GEOINFORMATICS 2021

EAGE

21150

Prospects lithium extraction from produced water in oil and gas fields of Ukrainian

***M. V. Reva** *(Taras Shevchenko National University of Kyiv, Institute of Geology)*, **D. F. Chomko** *(Taras Shevchenko National University of Kyiv, Institute of Geology)*, **F. Chomko** *(V. N. Karazin Kharkiv National University)*

SUMMARY

The article considers the urgency of the search for new lithium raw materials caused by a sharp increase in demand for this element. The authors consider the world's reserves of lithium raw materials and the main genetic types of origin of these deposits. The authors explored the world's leading lithium manufacturers and the main technologies used. The main suppliers of lithium raw materials are Argentina, Chile and the United States. These countries produce mainly lithium carbonate, which is obtained mainly from hydromineral raw materials. The article identifies Ukraine's interest in developing its own lithium deposits. Stocks of lithium raw materials in Ukraine are calculated mainly for pegmatite deposits. According to this amount of lithium reserves, Ukraine ranks first in Europe. The authors highlight that in Ukraine lithium reserves are concentrated not only in pegmatites but also in associated reservoirs of oil and gas fields. Ukraine has been developing oil and gas fields for a long time, as a result of which the extracted water together with the hydrocarbon sometimes reaches 95% in terms of water content. Due to geological and hydrogeological conditions, the waters of these deposits have high mineralization and with rather significant concentrations of lithium. At the experimental deposits, the lithium concentration ranges from 10 to 20 mg/dm3, but these values can vary greatly. These indicators are approximate but clearly indicate that the associated watershed is a promising resource. For efficient and rational use of this type of lithium raw material deposits, the authors identify the main tasks facing modern geologists

Introduction.

Lithium and lithium raw materials are strategic for the modern development of industry and electrical engineering both in the world and in Ukraine. This is stated in the law " On Ratification of the Nationwide Mineral Resources Base Development Program of Ukraine for the Period until the Year 2030 " ("Pro zatverdzhennia Zahalnoderzhavnoi prohramy... ", 2012). The issue of prospecting, exploration and calculation of lithium reserves is a priority for modern geologists.

Lithium is extracted from pegmatites or brines in salt lakes. Its total reserves are estimated at more than 53 million tons: Argentina - 9.8 million tons; Bolivia - 9 million tons; Chile - 8.4 million tons; China - 7 million tons; USA - 6.8 million tons, Australia - 5 million tons; Canada - 1.9 million tons; Congo (Kinshasa), Russia and Serbia - 1 million tons each; Czech Republic - 840,000 tons; Zimbabwe - 500,000 tons; Spain - 400,000 tons; Mali - 200,000 tons; Brazil and Mexico - 180,000 tons each; Portugal - 100,000 tons; Austria - 50,000 tons, according to the US Geological Survey (USGS) (National Minerals Information Center, n.d.).

World production of lithium raw materials (lithium carbonate and lithium chloride) is almost 67% from hydromineral raw materials (HRM) or brines of salt lakes.

Theory.

World production of lithium raw materials (lithium carbonate and lithium chloride) is almost 67% from hydromineral raw materials (HRM) or brines of salt lakes.

The largest part of the hydromineral reserves of lithium in the world is accounted for by Chile in the form of the Salar de Atacama deposit with an area of about 3000 km^2. Salar de Atacama brine differs from other HRM deposits in that the concentration of lithium in the original natural brine is 1.0-2.5 g/dm^3, and by evaporation according to a special scheme, it is possible to obtain concentrates with a lithium content above 40 g/dm^3. The peculiarity of the effective development of this field is due to natural conditions, namely the high evaporation of water and shallow raw materials. The evaporation of water in the area of the field is 3200 mm/year, the amount of precipitation is 15 mm/year. Useful brines are at a depth of 30-40 m (Reva, 2019). The production technology is based on staged solar evaporation of brine, which increases the concentration of lithium from 1.7 to 43 g / dm^3. The process is implemented in 12 pools. This scheme highlights the high profitability of the integrated scheme, which allows you to set the price of lithium carbonate produced by this technology is not higher than 2 USD, it is the lowest price in the world (Reva, 2019). This lithium deposit is the largest in the world in terms of lithium reserves and production. Chile's total lithium reserves are estimated by the USGS at 7.5 million tons (Lithium Statistics and Information, n.d.).

The United States is developing salt lakes located in the western states, they have an average content of lithium oxide in brine from 0.0075 to 0.015%. Albemarle Rockwood Lithium produces lithium carbonate from brine at Silver Peak. Total reserves of lithium in the United States are estimated by the USGS at 38 thousand tons (Reva, 2019).

