

**LITHIUM IN NATURE, APPLICATION, METHODS OF EXTRACTION  
(REVIEW)**

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**ABSTRACT**

The present review is dedicated to the world's lithium resources, and application areas of lithium and its compounds in everyday life and technology. Lithium is the lightest representative in the group of alkali metals. In its geochemical properties lithium refers to a group of lithophilic elements. Lithium is found in more than 150 minerals, although only 28 lithium minerals per se are known. Many of them are extremely rare. The main lithium minerals are the following: amblygonite, lepidolite, petalite, spodumene, zinnwaldite and Jadar. A review of the world's largest lithium deposits, made the analysis of its global production and reserves. Deposits of lithium are known in Chile, Salar de Uyuni in Bolivia, United States, Argentina, Congo, Lake Chabyer in China, Brazil, Serbia, and Australia. The estimates of reserves were made on the basis of information received from government and industry sources. Separately was presented analysis of the resources and reserves of lithium in the associated petroleum waters of Russia. It also shows that a large source of lithium is the Dead Sea in Israel. Due to the market development of lithium power sources, the most promising lithium resource is secondary resources. The necessity of creation of processes for recycling of spent lithium power sources. In connection with rapid growth in lithium consumption, it is very urgent task of lithium extracting, and receive it in the form of salts, and metal. Have been described, modern sorption methods of lithium extraction from poor on the composition of natural waters and brines with the use of inorganic ion exchangers highly selective to lithium. We present the results of their tests on real natural brines. Particular attention is given to the review of the lithium and its compounds application areas. The most important and rapidly growing area is lithium power sources. Next in importance and volume of consumption lithium is glass and ceramics. Also, large application areas of lithium are lubricants, regeneration of oxygen in the autonomous life support systems, production of polymeric materials and catalysts in chemical technology, metallurgy, pharmaceuticals, medicine. In recent years, a number of promising new application areas of lithium and its compounds: hydrogen energy, electronics and nonlinear optics, nuclear power, and used as rocket fuel. At the end of the article, it provided an overview of prices and demand for lithium and its compounds.

**Keywords:** Lithium, Lithium geochemistry, Lithium application, Extraction methods of Lithium,

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## **LITHIUM GEOCHEMISTRY**

Lithium is the lightest representative in the group of alkali metals. In its geochemical properties lithium refers to a group of lithophilic elements. The ions of these elements have large dimensions. These include the potassium, rubidium and cesium. The lithium content in the upper continental crust is 21 *g/ton* and in the seawater is 0.17 *mg/l* [1].

Lithium is found in more than 150 minerals, although only 28 lithium minerals per se are known. Many of them are extremely rare. The main lithium minerals are the following: amblygonite, lepidolite, petalite, spodumene, zinnwaldite and Jadar. The most common one is: lepidolite -  $\text{KLi}_{1,5}\text{Al}_{1,5}[\text{Si}_3\text{AlO}_{10}](\text{FOH})_2$ , which belongs to a group of mica minerals, i.e., aluminosilicates having a layered structure, and the spodumene -  $\text{LiAl}[\text{Si}_2\text{O}_6]$ , referring to a group of pyroxenes, i.e., chain silicates. In many cases, lithium does not form independent minerals and is isomorphic to replace potassium in wide-spread rock-forming minerals. Deposits of lithium are associated with rare-metal granitic intrusions, which result in development of lithium-carrying pegmatites or hydrothermal complex deposits of other metals. Lithium also occurs in the underground thermal waters with extremely high concentrations of various trace elements. Other common type of lithium deposits are natural brines of some highly saline lakes.

## FIELDS. WORLD PRODUCTION AND RESERVES

Deposits of lithium are known in Chile, Bolivia, United States, Argentina, Congo, China, Brazil, Serbia, and Australia. The estimates of reserves were made on the basis of information received from government and industry sources [3, 6] and are presented in Table 1. Data in terms of US domestic production has not been published, and, in order to protect our own data, we evaluated them on the basis of data published on reserves.

**Table 1.** Global production, reserves and resources in lithium

Country	Production by years		Reserves, ton	World resources	
	2014	2015		ton	%
Bolovia				9 000 000	21.4
Chili	11 500	11 700	7 500 000	7 500 000	17.8
USA	<sup>1</sup> 130	<sup>1</sup> 130	38 000	6 700 000	15.9
Argentina	3 200	3 800	2 000 000	6 500 000	15.4
China	2 300	2 200	3 200 000	5 100 000	12.1
Australia	13 300	13 400	1 500 000	1 700 000	4.0
Israel <sup>3</sup>				1 000 000	2.4
Canada				1 000 000	2.4
Congo (Kinshasa)				1 000 000	2.4
Russia				<sup>4</sup> 1 000 000	2.4
Serbia				1 000 000	2.4
Brazil	160	160	48 000	180 000	0.4
Mexico				180 000	0.4
Austria				130 000	0.3
Portugal	300	300	60 000	60 000	0.1
Zimbabwe	900	900	23 000	23 000	0.1
Total in the world <sup>2</sup>	32000	33000	14 400 000	<sup>3</sup> 42 000 000	100

<sup>1</sup> – author’s estimates, official data are not available;

<sup>2</sup> - approximated;

<sup>3</sup> - calculated by the author;

<sup>4</sup> - without taking into account underground brines.

### Salar de Uyuni in Bolivia

Salar de Uyuni in Bolivia is the world's largest deposit of lithium, which is also suitable for the extraction of lithium chloride by a halurgical method. The Bolivian press reported that in this saline lake contains about 100 million tons of lithium. However, this value is 10 times higher than the estimates of American experts [2]. According to experts from the U.S. Geological Survey (USGS) the aforementioned deposit contains 50 to 70% of the world's lithium reserves [4].

### Chile

Reserves of lithium ore In Chile takes second place among the industrialized capitalist and developing countries (50% of proven reserves). Deposits (Salar de Atacama, Askotan, etc.) are located in the Central Valley and are associated with mineralized water of salars mountainous

undrained lakes. In the Salar de Atacama field, lithium resources in the "caliche" (porous gypsum-halite rocks soaked in brine) are estimated in excess of 3 million *tons* with 0.3% Li<sub>2</sub>O content.

### **United States of America**

In the United States two companies operate in the fields of extracting and processing lithium raw materials. One of these companies is Rockwood Lithium Inc., Kings Mountain, North Carolina, and Lithium Corporation in Nevada that uses a salt lake in Fish Lake Valley.

Rockwood Lithium, Inc. is a world leader in the market for lithium compounds and one of the largest manufacturers of lithium raw materials. The company is also the world's leading supplier of special metal compounds based on cesium, barium or zirconium. Access to raw materials is fundamental to the economy and is vital to ensure supplies. Rockwood Lithium, Inc. is fully backward integrated and has to use three independent resources of primary lithium.

Chilean resource in Salar de Atacama, which is the most attractive in the world, is in the activities of Rockwood Lithium, Inc. since 1980. Since 1960's, Rockwood Lithium, Inc. exploits one more plants, which is located in Silver Peak, Nevada and operates on brine. In 2014, the company acquired a stake of 49% from Talison Lithium in Australia with access to its spodumene resources. In addition, Rockwood Lithium, Inc. is constantly working on innovative methods of operation to improve the efficiency and sustainability of its resources [9].

