Short communication

Extraction of lithium from β-spodumene using chlorination roasting with calcium chloride

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A B S T R A C T

Chlorination roasting was used to extract lithium as lithium chloride from β-spodumene. The roasting was carried out in a fixed bed reactor using calcium chloride as chlorinating agent. The mineral was mixed with $CaCl_2$ on a molar ratio of 1:2. Reaction temperature and time were investigated. The reactants and roasted materials were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD) and atomic absorption spectrophotometry (AAS). The mineral starts to react with $CaCl_2$ at around 700 °C. The optimal conditions of lithium extraction were found to be 900 °C and 120 min of chlorination roasting, under which it is attained a conversion degree of 90.2%. The characterization results indicate that the major phases present in the chlorinating roasting residue are $CaAl_2Si_2O_8$, SiO_2, and $CaSiO_3$.

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1. Introduction

The successful use of lithium-ion batteries in electric vehicles (EVs), hybrid electric vehicles (HEVs), and plug-in-electric vehicles (PHEVs) could greatly increase consumption of lithium. Lithium's unique properties are also underpinning growth in other markets, including grease, glass-ceramics, primary batteries and metallurgical powders. If the rate of consumption increases faster than supply, prices could increase, and spodumene ($LiAlSi_2O_6$) and other lithium resources that had been considered uneconomic might once again yield economically feasible raw materials for the production of lithium carbonate [1].

There are many different lithium containing minerals. Currently, spodumene is the preferred mineral because it has a high lithium theoretical content (8.03% Li_2O) and is comparably easy to process [2]. Presently, the most important process for extraction of lithium from lithium alumino-silicates is the lime method [3]. However, it is known that too much limestone and high energy are consumed. Chlorination roasting is emerging as an alternative process; it has been an important process step in the extraction of many nonferrous metals from their ores and concentrates [4].

Chlorination process with chlorine as a reactant gave high yield for the extraction of lithium as lithium chloride from β-spodumene (β-$LiAlSi_2O_6$). However, such process requires temperatures as high as 1100 °C [5,6].

Calcium chloride has been used as a chlorinating agent for the extraction of metals from different sources [3,4,7–12]. Moreover, calcium chloride has been found to be the most effective chlorinating agent in presence of silica. Accordingly, calcium chloride was evaluated as a chlorinating agent to extract lithium as lithium chloride from β-spodumene in this work. The effect of temperature and time of the reaction between β-spodumene mineral and $CaCl_2$ was studied to optimize the conditions of the process.

2. Thermodynamic analysis

The thermodynamic calculations for the chlorination reaction of β-$LiAlSi_2O_6$ with $CaCl_2$ were performed within the temperature ranging from 25 to 900 °C. Considering that $CaCl_2$ is in excess, the equilibrium composition of the system Si–Al–Li–O–Ca–Cl as a function of temperature can be calculated using HSC thermochemical database software [13]. This calculation was performed using the system free energy minimization method and the results are presented in Fig. 1. The compound O_2 was not considered in the calculation as a reactive gas.

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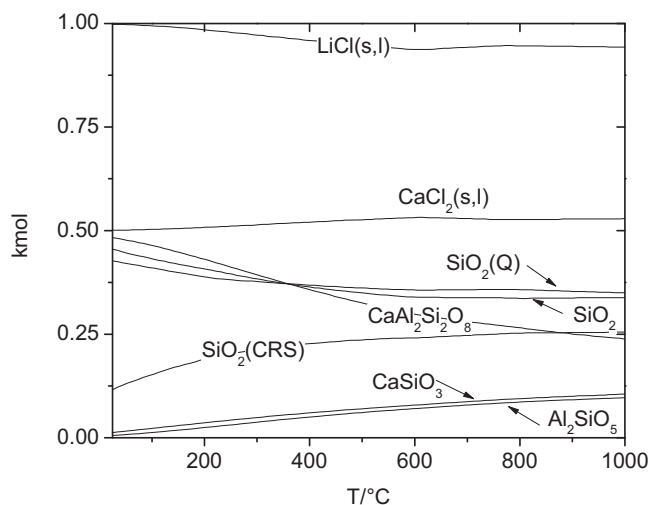E-mail address: lbarbosa@unsl.edu.ar (L.I. Barbosa).

