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RECOVERY OF LITHIUM FROM NATURAL RAW MATERIALS. MINIREVIEW

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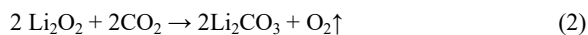
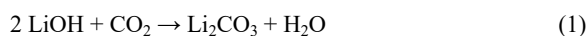
Abstract

This review briefly discusses acidic, basic, and saline methods of lithium salt recovery from mineral spodumene, methods of processing natural chloride brines by alternative removal of attendant elements of the first and second groups as well as the recovery of lithium salts by using DALH-Cl based on $\text{Al}(\text{OH})_3$. A suggested hypothesis provides the explanation for some unusual properties of the material by the influence of hydrogen bonds and dissociation of $\text{Al}(\text{OH})_3$ in an aqueous medium.

Key words: spodumene, brine, aluminum hydroxide, DALH-Cl.

1. Introduction

Metallic lithium and its compounds are widely used in different fields of human activity almost throughout the world. Nowadays, according to the US Geological Survey, the largest volume of lithium products is used in the production of chemical power sources. Everyone knows lithium batteries, which are used in spaceships, mobile phones, and for many other consumers of electrical energy. Lithium products are needed for the production of ceramics and glass, they are used in electronics, metallurgy, medicine, and for in the production of alloys. Since LiOH and Li_2O_2 rapidly react with CO_2 , the former absorbing carbon dioxide (1) and the latter releasing oxygen (2), both are used to maintain normal air composition on submarines and space stations.



The great demand for lithium products has contributed to the active processing of natural resources in all developed countries around the world, including the USA, Chile, and China as the top three producers. Unfortunately, after the collapse of the USSR, Russia stopped lithium mining, although currently the country has begun organizing large-scale production of this valuable metal based on the Russian raw materials.

There are two main sources of lithium known in the world: lithium-bearing ore deposits and hydromineral sources.

There are about 150 lithium-containing ores on Earth, but only spodumene and lepidolite contain lithium in quantities acceptable for industrial processing, with spodumene bearing from 1% to 8% of lithium [1]. Both minerals are aluminosilicates. The structure of the main core of spodumene is given in Fig. 1 [1].

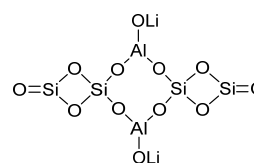
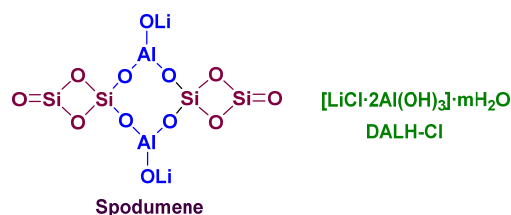
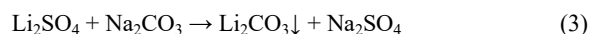


Fig. 1. Structure of the spodumene main core.

2. Processing of lithium-containing ores

The methods for extracting lithium from natural ores have been known for a long time and are well studied, so we will describe only the main underlying approaches [1, 2].

The sulfuric acid method of lithium extraction involves treating spodumene annealed at 1200–1300 °C with sulfuric acid at 250–300 °C. This affords sulfates of lithium, aluminum, and impurity metals, namely, Mn, Ca, Fe, as well as silicic acid. After removal of the latter, aluminum is extracted in the form of potassium alum, while the metal impurities are removed in the form of hydroxides. Lithium sulfate is converted to lithium carbonate, which is the main product of industrial processing of spodumene.



In the alkaline method, spodumene concentrate is sintered with calcium oxide at 1000 °C. The products are lithium oxide, calcium aluminate, and dicalcium silicate. After treatment with water, lithium hydroxide crystallizes in the form of a monohydrate.

A salt method for lithium recovery from a spodumene concentrate is also known that consists in its sintering with potassium sulfate at 100–150 °C followed by leaching, precipitation of aluminum and iron hydroxides, and, after separation of by-products, precipitation of lithium carbonate

with sodium bicarbonate. The resulting salt (Li_2CO_3) distinguishes from the salts of other alkali metals by high solubility in water at low temperatures (even at slightly negative temperatures), but precipitates from the solution at 80–90 °C. If the salt precipitate is filtered at the same temperature, its losses will decrease, but the salt concentration in the mother liquor remains significant. The patent literature [3] suggests using the mother liquor from lithium carbonate crystallization to precipitate traces of magnesium and calcium in the form of water-insoluble MgCO_3 and CaCO_3 . The authors state that these methods allow for recovery of up to 90% of lithium.

