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Allen Yushark Fosu, Ndue Kanari, James Vaughan, Alexandre Chagnes. Literature Review and Thermodynamic Modelling of Roasting Processes for Lithium Extraction from Spodumene. *Metals*, 2020, 10 (10), pp.1312. 10.3390/met10101312 . hal-02953994

HAL Id: hal-02953994

<https://hal.science/hal-02953994>

Submitted on 30 Sep 2020

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Literature Review and Thermodynamic Modelling of Roasting Processes for Lithium Extraction from Spodumene

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Received: 24 August 2020; Accepted: 28 September 2020; Published: 30 September 2020

Abstract: This review adds to the public domain literature on the extraction of lithium from mineral ores. The focus is on the pyrometallurgical pre-treatment of spodumene. Information on the phase transformation from α to β , the heat treatment methods as well as the behavior of various compounds in the roasting processes are evaluated. Insight into the chemical thermodynamics of the baking process is evaluated using HSC Chemistry software up to 1200 °C. It was observed that the alkaline, sulfation, chlorination (using Cl_2 and CaCl_2), carbonizing (to form Li_2CO_3) and fluorination processes were feasible either throughout or at a point within the temperature range considered. Chlorination using KCl and carbonizing to form Li_2O are the processes found to be nonspontaneous throughout the temperatures considered.

Keywords: spodumene; thermodynamics; lithium; roasting

1. Introduction

Lithium is used in several industries as a component of products such as glass–ceramics, greases and casting-alloys. Over the last two decades, lithium’s use in batteries, particularly for making vehicles, has resulted in an increased need for lithium compounds. Global lithium demand has risen to about 60% in this time and a 20% yearly increase is expected over the next few decades [1,2]. Such a boom in lithium production is accompanied by a drastic increase of its price, which has tripled in a little more than three years (from 5000 US dollars per ton in 2014 to more than 15,000 US dollars per ton by the end of 2017) [3]. The astronomical demand for the metal has caught the attention of metallurgists around the globe and has prompted the development of novel beneficiation approaches to meet this demand by focusing on extraction from mineral ores. Extracting lithium from ores has higher operating costs than conventional extraction from brine, however, the theory of supply and demand makes the processing economically prudent because of the increasing price of lithium.

Spodumene is the main ore of interest due to its high lithium content (~8 wt.% as Li_2O in a pure mineral specimen) [4,5]. Table 1 shows the mineralogical composition of a typical spodumene ore sample with 2.14 wt.% Li_2O . The concentration of Li_2O in this ore indicates that it is low grade. Spodumene is a lithium aluminum silicate ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ or $\text{LiAlSi}_2\text{O}_6$) of the pyroxene group; it is found in close association with quartz, feldspar and micas [6]. Its color may vary from purple, green, yellow, gray or white, depending on the presence and concentrations of sodium, manganese, iron, magnesium or titanium [7–9].

Table 1. The mineralogical composition of a typical spodumene ore sample.

Mineral	Cr ₂ O ₃	MgO	MnO	Li ₂ O	SO ₃	Fe ₂ O ₃	K ₂ O	Na ₂ O	TiO ₂	P ₂ O ₅	SiO ₂	Al ₂ O ₃	CaO
%	0.03	1.30	0.32	2.14	0.15	4.29	1.26	1.14	0.10	0.33	61.31	20.79	1.72

Spodumene is naturally present in the stable α -monoclinic (highly packed crystal structure) form with high grindability and hence the mineral is difficult to leach without pretreatment. It is made amenable to lixiviation by calcination at 1000 °C to the β -tetragonal form [5]. During the thermal process, there is a dislocation of Al³⁺ in the α -spodumene leading to a β -spodumene crystal structure with a comparably larger crystal volume. This increases the mobility of lithium atoms which then become easily accessible to aqueous lixiviant solutions [4,10,11]. The phase transformation has also been shown to improve comminution, as β -spodumene is relatively soft and flaky [9,10,12]. Recently, an intermediary hexagonal metastable γ -phase was discovered during calcination. This phase is predicted to influence the extraction of lithium. Therefore the sequence of the phase transformation is now understood to be $\alpha \rightarrow \gamma \rightarrow \beta$ [4,10,13]. Though interlocking gangue in spodumene can adversely affect downstream beneficiation processes, Salakjani et al. [9] as well as White and McVay [14] indicated that these impurities facilitate heat conduction and efficient transformation since spodumene itself exhibits low thermal conductivity.

Prior to the hydrometallurgical treatment of the ore after calcination, the β -spodumene phase is baked or roasted with additional compounds which define the next processing route as acidic, alkaline or chlorination.

This review focuses on the various methods of processing spodumene ore, providing theoretical insight from the thermodynamic point of view using the reaction equation and the equilibrium module of HSC Chemistry software version 5.1 (Outokumpu Research Oy, Pori, Finland).

2. Decrepitation of Spodumene Ore

The amenability of spodumene to lixiviation is greatly enhanced by its transformation from the α -form to β -form at elevated temperature, however, a process for direct extraction of lithium from α -spodumene using the HF/H₂SO₄ system was introduced by Guo et al. [15]. The thermal behavior of spodumene has been studied extensively by a number of researchers [4,5,10,11,16] and it is worthy to note that the process is carried out below 1040 °C which is the fusion temperature of spodumene [17].

It has been established that the phase change of α -phase spodumene starts at 800 °C and is completed by 1100 °C, though there is a report of the phase transformation commencing above 634 °C using microwave heating [5,10]. Peltosaari et al. [10] considered the effect of particle size to be insignificant with respect to the conversion rate of spodumene. Salakjani et al. [4] revealed that heating leads to volumetric expansion and makes the ore porous. The final β -spodumene consequently has a larger surface area which enhances subsequent chemical processing. They found that a greater extent of the β -spodumene formed corresponded to a higher surface area produced but a relatively low density. It is anticipated that the inversion of α -spodumene to γ -spodumene is exothermic and that the heat released helps to offset the heat requirement of the process, however, the phase change from α directly to β is endothermic [9,18]. Investigations by Moore et al. [16] indicate that the temperature and the heating method have negligible effect on the mass fraction of the phases transformed during the decrepitation process and that the quantities of inversion products are almost equal at the initial stage before the final conversion to the β -phase. Conversely, Salakjani et al. [5] explained that temperature and residence time are the major factors that determine the inversion of the phases in spodumene; the temperature requirement is subsequently influenced by the chemical composition and the feed particle size of the spodumene sample.