Lithium Corporation is a young mining company that is focused on creating a shareholder value through the discovery and development of deposits of lithium and other associated minerals. Currently, Lithium Corporation studies two fully owned promising fields located in Nevada, USA, and two fields located in British Columbia, Canada. In each of the Nevada fields the company discovered an anomaly on the content of lithium in the brine. In its flagship mine, which is located in Fish Lake Valley, in addition to lithium, the company found reserves of potassium and boron. In 2011, near the surface of the lake, the company ran onto brines enriched in lithium and boron and containing up to 140 *mg/l* of lithium. In addition to these highly anomalous values of the content of lithium and boron, the deposit has an increased content of potassium which reaches 2500 *mg/l*. The company undertook a drilling program that was conducted during the autumn of 2012. Significant works in this direction are included into the plans of 2016 [10].

### **China, Lake Chabyer**

A third unique source of lithium is Zabuye salt Lake – mountainous undrained highly-saline soda lake in the county of Shigatse, Tibet Autonomous Region, China. Besides the enormous amount of lithium carbonate, Lake Zabuye contains appreciable quantities of sodium tetraborate, Glauber's salts, and other alkali metal salts. The content of the chemical elements (*g/l*): Na<sup>+</sup> - 160, Cl - 120, K<sup>+</sup> - 60, Br<sup>+</sup> - 3, B - 3, Li<sup>+</sup> - 1,2 ÷ 1,53, Rb<sup>+</sup> - 0,25, Cs<sup>+</sup> - 0 1, I<sup>-</sup> - 0,02; - 90, CO<sub>3</sub><sup>2-</sup> - 20. The density of water is 1.4 *g/cm<sup>3</sup>*, pH 10. In 2008, Zabuye (Shenzhen) Lithium Trading Co., Ltd. produced 1556.5 tons of lithium carbonate. The company plans to increase the capacity of its plant in the near future from 5,000 to 20,000 tons per year, assuming that the lake reserves are 8.300.000 tons of carbonate (1.530.000 tons of lithium). However, many experts believe these numbers are overestimated [5].

In the 1984, a mineral known as Zabuyelite (lithium carbonate, Li<sub>2</sub>CO<sub>3</sub>) was discovered in the area of this lake, however, only in 1987 it was proved that this mineral can be used for the production of lithium in industrial quantities. In 1999, a company known as Zabuye (Shenzhen) Lithium Trading Co., Ltd was founded here and started production of lithium, and in 2005 [5] this salt lake mine was recognized as the largest source of lithium throughout China. In 2008, Zabuye (Shenzhen) Lithium Trading Co., Ltd. had a staff of 50 employees. In 2008 the company's plant on the shore of the lake produced 1556.5 tons of lithium carbonate. In the near future, the company plans to increase the capacity of its plant from 5000 to 20 000 tons per year [2], evaluating lake stocks as 8.3 million tons

of carbonate (1.53 million tons of lithium). However, many experts believe these numbers are exaggerated [5].

Tibet's government is actively investing in the development of the lake. According to the government estimation, in addition to 20,000 tons of lithium carbonate, the plant will be able to produce annually 5,000 tons of lithium chloride, 500 tons of conventional lithium, 200 tons of ultra-pure lithium, and 520 tons of other lithium-containing substances.

## **Russia**

In Russia more than 50% of lithium reserves are concentrated in rare metal fields of the Murmansk region. However, in our opinion the data presented in Table 1 is too low; since this data does not take into account the resources of lithium found in subsurface brines and associated petroleum waters. Practically, in many regions of Russian Federation there are deposits of salt groundwater with lithium having concentration of 5 to 50 mg/l.

## **Israel, Dead Sea**

Saline Dead Sea basin is a part of one of the largest global zones of salt accumulation - Afro-Arabia, which is inside the Intercontinental rift (submeridional). The African-Arabian rift belt is characterized by salt-bearing basins of different types of rift structures: inland rifts (Suez Graben, separate branches of the East African System) of within shear zones (the Dead Sea) and intercontinental rifts (Red Sea). Saline Dead Sea basin began to form in the first stage of the Late Triassic period, about 230 million years ago. The second stage of its formation took place in the Cenozoic era, between Pliocene and Holocene, i.e., from 6.7 million to 10000 years ago. Accumulation of salts continues also in the modern era. In addition, the structure of the salt basin of the Dead Sea is complicated by hydrochloric dome tectonics. In geodynamic classification of sedimentary basins of salt, it is characterized by the formation of the spreading rift geodynamic regime [24]. In this regard, the Dead Sea is just a small external surface manifestation of giant salt deposits stretching from the southern tip of the Arabian Peninsula to the Strait of Gibraltar. Hence, the water of the Dead Sea is a product of dissolution of a small element of this salt bed that comes to the surface. Therefore, our evaluations of lithium resources in the Dead Sea area are underestimated and relate only to the territory directly near the Dead Sea.

The content of mineral substances in the Dead Sea water is up to 340-350 ‰, 300 ‰ in average (for comparison, in the Mediterranean Sea - 40 ‰). The Dead Sea is one of the most saline lakes in the world. The mineralogical composition of salts of the Dead Sea is significantly different from the composition of the salts of other seas. It contains about 50.8% magnesium chloride, 14.4% calcium chloride, 30.4% sodium chloride, and 4.4% of potassium chloride. It contains a relatively small amount of sulfates, but relatively large amount of bromides.

In its borders the Dead Sea exists for about 15,000 years, and during this time a 100 meter thick salt and mud sediment layer has accumulated at the lake's bottom. The volume of water in the Dead Sea is about 110 km<sup>3</sup>, and it contains about 50 billion tons of dissolved mineral substances. It contains 21 different minerals. The chemical composition of the Dead Sea is shown in Table 2.

We evaluated lithium resources in the Dead Sea on the basis of published data on reserves of magnesium, potassium, and bromine [25], and the concentration of these elements in the water of the Dead Sea (Table 2). The results are shown in Table 1.

**Table 2.** Chemical Composition of the Dead Sea Water

Components of the Dead Sea Water Composition	Concentration					
	General Data		Nissenbaum, (1974) [26]		Nissenbaum, (1977) [27]	
	(1), g/l	(2), mg/l	mg/l	mkg/l	mg/l	µg/l
Na <sup>+</sup>	34.9	39158	39200			
K <sup>+</sup>	75.60	7956	7300			
Rb <sup>+</sup>	0.06					
Ca <sup>2+</sup>	15.8		16900			
Mg <sup>2+</sup>	41.96	45345	40700			
Cl <sup>-</sup>	208.02	227545	212400			
Br <sup>-</sup>	6.92	5360	5100			
SO <sub>4</sub> <sup>2-</sup>	0.54		500			
CO <sub>3</sub> <sup>2-</sup>	0.24		200			
Li <sup>+</sup>			20		17÷21	
Sr <sup>2+</sup>			300		308÷330	
Mn <sup>2+</sup>			4.0÷7.1		3.1÷8.0	
Cu <sup>2+</sup>				300÷500		300÷500
Zn <sup>2+</sup>				500		500
Fe <sup>2+</sup>				10÷15		10÷15
Ni <sup>2+</sup>						20÷25
Co <sup>2+</sup>				8		8
Cd <sup>2+</sup>				8÷10		8-10
Pb <sup>2+</sup>				120÷300		120÷300
I						80÷120
U(VI)				1.3÷2.5		1.5÷2.5
Salinity	315	343202				

### Secondary lithium resources

One aspect of the efficient use of the lithium resources is possibility of recycling of lithium-containing wastes. Historically, recovery of lithium from secondary resources was insignificant, but it is constantly increasing due to the growth of consumption of lithium by lithium batteries. Thus, reprocessing or use of secondary resources will become increasingly important over time. This trend needs to be developed in the present time. As an example of such a development, we can refer to the activity of Rockwood Lithium, Inc. in the USA.