Of course, in addition to the main elements, the ore, depending on the deposit, may also contain impurities of valuable metals, such as rhenium or beryllium. Their extraction complicates the overall process technology, but given the value of the entire product, it does not affect significantly the production cost-effectiveness.

3. Recovery of lithium salts from brines

World reserves of lithium in the form of minerals make up only 22% of the total volume of deposits of this metal, whereas 78% of the lithium reserve is concentrated in hydromineral sources. The latter are widespread throughout the world. Ryabtsev [4] proposed a classification of sources, which he divided into two main groups: sources located in the regions with a pronounced arid climate (climate of hot deserts) and sources located in the areas with a climate unfavorable for natural evaporation (Table 1).

The first group includes brines from the USA and South America, Turkmenistan (Kara-Bogaz-Gola) and the Dead Sea brines off the coast of Israel and Jordan. The author also includes brines from Dagestan in this group.

The second group involves underground brines from Eastern Siberia, associated petroleum waters from Western Siberia, thermal waters of New Zealand, Japan, the USA, and Russia.

From the viewpoint of feasibility of lithium extraction from brines on an industrial scale, hydromineral raw materials can be divided into target, in which the lithium concentration exceeds 0.01 g/L, and non-target, containing lithium in an amount of less than 0.01 g/L.

Of course, brines with increased or reduced lithium concentrations can be found in regions with any climate. The prospects of a particular source for development can be assessed not so much with recourse to the mentioned classification, but using the parameter R , being equal to the ratio of the sum of the concentrations of alkaline earth elements to the lithium concentration. It can be as low as 2.9 like for the water of Silver Peak Lake in Nevada or as high as 2400 for a source on the coast of the Dead Sea (Table 1). It is obvious that the processing the latter brine requires large investments.

The qualitative composition of all traditional brines is almost the same. First of all, in addition to lithium, it includes Na, K, Mg, Ca, iron, Cl^- , Br^- , I^- , SO_4^{2-} , and boric and silicic acids. Russian brines often contain 0.8–3.3 g/L of strontium. Sometimes the source contains an admixture of organic compounds. Before extracting the lithium salt, sodium, potassium, calcium, magnesium and boric acid salts must be removed, since they reduce the efficiency of lithium power sources.

It should be noted that our country has non-traditional sources of lithium, such as waste burial sites. The burial site has a simple construction. The waste is placed on a special base and covered with earth. Rainwater passes through it and accumulates under it in the form of a lake. In warm weather, the burial sites are specially watered to prevent possible combustion of the waste. Unfortunately, lithium batteries that are out of use are also end up in the waste, leading to the accumulation of lithium salts in the lake. According to the protocols of the Federal Service for Supervision of Natural Resources available to the authors, the lithium concentration can exceed 300 mg/L in the lake under the burial site. This lake also contains cations of many other metals and organic compounds. The recovery of lithium from these sources is not an easy task, but, if necessary, difficulties can be overcome.

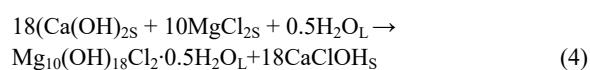
3.1. Successive processing of brines

Although the qualitative composition of brines is approximately the same, methods for isolating lithium salts have been developed specifically for each source, and, as a rule, imply the successive removal of each of the impurity components from the brine. In this work, we will mention only those basic techniques that are described in the patent literature and are used in practice to recover lithium from a mixture with other components of the brine.

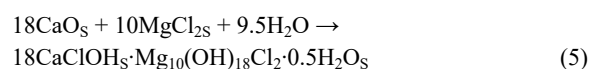
The concentrations of sodium and potassium cations in chloride brines are many times higher than that of lithium cations (Table 1). A very simple method for separating LiCl from sodium chloride and other chloride salts was proposed as early as 1981 [5]. Using a system of successively connected small reservoirs with a large water surface area, it was possible to increase the lithium concentration in the brine of one of the sources in Nevada to 40% due to natural evaporation in the sun. In this case, sodium and potassium salts predominantly precipitated due to their relatively low solubility in water. The precipitate was separated, and the solution of the target component was evaporated under vacuum until the precipitation of lithium chloride monohydrate. The experiments confirmed that concentration of various brines to 3% of lithium chloride [6], 6% of lithium [4, 7] and 40% [8] of lithium chloride, already at the first stage of their processing leads to the precipitation of sodium and potassium chlorides, and, therefore, to the removal of these salts from the brine. However, these salts still remain in the mother liquor. In this case, the liquid is evaporated completely, and LiCl contained in the residue is then extracted with a selective solvent—*isopropanol*. As is known, alcohols, in particular *n*-propanol, dissolve LiCl 750 times better than NaCl, and 1500 times better than KCl [1].