The phase transformation process at the elevated temperature is known to be influenced by many factors including the heating method employed, the morphology of the sample after comminution and the quantity of gangue minerals present [4,10,11,16].

Recently, microwave heat treatment of spodumene has been studied extensively by several authors and compared with conventional methods [4,5,10,16,19]. Spodumene is passive to microwave irradiation so the heat treatment with this method is made possible by hybrid microwave heating with the aid of SiC [9,10]. It was found that β -phase spodumene absorbs significantly higher microwave energy than the α -phase spodumene, resulting in local sintering when the β -phase is reached [9]. Treatment of spodumene using microwave irradiation is still under development and much additional research is required to overcome challenges such as local sintering that results in unequal heating, transparency of spodumene to microwave irradiation and other factors that generally affect the treatment of ores using microwave irradiation. Salakjani et al. [9] suggested that mechanical stirring and the addition of additives (which do not affect downstream processes) could be a remedy for the sintering and passive behavior of spodumene to microwave irradiation, respectively. The microwave heat treatment was found to have a fast transformation rate compared with conventional heating. The transformation of α -spodumene commenced and was almost complete at 110 and 170 s of microwave irradiation respectively [10], but it appears that an hour of heating in a muffle furnace is needed to achieve a 100% conversion to the β -phase [9]. The operating temperature was, however, found to be invariant with regards to the heating methods. There appears to be an inconsistency in the inversion temperatures of these two investigations during the conventional approach. According to Salakjani et al. [9], no phase change was observed for temperatures below 950 °C irrespective of the heating time. They observed the first γ and β -phases at 950 °C for at least 30 min of residence time but Peltosaari et al. [10] observed the first γ -phase at 800 °C. This inconsistency might be due to some factors such as the concentration of impurities, the amorphous nature created due to the mechanical treatment and even particle size to a lesser degree. A minimum of 5 min of conventional heating at 1100 °C was observed by Salakjani et al. [4] to almost complete the conversion of α to β -spodumene while Peltosaari et al. [10] indicated that 100% conversion was achieved within 15 min. However, Salakjani et al. [4] observed some γ -phase present even after 1-h of residence time at 1100 °C.

Comparing the energy requirement for the microwave and the muffle furnace heating for the phase conversion process shows that the microwave approach requires a relatively low energy input for the transformation compared to the conventional method [5]. The conversion to the β -phase requires 5 times less energy by using microwave heating than conventional furnace. The reason for the high energy requirement in the conventional process can be due to the fact that heating begins from the outside and moves to the inside of the sample by conduction (the furnace needs to heat up evenly before the sample undergoes heating) therefore, most of the energy is wasted while in the microwave process, heating starts from the inside of the sample and extends radially outside (the sample absorbs the microwave radiation directly for heating), leading to little or no loss of energy. In another paper [19], the comparison of the microwave and conventional heat treatment for acid roasting of β -spodumene showed that microwave heating resulted in higher lithium extraction than the muffle furnace with regards to key parameters like processing time, excess acid and energy requirement. Indeed, 10.4 MJ of energy was needed for the conventional process whereas only 15.4 kJ was required for the microwave for the same quantity of lithium extracted. Microwave irradiation again required shorter time (20 s) to achieve this goal while an hour was needed in the muffle furnace for the extraction. Particle size was found to have an important effect on the amount of lithium extracted by microwave heat. Finer particles have been confirmed to enhance maximum (93%) lithium extraction with as low as 15% excess acid requirement as compared to 80% excess acid, which is normally used in roasting.

3. Roasting of Spodumene Ore

Roasting β -spodumene with appropriate reagents results in a chemoselective ion exchange reaction where lithium is exchanged for atoms of similar characteristics in the reagent used. This may be done after decrepitation where β -spodumene is roasted with chemicals, or may be performed in-situ during decrepitation. This leads to the formation of soluble lithium salt (such as LiCl, Li₂SO₄ or LiOH). Various reagents have been employed for forming the lithium salt during roasting and

rigorous investigations are ongoing for optimization. Unlike roasting, the decrepitation process appears to be nearly optimized and little can be done to further adjust parameters like the operation temperature and granulometry of the comminuted ore [13]. The reagent used for the roasting determines the name of the process. Generally, at a given pH, reagents are selected based on their selectivity for the metal of interest, stability in the aqueous phase, environmental friendliness, cost and ease of regeneration after dissolution. These reasons have resulted in a series of investigations in search of suitable chemicals that satisfy a majority of these criteria during lithium ore beneficiation.

There are three well-known methods for roasting spodumene. The first is acid roasting, which involves baking the calcined spodumene product with an excess of concentrated sulphuric acid at a temperature of about 250 °C (for conventional heat treatment) or 320 °C (for microwave irradiation for 20 s) [19]. The second is the alkaline process which utilizes limestone (CaCO_3) or lime (Ca(OH)_2 or CaO) and lastly, the chloride route which uses various chlorinating reagents. There are other new approaches such as the carbonizing (using Na_2CO_3 in the presence of CO_2 and other additives) and fluorination (using NaF). Figure 1 shows the main high-temperature routes for spodumene treatments which are described below (sulfation, alkaline and chlorination processes for processing spodumene).

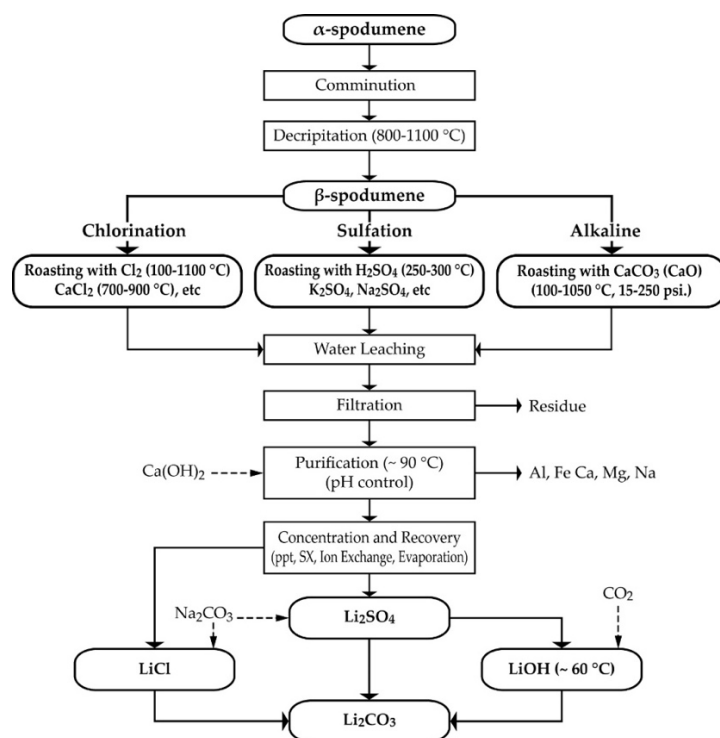


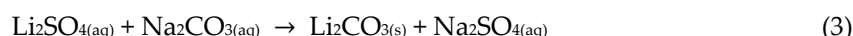
Figure 1. The flow diagram of the major treatment processes for spodumene (chlorination, sulfation and alkaline processes).