Fig. 1. Equilibrium composition of the system Si–Al–Li–O–Ca–Cl as a function of temperature.

Fig. 2. XRD pattern of the β-LiAlSi$_2$O$_6$/CaCl$_2$ mixture.

Fig. 1 shows that the chlorination reaction of β-LiAlSi$_2$O$_6$ is favored in the whole temperature range studied yielding lithium chloride, anorthite (CaAl$_2$Si$_2$O$_8$), and silica (SiO$_2$). Lithium chloride is a solid or liquid product depending on the chlorination temperature. Silica is present at equilibrium with quartz (SiO$_2$(Q)) and cristobalite (SiO$_2$(CRS)) in the whole temperature range studied. The crystalline phases, wollastonite (CaSiO$_3$) and andalusite (Al$_2$SiO$_5$) are also present at equilibrium. Thus, the thermal decomposition of anorthite may be favored within the investigation temperature range because the number of moles of anorthite decreases as the number of moles of wollastonite and andalusite increases with temperature increase.

3. Experimental

3.1. Materials

The spodumene ore was collected from San Luis Province in Argentina and contains 7.2% Li$_2$O and approximately 2% impurities such as Fe$_2$O$_3$, CaO, and MgO. This rock ore was grounded in a ring mill, sieved to a particle size smaller than 50 μm, and then calcined at 1180 °C for 2 h so as to transform it into its β phase. Then, it was mixed with calcium chloride dehydrate 99% purity (Mallinckrodt Chemical Works) in a mortar to obtain a mixture with a β-LiAlSi$_2$O$_6$/CaCl$_2$ molar ratio of 1:2. The mixture was dried at 200 °C in a muffle furnace until reaching constant mass. Then, it was put into a desiccator because of the hygroscopic nature of calcium chloride. The chemical composition analysis results of the mixture are recorded in Table 1. The X-ray diffraction (XRD) pattern of the dried mixture is shown in Fig. 2. The main minerals are β-LiAlSi$_2$O$_6$, CaCl$_2$, and sinjarite (CaCl$_2$·2H$_2$O). The presence of hydrated crystalline phases of CaCl$_2$ is due to the hydration process that occurs during the XRD experiment.

The gas used in the chlorination roasting assays was nitrogen 99.99% (Air Liquide, Argentina). The reagents used to prepare the solid samples to measure lithium concentration by AAS were 95–98% H$_2$SO$_4$ (Sigma–Aldrich, Argentina) ACS reagent grade, CAS:

7664-93-9, and 40% HF (Merck, Argentina) GR for analysis, CAS: 7664-39-3.

3.2. Equipment

The reactor consisted in a quartz tube placed inside an electric furnace equipped with a temperature controller. The sample was held in a quartz crucible which was contained inside the quartz tube. The temperature was measured with a chromel–alumel thermocouple to within ±5 K. Nitrogen was fed to the reactor during the chlorination roasting experiment and the flow rate was controlled using a mass flowmeter and a metering valve.

The XRD analysis of reactants and products was performed on Rigaku D-Max-IIIC equipment with Cu Kα, operated at 35 kV and 30 mA. SEM and EPMA characterizations were carried out using a LEO 1450VP microscope equipped with an EDS spectrometer (EDAX Genesis 2000). An analytical balance (Mettler Toledo AB204-S/FACT, maximum sensitivity of 0.0001 g) was used for the measurement of the sample mass before and after each experiment.

The chemical composition of the ore, the β-LiAlSi$_2$O$_6$/CaCl$_2$ mixture, and the chlorination residues was determined by XRF with Philips PW 1400 equipment. The concentration of lithium present in the ore and in chlorination residues was determined by AAS using a Varian SpectrAA 55 spectrometer with a hollow-cathode lamp.

The thermal behavior of the β-LiAlSi$_2$O$_6$/CaCl$_2$ mixture was studied by simultaneous TG/DTA, using a Shimadzu DTG-60 analyzer.

