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Selective Extraction of lithium from low-grade Gypsiferous Clays by reduction of Calcium and Magnesium content in the pregnant leach solution (PLS).

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Abstract

Lithium extraction from all deposits is associated with magnesium and calcium ions as main impurities. In this study, an effective way provided to extract the maximum amount of lithium from clay deposits while minimizing extraction of magnesium and calcium ions. After pre-feasibility studies on extraction methods, the limestone-gypsum roasting with water-leaching technique was selected for final studies. After identifying effective parameters including furnace temperature, roasting time, the ratio of calcium carbonate to feed and the ratio of calcium sulfate to feed, Taguchi experimental design was used to optimize experimental conditions and variables. For this purpose, DX7 software and L25 array were used. A furnace temperature of 800 ° C, roasting time of 2 h, a calcium carbonate to feed ratio of 1:5 and a calcium sulfate to feed ratio of 4:5 were obtained as the optimal technical and economic conditions with a lithium recovery of 68.7%. The highest lithium recovery of 75.65% was obtained at a furnace temperature of 1100 ° C, roasting time of 5 h, a calcium carbonate to feed ratio of 1:5 and a calcium sulfate to feed ratio of 1:5. In both cases, magnesium was completely removed and the maximum content of calcium (in optimal technical and economic conditions) in the leach solution was 0.1%.

Keywords: Lithium, Gypsiferous Clays deposits, limestone-gypsum roasting, water leaching.

Introduction

Lithium

Lithium has raised for electrical machines and this is not an unreasonable expectation. Lithium batteries were not known to anyone before 1990. Thereafter, lithium batteries are found in all portable electronic equipment. Ignoring their cost and high capacity, lithium batteries are used in mobile phones and laptops as well as high performance electronics (Garrett, 2004). Lithium with a density of 0.53 g/cm^{-1} is the lightest metal. Lithium is similar to sodium with a relatively lower reactivity with water and oxygen. Due to the increasing use of lithium in various industries such as electronics, chemical industry, engineering projects, industrial optics, aerospace and medicine and its strategic role in the future energy crisis as well as the need for access to deposits and justifiable extraction methods in terms of technical and economic parameters, many studies are currently conducted in international industrial and research centers (Barzegari, 2012).

Lithium deposits

Lithium is a relatively rare element, although very low concentrations of lithium are found in many rocks and some brines. There are three type of lithium deposits including ore (pegmatites), brine and sedimentary clay deposits (Evans, 2008). Elements found in lithium deposits vary depending on the type of deposits. Therefore, common elements in these three types of lithium deposits will be evaluated. The most important elements in the brine deposits include sodium, potassium, calcium, magnesium and boron. The most important elements of ore deposits include magnesium, boron and aluminum (Hykawy, 2009).

Associated elements in clay deposits vary, but the main elements include magnesium, calcium and aluminium. In some cases, heavy metals of the first and second groups in the periodic table are rarely found. Table 1 shows the analysis of a sample from a clay deposit containing four types of lithium mineral (Garrett, 2004).

Table 1: Physical and Chemical Properties of Some Lithium Clays (Garrett, 2004)

Minerals name	**Li**	**Al**	**Mg**	**F**	**Relative dispersion of clay in water**	**Relative Li solubility in water**
	Percent or relative amount					
Hectorite	0.5	rarely	Major	5.0	Very high	Low
Li-stevensite	0.4	Low	Major	5.0	Variable	High
Li-smectite	0.7	Medium	Low	Low	Poor	Low
Li-bearing high-alumina clay	0.5	High	None	None	Very poor	Very low

As was mentioned, in addition to the brine and ore deposits, lithium is also found in clay and lacustrine evaporates usually as part of clay minerals such as smectite. One of the best examples of this type of deposits is Kings Valley in Nevada which contains hectorite. Hectorite is a kind of smectite that is rich in lithium and magnesium (Crocker *et al.*, 1988). Table 2 shows lithium deposits and their cut-off grades.