This company recycles lithium metal and lithium-ion batteries already since 1992 at its plant in British Columbia, Canada. In 2009, the US Department of Energy gives the company a grant of \$ 9.5 million for construction of the first US center for utilization of lithium-ion batteries for vehicles. The company provides technology for recovery of lithium or cesium contained in the waste from different industries, and manufactures products from these secondary sources. It is safe to predict that car batteries from hybrid or electric vehicles with expired service-life, will in the near future become the most important secondary raw material for the lithium industry. In order to be ready for this, Rockwood Lithium, Inc. is now developing appropriate processes and began to build a pilot plant for reprocessing lithium salts of EV batteries. The construction is nearing completion.

## THE USE OF LITHIUM ISOTOPES

Natural lithium consists of two stable isotopes:  ${}^6\text{Li}$  (7,5%) and  ${}^7\text{Li}$  (92,5%); in some samples of lithium the isotope ratio may be much disturbed as a result of natural or man-made isotope fractionation.

${}^6\text{Li}$  has a greater affinity with mercury than  ${}^7\text{Li}$ . This is the basis for the enrichment process COLEX [7]. An alternative process is vacuum distillation that occurs at temperatures around 550°C. Normally, separations of lithium isotopes are needed for military nuclear programs (Russia, USA, China). In the USA,  ${}^7\text{Li}$  was produced only as a byproduct of a military nuclear program, namely, in the process of lithium enrichment in the isotope  ${}^6\text{Li}$ . Currently, only Russia and China [8] have functioning capacity for the separation of lithium.

In the United States, the  ${}^7\text{Li}$  is actively used in reactors PWR, analogues of Russian Water-Water Energetic reactors. There are 100 nuclear reactors in operation, of which 65 have installed tank reactors PWR. The water-chemistry mode with PWR units requires the use of lithium hydroxide, enriched in the isotope  ${}^7\text{Li}$ . In addition, the lithium-enriched compounds are used in demineralizers for cleaning the primary coolant circuit. The use of lithium enriched in the isotope  ${}^7\text{Li}$ , rather than natural lithium, is necessary because isotope  ${}^6\text{Li}$  interacts with neutron by the reaction (n; $\alpha$ ) to form tritium.

Previously it was thought that China and Russia have produced  ${}^7\text{Li}$  in an amount sufficient to meet the current needs of the United States, which is unlikely to increase significantly in the foreseeable future. However, supply volumes from China may be reduced due to the active construction in the country of new nuclear units. In addition, China has plans to develop molten-salt reactors, whose operations will require large amounts of  ${}^7\text{Li}$ . China has developed two types of molten-salt reactors which may require large volumes of  ${}^7\text{Li}$ . For comparison, the annual demand of all 65 US units with PWR in  ${}^7\text{Li}$  is approximately 300 kg. Furthermore, molten-salt reactors require significantly higher concentration of lithium  ${}^7\text{Li}$ , namely - 99.995%. Currently, there is no  ${}^7\text{Li}$  of such purity in China.

China has built a small laboratory, whose mission is to enrich the Chinese stocks of  ${}^7\text{Li}$ . Functioning of this laboratory would inevitably lead to a decrease in volumes of the sales of  ${}^7\text{Li}$  from Chinese side. Moreover, it is known that China has already started to acquire  ${}^7\text{Li}$  in Russia.

Unlike China, Russia has low need in domestic consumption of  ${}^7\text{Li}$  and can be a supplier. On the Russian units corrosiveness of  $\text{H}_3\text{BO}_3$  is reduced by using potassium hydroxide instead of lithium.

The auditors of US Government Accountability Office proposed three solutions to the problem of potential risks of interruptions in the supply of  ${}^7\text{Li}$  [11].

First, the cheapest way is to create a national reserve of  ${}^7\text{Li}$  by increasing the volume of imports and to clean the remaining reserves of lithium at the Factory Y-12 (1300 kg of lithium-7). The cost of such an approach can be determined based on the current price of less than \$10 000 for 1 kilogram of lithium-7. However, buying should be done carefully so as not to cause a sharp rise in prices and not to cause other damage to the market. The cost of cleaning of  ${}^7\text{Li}$  obtained from the military Factory Y-12 can be judged based on the known data stating that cleaning of the first 200 kg cost \$ 3,000 per kilogram. It is possible that cleaning of the remaining 1100 kg will have a higher rate per kilogram.

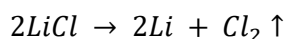
The second way is restoration of production of  ${}^7\text{Li}$  in the USA. According to the estimate by specialists of the Factory Y-12, creation of manufacture capable of delivering only 200 kg of  ${}^7\text{Li}$  per year will take five years and require investment of 10-12 million dollars.

Finally, the third way is to reduce the needs of PWR-containing blocks in  ${}^7\text{Li}$ . This can be achieved at the expense of recovery of  ${}^7\text{Li}$  from demineralizers. Next reserve is to reduce a need in  ${}^7\text{Li}$ , i.e., to switch to the use of potassium hydroxide as is customary in Russian VVERs. Industry estimates the time for such transition as 10 years [11].

## **EXTRACTION OF LITHIUM, AND ITS PREPARATION IN THE FORM OF SALTS AND METALS**

Currently, to extract lithium from its natural minerals, they are decomposed by the action of sulfuric acid (acid method), or sintered with CaO or CaCO<sub>3</sub> (alkali method), or treated with potassium sulfate K<sub>2</sub>SO<sub>4</sub> (salt method), and then leached with water. When a lithium raw material is comprised of natural brines, it is extracted by a halurgical method based on the difference in solubility's of sodium and lithium chlorides in concentrated solutions and in the presence of other metal salts. Brines poor in lithium require the use of a sorption lithium extraction method with the use of selective sorbents. Since the lithium-rich brines can be quickly exhausted, an agenda will be a question of lithium extraction from relatively lithium-poor sources of raw materials.

In any case, a preprocessing produces a concentrate solution of lithium salts. The resulting solution is used for recovery of poorly soluble lithium carbonate Li<sub>2</sub>CO<sub>3</sub>, which is then converted into chloride LiCl. Melt electrolysis of lithium chloride is carried out in admixture with KCl or BaCl<sub>2</sub> (these salts are used to lower the melting temperature of the electrolyte mixture):



Further, the resulting lithium metal is purified by vacuum distillation at a temperature of about 550°C.

Lithium can be leach out of the rocks, and the most common raw source of this element is natural waters. The content of lithium in seawater averages 1.5 to 10<sup>-4</sup> g/l. From a technological point of view such concentration is low. Much more promising are some lake brines. The maximum known lithium concentration of 56 mg/l is observed in chloride-type lake waters. Accordingly, lakes are considered as real sources of a lithium raw material. For example, in the Great Salt Lake (Utah, USA), the total lithium content reaches 4 million tons (based on LiCl) with lithium concentration of 20 mg/l and higher.

It has been shown that a content of lithium in brines can be concentrated by natural evaporation. Experiments made still in the USSR confirmed increasing the lithium concentration in the brine during its evaporation from 2.1 to 32.5 mg/l, but the total mineralization of brine in this case was increases from 280 to 582 g/l.

