# ФІЗИКА ТВЕРДОГО ТІЛА, ЗБАГАЧЕННЯ КОРИСНИХ КОПАЛИН

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**С.Р. Боблях**, **канд. техн. наук,**
**Р.М. Ігнатюк**

Національний університет водного господарства та природокористування, м. Рівне, Україна,
e-mail: Sergii_Bobliakh@yahoo.com

## ОТРИМАННЯ РІДКОЗЕМЕЛЬНИХ МЕТАЛІВ ІЗ ВТОРИННОЇ СИРОВИНИ

**S.R. Bobliakh, Cand. Sci. (Tech.),**
**R.M. Ignatiuk**

National University of Water Management and Nature Resources Use, Rivne, Ukraine,
e-mail: Sergii_Bobliakh@yahoo.com

## RARE-EARTH METALS PRODUCTION FROM SECONDARY SOURCES

The purpose of the article is an analysis of use and extraction technologies of rare-earth metals. Examples of the impact of those metals on the world economy and politics are showed. In addition, the impact of the mining industry on the environment and questions of provision of countries with secondary raw materials were observed. The results of cerium production from the secondary raw materials are presented in the article. $CeO_2$ was the final product we wanted to obtain from the recyclable material ($CeAlO_3$) during the research. There were two ways to obtain it. For each way all possible reaction chains were determined. The chemical equations were provided for each reaction chain. Also, the types of reaction were indicated. Eh-pH diagrams for the Ce-Al-$H_2O$ (Al-$H_2O$, Ce-$H_2O$, Ce-Al-$H_2O$) system were created. For each reaction redox windows were calculated using the corresponding log(K) values at appropriate temperatures. The production/consumption analysis was made for considered processes. The economic analysis and diagrams shoved the advantages of the process no.1. Modeling was done by means of HSC 5.1 program.

**Keywords:** *rare-earth metals (REE), cerium, catalyst, converter, dissolution, precipitation*

**Problem.** Nowadays, people use a number of the modern technological devices consisting of rare-earth metals. For example, europium is used in production of cathode ray tubes and liquid crystal displays of TV sets and computers [1]. Cerium is one of the most common and inexpensive among rare-earth elements and it is used as a glass polishing agent and in catalytic converters for air purification in vehicles (fig. 1, 2).

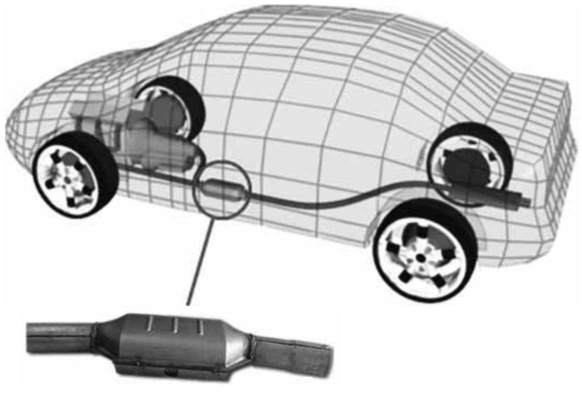

*Fig. 1. Catalytic converter*

Small light magnets made from rare-earth elements (REE) allowed miniaturization of numerous electrical and electronic components used in audio and video equipment, computers, automobiles, communication systems, and military devices [1]. Magnets containing neodymium, samarium, gadolinium and dysprosium allowed manufacturing of advanced electronic devices such as iPod’s, iPad’s and cell phones. Neodymium-based magnets are also used in microphones, loudspeakers, headphones, computer hard drives and can be found in wind and tidal electricity turbine generators [2].

Environmental aspects of the REE production technology become more and more important with the growing interest to green energy and ongoing debate over global warming. For example, REE used in catalytic converters of automobiles are the main issue in exhaust gases pollution control [1]. Batteries, which are used now as a power source in almost every electronic device we use today, also make a challenge for our environment. Lanthanum-nickel-hydride batteries replaced Ni-Cd batteries in computers and communication applications and possibly the lead-acid batteries in automobiles. Those batteries have better energy density, charge-discharge characteristics and cause fewer environmental problems (U.S Geological Survey, Gordon Haxel, James Hedrick, Greta Orris, 2002). Due to the increasing demand for electric automobiles lanthanum

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is in demand used as an intermetallic component of Nickel-Metal-Hydride batteries which are the heart of the electrically powered vehicles [2].