3.1. Sulfation Processing of Spodumene

In this process, alkali metal sulfates, sulfuric acid or SO_3 gas in the presence of water and oxygen are employed as reagent (s) to produce soluble lithium sulfate which can be water leached. This process benefits from the high stability and solubility of lithium sulfate in the aqueous phase during leaching. The drawbacks are the difficulty in producing high purity lithium carbonate resulting from the unselectivity of sulfate reagents towards other metals such as Al, Na, Mg, Fe and K. Aluminum and iron impurities may be significant such that precipitating them from the leachate carries along some lithium, decreasing overall lithium recovery [17]. The presence of some alkali metals also affects the purity of the final product since they are leached alongside lithium and separating them becomes complicated due to their similar chemistry to lithium in aqueous solution.

The sulfation process consumes a large amount of reagent which affects the economic viability of the process [20,21]. Sulfates of potassium, ammonium and sodium have been successfully used for the extraction of lithium from several lithium bearing minerals. Sulfate roasting of lepidolite followed by water leaching has been studied widely using $\text{Na}_2\text{SO}_4/\text{K}_2\text{SO}_4/\text{CaO}$, Na_2SO_4 and FeSO_4 at roasting temperatures of 880, 1000, 850 °C respectively. The corresponding approximate extraction extents were 95, 99.5 and 90% extraction, respectively [21–24]. The sulfating behavior of zinnwaldite, petalite and montmorillonite have also been discussed elsewhere [21,25–27] using Na_2SO_4 and H_2SO_4 and yielding 90, 97.3 and 90% lithium extraction, respectively.

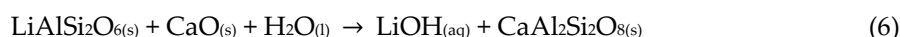
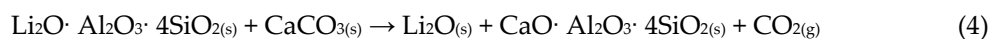
In the case of spodumene, the transformation from the α to the β -phase is crucial before the application of sulphates as indicated above. Several authors have conducted systematic experimental studies to understand and optimize the amenability of sulfates to spodumene beneficiation [17,19,28–31]. The use of sulfuric acid is renowned and currently, the commercialized process for lithium extraction while the others are still undergoing research. In the acid process, the ore is roasted with sulfuric acid at a temperature of about 250 °C. Investigations by Salakjani et al., [19] indicate that one hour is optimal for conventional heating while only 20 s is needed with microwave roasting. It is essential that this process is operated below 337 °C to prevent the evaporation of the acid [19]. During this process, the H^+ of the acid is chemoselectively exchanged with Li^+ of spodumene as indicated in Equation (1) to form water soluble $\text{Li}_2\text{SO}_4(\text{s})$. The water-soluble part of the roasting process is water leached according to Equation (2), lime precipitation is conducted at 90 °C for pH adjustment and removal of impurities from solution. Lithium carbonate is recovered by the addition of sodium carbonate solution to the extract as indicated by Equation (3):



It must be noted that the diffusion of the acid through the ore for the ion exchange is the rate determining step for the reaction. Unlike gaseous reagents, the viscous nature of the liquids (acid and lithium bisulphate produced around 170 °C) slows their penetration through tiny pores and cracks, thereby slowing down the reaction [32].

3.2. Alkaline Process

This process benefits from the economics and the nonaggressive nature of the salt used as a reagent compared to the acid process which requires the use of concentrated acid [33]. It involves roasting the lithium bearing ore with lime or limestone within the temperature range of 100–205 °C or 825–1050 °C respectively. Roasting with limestone is specified by Equation (4) where water soluble $\text{Li}_2\text{O}(\text{s})$ is formed with calcium aluminosilicate and carbon dioxide. $\text{Li}_2\text{O}(\text{s})$ is water leached to produce aqueous LiOH [21,34], which is separated from residual solids by filtration. Instead of direct baking of spodumene with limestone to produce $\text{Li}_2\text{O}(\text{s})$, limestone can initially be decomposed thermally to produce CaO (Equation (5)). The CaO that was produced is then roasted with spodumene in the presence of water to produce LiOH (Equation (6)).



The lithium hydroxide that is produced can be converted to LiCl or LiCO_3 by reaction with hydrochloric acid or carbon dioxide, respectively, if they are the final products desired. This process has been used by Jandova et al. [35] to recover 90% lithium from zinnwaldite waste. Some additives such as gypsum, lithium carbonate and sodium sulphate may be employed in the baking process to enhance lithium recovery; recording 96%, 96% and 90%, respectively [33,36,37]. The downside of this approach is the high energy requirement for the decomposition of limestone and dicalcium silicate. This may result in the evolution of unbearable heat which makes temperature control in the system difficult [14].

3.3. Chlorination Process

The use of chlorine gas and chloride bearing salts in mineral beneficiation is the least considered process due to the toxicity of chlorine gas that may be generated alongside the products, and the high cost of corrosion resistant equipment needed for the process. However, there are several benefits of chlorine metallurgy in minerals processing. The main benefit is the high selectivity of chlorine and the comparatively lower operating temperature. The generated chlorides have low melting and boiling points and are easily separated from the wastes due to the vapor pressure difference [38–40]. In addition, the use of chlorine results in high recovery of metals, which makes it easy for treating low grade ores. Lastly, the process results in the generation of environmentally green waste. These advantages call for a closer look at chlorine for beneficiating lithium ores, however, it has attracted little attention and few literature articles have been written about it [41–46].

Peterson et al. [41] patented a blend of muriate of potash and sylvinitic ore (sodium and potassium chloride) to recover lithium from its ores at 980–1100 °C. The reaction of this invention is an exchange reaction between the alkali metals of the chlorides and the lithium of the ore, thereby forming soluble LiCl, which was further converted to lithium carbonate by reaction with sodium carbonate. About 97.5% of the lithium carbonate was recovered by this approach. Chlorination of lepidolite using sodium and calcium chloride at 880 °C yielded 93% lithium recovery [42]. Recently, the same approach was applied to recover the lithium value in spodumene using chlorine gas and calcium chloride, respectively; 900 °C and 120 min were suggested as the optimal chlorination conditions, which resulted in 90% lithium extraction when calcium chloride was used [43,44].