A study has been conducted regarding a possibility of extracting lithium from free petroleum waters of Dagestan (in the area of South Sukhokumsk). A mixture of free saline waters had the following composition (g/l): NaCl - 75,5; KCl - 15,8; CaCl<sub>2</sub> - 20,3; MgCl<sub>2</sub> - 2,20; SrCl<sub>2</sub> - 1,22; and LiCl - 0,52. It was planned to carry out complex processing of these raw materials. However, the studies have ceased in the early 90s.

Schemes of the existing industrial complexes for processing lithium-containing brines are oriented on Li-rich sources (with Li content in the range of 300 to 500 mg/l), and are based mainly on evaporation and sequential crystallization of different compounds [18-19]. The sorption methods appear to be most promising for the brines with poor content of rare elements [20-23]. Separation of lithium from solutions in the form of carbonate is effective when its content in the solution is not less than 20 to 25 g/l. For brines with the lithium concentration of 40 mg/l this corresponds to a concentration degree of 500. On the other hand, ion exchange processes developed for the above purpose provide not only a required degree of concentration but also specified production efficiency.

The problem of extracting lithium from salt brines is largely connected with their molar ratio of ion Na<sup>+</sup> to Li<sup>+</sup>, i.e., the value of Na/Li. Sodium is one of the elements which is the closest to lithium in its chemical properties and which, as a rule, also has the highest content in natural waters. In some classes of chloride brines the Na/Li ratio can reach 93000. Under such conditions conventional methods based on the precipitation of sparingly soluble compounds of lithium, such as phosphates, are not effective. Promising are only sorbents, which are highly selective to Li<sup>+</sup> ions.



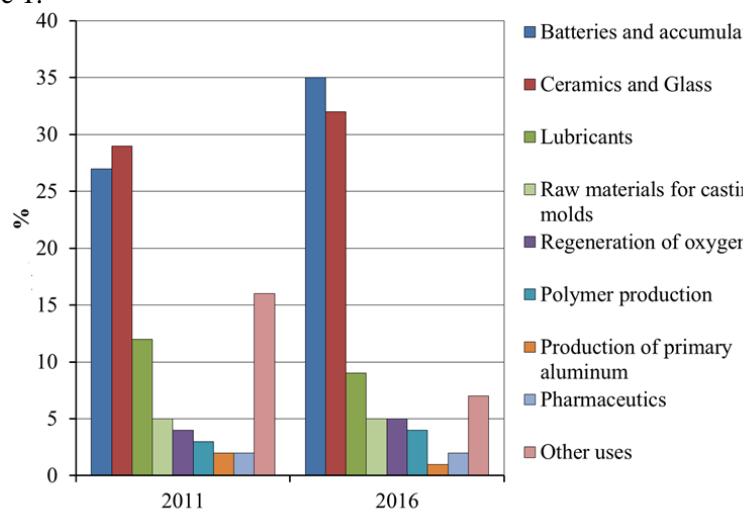
Inorganic sorbents such as ICM-1 have been developed for the extraction of lithium from highly mineralized natural brines. The basis of these sorbents is manganese dioxide. Under the effect of thermal recrystallization the manganese dioxide acquires a structure in which the cation-exchange positions strictly correspond to  $\text{Li}^+$  ions, while access of  $\text{Na}^+$  ions inside the crystal grains is limited due to the "ion-sieve" effect. The sorption-desorption processes are accompanied only by  $\text{H}^+ \leftrightarrow \text{Li}^+$  type exchange. Main features of the ICM-1 sorbent are partition coefficients for the  $\text{H}^+ - \text{Li}^+$  ion pair, which reach  $(1 \div 5) \cdot 10^4$ ; the exchange capacity of  $4 \div 5 \text{ mol Li}^+/\text{kg}$  (full); and  $1,0 \div 2,0 \text{ mol Li}^+/\text{kg}$  (working capacity in solutions of complex salt compositions); and the residual concentration of  $\text{Li}^+$  ions in the filtrate after sorption in the range of  $0.1$  to  $0.3 \text{ mg}/\text{dm}^3$ .

The modified sorbent ISMA-1 was tested in the process of lithium extraction from the underground solution of iodine-bromide production (Perm, Russia). The solution had the following composition ( $\text{g}/\text{dm}^3$ ): NaCl - 189;  $\text{CaCl}_2$  - 56.05;  $\text{MgCl}_2$  - 14.9; KCl - 2.47; NaBr - 1.12;  $\text{SrCl}_2$  - 0.42;  $\text{Na}_2\text{B}_4\text{O}_7$  - 0.12; KI - 0.02;  $\text{Li}^+$  -  $11 \cdot 10^{-3}$ , pH 8,2. Sorption was performed prior to breakthrough of  $\text{Li}^+$  ions to the filtrate -  $0.9 \text{ mg}/\text{dm}^3$ . Test results: sorption capacity was  $17 \text{ g Li}^+/\text{kg}$ , the degree of lithium extraction was 91.5%. The author took active part in the development of technology for these and other similar sorbents, as well as in the test of their properties in case of real industrial and natural solutions [12-16].

## THE USE OF LITHIUM AND ITS COMPOUNDS

The scheme of lithium consumption has not changed much over the past few decades. However, major changes have occurred in the proportions.

In recent years the consumption of lithium for the batteries has significantly increased. This is because the market has grown for rechargeable lithium batteries to be used in portable electronic devices, electric tools, electric vehicles, and applications to network storage circuits. Lithium minerals, as before, are used worldwide directly as ore concentrates in the ceramic and glass industries. The structure of the largest areas of use of lithium and its compounds in the world in 2011 and 2016 is presented in Figure 1.



**Figure 1.** Assessment of the largest areas of use of lithium and its compounds in the world in 2011 and 2016. [3].

### Lithium power sources

For many years, the first and most important application of lithium and its compounds was the sphere of chemical current sources. Ever since the middle of last century, lithium hydroxide began to be added to the electrolyte of alkaline batteries. It was found that the addition of this substance to the electrolyte alkaline battery increases the battery capacity approximately by 20% and makes the

service life 2 ÷ 3 times longer. In recent years, this area has dramatically expanded in connection with the creation of lithium power sources required for the operation of cell phones and other small consumer electronics devices.

Lithium is used in manufacturing anodes for chemical current sources of accumulator batteries and battery cells with solid electrolyte working on the basis of non-aqueous solid and liquid electrolytes. Examples of such batteries are lithium-chromium-silver accumulators. Electrochemical cells with solid electrolytes are represented by the following designs: lithium-bismuth, lithium-copper oxide, lithium dioxide-manganese, lithium-iodine-lead, lithium-thionyl-chloride, lithium-oxide-vanadium, lithium-fluorine-copper, and lithium-dioxide-sulfur elements. In case of liquid electrolytes the following organic polar liquids are used as solvents: tetrahydrofuran, propylene carbonate, methyl formate, acetonitrile, and others.

When used in lithium batteries as positive electrodes, such solid electrolytes as lithium cobaltate and lithium nickelate showed the best performance and energy consumption characteristics. Currently, the following several classes of cathode materials are used in mass production of lithium-ion batteries:

- lithium cobaltate  $\text{LiCoO}_2$  and solid solutions on the basis of isostructural nickelate  $\text{LiNiO}_2$ ;
- Lithium-manganese spinel  $\text{LiMn}_2\text{O}_4$ ;
- Lithium-ferrophosphate  $\text{LiFePO}_4$ .
- Carbon-coated nanotubes of lithium molybdate, which can be used as an anode in lithium-ion accumulators [33].