Magnesium is usually precipitated as magnesium hydroxide by treating concentrated brines with slaked lime [8].

The following reactions occur during the process [4]:



The precipitation of alkaline earth metals can also be carried out using quicklime:



In both cases, filtering the liquid phase from gel-like pre-

Table 1. Compositions of the most popular brines [3]

Country (deposit)	Concentration, g/L									R
	Li ⁺	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	Br ⁻	Σ _{salts}	
Target raw materials with high lithium content, arid climate										
USA, Nevada (Silver Peak Lake)	0.44	88.0	11.0	0.7	0.6	128.5	n/a	–	220	2.9
Chile (Atakama)	0.5–0.2	113.4	32.1	11.4	0.5	210.6	17.2	–	~400	6...24
Bolivia (de Uyuni)	0.8–2.0	105.2	24.2	16.6	0.5	190.5	9.1	–	400	9...21
Russia (Tarumovskoe)	0.2	67.0	3.8	0.8	10.1	127.3	n/a	0.6	210	60 ^a
China, Qing Hai (Duong-Toi)	0.49	68.6	17.7	29.3	–	190.4	23.1	–	330	60
China, Qing Hai	0.96	1.4	1.1	107.8	4.3	326.0	0.1	–	450	117
Target raw material with high lithium content, boreal climate										
Russia, Sakha (Complex Udachnyi)	0.414	35.6	20.3	11.2	65.5	220.0	–	4.8	360	192 ^a
Russia, Krasnodar Krai (Sukhotungusskoe)	0.22	46.8	23.1	9.5	58.8	233.9	–	3.2	375	310 ^a
Russia, Evenkiya (Verkhnekostinskoe)	0.45	50.2	19.7	11.2	81.7	271.8	–	5.6	444	210 ^a
Russia, Irkutsk Oblast (Znamenskoe)	0.48	2.4	4.3	28.5	134.3	322.5	–	10.6	503	340 ^a
Russia, Irkutsk Oblast (Kovyktinskoe)	0.39	1.9	11.7	29.0	154.0	338.9	–	6.3	544	470 ^a
Target raw materials with low lithium content, arid climate										
Russia, Dagestan (Berikeyskoe)	0.039	24.0	0.6	1.4	0.3	41.0	–	0.2	70	55 ^a
Russia, Dagestan (Yuzhno-Sukhokumskoe)	0.041	31.5	0.6	0.7	7.2	65.5	–	0.3	110	213 ^a
USA, Utah (Great Salt Lake)	0.07	85.4	4.9	9.8	0.4	170.8	18.3	7.8	300	146
China, Qing Hai (Chaerhan)	0.027	67.5	736	36.7	1.3	219.5	–	n/a	340	1400
Turkmenia (Kara-Bogaz-Gol)	0.026	70.0	4.6	33.0	–	74.6	64.8	0.4	247	1270
Israel, Jordan (Dead Sea)	0.018	30.3	7.3	40.3	3.0	190	0.5	4.0	275	2400
Non-target raw materials, boreal climate										
Russia, Tyumen Oblast (associated petroleum waters)	0.004	8.5	0.1	0.03	0.74	8.3	0.02	–	18.0	192.5
Russia, Tyumen Oblast (Senoman)	0.0004	6.6	1	0.18	0.80	12.9	0.04	–	21.0	2050

^a the values were calculated taking into account the strontium content.

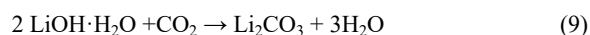
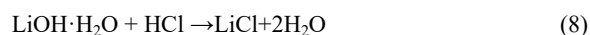
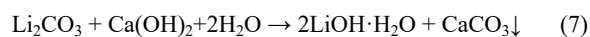
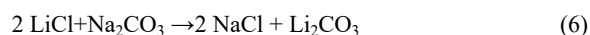
precipitates is very difficult. The use of quicklime and cooling the mixture make filtering somewhat easier, but in the latter case the probability of precipitation of LiCl·H₂O increases, so that lithium losses are significant. Calcium cations can be removed from the brine with oxalic acid [4] or by converting Ca²⁺ into insoluble gypsum, and *vice versa*, if there is a need to remove sulfate anions, an equivalent of calcium ions is added. It was also suggested to use barium instead of calcium to remove SO₄²⁻ [9].