In Argentina, FMC Corp. operates at the Salar de Hombre Muerto field (total lithium reserves 800 thousand tons) produces 12 thousand tons/year of lithium carbonate and 5-7 thousand tons/year of lithium chloride. Argentina's total lithium reserves are estimated by the USGS at 2 million tons.
Lithium is also produced in China. Tibet Lithium New Technology Development Co. produces 5,000 tons/year of lithium carbonate from brine from the Zabayu Salt Lake field in eastern Tibet. CITIC Guoan Lithium Science & Technology Co. produces 35,000 tons / year of lithium carbonate at the Taijinaier Salt Lake deposit (940,000 tons of lithium reserves) in Qinghai Province. It is the largest lithium plant in China.

In Israel, potassium chloride, bromine compounds are extracted from the Dead Sea brine (mineralization 300-320 g/dm^3) and lithium chloride (whose reserves are estimated at 17.5 million tons) is intended to be extracted.

In Ukraine, the search for and exploration of lithium deposits has been conducted since Soviet times. Ukraine is considered to be the richest in Europe in terms of reserves of this raw material. According

to expert estimates, its number is from 500 thousand to 5 million tons. In Ukraine there is no brine salt lakes with a high lithium content, these reserves are calculated only for pegmatites (petalite ($Li[AlSi_4O_{10}]$)). Now, given the increased demand for lithium, special permits have been issued in Ukraine for the development of two deposits explored since Soviet times. These are Shevchenkivske (Donetsk region) and Polokhivske (Kirovohrad region) deposits (SSGSU, 2019). The development of these new deposits is still not carried out due to the use of specific technologies for the enrichment of petalite. Another negative point is that well-known world technologies have been developed for spodumene ($LiAl(Si_2O_6)$) (Syrovyna dlia…, n.d.).

However, the reserves of lithium raw materials in Ukraine can be represented not only by pegmatites. We are talking about the use as a raw material for lithium production of associated produced water of oil and gas fields.

Results.

Ukraine has a long history of oil and gas industry, some oil fields have been developed for more than 50 years. Oil production at these fields is accompanied by significant production of associated produced water (PW). The water ratio of the extracted fluid is more than 95%. PWs of oil fields in Ukraine, and especially in the Eastern oil and gas region, have a high degree of mineralization due to the chemical components and their compounds dissolved in it in high concentrations (Reva, 2016). Table 1 shows the concentrations of chemical components in the PW of some deposits that may be of industrial value.

Table 1

Concentrations of valuable chemical elements in some deposits (Reva, 2019)

Component	Deposit					
	Rybalske	Kachanivske	Chutivske	Lutsenkivske	Skorobahatkivske	Rusko-Komarivske (Zakhidnyi NHR)
	Concentration, mg /dm^3					
Chlorides	102150	97219	188654,40	75279,65	127656,00	18027,64
Sulfates	48	28,89	1170,31	216,45	431,66	624,65
Bromine	110	143	294,7	105,23	35,96 – 275,72	6,35 – 16,40
Iodine	3,98	5,3	72,18	6,35	1,05 – 12,69	2,5 - 5,5
Boron	75	147	54,8	9,88	18,52	18,6
Lithium	**4,75**	**4,2**	-	-	-	**5,10 – 9,85**
Potassium	618,8	335,0	-	-	-	737,2 – 858,5
Magnesium	1875,02	1518,9	6487,02	3648,0	4864,00	-
Strontium	330	444,4	-	-	-	-
Rubidium	-	0,3	-	-	-	0,47
Cesium	0,2	0,27	-	-	-	0,38

The table shows that the lithium content is not reflected in all deposits. This is not due to its absence in the PW of these deposits, but rather the lack of information due to the lack of determination of concentrations of this component. As the data on lithium concentrations in PW did not have any practical result (neither industrial value, nor assistance in prospecting and exploration of oil and gas fields), therefore, according to the existing industry regulations, the definition of this element is not mandatory. However, the determination and collection of information on lithium concentrations in PW was carried out at some deposits. Using these data, we performed a preliminary analysis of the possibility of industrial extraction of lithium from PW (table 2).

Given the experience of lithium extraction from hydromineral raw materials of salt lakes, we can say that the technological process of lithium extraction from oilfields is a reasonable and promising direction. The main condition for the use of PW as HRM in comparison with the brine of salt lakes is the technological concentrations of chemical components (minimum cut-off grade of the chemical

component in the water). The constant development of technology reduces the minimum concentrations, which makes it possible to consider PW as a valuable raw material.