Lithium aluminate (lithium  $\beta$ -alumina) is one of the most effective solid electrolytes, along with sodium and cesium- $\beta$ -alumina.

Lithium hydroxide is used as a component for preparation of an alkaline battery electrolyte. Due to the formation of lithium nickelates an addition of lithium hydroxide to an electrolyte traction iron-nickel, nickel-cadmium, or nickel-zinc rechargeable battery increases the battery capacity by 12%, the resistivity at 21%, extends the service life of nickel-iron battery 2 ÷ 3 times, and increases its capacity by 21 %.

Almost the same area includes the use of lithium compounds as thermoelectric materials. Thus, the alloy of lithium sulfide and copper sulfide is an effective semiconductor for thermoelectric converters. It has the EMF about  $530 \mu\text{V/K}$ .

## **Glass and Ceramics**

Ceramics and glass are the second most important areas of application of lithium and its compounds. Ceramics that are solidify at room temperature and used in military equipment, metallurgy and, in the long term, in fusion energy is made on the basis of lithium aluminate and lithium silicate. Glass based on lithium-aluminum-silicate reinforced with silicon carbide fibers has a tremendous strength.

A significant number of lithium compounds are used to produce glass having such properties as improved chemical resistance, transparency to ultraviolet or infrared radiation, and photosensitivity. The introduction of lithium compounds contributes to the production of high-quality ceramics. In particular, lithium is included in the high voltage porcelain composition, and the composition of specific ceramic coatings having exceptional heat resistance (Stupalit) that are used to extend the life of combustors and nozzles of jet engines. In enamels lithium compounds reduce viscosity of the melt and facilitate formation of smooth and thin coatings. Lithium is a component of a high-quality glaze.

Lithium and its compounds are widely used in the silicate industry for the production of special types of glass and for application of porcelain coatings.

Lithium oxide comprises a widely used flux for treatment of silicon dioxide by reducing the melting point and viscosity of the molten material and thus improving physical properties of glaze coatings, as well as reducing the thermal expansion coefficients. Lithium oxide is a component used

in the manufacture of glassware. As a rule, lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) is used in the art since it is converted into an oxide by heating.

Liquid lithium glass is among the most tonnage of lithium products. It is widely used in a variety of silicate cements in construction industry. In metallurgy it is used as a binder for foundry forms. When lithium silicates lose moisture at a temperature in the region of 150–200 °C, they begin to convert into forms insoluble in water and quickly become waterproof. Lithium polysilicate solutions are mainly used as a binder in zinc anticorrosion coatings, providing stability and storability of paints. Furthermore, these solutions are suitable for depositing thin silica films on a variety of surfaces, including glass surfaces of optical devices. Lithium hydroxide, as well as lithium silicate or polysilicate are good additives to the sodium or potassium silicate systems modifying their properties.

## **Lubricants**

The third most important area of application of lithium compounds includes lubricants. Lubricants can be solid, plastic, liquid, or gaseous substances that are used in friction units of motor vehicles, industrial machinery, as well as in everyday life for reducing wear of moving mechanisms and structures caused by friction. Lubricants are presented by lubricating oils and greases. Greases are substances that are in a pasty state at ordinary temperatures and in a liquid state when heated. They are complex colloidal systems having a solid phase consisting of a thickener (sometimes filler) and a liquid phase consisting of a mineral oil.

The most important properties of greases are consistency, i.e., the degree of density of grease; melting point that characterizes the upper limit of the working temperature of the lubricant; chemical and mechanical stability; colloidal stability, i.e., resistance against decay into liquid and solid phases; and thermal stability, i.e., the ability to retain its structure and properties during prolonged heating.

Examples of such materials are *Litol* and CIATIM-201. They are mixtures of low-viscosity petroleum oils thickened with lithium salts of fatty acids. One of the most common compounds of this type is lithium stearate ("lithium soap"), which is used as a thickener for pasty high temperature greases for machines and mechanisms. Lithium salts of higher fatty acids are the basis of most high quality greases with an unusually wide operating temperature range (-60 to + 160°C).

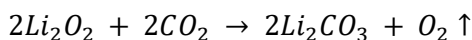
Thickeners are important components for preparation of greases. Soaps may also be used as thickeners for increasing viscosity of oils. The major components of most grease are usually emulsions of mineral oils and calcium or lithium soaps. Widely used are calcium and lithium greases. The lithium soaps are also used as thickeners for increasing the viscosity of oils.

Soaps are the most common emulsifying agents, and a choice of a specific type of soap depends on its specific application. The soaps typically comprise calcium, sodium and lithium stearates or mixtures of these components. Frequently used are soaps based on fatty acids which differs from stearate derivatives. For example, particularly widely used is lithium 12-hydroxystearate. The lithium 12-hydroxystearate exhibits high stability to oxidation approximately to about 200°C. Most lubricants used today in cars, airplanes and heavy equipment include stearates of lithium, mainly lithium 12-hydroxystearate [34]. Greases may be prepared with the addition of several different metallic soaps. Lubricants based on lithium soaps are preferred because of their resistance to water, as well as their mechanical and oxidative stability. They also have good characteristics, both at high and at low temperatures. Greases based on lithium have a higher melting temperature than calcium-based greases. Lithium lubricants have melting points in the range of 190 to 220 °C. However, the maximum usable temperature for lithium grease is 120 °C.

Being a strong base, lithium hydroxide, when heated with fat, forms a soap containing lithium (lithium stearate). Lithium soap has the ability to thicken oil, and it is used for the production of universal, high-temperature greases [35].

## Regeneration of oxygen in the autonomous life support systems

In its importance this area takes the fourth place among the fields in which lithium compounds are used and is one of the most underdeveloped applications of lithium. Lithium hydroxide LiOH and lithium peroxide Li<sub>2</sub>O<sub>2</sub> are used to clean the air from carbon dioxide and, when the latter compound reacts, it evolves oxygen

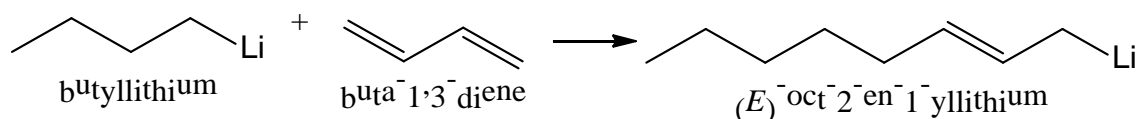


Due to this effect, it is used in insulating gas masks, cartridges for purification of air in submarines, manned spacecraft, etc.

Anhydrous lithium bromide LiBr and lithium chloride LiCl, which possess high hygroscopicity, are used to maintain constant humidity by drying air and other gases.

## Polymer materials and chemical technology

Fifth place in the structure of the lithium consumption takes lithium organic synthesis and especially production of polymeric materials and in particular synthetic rubber. The basic lithium compound used in these processes is butyllithium (BuLi). Organic lithium compounds and, in particular butyl lithium, are obtained from metallic lithium and alkyl halides [32]. The main area of application of butyllithium for industry is use thereof as a catalyst for anionic polymerization in the manufacture of polyisoprene, polybutadiene and butadiene/styrene, which play an important role in the production of plastics and rubber. Thus butyllithium is used as an initiator of anionic polymerization of dienes such as butadiene. This reaction is called a reaction of carbonylation:



Thus, stereospecific polymerization of isoprene can occur. Also commercially important is the use for the manufacture of butyllithium styrene-butadiene polymers. Even an ethylene can be polymerized under the influence of BuLi.