Table 2: Lithium deposits and Grade "cut-offs." (Gruber, 2010)

Type	Lowest Productive Grade (%Li)	Reasoning
Brine	0.02	- Searles Lake closed at avg. 0.008% Li - Lowest content is Silver Peak, operating at avg. 0.02% Li since 1966
Pegmatite (Spodumene)	0.59	- Lowest content is Jiajika, operating at 0.59% Li - Kings Mountain closed at avg. grade of 0.69% Li - Note: Bikita and Yichun are operating and may have lower Li content, but their Li content could not be verified
Sedimentary Rock (Hectorite)	0.27	- Kings Valley being explored, avg. 0.27% Li content - Western Lithium used avg. 0.27% Li as cutoff
Sedimentary Rock (Jadarite)	0.096	- Jadar Valley being explored, avg. 0.096% Li content - No other jadarite deposits

Many studies have been conducted to extract lithium from low grade clay deposits. Accordingly, various techniques have been used to optimize conditions to achieve the highest lithium recovery and separation (Suri, 1996; May *et al.*, 1980; Meshram, 2014; Nogueira, 2014). These methods include:

- Water disaggregation
- Hydrothermal treatment
- Acid leaching
- Acid pug - water leaching
- Alkaline roasting- water leaching
- Sulfate roasting- water leaching
- Chloride roasting- water leaching
- Multiple-reagent roasting- water leaching
- Sulfur dioxide atmosphere roasting - water leaching
- Chlorinating roast with hydrochloric acid
- limestone -gypsum roasting- water leaching

Although the main priority in these studies is to extract lithium from its structure, due to the necessity of high purity lithium for downstream products, purification of lithium salts, especially lithium carbonate has also been studied (Amouzegar, 2000). These methods include precipitation, solvent extraction (Bukowsky, 1992) and ion-exchange methods (Bukowsky, 1991).

In this study, the above methods were first studied on a small scale. Then, the recovery of magnesium and calcium was studied in methods with the highest lithium recovery. After reviewing the final approach and identifying effective parameters, Taguchi experimental design was used to optimize experimental conditions and variables. A conceptual flowsheet was developed according to the results.

Experimental

Representative sample

Since the beginning of lithium industry in Iran in 2008, exploration activities in the lithium industry, particularly from brine and ore-pegmatite deposits thrived. The most important exploration activities include Pars Hoorakhsh Mines in Khorasan Razavi province in Faizabad, Kashmar and Bardaskan. To select the representative sample, a total of 19 sample groups with different weights (each of 100 kg) were taken by the company. After determining the lithium grade, the samples were sent to the laboratory. According to the assay grade, the amount of lithium in the samples ranges from 100 to 400 g per ton. Given the gypsiferous Clays type

of samples and to confirm lithium content, only high grade samples were characterized. It is worth mentioning that average magnesium and calcium levels were 5 and 23%, respectively.
The size of the agglomerated sample was 10 to 20 cm. After drying and three crushing stages and preparing backup sample in every step of the grinding, all samples were grinded to d80 =75 μm. Subsamples were prepared for assay grade, mineralogical and process studies.

Procedure

First of all, the feed was again dried at 70 ° C and stored in a desiccator. Due to the variable solid content, a maximum solid content of 30% in final leaching was considered in all feasibility experiments. The roasted samples were cold in the laboratory for 24 h. Water leaching was performed for 3 hours at pulp stirring rate of 400 rpm (with a tolerance of 15 rpm due to machine error). Rotational mixing was carried out along the main axis of a two-blade impeller with a diameter of 5 cm.
All above procedures were first studied. After matching data with conditions mentioned in literature and determining the testing method, all methods other than hydrothermal treatment (due to the impossibility of using an autoclave) were studied. To achieve optimal conditions based on the optimal parameters of "maximum extraction of lithium" and "minimum extraction of calcium and magnesium", three methods were identified. Based on complementary tests, one of the methods was selected for lithium extraction and experimental design studies. Taguchi experimental design and DX7 optimization software were used for optimizing lithium extraction process from gypsiferous clays ore. Testing conditions were similar to the above paragraph, but the solid content in leach pulp was 20% in all tests of experimental design. In all experimental design tests, the sample contained 200 mg of lithium.

Reagents and chemicals

All chemicals prepared with analytical grade and purchased from Merck, Germany. All titration solution were prepared from Merck Titrisols.

Laboratories and Equipment

All characterization analyses were conducted in the laboratories of the Geological Survey of Iran. All major cations were measured by flame atomic absorption spectroscopy (Varian AA240FS). Lower contents of cations and anions were measured by ion chromatography (Metrohm 861 Advanced Compact IC). A 20 litre electric furnace without aeration and exhaust and fire assay pots were used for roasting studies. Rotational mixing along the axis in a handmade two-blade glass mixer with a diameter of 5 cm (complete mixing) was performed in all leaching experiments.
To validate the results of filtered samples, both solid and solution samples were analysed after filtration. In the case of significant difference between the solid and solution, three solid samples were re-analysed to validate the results.