3.4. Other processes to Spodumene Treatment

Other less known processes for beneficiating lithium ores worthy of discussion are the carbonizing and fluorination processing. Lithium carbonate can be produced by carbonizing lithium bearing ore with sodium carbonate between 525 and 675 °C in a solid–solid intimate reaction followed directly by leaching or hydrothermal decomposition treatment (between 90 and 225 °C) prior to leaching [47]. The reactions of the process (Equations (7) and (8)) must be carried out above the minimum temperatures suitable for the individual lithium bearing ore (1080, 850, 980 and 870 °C respectively for petalite, lepidolite, eucryptite and spodumene). They indicated the need to carry out this roasting in the presence of alkali metal chlorides, alkali metal sulfate or carbon dioxide which act as a catalyst for the process. However, a specific preference for sodium and potassium chloride or sulfate was indicated. By this process, 75–97% of lithium contained in the ore could be leached for recovery. The inventors of this process [47] highlighted some advantages of this process which include the possibility of using Na₂CO₃ as the only reactant to produce Li₂CO₃ of high purity. They indicated that the reagent is ideally employed to decompose refractory ores into fragments to enhance leaching. The process is therefore expected to require serious purification steps since the decomposition may give rise to several impurities. Using it as a plant production of Li₂CO₃ with good recovery and high purity without major purification is therefore a breakthrough. This approach is also said to have a short processing time and to be economically viable. This is because, the reagent is added to the cooling calcined spodumene midway during the process, for it reacts with the mineral, thereby reducing the time for processing and also utilizing the energy which would have gone wasted.



Owing to this invention several other investigations have revolved around it for its optimization [48,49]. Chen et al. [48] employed pressurized roasting of spodumene concentrate with sodium carbonate in an autoclave, yielding 94% lithium carbonate production with 99.6% purity. Research by dos Santos et al. [49] using spodumene and sodium carbonate, promoted by sodium chloride, resulted in 70% lithium yield. The involvement of NaCl by dos Santos et al. [49] was to aid the extraction of the residual lithium bound at the interstitial positions of the ore. This reaction was conducted within 550–650 °C for 120 min.

The only fluorination roasting report available in literature was performed by Rosales et al. [50], though there are some hydrometallurgical processes of spodumene beneficiation using some fluorination agents [15,51]. In this approach, roasting of NaF with β -spodumene at 600 °C spodumene: NaF from 1:1 to 1:2.5 and 4 h was investigated. 90 % maximum lithium recovery was achieved and it occurred at spodumene: NaF of 1:2 and 2 h of roasting. Equation (9) illustrates the reaction process:



The processes discussed with some relevant information are summarized in Table 2.

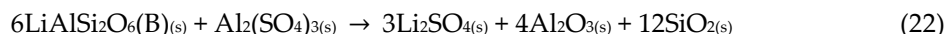
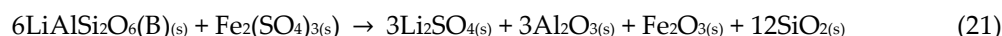
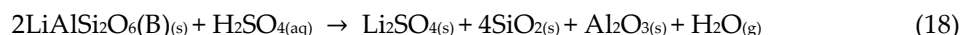
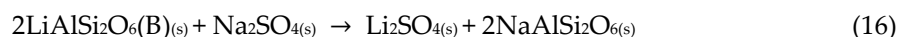
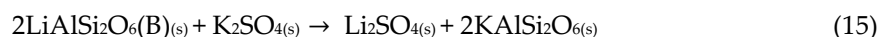
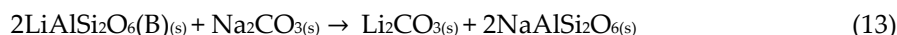
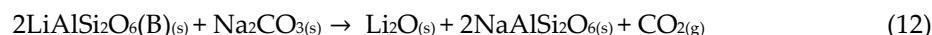
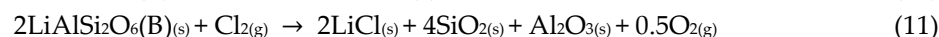
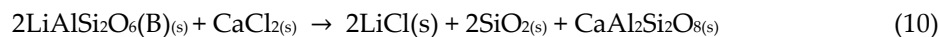
Table 2. Summary of literature for the recovery of lithium from spodumene using the major beneficiation processes.

Process	Experimental Conditions						Product	Recovery/%	Reference
	Roasting			Leaching					
	Reagent	Temp./°C	Time/min.	Time/hr	Temp./°C	Lixiviant			
Sulfating	Conc.·H ₂ SO ₄	200–300	30–60	-	-	H ₂ O	Li ₂ SO ₄	85	[52]
	Na ₂ SO ₄ + CaO	-	-	3	230	Na ₂ SO ₄ + CaO	Li ₂ SO ₄	93.30	[28]
	Na ₂ SO ₄ + NaOH	200–300	-	3	230	Na ₂ SO ₄ + NaOH	Li ₂ SO ₄	90.70	[28]
	(NH ₄) ₂ SO ₄	150–370	-	-	-	NH ₃ (aq)	Li ₂ SO ₄	-	[17]
	CaSO ₄ + CaCO ₃	1000–1150	120–180	-	-	H ₂ O	Li ₂ SO ₄	85–90	[53] *
	Conc. H ₂ SO ₄	250–300	-	1	-	H ₂ O	Li ₂ SO ₄	86	[31]
	H ₂ O+O ₂ + SO ₃	350–425	10-40	-	-	H ₂ O	Li ₂ SO ₄	97	[32]
Alkaline	CaO + H ₂ O	100–205	60			H ₂ O	LiOH	~97	[34]
	CaO + H ₂ O	1000–1230			100	H ₂ O	LiOH	80	[34] *
Chlorination	KCl, NaCl	1000–1050	15–60	-	85	H ₂ O/HCl	LiCl	85–97.50	[41]
	Cl ₂	1100	150	-	-	-	LiCl	-	[43]
	CaCl ₂	900	120	-	60	H ₂ O	LiCl	90.2	[44]
	CaCl ₂	800–1200	-	-	-	Alcohol	LiCl	9.5–98.5	[46]
Carbonizing	Na ₂ CO ₃	525–675	10–120	-	-	H ₂ O, NH ₄ ⁺ (aq)	Li ₂ CO ₃	75–97	[47]
	Na ₂ CO ₃	150–250	10–120	--	-	H ₂ O	Li ₂ CO ₃	~94	[48]
	Na ₂ CO ₃ + NaCl	~923	120	-	-	H ₂ O	Li ₂ CO ₃	70	[49]
Fluorination	NaF	600	120	0.5	25	HF	LiF	90	[50]

* roasting of spodumene done in the alpha phase.