Some brines contain admixtures of organic compounds, which were suggested to be removed by heating the dry residue formed after separation of solid by-products of brine processing and evaporation of the liquid fraction at about 300 °C. Organic compounds either evaporate or undergo pyrolysis and then evaporate. When heated, boric acid salts are converted into the products insoluble in isopropanol, which is used to finally extract lithium chloride [6, 10].

Boric acid was suggested to be removed from a 40% brine concentrate by vigorously stirring it with a solution of octanol in kerosene [11]. It is known that lithium cations interact with alcohols, forming solvates. However, in the brine with such a high concentration there is no free water, but only water that has gone into the hydration of salts. In other words, lithium chloride is not dissociated in the concentrated solution, and, therefore, boric acid can be removed from this brine without affecting lithium chloride. Sometimes boron is also removed as CaO·3B₂O₃·3H₂O [12].

From the analysis of the above patent literature, it is clear that the separation of lithium from the impurities of other elements using simple chemical reactions is a multi-step process. Typically, the industrial processes end with the

reactions listed below [11]. Sometimes LiOH·H₂O is purified by recrystallization, and its conversion to lithium carbonate is carried out by passing carbon dioxide through the solution. Lithium carbonate can also be further purified by dissolving it in cold water and then heating the solution almost to boiling. Lithium carbonate precipitates from the solution, while the solubility of other salts only increases.



The stepwise extraction of lithium salts from brine allows for obtaining both technical products and pure LiCl, Li₂CO₃, and LiOH of the reagent and high purity grades. If lithium carbonate is produced for obtaining a power source, its purity should be no lower than 99.5% (chemical grade) and preferably 99.95% (high purity grade) [4]. It is obvious that the preparation of such products requires a large consumption of reagents and time, which cannot but affect the yield and cost of the final product. In this respect, new approaches to the extraction and purification of lithium salts have recently begun to develop. The method for isolating pure lithium carbonate from the original brine was described in the Russian patent [13]. First, the brine is treated with a group reagent, most likely sodium carbonate, which precipitates all alkaline earth carbonates that poorly dissolve in water, while lithium carbonate remains in the solution. After removing the precipitate, the selective crystallization of lithium carbonate from the liquid phase is carried out, slightly increasing its temperature and filtering out the precipitated

lithium carbonate at the first stage of crystallization, and then repeating the procedure of a gradual increase of the mother liquor temperature twice and removing the salt. As a result, Li_2CO_3 with a purity of 99.5% is obtained.

Ryabtsev *et al.* [14] suggested the application of membrane electrolysis of aqueous solutions of LiCl , Li_2SO_4 , and Li_2CO_3 of any origin to obtain very pure lithium hydroxide monohydrate. To accomplish the process, the authors proposed using cation-exchange membranes that separate the cathode and anode circuits of electromagnetic cells. During electrolysis, solutions constantly circulate through the cathode and anode circuits, and due to the presence of the cation-exchange membrane, the solution in the anode circuit is depleted of lithium salt. Lithium hydroxide accumulates in the solution circulating through the cathode circuit, from which a portion of the lithium hydroxide solution is periodically withdrawn for its purification mainly from calcium and magnesium using standard methods. The cathode solution is supplemented with a fresh portion of the initial solution. As a result, the authors obtained chemically pure lithium hydroxide monohydrate.

3.2. Sorbents for the lithium salt recovery from brines

As follows from the previous section, the technology of stepwise purification of brines from lithium-associated components is well developed; the chemical reactions in use are simple and are utilized in a sequence that depends on the source composition. However, the multi-stage processes not only complicate the isolation of the target component, but also increase the cost of the final product. The use of sorption processes can, if not completely, then at least partially reduce a number of stages of separate precipitation of the components. The use of ion-exchange resins for this purpose could be an obvious solution. Indeed, a complex industrial technology for the purification of polluted waters of different origins, including brines, from alkaline earth elements, heavy metals, oil products, and organic impurities was suggested in the recent patent [15]. The brine processing includes the precipitation of the main amount of calcium and magnesium, and to remove their traces, the process scheme implies the use of a carboxyl cationite and a chelate resin containing iminodiacetate groups. When such a resin in lithium form comes into contact with MgCl_2 , the cation coordinates with two carboxy groups, displacing two lithium chloride molecules into the solution. Such a resin was also used in other cases, for example, when working with the DALH-Cl sorbent.