The profitability of extraction of this component in addition to concentrations of lithium in PW can be affected by other indicators, such as the volume of production of PW, time constancy of concentrations of useful component in PW, service life of the field, polycomponent extraction (except lithium can extract iodine, bromine, boron, magnesium and others), as well as a number of other indicators.

These indicators are stable and predictable in determining the economic efficiency of extraction of lithium or other components from water (Reva, 2019). Therefore, the main criterion remains the cut-off grade of the component in the PW.

The relevance and prospects of lithium production from oil and gas fields are further enhanced by the fact that leading investment geological companies are beginning to invest and enter into agreements to conduct research in this area. For example, in the United States, MGX Minerals has signed an agreement with Major Oil and Gas Operator, which is developing Sturgeon Lake oilfield, to study PW for lithium and other components (MGX Minerals Signs Lithium Brine Agreement with Major Oil and Gas Operator - Junior Mining Network, n.d.). Also, in October 2018, MGX Minerals announced the extraction of lithium from the Alberta field (MGX Minerals Brings Rapid Lithium Extraction to Alberta's Oil Patch, n.d.) .

Table 2

Lithium content in PW at some deposits (Atlas, 1998)

Deposit	Layer collector	Mineralization g/dm^3	Lithium concentration (Li^+) mg/dm^3	Production volume tons/day	
				oil/gas/condincate	water
Vasylkivske oil and gas condensate	B-15	209	10	25 000	X
	B-17C	253	23		
	B-17H	241	11,3		
	B-18b	242	13,9		
Andriiashivske gas condensate	B-19b	244	0,99	50 000	X
	B-19H	224	20,0		
	B-20-21	215	18,0		
Kampanske oil and gas condensate	B-15b	224	15,1	±40 000	800
	B-19H	282	16,25		
Shatrovynske oil	B-26	223	19	100	31
	T	197	19		
Lipovodolinske oil and gas condensate	B-20	223	10	110	28
	B-22	247	12		
	B-26	252	18		

PW are mined in the fields of Ukraine in the amount of about 300 thousand tons per day. The minimum concentrations of lithium in PW are 4.0 mg/dm^3. A minimum of about 430 thousand tons of lithium raw materials can be produced annually. Compared to the production of solid lithium ore that is planned to be developed at the Polokhiv deposit in the amount of 1000 thousand tons per year, it is 28/72% (Figure 1). The advantage of extracting lithium raw materials from PW is that it is an inexhaustible resource but the balance reserves of lithium ore at the Polokhiv deposit are estimated by geologists at 28,000 thousand tons («Ukrlitiivydobuvannia» … — EXPRO Consulting, n.d.)

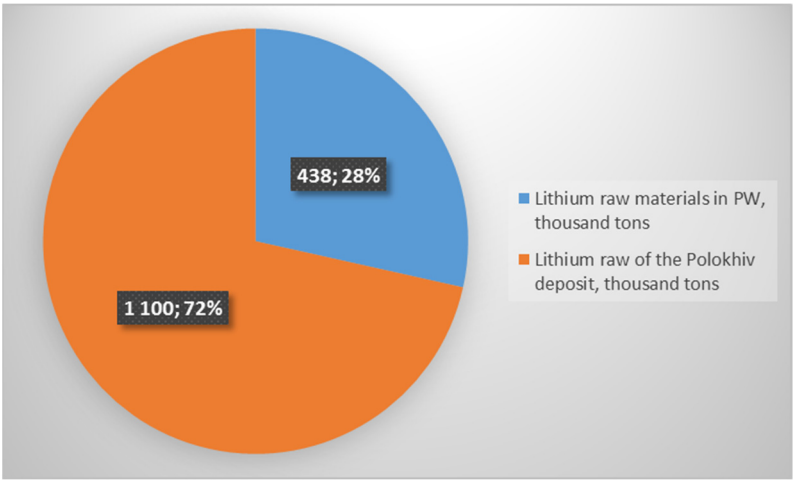

Figure 1 *The ratio of the development of different lithium resources*

Conclusions

Given all the above, we can talk about the real prospects for the extraction of lithium from oil and gas fields in Ukraine. However, a number of important issues need to be addressed for the successful implementation of this project. First of all, it is the conduct of specialized research on the lithium content in PW in all oil and gas fields, the selection of appropriate cost-effective technologies for PW fields in Ukraine. In order to successfully collect information on the concentration of lithium in reservoir and associated produced waters, it is necessary to change the rules of chemical analysis for such waters and oblige oil and gas companies to include lithium in the list of mandatory elements during chemical analysis. In the future, this will allow to enter in a special database of deposits and the lithium content along with other components (Reva and Chomko, 2018). The availability of this information will allow specific investors to make decisions about investing in the introduction of certain technologies and the actual extraction of lithium.