4. Chemical Thermodynamics of Spodumene Processing

Insight into thermodynamics of the beneficiation approaches of spodumene are scarce in literature. This section looks at the thermodynamic modelling of the various approaches of lithium processing encountered in literature using the HSC Chemistry software version 5.1 reaction equation and equilibrium module. The standard Gibbs free energy changes as a function of temperature for the following reactions involved during spodumene roasting with various reagents (sulfating, alkaline, fluorinating, carbonizing and chlorinating agents, Equations (10)–(22) are found in Figure 2:



It is worth noting from Figure 2 that all the reagents used in literature for alkaline, sulfating, fluorination, chlorination (with the exception of KCl) and carbonizing to yield Li_2CO_3 were spontaneous at a point or throughout the operating temperature for roasting spodumene. Chlorination with KCl and carbonization to produce Li_2O were the only processes which are not thermodynamically favorable throughout the temperature range. All reagents for sulfating roasting except K_2SO_4 and the feasible carbonizing process showed a major variation of spontaneity with temperature while reagents for other processes did not. Sulfation and chlorination using Na_2SO_4 , SO_3 and Cl_2 as well as the spontaneous carbonizing process benefit from feasibility only at low temperatures; they are not feasible at high temperatures. The observed spontaneity of CaCl_2 chlorination parallels observations by Barbosa et al. [44]. However, those observations are contrary to observations made by the same authors earlier, which indicated feasibility with Cl_2 even at higher temperatures [43]. The reason for this difference is not yet apparent.

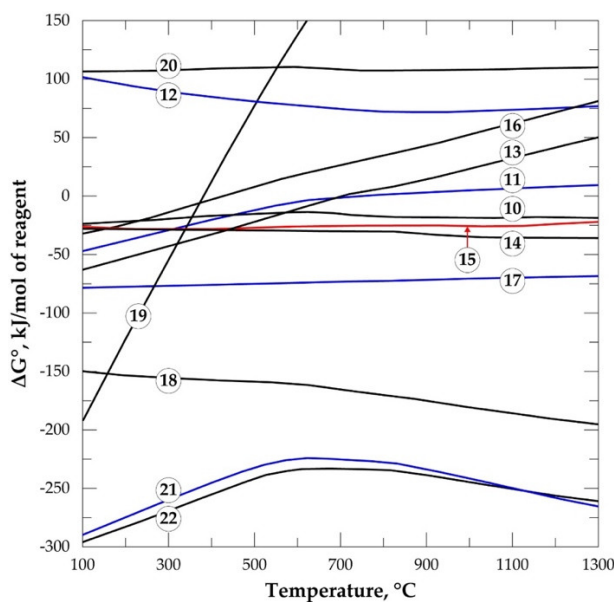
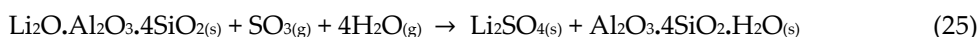


Figure 2. The standard Gibbs energies for roasting of spodumene for processes encountered in the literature (reactions (10)–(22)) versus temperature (data from the HSC Chemistry 5.1 software).

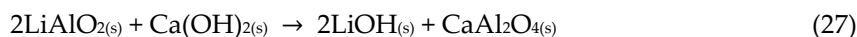
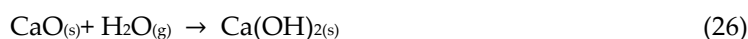
To gain a deeper understanding of the approaches outlined in literature, the HSC Chemistry 5.1 software equilibrium module was further employed to investigate the equilibrium amount of each process as a function of temperature. Figure 3 displays the equilibrium moles for the sulfating process using Na_2SO_4 , K_2SO_4 , H_2SO_4 , $\text{SO}_3(\text{g})/\text{H}_2\text{O}(\text{g})$, $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Al}_2(\text{SO}_4)_3$ as reagents. As indicated earlier (Figure 2), Na_2SO_4 is feasible only below 400 °C. It is only below this temperature that the equilibrium moles of the products (lithium sulfate and sodium aluminosilicate, NaAlSiO_6) are higher than spodumene (Figure 3a), confirming feasibility. It can be inferred that the highest amount of lithium sulfate can be obtained below 200 °C above which it starts decreasing until 400 °C, where the reaction ceases feasibility. Around 400 °C and above, solid lithium sulfate begins to change into a liquid state due to the increasing temperature but the amount is relatively smaller in the system; resulting from the decreased feasibility of the reaction. Temperatures less than 400 °C appear to be the best for Na_2SO_4 /spodumene roasting, however, 1000 °C was required to achieve 90.4% lithium extraction according to Luong et al. [23] for Na_2SO_4 /lepidolite roasting for 30 min. Unlike Na_2SO_4 , K_2SO_4 drives the reaction to the right within the whole temperature range considered, forming lithium sulfate in the solid phase (Figure 3b), moles of lithium sulfate then are at levels higher than spodumene within the entire temperature range considered. There is a steady decrease in moles of solid lithium sulfate and a simultaneous increase of the liquid phase with increasing temperature. This is a result of the conversion of the solid into liquid as liquid is formed until around the melting point (859 °C); where all the solid phase changes to liquid and remains constant. Thermodynamics of the sulfuric acid process predicts feasibility throughout the entire temperature range considered (Figure 2) with ΔG° becoming more negative with increasing temperature. The highest amount of soluble Li_2SO_4 produced by modelling of this process occurs around 200 °C. When the temperature is close to 300 °C and beyond, there is a steady decrease in quantity. These observations are in line with observations by Salakjani et al. [19] whose maximum recovery occurred at 250 °C, but a decrease in lithium recovery was observed at 300 °C and beyond. This occurrence is as a result of the decomposition of sulfuric acid between 300 and 400 °C (Figure 3c). However, the process remains spontaneous even after the decomposition of the acid because the products of the decomposition (SO_3 and H_2O) from Equation (23) are capable of driving the reaction to the product in Equation (25) but with a limited amount of lithium sulfate production. SO_3 breaks down further into SO_2 and O_2 (Equation (24)), which remain as spectator species. Precautionary measures are advised at this point due to the toxicity of SO_2 produced. Thus above 400 °C the sulfuric acid process has thermodynamic behavior similar to the sulfation process using $\text{SO}_3(\text{g})/\text{H}_2\text{O}(\text{g})$ invented by Archambault et al. [32].