3.3. Procedure

The chlorination roasting stage was conducted by placing 500 mg of the β-LiAlSi$_2$O$_6$/CaCl$_2$ mixture in the reactor at a certain temperature in N$_2$ flow (50 cc/min) during the period of time set for each experiment. Upon attainment of this period, the chlorination roasted sample was taken out from the reactor, cooled down in a desiccator and weighted. Then, the roasted sample was leached with water at 60 °C. The liquid and solid phase were separated by filtration and the residue was washed thoroughly with distilled water several times. The leach solution was analyzed by AAS to determine the concentration of lithium. The leach residue was dried in an oven at 120 °C. The dried residue was weighted and dissolved with 98% H$_2$SO$_4$ and 40% HF acid

Table 1
Chemical composition of the β-LiAlSi$_2$O$_6$/CaCl$_2$ mixture (mass fraction, %).

Li$_2$O	Fe$_2$O$_3$	K$_2$O	CaO	SiO$_2$	Al$_2$O$_3$	TiO$_2$	MgO
3.9	0.33	0.01	37.93	20.65	8.98	0.02	0.08

according to the method of Brumbaugh and Fanus [14]. The resultant solution was analyzed by AAS to determine the content of lithium in chlorination residues. The conversion of the chlorination reaction for each experiment was calculated according to Eq. (1).

$$X = \left[\frac{mLi_2O(1) - mLi_2O(2)}{mLi_2O(1)}\right] \times 100 \qquad (1)$$

where X is the conversion of Li_2O in percentage, $mLi_2O(1)$ is the initial mass of Li_2O in the β-$LiAlSi_2O_6/CaCl_2$ mixture, and $mLi_2O(2)$ is the mass of Li_2O in the chlorination residue.

4. Results and discussion

4.1. Effect of chlorination roasting temperature

Chlorination roasting test of β-spodumene mixed with calcium chloride was investigated from room temperature to 900 °C in N_2 atmosphere using TG–DTA. The results are shown in Fig. 3. Three endothermic peaks at about 113, 155, and 188 °C are observed in DTA curve. These peaks are associated with the release of adsorbed water of calcium chloride, and the corresponding mass loss is 10.5%. The endothermic peaks observed at about 700 °C and 763 °C are due to the ore starting to react with calcium chloride and the melting point of the calcium chloride, respectively. Thus, the envisaged chlorination reaction occurring at 700 °C may be β-$LiAlSi_2O_6 + CaCl_2 = 2LiCl + 2SiO_2 + CaAl_2Si_2O_8$ and the enthalpy of the reaction $\Delta H°$, 12.8 kJ/mol $CaCl_2$ (HSC, 2002). A sharp mass loss from the sample is observed between 696.3 °C and 900 °C; this phenomenon could be attributed mainly to the volatilization of lithium chloride.

4.2. Effect of chlorination roasting time

A series of experiments at 700, 800, and 900 °C were carried out for periods ranging from 30 to 120 min to study the effect of chlorination roasting time on the extraction of lithium. After each chlorination roasting experiment, the following sources of lithium can be identified: lithium staying in the β-spodumene structure; lithium chloride produced by the chlorination reaction, staying on the solid residue and leach by water after the chlorination roasting (LiCl(1)); and volatile lithium chloride dragged from the reaction zone by the flow of N_2, which condensates in the cold areas of the tubular reactor (LiCl(2)). Both, the degree of conversion attained by the chlorination reaction and the production of LiCl, are listed in Table 2 as a function of time at a given temperature. The conversion for each experiment was determined using Eq. (1). As observed, the conversion of lithium increases with increasing time at all temperatures investigated. Conversion and LiCl production reach maximum values of 90.2% and 47.2 mg, respectively, for the
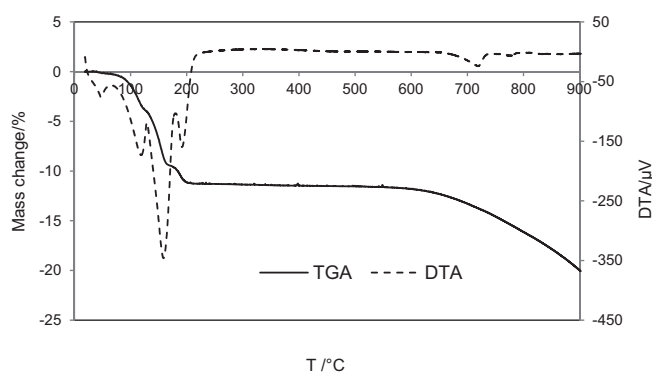
Table 2
Conversion degree and production of LiCl (using 500 mg β-$LiAlSi_2O_6/CaCl_2$ molar ratio of 1:2).