By using butyllithium it becomes possible to control a homogeneous polymerization for obtaining polymeric material having predetermined molecular weights, molecular weight distributions, given ratios of co-monomers, sequences of butadiene and styrene monomer units, and degrees of branching. Thus, it is possible to produce the most effective microstructure [29-31].

In addition, butyl lithium, which is a valuable tool in organic synthesis of active pharmaceutical ingredients (API), is used in the production of chemicals for agriculture and electronic materials. Due to distinct properties of its base, the butyl lithium can be used as a universal reagent for metallization (deprotonation or metal-halogen exchange) of organic matters.

n-BuLi belongs to a group of compounds called "superbases" and is one of the strongest bases which are used in organic synthesis. When dissociation constant ( $pK_a > 35$ ) is set as an acid, the n-butyllithium is capable of deprotonating a wide range of acidic compounds thus allowing further conversions, such as generation of C-C bonds. Mild reaction conditions, high yield, an insignificant amount of byproducts, and ease in detaching residual lithium salts are the main advantages of n-butyllithium in comparison with alternative reagents. For specific reactions of deprotonation can be used sec-butyl lithium or t-butyl lithium having even more pronounced basic properties.

Another common use of butyl lithium as a reagent in organic synthesis is use thereof in metal-halide exchange reactions. In this type of reactions, aliphatic or aromatic organic halides (generally iodides or bromides) are employed as substrates. A reaction with butyllithium generates fewer organolithium compounds, and this increases the scope for further intermediate reactions with suitable

electrophilic agents. Compared with other classical methods such as the use of magnesium-organic compounds, the halogen exchange with butyl lithium is characterized by mild reaction conditions, high yields, and a small amount of by-products, especially when using compounds with functional groups sensitive to harsh conditions.

Many other lithium compounds are used as reagents for the preparation of organic compounds. Examples of such compounds are lithium aluminum hydride ( $\text{LiAlH}_4$ ), lithium borohydride ( $\text{LiBH}_4$ ), lithium triethylborohydride ( $\text{LiBH}(\text{C}_2\text{H}_5)_3$ ), etc.

## **Metallurgy**

Ferrous and non-ferrous metals are also one of the great applications for metallic lithium, which is used for deoxidation and improving ductility and toughness of alloys. Lithium is administered as a single metal or with metals of different ligatures (e.g., 30% Li + 70% Ca) for deoxidizing, alloying, or modifying many brands of ferrous alloys and irons. It is used to increase the yield, strength, and hardness of carbon steel and stainless steel, for modifying the high-speed tool steel and austenite steel. In non-ferrous metallurgy, introduction of 1% lithium into magnesium alloy improves its corrosion resistance and resistance to tearing. Of great interest is the ability to create "floating" Mg-Li alloys containing more than 50% Li.

By using metallothermic methods, lithium is sometimes employed for recovery of rare metals. Metallothermy is recovery of metals at elevated temperatures from their compounds with other metals which are chemically much more active than the recoverable.

Special application of lithium in metallurgy is metallurgy of aluminum. Thus, lithium carbonate is an essential adjunct (for addition to electrolytes) in the smelting of aluminum, and every year its consumption grows in proportion to the volume of world aluminum production (consumption of lithium carbonate is  $2,5 \div 3,5$  kg per ton of smelted aluminum).

Lithium is also widely used for aluminum alloying. Introduction of lithium into the doping system makes it possible to obtain new aluminum alloys of high specific strength. Addition of lithium reduces the density of the alloy and increases its modulus of elasticity. However, high concentrations of lithium in aluminum alloys may affect their corrosive properties. At lithium content up to 1.8% the alloy becomes low resistant to stress corrosion and at 1.9% becomes not prone to stress corrosion cracking. The increase in lithium content up to 2.3% contributes to increase in the probability of formation of cracks and loose structures. This changes the mechanical properties of aluminum-lithium alloys. In other words, increase in limits of their strength and yield is accompanied by decrease in plastic properties of such alloys.

The most famous doping system are Al-Mg-Li (an example is alloy 1420 used in the manufacture of aircrafts) and Al-Cu-Li (an example is alloy 1460 used in the manufacture of tanks for liquefied gases). An alloy on the basis of aluminum, which is known as "Skleron" and which contains lithium, has found use in the aircraft industry. Tensile strength, elasticity and hardness of this alloy are higher than the same properties in duralumin-type alloys. Alloys of lithium with magnesium, scandium, copper, cadmium, and aluminum are new promising materials in aviation and astronautics (because of their lightness). Excellent mechanical properties are in lithium alloys with copper and lead. Lithium is very effectively strengthens lead alloys and gives them flexibility and resistance to corrosion. Alloys of lithium with titanium, beryllium, zinc, and silver also find application. Alloys of lithium with silver and gold, as well as with copper, are very effective solders.

Lithium is sometimes used for recovery of rare metals from their halides by metallothermic methods.

## **Pharmaceuticals, medicine and biological importance of lithium**

Lithium salts exhibit normothymic and other therapeutic properties. Therefore, they are used in medicine.

Lithium drugs are psychotropic medical substances from normothymics. Historically they are first drugs of this group, found yet in 1949; however, they remain essential in the treatment of affective disorders, especially manic and hypomanic phases of bipolar disorders, as well as in their preventive treatment and treatment of exacerbations of severe or resistant depressions, as they possess preventive properties. Lithium preparations have some other applications as well [36,37].

Lithium is an alkaline metal, so it is used in medicine in the form of salts, mostly as carbonates and also as citrates, succinates, orotates, chlorides, and sulphate of lithium. Lithium bromide is no longer used in medicine, as it causes chronic poisoning - bromism - already at a dose of 250 mg per day. In Russia, only carbonates are used now from the salts of lithium, and hydroxybutyrate and lithium nicotinate were used previously.

Human body needs lithium in small quantities (about 100 mg/day for adults). Lithium is present in the human body predominantly in the thyroid, lymph node, heart, liver, lungs, intestine, blood plasma, and adrenal glands.

Lithium is involved in important processes:

- participates in carbohydrate and fat metabolism;
- supports the immune system;
- prevents the occurrence of allergies;
- decreases nervous excitability.

Lithium is evolved mainly by kidneys.

Some lithium compounds are used as catalysts in medicine for drug development. Lithium soaps are used for impregnation of water-repellent fabrics.

Other areas which are close by use of lithium to pharmaceuticals are the textile industry where lithium compounds are used for bleaching fabrics, and the food industry where lithium compounds are used for food preservation. Lithium compounds are also used in the manufacture of cosmetics.