Solid lithium sulfate in the reaction medium melts above 800 °C. The equilibrium amount of lithium sulfate decreases after the decomposition of the acid but the kinetics of the process is expected to be favored due to the production of the gaseous reactants which easily access reaction sites by diffusion compared to the percolation of sulfuric acid as a result of its viscosity. Around 900 °C and above the sulfation process with sulfuric acid and $\text{SO}_3(\text{g})/\text{H}_2\text{O}(\text{g})$ ceases spontaneity, signified by a sharp increase in the amount of spodumene in Figure 3c,d. This observation is attributed to the sintering effect and the formation of lithium silicate, which has close resemblance to β -spodumene [54,55].

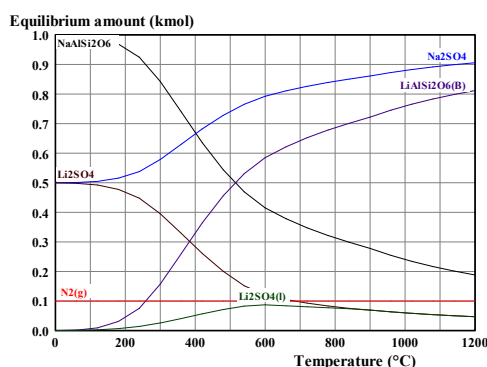


Spodumene roasting using $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Al}_2(\text{SO}_4)_3$ have similar behavior (Figure 3e,f), except for a constant production of Li_2SO_4 in the case of $\text{Fe}_2(\text{SO}_4)_3$, but its amount is higher only at temperatures below 500 °C for $\text{Al}_2(\text{SO}_4)_3$. Metal sulfates also break down, producing SO_3/SO_2 at higher temperatures, which may influence the roasting process. According to Luong et al. [24], Na_2SO_4 like K_2SO_4 has high thermal stability, ergo they break down at higher temperatures, producing a small amount of SO_3/SO_2 , which apparently has no effect on the process. This is confirmed by the absence of these gases in their modelled process (Figure 3a,b). For iron and aluminum sulfates, the amount of the gases generated during the decomposition is large enough to influence the process. From Figure 3e,f, the sulfate of these metals is observed to decompose around 700 °C, producing the gases but their effect is minimal in spodumene as compared to observation in lepidolite by Luong et al. [24], which may be due to the sintering of spodumene above 800 °C [54,55].

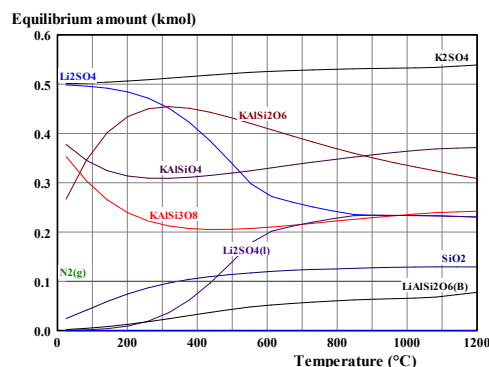
Calcium oxide was considered the reagent for alkaline roasting of spodumene. LiAlO_2 is predicted by HSC as a product of the reaction (Equation (17)). $\text{Ca}(\text{OH})_2$ produced from the reaction of Equation (26) reacts with LiAlO_2 (Equation (27)), producing LiOH in the solid or liquid phase depending on the temperature.



It can be found from Figure 2 that the process is feasible throughout the temperature range considered. This is confirmed by Figure 4 where soluble lithium hydroxide is formed as the useful product. Other products formed include silica, silicates and other aluminosilicate with traces of calcium hydroxide. The moles of lithium hydroxide in the solid phase decreases sharply with increasing temperature. This occurrence is attributed to the conversion of the solid into the liquid phase, confirmed by the sharp rise of the liquid phase with increasing temperature until around its melting point (462 °C), where there is a total transformation into the liquid phase (Figure 4).



(a)



(b)