T (°C)	t (min)	X (%)	mLiCl(1) (mg)	mLiCl(2) (mg)	mLiCl (mg)
700	30	64.9	14.8	19.2	34.0
	75	75.5	16.6	22.9	39.5
	120	76.6	19.6	20.5	40.1
800	30	78.9	20.4	20.9	41.3
	75	85.7	21.7	23.2	44.9
	120	86.5	22.8	22.5	45.3
900	30	80.7	15.9	26.4	42.3
	75	89.9	14.1	32.9	47.0
	120	90.2	0.7	46.5	47.2

Where mLiCl(1) is the mass of LiCl(1); mLiCl(2) is the mass of LiCl(2); and mLiCl is the total mass of LiCl.

experiment carried out at 900 °C for 120 min. At 900 °C, the amount of volatile LiCl is the greater because LiCl vapor pressure is the higher [5,15].

Figs. 4–6 show XRD patterns of the chlorination residues. The major minerals are β-$LiAlSi_2O_6$, $CaAl_2Si_2O_8$, $CaSiO_3$. When the chlorination roasting is carried out at 700 °C for 120 min, the phases of calcium chloride hydrates disappear. It is observed that as time increases, the characteristic peaks of calcium silicate become sharper, which may indicate that the decomposition of anorthite into different calcium silicates phases occurs in accord with thermodynamic results. The reaction product SiO_2 predicted by the thermodynamic analysis was not detected by XRD analysis; this fact could indicate that SiO_2 is in its amorphous phase. Thus, SEM and EPMA tests were carried out on chlorinated samples to verify the presence of SiO_2. These tests were conducted on the sample chlorinated at 900 °C for 120 min for being the experiment

Fig. 3. TG–DTA curves of the β-spodumene/$CaCl_2$ mixture (molar ratio 1:2).

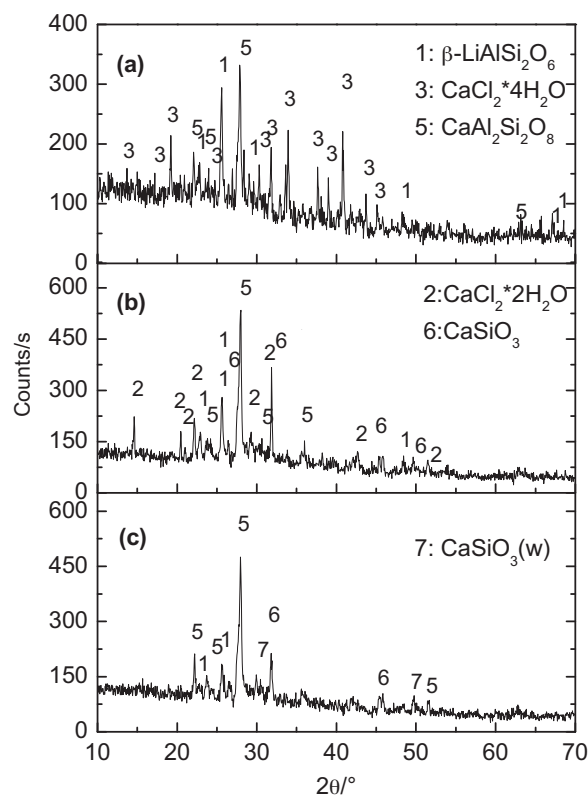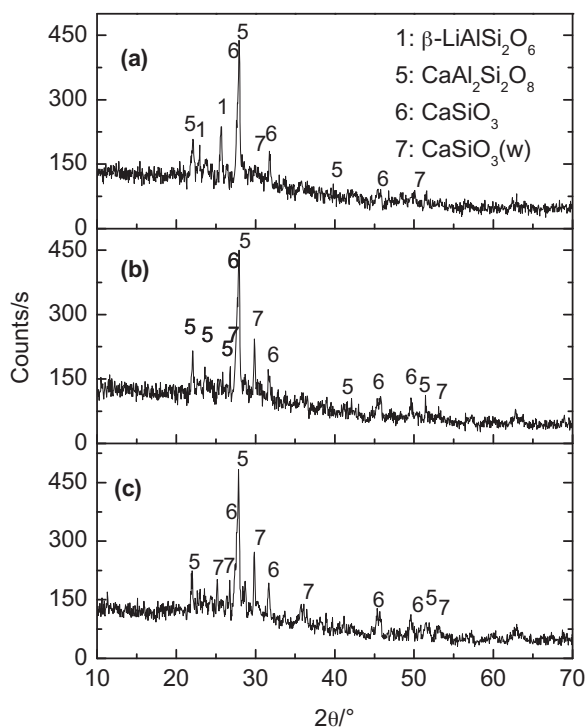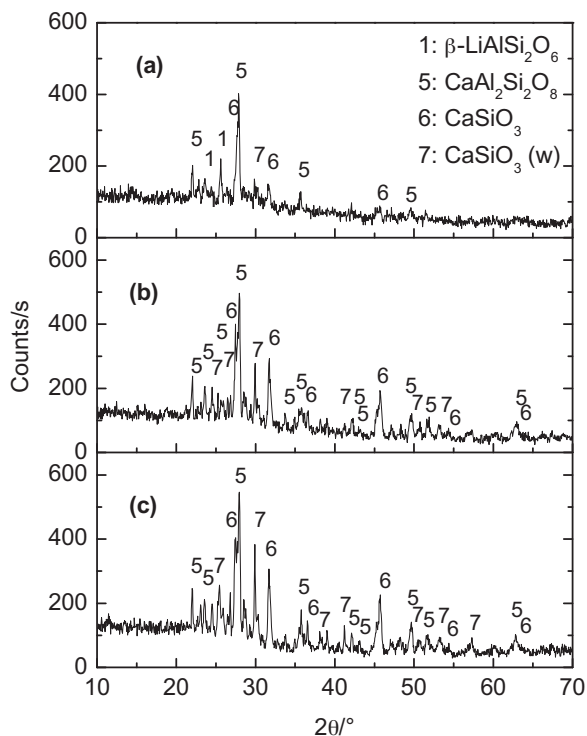**Fig. 4.** XRD pattern of chlorination roasted samples at 700 °C for (a) 30 min; (b) 75 min; (c) 120 min.

