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G.A. Kolobov [(1)], professor, c.t.s.
I.V. Nikolaev [(2)], professor, d.t.s.
T.N. Nesterenko [(1)], associate professor, c.t.s.
A.V. Karpenko [(1)], assistant

MODERN STATE OF TECHNOLOGIES OF RECEIPT EASY RARE METALS FROM SECONDARY RAW MATERIAL

[(1)] Zaporozhe state engineering academy, Ukraine,
[(2)] National research technological university «MISandA», Moscow, Russian Federation

There are considered application areas, volumes and pattern of consumption of lithium and beryllium in the real review. There are presented types of secondary raw material of easy rare metals and technologies of their processing with the purpose of extraction of connections of lithium, cesium and beryllium.

Keywords: lithium, rubidium, cesium, beryllium, application areas, consumption, technologies of secondary raw material

The elements of I (lithium, rubidium, and cesium) and II (beryllium) groups of the periodic system are included at the sub-group of easy rare metals.

Today in the world lithium market the next sorts of metallic lithium are present: technical, catalyst, battery and metallurgical. Metallic lithium of battery sort used as foil as anodic material in the primary sources of current. The metallurgical lithium can be divided into two sorts: *alloy grade* - for the receipt of different alloys and *high pure* - high-clean (99.99 % *Li*), for laboratory researches and receipt of high-clean alloys [1].

At the last fourth of XX century strong growth of production and consumption of lithium and his connections began in industries of industry, indicated higher. As a result the far of wastes is in which content of lithium made from 10 to 95 %. Secondary raw material of lithium is presented appeared gradually, mainly, scrap of lithiumcontaining alloys, first of all alloys of Al-Li, by the exhaust lithium chemical sources of current (CSC),

In works of university «MISandA» (V.K. Kulifeev, V.V. Miklushevsky, I.I. Vatulin etc) [2-5] the technological scheme of processing of hard and liquid lithiumcontaining wastes with a receipt as an intermediate product of fivelithium aluminate of Li_5AlO_4, from which get secondary lithium, and slag, containing, mainly, Al_2O_3, and also $LiAl_5O_5$ and no more than 1.0 % *Li* is offered. Such slag it is expedient to use for adjustment of electrolyte of aluminium baths: introduction to 3 % lithium in an electrolyte are increased by his conductivity, decrease viscidity and reduces on a 10…20 % temperature of fusion. Metallic lithium from Li_5AlO_4 it is suggested to get by an aluminothermic method in a vacuum. The secondary lithium got on this technology does not yield in quality to electrolytic lithium of grade LE-1 and excels lithium of grade LE-2.

Lithium accumulators got unprecedented development in the last few years; therefore most new works are sacred to processing of scrap of lithium batteries and extraction from it lithium and other valuable elements.

In work [6] the hydrochloric scheme for processing of storage-battery mass with the used lithium batteries is offered. Active cathode mass contains a cobalt, manganese, nickel and lithium as connections of $LiCoO_2$, $LiMn_2O_4$ or $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$. It is shown that 99 % extraction of metals in solution for one hour is arrived at in the mode: a 4 M *HCl*, 80 °C, S : L = 2 g/l. From chloride solution MnO_2 there are besiege by additions of $KMnO_4$. A nickel is extracted selective by a dimethylglyoxime. A cobalt is besieged by a 1 M solution of *NaOH* at pH = 11 as $Co(OH)_2$. Remaining in solution lithium is besieged as Li_2CO_3 by additions of Na2CO3. Cleanness of the distinguished reagents (%) made: *Li* 96.97, *Mn* 98.23, *Co* 96.94 and *Ni* 97.43 accordingly.

Exhaust lithium ionic batteries, containing a cobalt and lithium, are a valuable secondary resource. It is considered [7] ecofriendly process on the basis of a vacuum pyrolysis, oxalate lixiviating and besieging for extraction of cobalt and lithium. Oxalate, entered as a lixiviating reagent, operates and as precipitator of cobalt from $LiCoO_2$ and *CoO* as $CoC_2O_4 \cdot 2H_2O$ in a 1 M solution of oxalate at a temperature 80 °C and correlation of S : L = 50 g/l during 120 min.

At processing of secondary lithiumcontaining raw material lithium is extracted on hygrometallurgical technologies as different compounds depending on the type of the processed raw material.