An interesting inorganic ion exchange material $\text{Li}_4\text{Mn}_5\text{O}_{12}$ is described in the patent [16]. The ion exchanger particles with a diameter of 1 μm are covered with ZrO_2 . The coating thickness is 2 nm. This material is washed with dilute hydrochloric acid, during which lithium cations in the ion exchanger are replaced by protons and lithium chloride passes into the solution. A chloride brine is passed through the ion exchanger in the H^+ form, during which only lithium cations are extracted from the brine. After saturation of the cation exchanger with lithium, the material is rinsed with hydrochloric acid, and the process is repeated again. The exceptional selectivity of crystalline $\text{Li}_4\text{Mn}_5\text{O}_{12}$ is apparently associated with the structure of the ion exchanger, which contains cavities, the sizes and spatial configuration of which are complementary to the sizes and

spatial configuration of lithium cations. In other words, the ion exchanger can be attributed to the sorbent with a molecular recognition effect; it operates through the key-and-lock principle [17]. Coating the ion exchanger particles with zirconium oxide does not interfere with the interdiffusion of exchanging ions, but creates a barrier that prevents the material dissolution.

The above-mentioned patent also describes the principle of obtaining spherical particles of porous polyvinylidene difluoride (fluoroplast-2), the outer surface of these particles and the inner surface of the pores are coated with $\text{Li}_4\text{Mn}_5\text{O}_{12}$, which in turn is coated with ZrO_2 . The spherical particles of the composite have an average diameter of 2 μm , which allows them to be used under dynamic conditions.

Gavlina and Ivanov [18] developed a two-temperature reagent-free method for ion-exchange purification of lithium chloride from impurities of metals of the first and second groups. A column filled with methacrylate ion-exchange resin KB-4P2 in a lithium form was brought into equilibrium with a solution of 0.98 N LiCl + 0.02 N KCl + 0.01 N CaCl_2 with pH = 8.9 at 22 °C, passing the excess of this solution from top to bottom, after which the column was heated to 90 °C and the initial solution was again passed through it from top to bottom at the same temperature. Since at this stage calcium actively displaced lithium from the ion exchanger, the volume of solution, after which CaCl_2 breakthrough began, was determined and which should be taken for subsequent separation of the mixture using parametric pumping (this term means that the chromatographic front does not extend beyond the sorbent layer.) Then the column was cooled to 22 °C and the entire volume of the solution collected at 90 °C was passed through the column from the bottom up at 22 °C. The eluate was collected and passed through the ion exchanger from the bottom up at 90 °C. The separation at room and elevated temperatures was repeated several times, the process was stopped at 90 °C. As a result, it was found that at high temperatures the concentration of calcium in the eluate gradually decreased due to its selective extraction by the sorbent from the solution in about nine times. On the contrary, at 22 °C the concentration of calcium in the filtrate gradually increased due to the regeneration of the ion exchange resin.

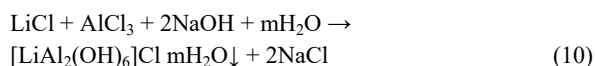
Unlike the polymer ion exchanger, purification of a 1.03 N LiCl + 0.020 N KCl + 0.0012 N CaCl_2 solution from potassium on zeolite A using a similar technique proceeds effectively at 20 °C. After several runs of parametric pumping, the concentration of potassium in the solution was reduced by 45 times. A thermodynamic description of two-temperature reagent-free separation of salts is given in the review [19]. We would like to believe that a non-trivial approach to purifying lithium chloride from impurities of alkali and alkaline earth metal salts will be in demand in the processing of brines.

All the above-described methods of processing natural hydromineral raw materials involve the extraction of a certain volume of brine, whereas natural sources continuously supply brine, for example, the daily volume of the Berikey deposit (Dagestan, Russia) reaches 1500 m^3 . The concentration of lithium cations in this source, according to various analyses, composes 39–44 mg/L. Simple calculations show that about 360 kg of lithium chloride are lost per day. It is clear that only adsorption of lithium chloride on a solid sorbent in the simulating moving bed mode can solve the problem of

continuous extraction of LiCl.

At the end of the 20th century, the Institute of Solid-State Chemistry and Mechanochemistry of the Siberian Branch of the Russian Academy of Sciences began active development of a sorbent based on the composite of aluminum hydroxide and lithium chloride: The material was called DALH-Cl (double aluminum lithium hydroxide) [19]. This was an important step towards solving the problem of continuous processing of brines. In this respect, the results obtained deserve a more detailed consideration.