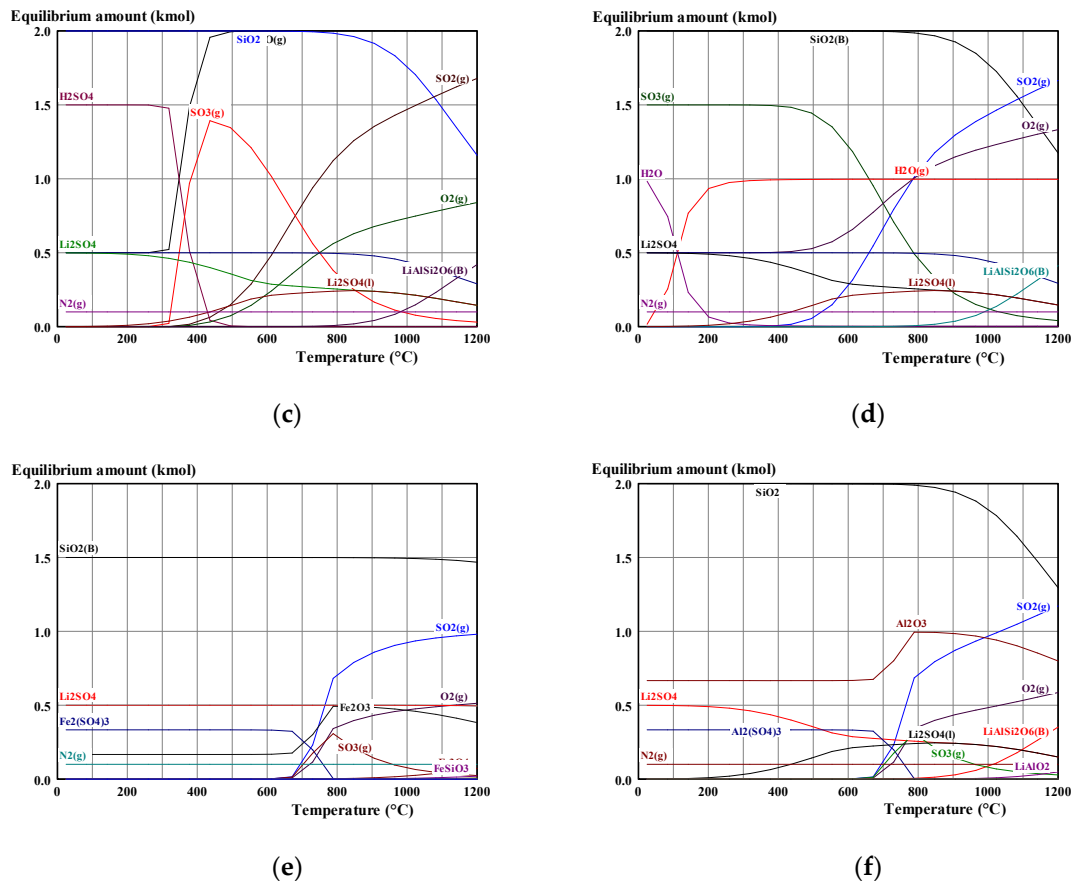


Figure 3. Equilibrium amounts versus temperature for sulfate roasting of spodumene using (a) Na_2SO_4 , (b) K_2SO_4 , (c) H_2SO_4 , (d) $\text{SO}_3(\text{g})$, (e) $\text{Fe}_2(\text{SO}_4)_3$ and (f) $\text{Al}_2(\text{SO}_4)_3$ (data from HSC Chemistry 5.1 software).

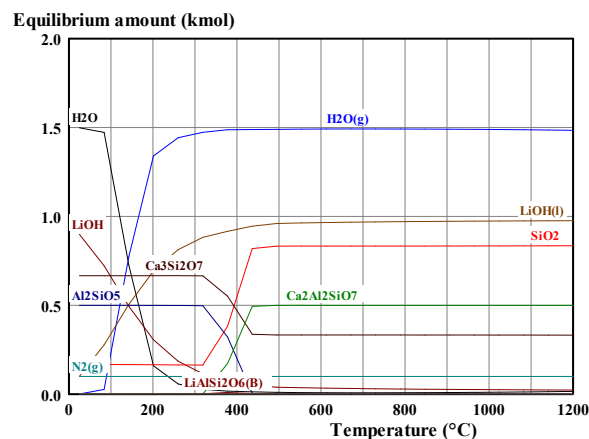


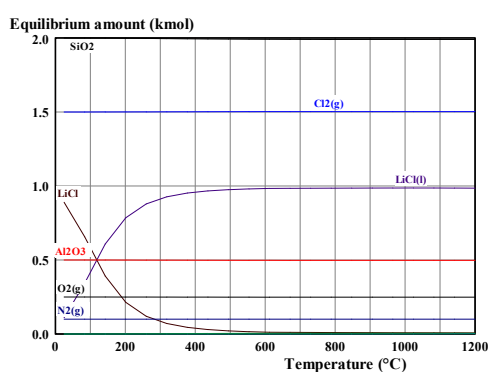
Figure 4. Equilibrium amounts versus temperature for alkaline roasting of spodumene using CaO (data from HSC Chemistry 5.1 software).

Figure 5a–c shows the modelling of chlorination roasting using CaCl_2 , Cl_2 and KCl , performed experimentally by several authors [41,43,44,46]. From Figure 2, it is observed that the reactions with CaCl_2 and Cl_2 are favored at a point or in the entire temperature range, however, it is not feasible with KCl . This infeasibility is confirmed in Figure 5a where an appreciable mole of spodumene is observed in the equilibrium mixture. There is an onset production of solid LiCl which is converted into the liquid phase as soon as it is produced (Figure 5b,c). At $\sim 610^\circ\text{C}$ (the melting point of lithium chloride) lithium chloride in the medium is predominantly in the liquid phase. A high volatilization

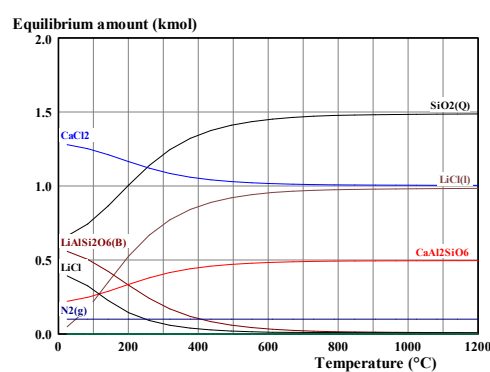
temperature is expected due to the high vapor pressure of LiCl. Barbosa et al. [43] observed the gaseous phase at ~1000 °C, however, it was not the case in the chlorination processes that were modelled.

Carbonizing roasting of spodumene using Na_2CO_3 as seen earlier in Equations (12) and (13) may yield either Li_2O or Li_2CO_3 . The Li_2O that is produced can be made to go into leaching to produce LiOH but the prediction from the HSC software indicates that the reaction is not spontaneous except for the production of Li_2CO_3 (Figure 2). The infeasibility of Equation (12) is confirmed in Figure 6a, where there is apparently, no leachable lithium product formed. The production of Li_2CO_3 from this process is feasible below 700 °C (Figure 2) which is confirmed in Figure 6b where Li_2CO_3 is observed below this temperature. Around 300 °C, the Li_2CO_3 that was produced decomposes, forming carbon dioxide, silicates, aluminates and aluminosilicates (Figure 6b). Thus, though there is feasibility until 700 °C, it is not recommended to operate up to this temperature due to the decomposition which occurs alongside the process. This confirms investigations by [47] that the ideal hydrothermal decomposition temperature for the process as 90–225 °C. It is mentioned that, the mixture of products from the decomposition process may be converted to sodic zeolite which when tapped increases the recovery and the purity of lithium carbonate produced. 94% and 70% lithium recovery were reached by working under high pressure and by adding sodium chloride, respectively, with this process [48,49].

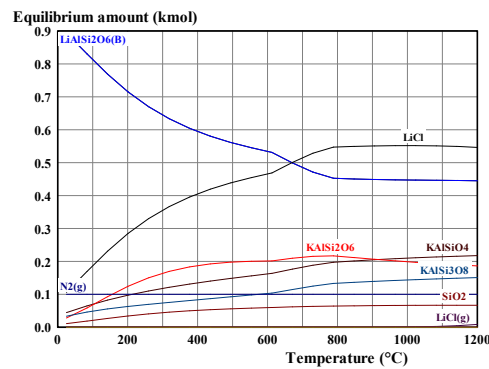
Fluorination roasting of calcined spodumene using NaF is found favored throughout the temperatures (Figure 2), which is confirmed by the formation of lithium fluoride in the solid or liquid phase (Figure 7) [50]. On the other hand, the predicted reversal of the process at higher temperatures, signified by the rise of spodumene in their model with increasing temperature, was not observed in this study. The disparity may be attributed to the absence of liquid lithium fluoride in their model. Solid lithium fluoride begins to form but it melts and its amount decreases due to the simultaneous formation of the liquid phase with increasing temperature. The liquid phase becomes the stable one at higher temperatures and its absence from the HSC equilibrium calculation leads to some errors in the result. There is a leveling of the liquid lithium Fluoride production at around 845 °C (the melting point of LiF) due to the transformation of all of the solid phase into liquid. Their maximum extraction (~90%) occurred at 600 °C, which is just around what is predicted in this study. Gaseous lithium fluoride was not observed within this temperature range, but it is expected to appear around its boiling point (1676 °C) and beyond.