Fig. 5. XRD pattern of chlorination roasted samples at 800 °C for (a) 30 min; (b) 75 min; (c) 120 min.

that showed the maximum conversion. Fig. 7 shows the micrographs of the particles that comprise the chlorinated sample and the chemical composition corresponding to those particles is presented in Table 3.

Fig. 7 shows that the particles that made up the chlorinated sample have different morphologies. The chemical composition

Fig. 6. XRD pattern of chlorination roasted samples at 900 °C for (a) 30 min; (b) 75 min; (c) 120 min.
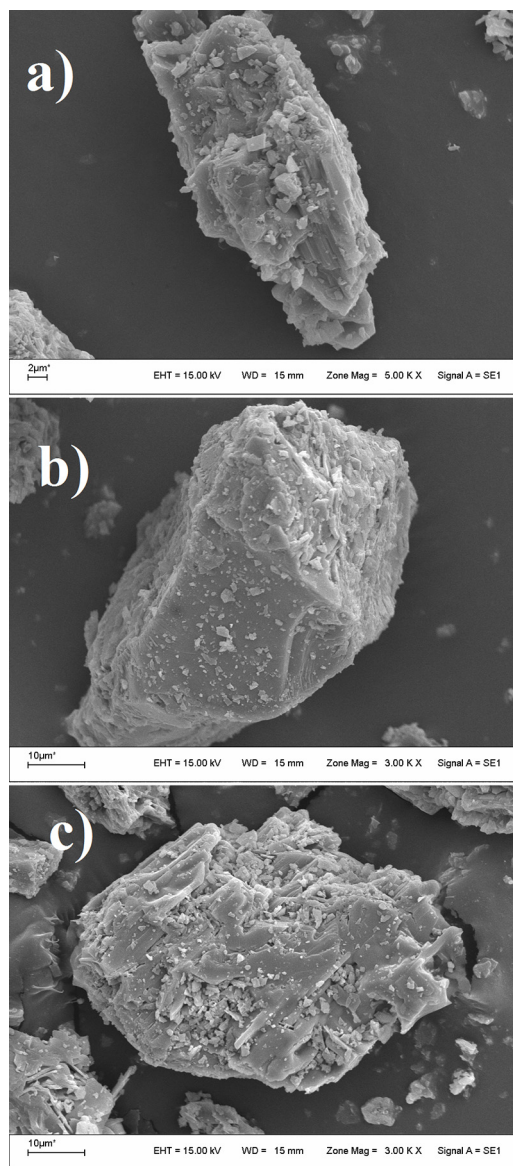