It was originally synthesized by mixing aqueous solutions of aluminum chloride, lithium chloride, and sodium hydroxide:



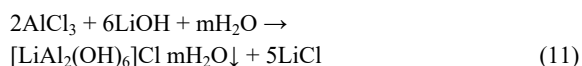
The co-precipitation of the lithium salt and amorphous aluminum hydroxide, which rather quickly acquires a crystalline form, apparently leads to the formation of an inclusion compound with an ordered structure (the authors of numerous works in this area call DALH-Cl an intercalation compound [20]).

In order to understand the crystal structure of DALH-Cl, hydrargillite particles (one of the crystalline forms of $\text{Al}(\text{OH})_3$) were placed in a 20 M LiCl solution at 90 °C. In several days, the crystals changed the appearance, and their chemical composition corresponded to the formula given in equation 10. Interestingly, even if DALH-Cl is obtained by dissolving Al in LiOH, it has the same composition. In principle, it is possible to increase the content of aluminum in DALH-Cl synthetically, but it is impossible to increase the content of LiCl. The investigation showed that the structure of DALH-Cl is a set of layered packets, each of which is formed by three layers: two layers of closely packed aluminum hydroxide and a third layer containing lithium and chlorine ions, as well as water molecules. No signs of starting hydrargillite were found.

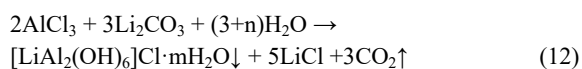
It should be noted that during investigation of DALH-Cl, the main focus was on the structural studies using modern physicochemical methods, while its properties, which are important for the extraction of lithium salts from brine, were relegated to the background, most likely because these properties are not easy to explain.

The composite with the composition exactly corresponding to the above formula (11) appeared to poorly extract lithium chloride from brine.

Later, Ryabtsev [21] proposed two other ways of obtaining DALH-Cl, the preferred option being the one that implies the use of cheaper lithium carbonate:



or



Both routes yield DALH-Cl with a defective, poorly crystallized, disordered, and single-phase structure. Apparently, a large excess of LiCl prevents complete crystallization of the product. The composition of a large batch of DALH-Cl (30 kg), obtained by reaction (12) with LiOH, corresponded to the formula $\text{LiCl} \cdot 2.6\text{Al}(\text{OH})_3 \cdot 4\text{H}_2\text{O}$ [22]. Finely ground powder of

the resulting dry DALH-Cl was mixed with polyvinyl chloride and methylene chloride, the resulting paste was extruded, and the product was obtained in the form of tablets with 2×2 mm sizes. 92% of the binding polymer was then removed from the tablets by extraction with methylene chloride [23]. In tablets, between the particles of the original sorbent in the form of powder, there remains free space (gigapores) with a diameter of 1000 nm and a small proportion of large mesopores with a diameter of more than 20 nm, while smaller pores are absent according to argon adsorption data in the granulated product [21].

The structure and properties of the initial DALH-Cl and granulated material based on it were studied in detail and presented in a generalized form in the book [24]. Three unusual properties of this double aluminum lithium hydroxide are noteworthy, which, unfortunately, remained unexplained.

Firstly, the equilibrium of lithium chloride absorption from an aqueous solution at 25 °C is reached only after 24 h (Fig. 2), whereas the removal of absorbed LiCl by washing with water at 50 °C occurs so rapidly that this difference cannot be explained by the influence of temperature alone.

Secondly, if DALH-Cl with a defective structure is washed with water, it easily releases only 30–40% of lithium being present in the material, and upon subsequent contact with chloride brine, it restores its composition.

Thirdly, the performed investigations showed that, if the molar ratio $\text{Al}(\text{OH})_3:\text{LiCl}$ in DALH-Cl with a defective structure exceeds 3 and in the material with a crystalline form—2.5, then the amount of lithium chloride removed during washing with water begins to exceed the amount of salt absorbed from the chloride solution [24].

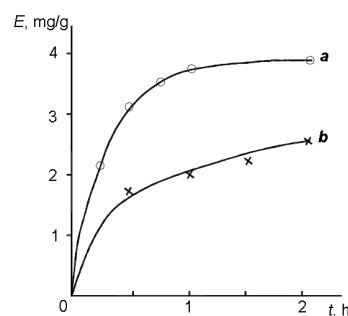


Figure 2. Kinetic curves of LiCl removal from DALH-Cl, obtained by reaction (11), by washing with water (a) at 50 °C and LiCl absorption from brine at 2 g/L salt concentration, 25 °C, and total salts of 450 g/L (b) [22].