Results and Discussion

The lithium content in the high-grade sample was 400 g per ton. In addition, the average concentrations of calcium and magnesium were 5 and 23%, respectively. The samples were sent for further studies by XRD analysis. Based on current conditions and predictions, two minerals were considered as lithium phase: hectorite and jadarite. Different fine fractions of the high-grade sample and the dried precipitate were studied under a microscope in the presence of ultraviolet light. In none of the fractions, there was no trace of fluorescence under UV light. On the other hand, due to lepidolite deposits (ore deposits) in Khorasan Razavi province, the presence of aluminosilicates is not too far-fetched.
25 g of the high-grade sample (400 g per ton) containing 15% solid was stirred for 3 h at a speed of 400 rpm at laboratory temperature. Lithium recovery in the aqueous media was less than 1%. The notable thing is severe dispersion (severe deterioration) of the sample in water. Due to the lack of fluorescence under UV light and the absence of boron (qualitative analysis), jadarite is less likely to be found in the sample. On the other hand, given

a trace amount of aluminium and severe dispersion (deterioration) of the sample in water, hectorite is more likely to be found in the sample.

The results of preliminary tests (characterization), sulfuric acid leaching tests, sulfuric acid pug-water leaching tests, leaching tests with sodium hydroxide at 60 °C, calcium carbonate and calcium sulfate dihydrate roasting-water leaching and calcium carbonate roasting with absence of calcium sulfate dihydrate -water leaching showed effective recovery of lithium. For this purpose, feasibility tests were performed on above procedures. After completion of the feasibility study, the samples were prepared from the pregnant leach solution and the remaining filtered precipitate. All samples were then analysed by atomic absorption spectroscopy. The results are shown in Table 3.

Table 3: The results of preliminary tests (characterization)

Experiment	Extraction (%)		
	Li	**Mg**	**Ca**
sulfuric acid leaching	35	42	12.6
sulfuric acid pug-water leaching	28	41	5.4
leaching with sodium hydroxide at 60 °C	13	< 1 ppm	< 1 ppm
calcium carbonate and calcium sulfate dihydrate roasting-water leaching	18	< 1 ppm	< 1 ppm
calcium carbonate roasting with absence of calcium sulfate dihydrate -water leaching	1.3	32	< 1 ppm

As it shown in table 3, although it looks very promising results with sulfuric acid leaching, but it shows very high recovery rate for magnesium. So if magnesium is not considered as a product of the company, this impurity will reduce the value of method. On the other hand, hot sodium hydroxide leaching does not show calcium and magnesium recovery, but is less efficient than the roasting - water leaching in the presence of calcium carbonate and calcium sulfate dihydrate. Thus, roasting - water leaching in the presence of calcium carbonate and calcium sulfate dihydrate was selected for further studies by Taguchi experimental design.

The mechanism of the process

Hectorite with a formula of $Na_{0.3}$ (Mg, Li)$_3Si_4O_{10}$ (OH)$_2$ belongs to phyllosilicate family. In other words, lithium exists in the silicate phase and is not water-soluble. For this purpose, lithium is thermally converted to lithium sulfate solution. To carry out the reaction in the furnace, calcium sulfate and calcium carbonate were added to the clay sample (Gruber, 2010). Therefore, the reaction mechanism is expected to be as follows:

$$(1)\quad 2CaSO_4.2H_2O+2SiO_2 \rightarrow 2CaSiO_3+2SO_2+O_2+4H_2O$$

So, we have:

$$(2)\quad 2Li_2Si_2O_5+2SO_2+O_2 \rightarrow 2Li_2SO_4+4SiO_2$$

Although the role of calcium carbonate is not shown in this process, it plays a key role in maximizing lithium recovery from lithium sulfate. Calcium carbonate reacts with free silicates and produces calcium silicate and thus prevents reverse reactions of formation of lithium sulfate (Gruber, 2010).

Effective parameters

After identifying and selecting the leaching process, parameters influencing the process were studied. Based on experimental studies, the effective parameters include: feed size, calcium sulfate content, calcium carbonate content, the ratio of clay to additives (including the first and second items), the purity of additives, roasting temperature, roasting time, furnace type and aeration, furnace charge, water leaching duration, pulp mixing speed, leach pulp solid content, leaching temperature, the agitator shape and other parameters that may not be

studies at a laboratory scale.

