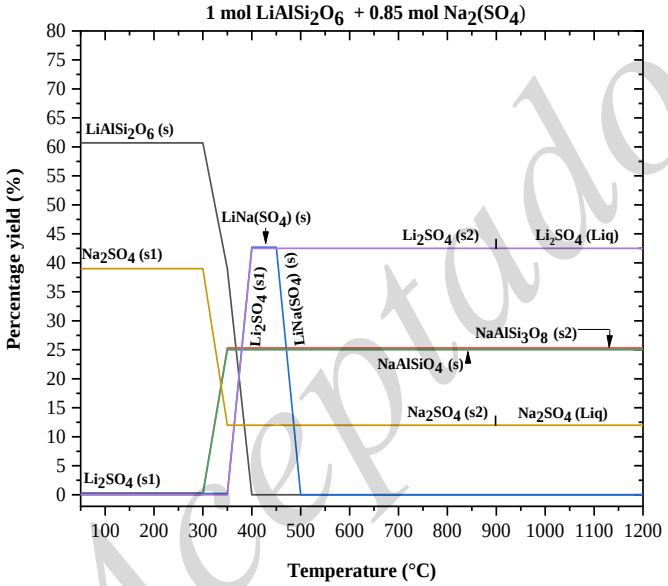

Figure 5: Percentage yield (%) for calcination of 1 mol $LiAlSi_2O_6$ with 0.85 mol Na_2SO_4.

Accordingly, the proposed reaction mechanism for the calcination of α-spodumene with Na_2SO_4 is as follows:

$$4LiAlSi_2O_6 + 3Na_2SO_4 = 2NaAlSi_3O_8 + 2LiNaSO_4 + 2NaAlSiO_4 + Li_2SO_4 \quad (3)$$

This reaction differs from that previously reported by Foss et al. (Foss et al., 2020), who only determined Li_2SO_4 as a reaction product but not the formation of $NaAlSi_3O_8$, $LiNaSO_4$ and $NaAlSiO_4$ during the calcination process.

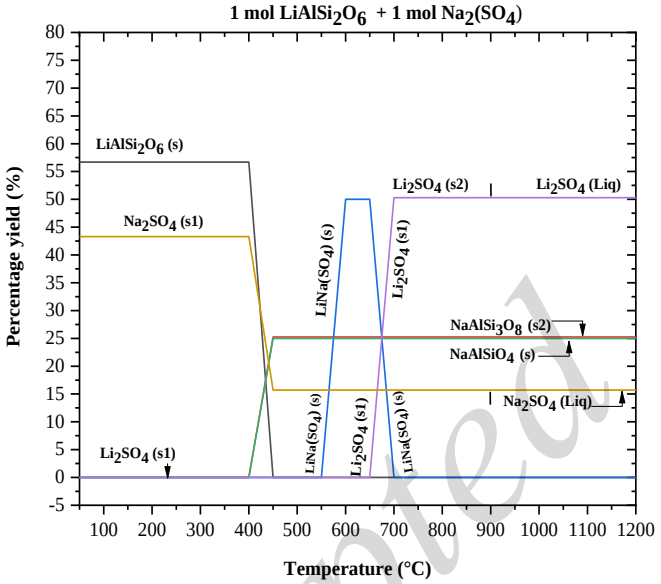

Figure 6: Percentage yield (%) for calcination of 1 mol $LiAlSi_2O_6$ with 1 mol Na_2SO_4.

On the other hand, in the literature it has been reported that the calcination of *α*-spodumene with a large excess of Na_2SO_4 melt (at 1000 ºC) extracted about 90 % of the total lithium content (Arne and Johan, 1941) and that the decrease in calcination temperature to 850 ºC resulted in a significant reduction in the lithium recovery in lepidolite to less than 60 %.

This reaction deserves further consideration, since in the results obtained in the present investigation, considering that the spodumene species is pure, the phase containing lithium, Li_2SO_4, melts at 900°C.

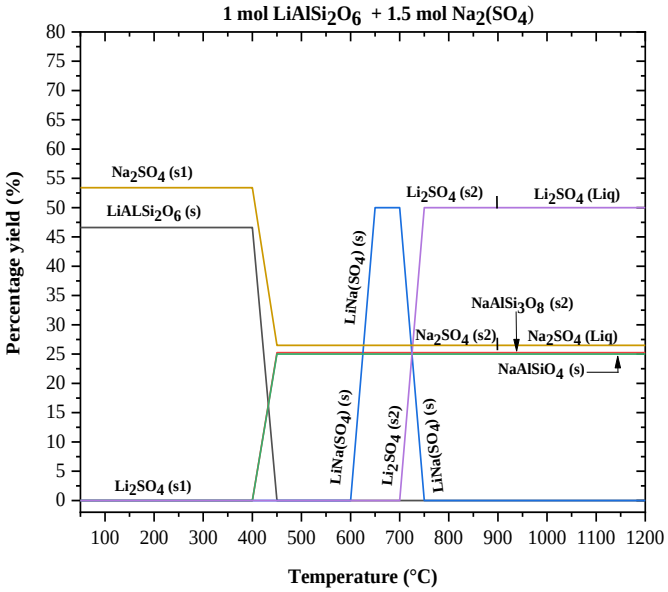

Figure 7: Percentage yield (%) for calcination of 1 mol $LiAlSi_2O_6$ with 1.5 mol Na_2SO_4.

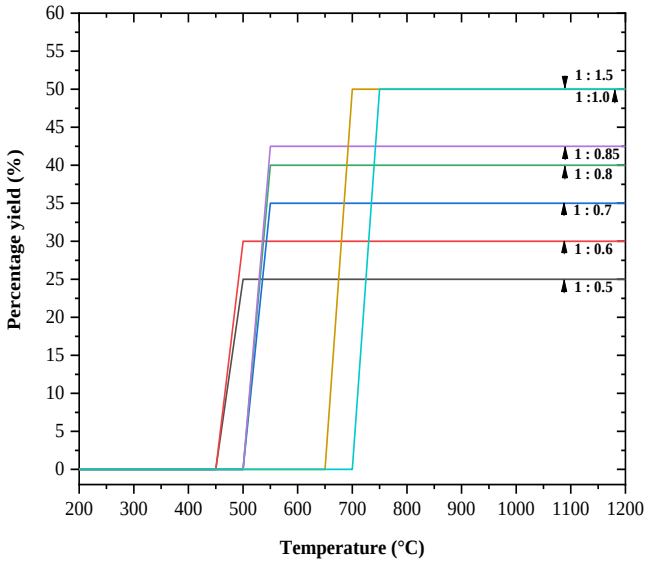

Figure 8: Percentage Yield (%) of Li_2SO_4 obtained at different molar ratios of $LiAlSi_2O_6$:Na_2SO_4.

4. Conclusions

This work simulated the calcination of α-spodumene with different molar ratios of Na_2SO_4 using the equilib module in the Fact Sage 8.2 software. The maximum percentage yield of Li_2SO_4 was 50% in the solid state obtained from 500°C and in the liquid state at ≥900°C for 1:1 $LiAlSi_2O_6$:Na_2SO_4 with an excess of $NaSO_4$. The formation Li_2SO_4 was preceded by the formation of $LiNaSO_4$ at 350°C which increased to 600°C with the increase in the molar amount of Na_2SO_4. $NaALSi_3O_8$ and $NaAlSiO_4$ reached equilibrium from 350°C to 500°C.

These results allowed us to propose the reaction mechanism of the calcination of α-spodumene with Na_2SO_4.

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