Finally, a very important property of DALH-Cl is its selectivity for extracting lithium chloride from brines containing salts of alkali and alkaline earth metals.

We took the liberty of expressing our hypothesis that explains the above non-trivial properties of DALH-Cl.

The incomplete extraction of lithium can be understood by turning again to reaction (11). The large amount of unreacted LiCl suggests that, after the reaction completion, it not only remains in the solution, but also precipitated DALH-Cl can mechanically capture LiCl, which remains in it after drying. Thus, the so-called molecularly imprinted material is formed. Menzheres *et al.* [22] rightly assumed that during rinsing, pure water simply washes out some of LiCl from defective DALH-

Cl, and upon contact with brine after equilibrium establishing, lithium chloride again occupies the vacated place. It is possible that it completely corresponds to the size and structure of the hydrated lithium chloride molecule (unfortunately, it is impossible to verify this assumption experimentally). In this case, the selectivity of the salt absorption can only be explained by the fact that "the place of lithium in this compound cannot be occupied by any other element" [22]. It can also be assumed that 60–70% of LiCl is included into the crystalline fraction of DALH-Cl and is not available to water.

However, it is also important to note that the absorption of LiCl from water and its removal with water at close temperatures is not an adsorption process, and DALH-Cl cannot be called an adsorbent. Indeed, adsorption is the process of concentrating the sorbate at the interface of two phases, caused by interactions such as dispersion, hydrophobic, ionic, *etc.* [25]. In our case, one phase is the solid material DALH-Cl or simply aluminum hydroxide, and the other is an aqueous solution. Water plays an important role in understanding the processes occurring during the extraction of lithium using aluminum hydroxide.

In the $\text{Al}(\text{OH})_3\text{-H}_2\text{O}$ system, there are multiple hydrogen bonds that compact the structure of DALH-Cl. Water and LiCl dissolved in it slowly diffuse between the small particles of this granular material, while lithium chloride, being a strong chaotropic agent, destroys the hydrogen bonds and thereby loosens the structure of DALH-Cl (presumably, even causing some swelling). The removal of lithium chloride by water occurs rapidly from the loose and more accessible structure, but after this, the hydrogen bonds are restored again.

In an aqueous medium, $\text{Al}(\text{OH})_3$ exhibits amphoteric properties and is therefore a weak electrolyte, up to 3% of its completely dissociated molecules dissolve in water. The remaining aluminum hydroxide molecules retain a tendency to dissociate, due to which a δ^+ charge appears on the Al cation and a δ^- charge on the OH group.

When LiCl comes into contact with $\text{Al}(\text{OH})_3$, the formation of the ionic Li–O bond is natural. It is this interaction that is responsible for the adsorption of lithium chloride on amorphous freshly precipitated $\text{Al}(\text{OH})_3$ [26–29] and on its crystalline analog [30]. Compared to other alkali metals, the Li–O bond is the shortest and strongest one [31, 32], and therefore LiCl is sorbed preferentially over other cations of the first group metals.

We performed two experiments confirming our ideas about the reason for the extraction of lithium chloride with aluminum hydroxide. In the first case, a macroporous chloromethylated copolymer of styrene with divinylbenzene was taken and molecules of tris(hydroxymethyl)aminomethane $\text{NH}_2\text{C}(\text{CH}_2\text{OH})_3$ were attached to the inner surface of the macropores *via* C–N bonds. A considerable number of OH groups on the surface of the macropores are accessible to LiCl, but no sorption from a 0.1 N aqueous solution was observed. In another experiment, we took polyvinyl alcohol of the general formula $-\{\text{CH}_2\text{CH}(\text{OH})\}_n-$ with a molecular weight of 86 kDa, it swells well in water, but also does not absorb the salt. A charge on the hydroxy group is really needed to implement the absorption of the lithium salt. The formation of ionic bonds is also confirmed by the fact that the desorption of lithium by water from amorphous $\text{Al}(\text{OH})_3$ is possible only at elevated temperatures [24] (DALH-Cl turned out to be a hydrolytically

unstable material and at 70 °C decomposes into LiCl and $\text{Al}(\text{OH})_3$).