Although all of the above parameters influence the leaching process, furnace temperature, roasting time, the ratio of calcium carbonate to feed and the ratio of calcium sulfate to feed were considered as the main parameters. Based on experimental conditions and to achieve the highest recovery, other parameters were considered to be constant. In other words, some parameters play a fundamental role in the process and other parameters can be adjusted in operational and even industrial stages. Since the main purpose of this study is to achieve maximum lithium recovery, the main parameters were selected accordingly. Regardless of interactions of parameters, roasting was inversely related with lithium extraction. In contrast, the ratio of calcium carbonate to feed and the ratio of calcium sulfate to feed were directly proportional to lithium recovery. However, the furnace temperature showed a dual behaviour so that lithium recovery increased up to 900 ° C and then decreased (Fig. 1).

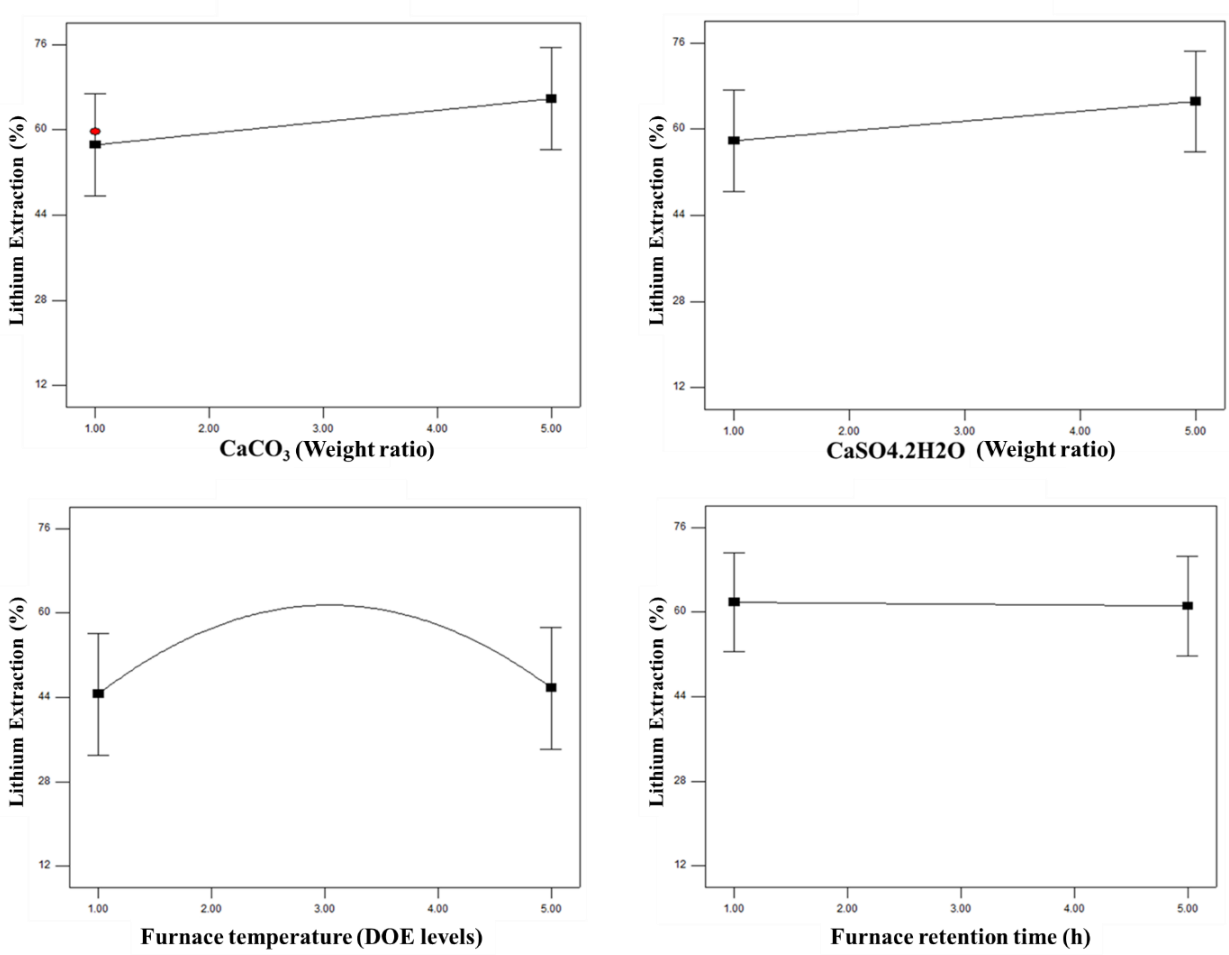


Figure 1: Parameters influencing lithium extraction

Experimental design

Taguchi experimental design with the help of DX7 software was used to optimize lithium extraction from gypsiferous clays ore. For this purpose, four variables were considered in five levels (L25 array). Table 4 shows the parameters and their levels in DX7.