(a)

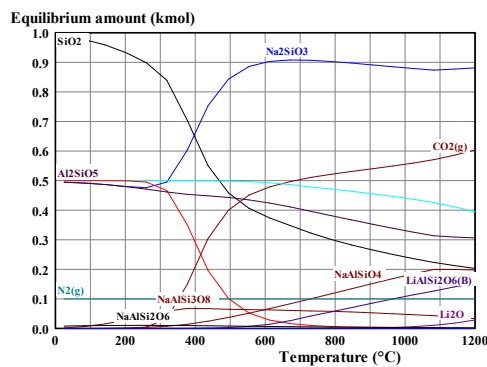


(b)

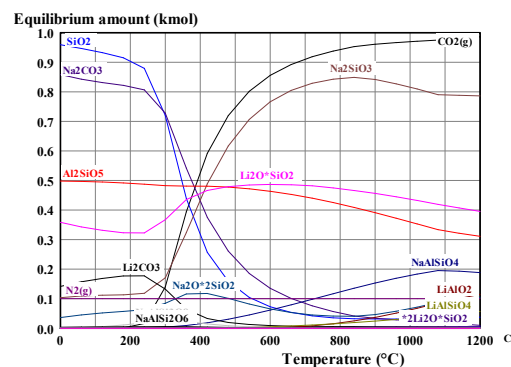


(c)

Figure 5. Equilibrium amounts versus temperature for chlorination of spodumene using (a) CaCl_2 , (b) Cl_2 and (c) KCl (data from HSC Chemistry 5.1 software).



(a)



(b)

Figure 6. Equilibrium amounts versus temperature for carbonizing roasting of spodumene using Na_2CO_3 by considering reactions reported in (a) Equation (12) and in (b) Equation (13), leading to the formation of Li_2O and Li_2CO_3 , respectively (data from HSC Chemistry 5.1 software).

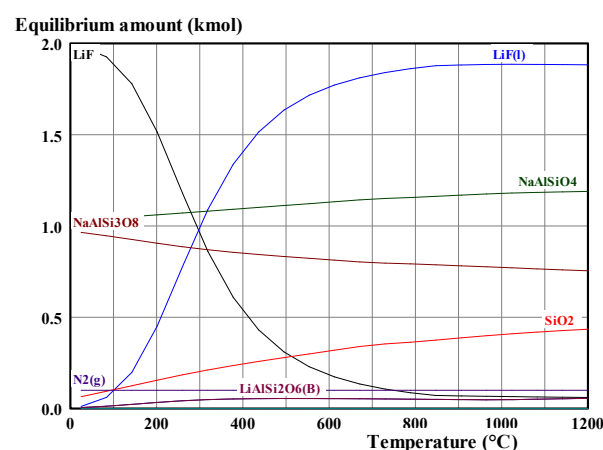


Figure 7. Equilibrium amounts versus temperature for fluorination roasting of spodumene using NaF (data from HSC Chemistry 5.1 software).

5. Conclusions

Besides the general review of the processes for spodumene treatment, an evaluation of the chemical thermodynamics reveals that, sulfation, alkaline, fluorination, chlorination as well as

carbonizing to produce lithium carbonate were processes which had the required thermodynamic driving force to move the reaction to the products for the reagents encountered in the literature. It is therefore not surprising sulfation (using sulfuric acid) and alkaline processes are considered as an industrial approach for lithium extraction. Looking at the mild nature of the reagents in the alkaline processes, it will be a real contender to the acidic process if the high energy requirement in the decomposition of limestone can be decreased by some means. Though roasting with lime is feasible even at lower temperatures, the decomposition of limestone is a precursor for the industrial production of lime which makes the overall process energy intensive. Future work must be focused on reducing the high heat needed for decomposing limestone to make the alkaline process economically viable. In the acid roasting process, SO_3 and H_2O from the acid decomposition may drive the reaction to produce at a faster rate due to the higher diffusion rate of gases compared to liquids. In spite of the expected faster rate of reaction of these gases (SO_3 and H_2O), little is known concerning their use for beneficiating lithium bearing minerals. It will be interesting if the behavior of these species as well as other gases are considered for processing lithium from ores. Sulfation as a method of spodumene beneficiation is mostly limited to sulfuric acid, with little focus on other sulfating reagents, but from the thermodynamics of this group of compounds it will also be interesting to pay attention to other members of this compound. There is considerable literature on the use of some alkali and alkaline earth metal sulfates as well as sulfates of ammonium for processing other lithium bearing minerals than spodumene. Even in those cases, there is minimal explanation of the chemical thermodynamics of the processes. Future work must therefore look at the use of other sulfating reagents for spodumene processing as well as their thermodynamics, both on spodumene and other lithium bearing minerals. Chlorination and fluorination have been found to be promising for lithium extraction. Few chlorination and fluorination agents are encountered in the literature for the process, despite their thermodynamic feasibility. More research should be pursued in search for new fluorination and chlorination agents and the processes should be optimized. The thermodynamics of the carbonizing process yielding lithium carbonate is very interesting; in particular its low operating temperature and the direct production of a considerably pure product. It is surprising that it has not attracted much attention. Further research must be pursued to optimize the process. From a thermodynamic point of view, temperatures below 300 °C are predicted for the acid process and the feasible carbonizing process due to the acid and lithium carbonate decomposition. For the other processes discussed, temperatures less than 600 °C are advised, except for fluorination, which works well a little above 600 °C.

Author Contributions: Conceptualization, A.C. and N.K. and software, A.Y.F. and N.K.; A.Y.F. writing—original draft preparation and writing—review and editing, A.C., N.K. and J.V.; Supervision, A.C. and N.K.; Funding acquisition, A.C. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the French National Research Agency through the national program “Investissements d’avenir” with the reference ANR-10-LABX-21-RESSOURCES21.

Conflicts of Interest: The authors declare no conflict of interest.

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