The propensity of $\text{Al}(\text{OH})_3$ for dissociation can explain another unusual property of DALH-Cl at first glance. The greater the molar ratio of aluminum hydroxide to lithium chloride, the greater the absolute amount of $\text{Al}(\text{OH})_3$ that dissolves in water, which is inevitably accompanied by the release of an additional portion of LiCl due to its leaching with water.

DALH-Cl appeared to be a complex object for studying and understanding its properties. The combination of the latter determines the practical significance of the material. The advantages of DALH-Cl include, first of all, the possibility of concentrating a brine without significant energy costs when the hydromineral source is located in a region with a boreal climate. Secondly, the brine passed through DALH-Cl is largely purified from the impurity components accompanying lithium chloride, although remaining MgCl_2 and CaCl_2 must be additionally extracted, for example, using a chelating resin taken in the Li form.

Over the past years, a technology for the production of DALH-Cl and a technology for the continuous production of the lithium chloride concentrate from chloride brines using a simulating moving bed system have been developed. The license for both technologies was sold to China, where a plant for the production of aluminum hydroxide and lithium composite was built in the city of Hoi Zhou, which has been used for several years for practical purposes. In Russia, a pilot plant for the production of lithium carbonate from associated waters of oil production was created in the Irkutsk Oblast. At the end of the discussion of the problems of DALH-Cl, it should still be noted that this material is short-lived; being constantly in dynamic contact with water, $\text{Al}(\text{OH})_3$ will gradually dissolve. However, only practice will show how important this problem is. For the future, however, it is more important to know what volume of brine of the known lithium concentration can be passed through one volume (or unit weight) of DALH-Cl under optimal conditions before lithium breakthrough and what capacity of the material is achieved in this case.

To replace the irregularly shaped particles of DALH-Cl, the authors of patents [33–35] suggested its analog in the form of spherical particles of macroporous anionite based on a copolymer of styrene with divinylbenzene. The authors filled the pores of the sorbent with a saturated solution of AlCl_3 , dried the granules, and treated them first with ammonia water to precipitate $\text{Al}(\text{OH})_3$ and then with a solution of LiCl or LiOH. The resulting composite withstood 60 cycles of lithium chloride absorption from chloride brine and subsequent removal of the lithium salt with water. However, the capacity of the sorbent subsequently began to gradually decrease due to the loss of aluminum hydroxide.

4. Conclusions

In this review, we briefly described the current state-of-the-art of the problem of lithium salt extraction from natural raw materials. We touched only on the scientific aspects of the problem and the chemical processes underlying the treatment of raw materials, leaving the problems of technology as such beyond the scope of this work.

In the world, lithium is concentrated, firstly, in lithium-bearing ores, and secondly, in hydromineral and geothermal sources. The processing of mineral ores, in particular spodumene, is actually the only method capable of meeting the state's need for valuable material.

At the same time, we cannot discount the processing of hydromineral raw materials, including sources, associated waters of oil production, and existing lakes. The processing of aqueous brines includes two directions: the sequential separation of each of the lithium associated components and the sorption processes.

The chemical methods for the stepwise separation of impurities have been studied for a long time, the optimal approaches have been developed, and currently the efforts of researchers are aimed primarily at improving the technology and using more modern equipment.

The sorption selective extraction of lithium salts from complex mixtures of elements of the first and second groups is attractive because all non-sorbed impurities leave with the flow of intergranular liquid, so the lithium salt desorbed afterwards should be practically free of contaminants.

Currently, only in Russia the method and technology for producing the lithium-selective sorbent DALH-Cl was developed, which represents a composite of lithium chloride and aluminum hydroxide. In addition, freshly precipitated $\text{Al}(\text{OH})_3$ exhibits good sorption properties. Aluminum hydroxide, although a disposable sorbent, is currently being actively introduced in Dagestan for processing the Berikey deposit. The authors of the process not only demonstrated the production of lithium carbonate in a short time, but also developed the method for converting spent $\text{Al}(\text{OH})_3$ into AlCl_3 , from which $\text{Al}(\text{OH})_3$ can be obtained again.

We also included two analytical papers that we found interesting, one devoted to the two-temperature reagent-free extraction of lithium chloride from its mixture with calcium and potassium chlorides on a carboxy-containing cationite and zeolite. The second paper is devoted to the synthesis and investigations of the sorption properties of the exclusively selective spinel sorbent $\text{Li}_4\text{Mn}_5\text{O}_{12}$, which is currently used as a cathode material in lithium-ion batteries [36].

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Conflict of interests

The authors have no conflicts of interest to declare.

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