Fig. 7. SEM micrographs of particles corresponding to the sample chlorinated at 900 °C for 120 min.

obtained for the particle shown in Fig. 7a agrees with that of anorthite. While, the proportions of Si and O present in particle from Fig. 7b are coincident with the chemical composition of SiO_2. This product may be in its amorphous phase given that none of the crystalline phases of SiO_2 were detected by XRD. Finally, the proportions of Ca, Si, and O present in particle from Fig. 7c agree with the chemical composition of wollastonite, which indicates that the thermal decomposition of anorthite into wollastonite is favored under the working conditions of the experiment.

At the end of the chlorination roasting test carried out at 900 °C and 120 min, the condensate accumulated in the cold areas of the

Table 3
Chemical composition of different particles of the sample chlorinated at 900 °C for 120 min (atomic %).

Element	Particle of Fig. 8a	Particle of Fig. 8b	Particle of Fig. 8c
O	49.19	57.43	31.04
Al	12.85		1.77
Si	25.36	42.57	35.82
Ca	12.6		31.36
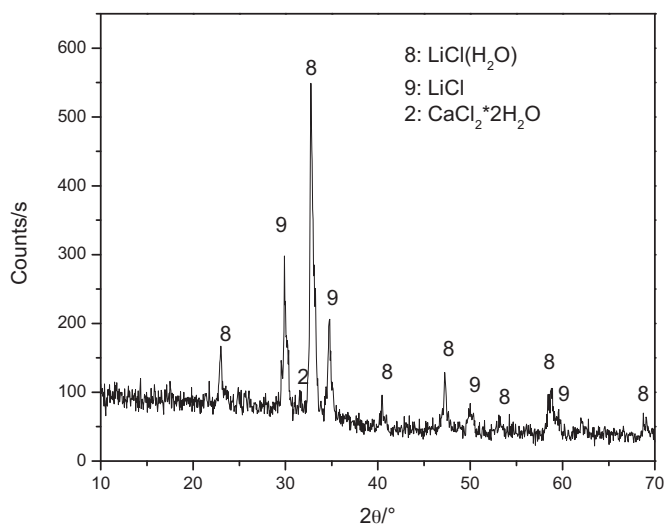
Fig. 8. XRD pattern of the chlorination roasting products collected from the reactor.

tubular reactor was collected, dried and analyzed by XRD. Fig. 8 shows the pattern of the collected product. These data indicate the presence of both anhydrous and hydrated LiCl, and a lower-intensity peak, which agree with the major peak of sinjarite. The presence of hydrated crystalline phases is due to the hydration process that occurs during the XRD analysis. The presence of $CaCl_2$ in the condensate indicates that part of it is also volatilized but the amount of volatilization should be very low because the vapor pressure values of $CaCl_2$ at 700, 800, and 900 °C are 7.13×10^{-12}, 1.59×10^{-10}, and 2.01×10^{-09} atm, respectively (HSC, 2002). The purity of LiCl present in the condensed product is 98.6% w/w. In the leach product, LiCl is present only in 10.8% w/w and the major constituent is $CaCl_2$. Under such conditions, $CaCl_2$ was not detected in the residual sample by XRD; this may be because it is present in its amorphous phase.

5. Conclusions

Lithium extraction from β-spodumene through chlorination roasting using $CaCl_2$ as chlorinating agent is favored with increasing time and temperature. The optimal conditions of the chlorination process are 900 °C and 120 min, conditions under which, it is reached a conversion degree of 90.2% and a LiCl

production of 47.2 mg using 500 mg β-$LiAlSi_2O_6$/$CaCl_2$ molar ratio of 1:2. The total products of the chlorination reaction are lithium chloride, anorthite, and amorphous silica. The decomposition of anorthite into wollastonite is favored in the operating conditions of the work.

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