In connection with the small scales of cesium production as his secondary raw material clipping of single-crystals of cesium iodide is used only. In accordance with technical requirements wastes of cesium iodide must contain no less than 98 % *CsI* (wastes with sodium) and 97 % *CsI* (wastes with thallium). Processing of these wastes is carried out on a next chart: dissolution in water; filtration of solution from mechanical admixtures; cleaning of solution from thallium by addition of $Pb(NO_3)_2$; the sulfide cleaning from lead and other heavy metals by a key-in through solution of H_2S; recrystallization of *CsI* and selection of crystals. As a result of the hygrometallurgical cleaning *CsI* of high-purity get as the prepared products.

A metallic beryllium is got the electrolysis of molten $BeCl_2$ and magnesiumthermic renewal of BeF_2. Cleanness of beryllium, got by a metallothermic method, below, than metal, got by electrolysis. A draft beryllium contains to 0.5 % admixtures (*Al*, *Fe*, *Si*, *Cu*, *Mn*, *Mg*) usually. The gas admixtures and magnesium is deleted from draft beryllium by meltback in a vacuum it. Such beryllium can be applied for making of technical alloys. For the further increase of beryllium cleanness it is apply distillation in a vacuum or electrorefining, the cleanness of beryllium here arrives at 99.98 %. Quality of the electrolytically refined metal is near to quality of the distilled beryllium and suits, produced to the nuclear metal.

Data about the production of secondary beryllium are not published, however it is known that it extraction is carried out both from a «new» berylliumcontaining crow-bar and wastes, got at the process of production of ready-to-cook foods and wares (wastes of folias, plastins, foil and powders) and from a being out of the use military equipment. Berylliumcontaining crow-bar is usually exposed to the refined melting in vacuum induction electric furnaces [8].

At processing of radio-active wastes, in particular uranium-beryllium compositions, is formed condensate from which beryllium takes by a method of a vacuum distillation.

LIST OF LITERATURE

1. Волегжанина, И. С. Мировой рынок лития и его соединений [Текст] / И. С. Волегжанина // Маркетинг в России и за рубежом. – 2006. – № 5. – С. 12-19.
2. Миклушевский, В. В. Технология переработки литиевых отходов [Текст] / В. В. Миклушевский, И. И. Ватулин // Экология и промышленность России. – 2003, Янв. – С. 23-25, 49.
3. Миклушевский, В. В. Установка для вакуумтермического получения лития из продуктов переработки литийсодержащих отходов [Текст] / В. В. Миклушевский, И. И. Ватулин // Экология и промышленность России. – 2003, Март. – С. 36-38, 49.
4. Miklushevsky, V. V. Basis for Lithium Extraction from technologenic Raw Material [Text] / V. V. Miklushevsky, I. I. Vatulin, V. K. Kulifeev / Proceeding Russian-Japanese Seminar «Material Research and Metallurgy. Advanced Technologies and Equipment». – Moscow, March 25, 2003. – M. : MSIU, 2003. – P. 252-268.
5. Физико-химические исследования в области переработки литиевых химических источников тока, монокристаллов на основе оксидов лития, галлия, РЗМ и отходов их производств [Текст] / В. К. Кулифеев, Л. В. Мякишева, В. П. Тарасов [и др.] // Производственные технологии/ – 2011: сб. статей и тезисов докладов. – М. : Изд-во МГУП, 2002. – С. 268-269.
6. Wang, R. C. A novel recovery process of metal values from the cathode active materials of the lithium-ion secondary batteries [Text] / R. C. Wang, Y. C. Lin, S. H. Wu // Hydrometallurgy. – 2009. – Vol. 99, No 3-4. – P. 194-201.
7. Sun, L. Organic oxalate as leachant and precipitant for the recovery of valuable metals from spent lithium-ion batteries [Text] / L. Sun, K. Qiu // Waste Manag. – 2012. – Vol. 32, No 8. – P. 1575-1582.
8. Кириченко, В. Ф. Комплекс оборудования для рафинировочной плавки вторичного бериллия [Текст] / В. Ф. Кириченко, В. Т. Дзуцев // Труды Свердл. НИИ хим. машиностр., 2006. – № 13. – С. 186-190.