Table 4: Parameters and their levels in DX7

parameters	units	levels				
		1	2	3	4	5
$CaCO_3$	g	5	10	15	20	25
$CaSO_4.2H_2O$	g	0	5	10	15	20
Temperature	°C	700	800	900	1000	1100
Furnace retention time	h	1	2	3	4	5

The experiments were conducted in 5 groups based on the furnace temperature. Five pots were simultaneously placed inside the furnace at each temperature. After reaching the desired temperature, a pot per hour was removed from the furnace. As listed in Table 5, the weight of clay sample used in each test was 25 g.

Table 5: Optimal conditions obtained from Taguchi experimental design

No.	**$CaCO_3$**	**$CaSO_4.2H_2O$**	**Temperature**	**Furnace retention time**	**Li Extraction**
Clay= 25 g	**g**	**g**	**^oC**	**h**	**%**
1	15	15	700	3	61.38
2	15	10	1100	2	71.29
3	10	0	800	3	69.05
4	10	5	900	4	74.75
5	15	5	1000	1	67.04
6	20	20	900	1	57.78
7	5	15	1000	4	72.54
8	15	10	1000	5	68.75
9	15	0	900	5	66.94
10	25	15	900	2	59.02
11	5	20	1100	5	73.64
12	10	20	700	2	62.93
13	25	10	800	1	60.07
14	20	5	1100	3	65.61
15	15	20	800	4	63.54
16	10	15	1100	1	70.43
17	5	5	800	2	63.21
18	20	10	700	4	62.20
19	25	5	700	5	62.47
20	25	0	1100	4	71.59
21	5	0	700	1	65.60
22	20	0	1000	2	63.87
23	25	20	1000	3	57.71
24	20	15	800	5	61.33
25	5	10	900	3	69.44

In all 25 tests, the leach solution and the precipitate remaining on the filter paper were analyzed by atomic absorption technique. If a significant error was observed (in this study, an error more than 5% was considered significant), the samples were studied again for validation.

According to predictions, the tests No 5, 11 and 25 were proposed as optimum conditions with maximum lithium recovery (the predicted lithium recovery was 78.94, 81.38 and 75.53%, respectively). In addition, five tests with the highest lithium recovery were studied. The results are shown in Table 6.

Table 6: Optimal conditions of experiments designed by DX7

No.	**$CaCO_3$**	**$CaSO_4.2H_2O$**	**Temperature**	**Furnace retention time**	Ion content in Pregnant leaching solution (ppm)				**Li Extraction**
Clay= 25 g	**g**	**g**	**^oC**	**h**	Na	Mg	Ca	Li	%
5	15	5	1000	1	76.60	< 1 ppm	688.62	13.47	67.35
11	5	20	1100	5	535.01	8.41	531.25	15.13	75.65
16	10	15	1100	1	450.31	< 1 ppm	429.00	13.18	69.00
17	5	5	800	2	70.50	< 1 ppm	1028.53	13.75	68.70
19	25	5	700	5	12.78	< 1 ppm	883.01	12.46	62.31
20	25	0	1100	4	71.07	< 1 ppm	291.75	13.60	68.00
25	5	10	900	3	78.69	< 1 ppm	891.32	11.93	59.65

Conclusion

After preliminary characterization of samples, the methods for extracting lithium from clay deposits were studied. In the methods with the highest rate of lithium recovery, magnesium and calcium were evaluated as impurities. After reviewing the final approach and identifying effective parameters, Taguchi experimental design was used to optimize experimental conditions and variables. According to literature (Meshram, 2014; Nogueira, 2014), lithium can be extracted by lime-gypsum roasting, water-leach from gypsiferous clays method deposits. The highest recovery rate of 75.65% has been reported on a laboratory scale. Although water leaching of furnace products has a relatively low recovery, the lack of magnesium recovery is as an advantage to this method and shows the need for further studies (in some clay deposits, a lithium recovery of more than 80% has been observed, Crocker *et al.*, 1988). Considering that in addition to recovery, other parameters such as furnace temperature, residence time and the ratio of ingredients have a key role in the economy of process, the test No 17 (a furnace temperature of 800 °C) was considered as the optimal point due to technical parameters.