### **Prospective application field of lithium and its compounds**

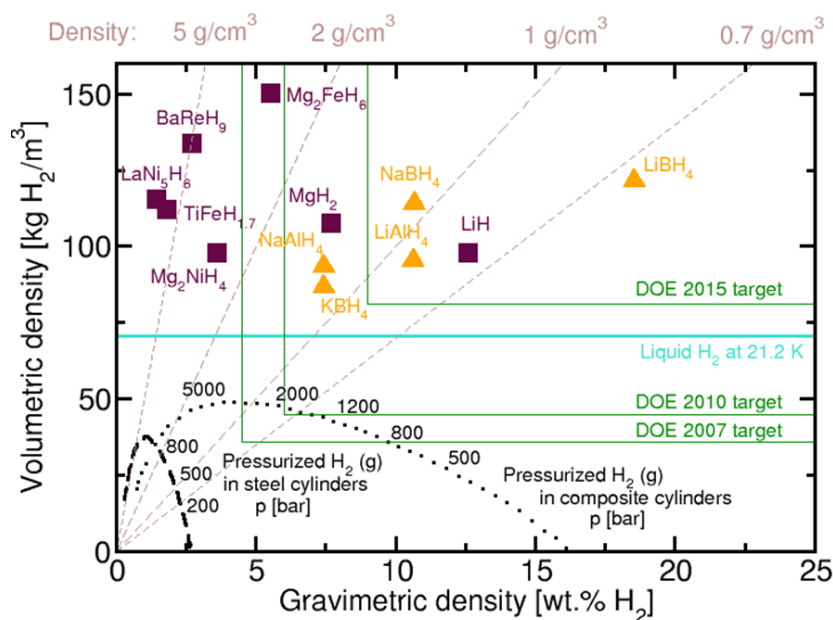
There are a variety of other applications for lithium compounds. Many of them are historically developed, and some are new as they arise from the development of science and technology in recent years. These applications are also in the near future may be at the forefront of lithium consumption and its compounds. It is therefore necessary to carry out intensive research in these areas, as the most promising.

### ***Hydrogen energetics***

The main problem of hydrogen energetics is the problem of hydrogen storage. Methods of storing hydrogen for later use cover a variety of approaches, including high-pressure, cryogenic techniques, and chemical compounds that reversibly release H<sub>2</sub> under certain influences. Most researches on hydrogen storage are focused on storing hydrogen in the form of solid compounds - hydrides as light and compact energy sources for mobile applications. Comparison of different methods of hydrogen storage is presented in Figure 2.

Metal hydrides are represented by squares and complex hydrides (including LiAlH<sub>4</sub>) by triangles. BaReH<sub>9</sub> has the highest known ratio of metal and hydrogen (4.5), Mg<sub>2</sub>FeH<sub>6</sub> has the highest known bulk density of H<sub>2</sub>, LiBH<sub>4</sub> has the highest weight density. The values presented for the hydrides exclude the role of capacity. Objectives are DOE including the weight of the container [40].

Lithium hydride LiH has the higher hydrogen content out of other hydrides, and more than three times exceeds content of hydrogen in sodium hydride NaH. The LiH is of great interest for hydrogen storage, but its resistance to decomposition is an obstacle to practical use. Thus, removal of H<sub>2</sub> requires temperatures above 700°C needed for its synthesis, and such temperatures are costly to build and maintain.



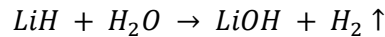
**Figure 2.** The volume and weight densities of hydrogen at different methods of storage

Metal hydrides such as MgH<sub>2</sub>, NaAlH<sub>4</sub>, LiAlH<sub>4</sub>, LiH, LaNi<sub>5</sub>H<sub>6</sub>, TiFeH<sub>2</sub> and palladium hydride which were used with varying degrees of success, also may be employed as hydrogen storages, often reversible [38]. These materials have a good energy density in volume, although their weight energy density is often worse than that of the basic hydrocarbon fuels. Most metal hydrides have very strong bind to hydrogen. As a result, the hydrogen contained therein is released at high temperatures of about 120 ÷ 200 °C. The energy costs can be reduced by using mixed compounds, such as in LiNH<sub>2</sub>, LiAlH<sub>4</sub> and NaBH<sub>4</sub> [39].

LiAlH<sub>4</sub> contains 10.6% by weight of hydrogen, which makes it a potential hydrogen storage medium for future use in vehicle fuel cells. The high content of hydrogen, as well as finding of the reversible hydrogen storage properties in NaAlH<sub>4</sub> doped with Ti [36] called over the last decade for the resumption of LiAlH<sub>4</sub> research. Significant research efforts have been directed to acceleration in decomposition kinetics by catalytic doping and grinding in a ball mill [37]. In order to take advantage of the total capacity of the hydrogen, the intermediate LiH must be dehydrogenated as much as possible. Because of high thermodynamic stability of the product of hydrogenation, the temperatures should exceed 400°C, which is not considered feasible for transport purposes. Receiving LiH + Al as a final product reduces the hydrogen storage capacity to 7.96 wt. %. Another problem associated with hydrogen storage is inverse recirculation of LiAlH<sub>4</sub>, which, due to its relatively low stability, requires extremely high hydrogen pressure in excess of 10,000 bar [37].

Lithium borohydride NaBH<sub>4</sub> is known as one of chemical energy carriers that has the highest energy density. The high specific energy density of lithium borohydride made it an attractive candidate that can be offered for automotive and rocket fuel, but, in spite of the research and advocacy, it is not yet widely used. Like all energy-based hydrides, lithium borohydride is very complex for utilization (i.e., recharge) and therefore suffers from low efficiency of energy conversion. At a density of 0.67 g/cm<sup>3</sup>, solid lithium borohydride releases 65 MJ/kg of heat by reaction with oxygen. For comparison, gasoline gives 44 MJ/kg, whereas the liquid hydrogen provides 120 MJ/kg. Thus lithium-ion batteries have power density up to 0.72 MJ/kg, but the efficiency of energy conversion can reach 90%. In view of the complexity in the mechanisms of cyclic use of metal hydrides, such high energy conversion efficiency is beyond the practical reach. However, due to the high energy consumption, their use will probably be in the region schemes of compromise.

It is well-known that in a reaction of lithium hydride with water:



1 kg of lithium hydride may evolve 2.8 m<sup>3</sup> hydrogen. Therefore hydride for many years is used as a solid source of hydrogen to fill the survival crafts, balloons, etc. Thus, lithium hydride and lithium aluminum hydride can be easily used to generate hydrogen by reacting them with water. It is hoped that such their use will have great prospects for hydrogen energetics.

### **Electronics and nonlinear optics**

Mixed cesium lithium borate is used as an optical material in electronics. Single crystals were obtained from triborate lithium - LiV<sub>3</sub>O<sub>5</sub> (LBO) and double-cesium lithium borate - CsLiB<sub>6</sub>O<sub>10</sub> (CLBO). These single crystals, having a relatively high non-linear optical properties, a wide area of transparency and high radiation resistance, quickly found a wide application in laser instruments [17].

The crystalline lithium niobate LiNbO<sub>3</sub> and lithium tantalate LiTaO<sub>3</sub> are non-linear optical materials which are widely used in nonlinear optics, acoustic optics, and optoelectronics. In particular, they are used in electro-optical modulators, pyroelectric detectors, and piezoelectric transducers.

Lithium is also used in filling gas-discharge metal halide lamps.

Single crystals of lithium fluoride LiF are used for the manufacture of high-performance (80% efficiency) lasers in free color centers and for the manufacture of optics with a broad spectral bandwidth.

Lithium sulfate is used for the manufacture of detectors in ultrasonic defectoscopy.

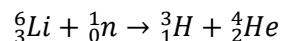
### **Nuclear energy**

The isotopes <sup>6</sup>Li and <sup>7</sup>Li have different nuclear properties - cross section of thermal neutron absorption and scope of their application are different. Lithium hafnate is a part of special enamel intended for the disposal of high level nuclear waste that contains plutonium.

Lithium-6 is used in nuclear energetics.

An important area of nuclear applications of lithium is the use of hydride <sup>6</sup>LiH in light shields against neutron radiation.

Irradiation of <sup>6</sup>Li nuclide with thermal neutrons produces radioactive tritium <sup>3</sup>H:



Therefore, lithium-6 can be used as a replacement for tritium, which is radioactive, unstable, and inconvenient in handling. Such a replacement takes place both for military purposes in the production of thermonuclear weapons and for peaceful purposes in control of thermonuclear fusion. In thermonuclear weapons it is generally used in the form of lithium deuteride - <sup>6</sup>LiD.