The issue of technology selection is important, today there are several different technologies, among which the most famous are "solar evaporation", "ionic extraction method", "membrane extraction" and others. However, the most promising is "rapid lithium extraction technology" from MGX (Extraction of Lithium from Oil and Gas Well Sources Is a Broad Paradigm Shift, 2021). Also, a number of scientific publications say that it is most effective to use complex methods (Jang et al., 2017; Murodjon et al., 2020).

References

Atlas rodovyshch nafty i hazu Ukrainy: V 6t. T.1-3.: Skhidnyi naftohazovyi rehion /[Ukrainska naftohazova akademiia]. – Lviv, 1998. (in Ukrainian).

"Extraction of lithium from oil and gas well sources is a broad paradigm shift" - Mining Journal. (n.d.). Retrieved April 9, 2021, from https://www.mining-journal.com/energy-minerals-news/news/1357992/"extraction-of-lithium-from-oil-and-gas-well-sources-is-broad-paradigm-shift"

Jang, E., Jang, Y., and Chung, E. [2017] Lithium recovery from shale gas produced water using solvent extraction. *Applied Geochemistry*, *78*, 343–350. https://doi.org/10.1016/j.apgeochem.2017.01.016

Lithium Statistics and Information. (n.d.). Retrieved April 9, 2021, from https://www.usgs.gov/centers/nmic/lithium-statistics-and-information

MGX Minerals brings rapid lithium extraction to Alberta's oil patch. (n.d.). Retrieved April 9, 2021, from https://magazine.cim.org/en/news/2018/mgx-minerals-brings-rapid-lithium-extraction-to-albertas-oil-patch/

MGX Minerals Signs Lithium Brine Agreement with Major Oil and Gas Operator - Junior Mining Network. (n.d.). Retrieved March 25, 2021, from https://www.juniorminingnetwork.com/junior-miner-news/press-releases/28-cse/xmg/27474-mgx-minerals-signs-lithium-brine-agreement-

with-major-oil-and-gas-operator.html

Murodjon, S., Yu, X., Li, M., Duo, J., and Deng, T. [2020] Lithium Recovery from Brines Including Seawater, Salt Lake Brine, Underground Water and Geothermal Water. In *Thermodynamics and Energy Engineering*. IntechOpen. https://doi.org/10.5772/intechopen.90371

National Minerals Information Center, U. (n.d.). *LITHIUM (Data in metric tons of lithium content unless otherwise noted) Domestic Production and Use: The only lithium production in the*.

Pro zatverdzhennia Zahalnoderzhavnoi prohramy rozvytku mineralno-syrovynnoi bazy Ukrainy na period do 2030 roku, Zakon Ukrainy № 3268-VI [2012] (Ukraina). https://zakon.rada.gov.ua/laws/show/3268-17 (in Ukrainian).

Reva, M. [2016] Produsedwater – source of pollution or valuable resource in the Eastern oil region, Ukraine. *Visnyk of Taras Shevchenko National University of Kyiv. Geology*, *72*, 81–85. https://doi.org/10.17721/1728-2713.72.12 (in Ukrainian)

Reva, M. V. [2019] The geological and economic assessment of produced waters of oil and gas fields of Eastern oil and gas field region of Ukraine as a valuable hydro-mineral raw material. Taras Shevchenko National University of Kyiv. (in Ukrainian)

Reva, M.V. and Chomko, D. F. [2018] Hydrogeochemical database of reservoir waters of oil fields in the Eastern region of Ukraine as the first way to the effective using produsedwater. *17th International Conference on Geoinformatics - Theoretical and Applied Aspects*. https://doi.org/10.3997/2214-4609.201801765

Syrovyna dlia elektrokariv: yakymy zapasamy kolorovykh metaliv volodiie Ukraina? (n.d.). Retrieved April 9, 2021, from https://www.geo.gov.ua/sirovina-dlya-elektrokariv-yakimi-zapasami-kolorovix-metaliv-volodiye-ukraïna/ (in Ukrainian).

«Ukrlitiivydobuvannia» planuie vykorystaty potuzhnosti Skhidnoho HZK dlia vydobutku ta zbahachennia litiievoi rudy — EXPRO Consulting. (n.d.). Retrieved April 11, 2021, from https://expro.com.ua/novini/ukrltyvidobuvannya-planu-vikoristati-potujnost-shdnogo-gzk-dlya-vidobutku-ta-zbagachennya-ltvo-rudi (in Ukrainian).