As seen in Table 6, extraction of magnesium is completely stopped. However, due to the presence of large quantities of calcium sulfate in the input tailing, calcium extraction is not completely stopped, but its content in the pregnant leach solution is minimum.

As was mentioned, the deposit surveyed is probably a hectorite deposit. But to distinguish assumptions, prospecting and exploration studies are recommended to obtain representative samples. With more sampling and proper pre-concentration, samples can be prepared for characterization of phases. On the other hand, XAFS technique is recommended for the detection of lithium phase in higher grade or by pre-concentrating samples. Since more precise data is required on larger scales, the experimental conditions listed in Table 6 appear to be repeated. Based on the above conditions and data, the following conceptual flowsheet (Fig. 2) is provided for future studies on the ore deposit. According to the conceptual flowsheet in Figure 2:

1. The feed is initially dried by air flow and then is crushed to a size of 10 mesh.
2. Based on optimal conditions, certain amount of gypsum with a particular size is added to the feed.
3. Based on optimal conditions, certain amount of limestone with a particular size is added to the feed.
4. The mixture of raw materials is crushed to less than 200 mesh by a closed circuit crusher.
5. The furnace output is transferred to the leaching unit after the preparation.
6. The filter effluent is reused for leaching to maximize lithium recovery.
7. The product on the filter is washed as much as possible to be depleted of lithium and is transferred to the tailings dam.
8. The pregnant leach solution (PLS) is sent to the evaporator for the removal of calcium and increasing PLS concentration.

9. With increasing concentration of pregnant leach solution, the soluble calcium become insoluble and is removed after filtration.
10. The calcium-free filtrate is sent to the evaporator for pre-concentration and at boiling point.
11. A stoichiometric ratio of sodium carbonate is added to the boiling solution containing lithium.
12. Lithium carbonate is removed by filtration (it is anticipated that the final product will have a lithium grade more than 90%).

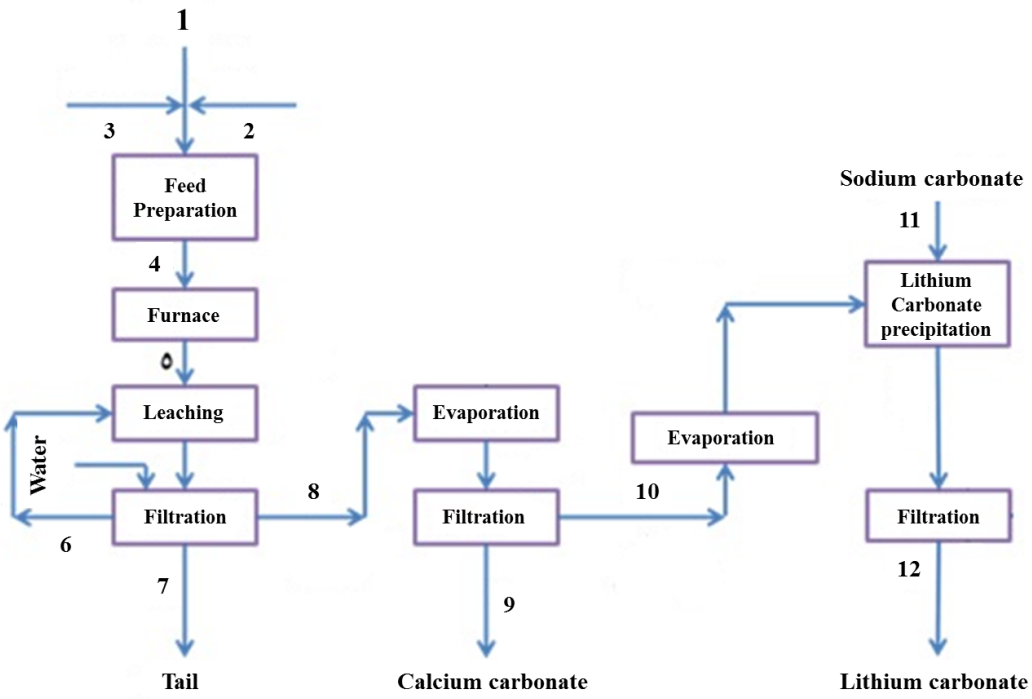


Figure 2: The conceptual flowsheet for lithium extraction from the clay deposit

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