Promising also is the use of lithium-6 for the production of helium-3 through tritium for the purpose of further use in deuterium-helium fusion reactors.

Creation of an economic and safe fusion reactor requires a development of special structural materials for the first wall, blanket, breeders and for elements working in the conditions of high heat fluxes. Materials must be chemically compatible with the coolant and tritium reproducing materials, such as lithium. The breeder's function is an effective, safe and reliable production of tritium from lithium under neutron irradiation. Since the heat generated by a nuclear reaction is absorbed by the blanket and is transferred to the coolant, it is important to know the structure and physical-mechanical properties of the breeder material and the breeder and changes occurring in this material during burning lithium out from this material.



Currently, the following basic materials are planned to be used in ITER reactor (International Thermonuclear Experimental Reactor):

- low-activated steels, vanadium alloys, and ceramics based on lithium for solid blankets of  $\text{Li}_2\text{TiO}_3$ ,  $\text{Li}_2\text{SiO}_4$ , etc.; and
- eutectic based on lithium for the blanket of the eutectic alloy Li-Pb [41].

Oxide ceramics based on lithium are considered as materials perspective for solid breeder blankets in future fusion reactors. It is believed that one of the materials is basic perspective breeder material such as lithium methatitanate  $\text{Li}_2\text{TiO}_3$  which lately attracts most attention because of the high rate of release of tritium at relatively low temperatures (from 200 to 400°C) and chemical stability.

Studies over the prospects for the use of lithium in ceramics in the tritium breeder of installation of controllable thermal nuclear units are held in Europe, Japan, and Russia [42].

Lithium-7 is used in nuclear reactors which have a reaction involving heavy elements such as uranium, thorium, or plutonium.

Due to a very high specific heat and low thermal neutron capture cross-section, liquid lithium-7, often serves as an effective coolant in the form of an alloy with sodium or cesium. Lithium-7 fluoride-7 in an alloy with beryllium fluoride (66%  $\text{LiF}$  + 34%  $\text{BeF}_2$ ) is called «flibe» (FLiBe) and is used as a highly efficient heat transfer fluid and solvent for fluorides of uranium and thorium in high-temperature molten-salt reactors and in production of tritium.

Liquid lithium-7 can be used as a coolant in a nuclear reactor due to its large temperature range in the liquid state (179 ÷ 1317 °C), low density ( $\rho = 0,534 \text{ g/cm}^3$ ), high heat capacity, relatively low viscosity, high heat of vaporization, and a small thermal neutron capture cross section (up to 16 times less than that of sodium). An obstacle to the use of liquid lithium is its strong corrosive action.

Lithium-7 deuteride may serve as a more effective neutron moderator, better than hard water.

The compounds of lithium enriched in the isotope of lithium-7, is used in PWR reactors to maintain water-chemistry regime, as well as in the desalter of the first reactor cooling circuit. Annual demand of the United States is estimated as 200-300 kg. This product is manufactured only in Russia and China [11].

### ***Rocket fuel***

According to foreign experts, a possible field of application of lithium compounds is missiles where the propellant may be comprised of lithium hydride, lithium boride and metallic lithium. Combustion of 1 kg of lithium or some of its compounds gives up to 4000 kcal (conventional rocket fuel - kerosene - 2300 kcal/kg). Perchlorate and lithium nitrate are characterized by a high oxygen content (60.1 and 69.5%, respectively), and may be used as an oxidant, while ammonium perchlorate which is used in the solid rocket fuel as an oxidizer contains only 54.4% oxygen.

Metallic lithium has been tested as a fuel in rocket engines. The results of these tests with various oxidants gave positive results which are presented in Table 3.

Lithium hydride  $\text{LiH}$  and lithium aluminum hydride  $\text{LiAlH}_4$  were tested as solid propellants for some models of rockets [28]. In addition, lithium nitrate is a classic product that is used in pyrotechnics for coloring in red lights.

### **Other applications**

A very promising use of lithium is filler for a bathyscaphe float because this metal has a density that is almost two times lower than water (more specifically,  $534 \text{ kg/m}^3$ ). This means that one cubic meter of lithium can keep afloat almost by 170 kg more than one cubic meter of gas. However, lithium is an alkali metal and therefore actively reacts with water. Therefore it should be reliably isolated from water in order to prevent their contact.

A saturated solution of LiCl is used as a de-ice because it has a very low freezing point -55 °C.

**Table 3.** Theoretical characteristics of rocket fuels formed by lithium with various oxidants

Oxidizer	Specific pulse ( $P_1$ , c)	Combustion temperature, °C	Fuel density, $g/cm^3$	Mass content of fuel, %
Fluorine	378.3	5350	0.999	28
Tetra-fluoro-hydrazine	348.9	5021	0.920	21.07
ClF <sub>3</sub>	320.1	4792	1.163	24
ClF <sub>5</sub>	334	4946	1.128	24.2
Perchloro fluoride	262.9	3594	0.895	41
Oxygen fluoride	339.8	4595	1.097	21
Oxygen	247.1	3029	0.688	58
Hydrogen peroxide	270.5	2995	0.966	28.98
N <sub>2</sub> O <sub>4</sub>	239.7	3006	0.795	48
Nitric acid	240.2	3298	0.853	42

### COST OF LITHIUM

The price of lithium has not been widely published. By various sources, on the average for the period of 2007- 2008, the price of metallic lithium (99% purity) was \$63-66 per 1 kg. By August 2009, it did not change and amounted to about US \$6,600 per ton. These prices can be compared with the price at the beginning of the last decade, when it was about \$ 2,500 per ton.

Currently Public Broadcasting states that "the cost of lithium is an eightfold increase in the last six years". It is also predicted that the price of lithium will continue to actively grow with increasing demand for energy sources containing lithium.

After the financial crisis of 2007, the cost of lithium from major suppliers such as Sociedad Química y Minera (SQM) dropped by 20% [43]. Prices rose in 2012. In 2012, an article in Business Week outlined the oligopoly in the area of lithium – a market form, which is dominated by a small number of sellers. Thus SQM controlled by billionaire Julio Ponce, is the second largest, following Rockwood Lithium Inc., which operates with the support of KKR & Co. of Henry Kravis and of FMC which is based in Philadelphia. To meet the demand for lithium batteries, which is growing at 25 percent per year, the global lithium consumption may rise from about 150 000 tons of 2012 to 300,000 metric tons per year by 2020. Demand growth is ahead by 4 ÷ 5% of the total growth of lithium production [44].

### DEMAND FOR LITHIUM

Lithium market has steadily grown over the past decade due to the increasing use of lithium batteries in consumer electronics, such as cell phones, laptop computers, and other portable electronic devices. Known devices such as iPods and Blackberries, quickly turn to lithium as a component of the main sources of energy, as such sources are comfortable, light in weight, and reliable in operation.

But excitement among many investors results mostly from the expected models of electric cars that may be created by Chevy Volt, Nissan Leaf, and Mitsubishi. Some automobile companies are all speculating on the fact that pure electric cars could account only for 10% of purchases of cars by 2020. Despite this, the automobile giant such General Motor tries to get a large piece of the lithium pie.

Companies such as Apple, Motorola, Research in Motion, Hewlett-Packard, Dell, Samsung and Sony all use lithium in majority of their products.

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