Mentioned cases are just a few of the uncountable ways of implementation of REE today (fig. 2) and it is obvious that it would be impossible to have the advanced technological devices and applications that without REE. REE proved to be incredibly important in the production of thousands of electronic gadgets, and contributed to the production of more efficient green energy sources.

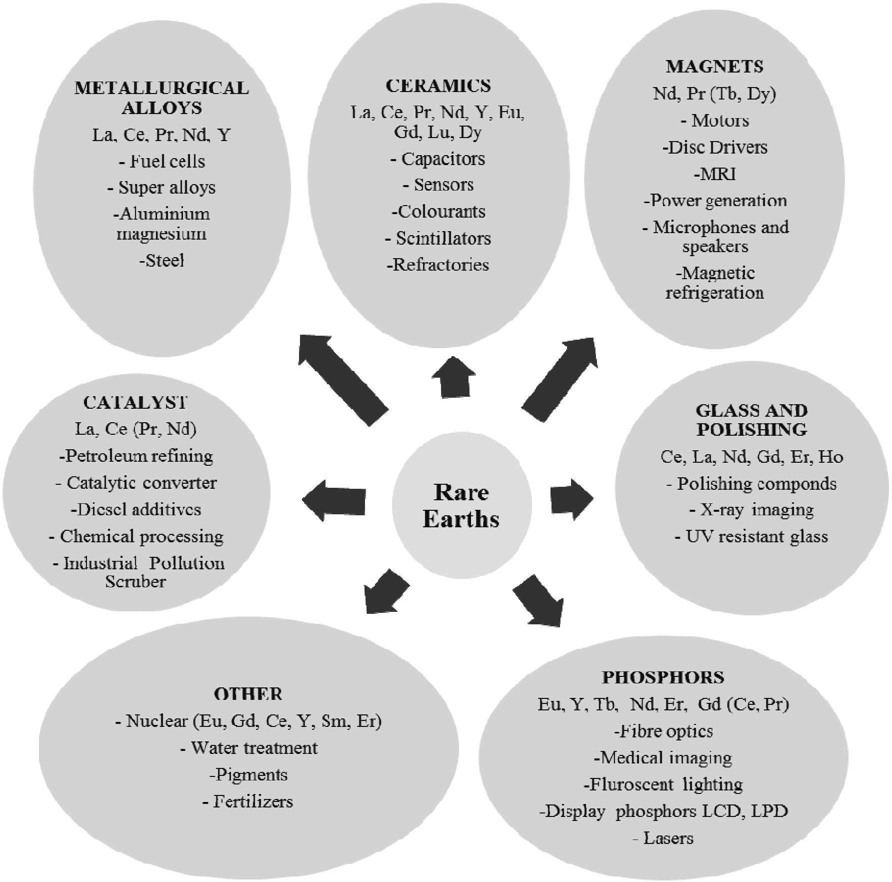

*Fig. 2. Application of rear-earths elements*

**Analysis of REE world market.** REE include seventeen chemical elements such as cerium, lanthanum, neodymium etc. which are one of the most imported and exported products in the world [3]. The leader of REE market is China. It meets a more than 97% of world's demand on REE [3]. But China reduces the amount of rare-earth metals produced and started enforcing embargoes on REE export to certain countries [3]. In 2011 China adopted a series of regulations concerning environmental protection, tightened limits of allowed pollution and increased taxes for mining enterprises. Strict control of REE export and increase of operational costs in China will result increase of prices [3]. Being the largest producer of REE China at the same time is one of the largest REE consumers [4].

Rare-earth elements are extremely important for electronics industry, military industry and green energy production technologies. The demand for REE is expected to increase each year encouraging Chinese economy. U.S. Government Accountability Office report, released in 2010 stated that establishing of a rare earth metal production supply chain in the United States could take fifteen years and would include creation of new technologies and obtaining patents that are currently owned by international companies [3].

**Background.** Cerium is an important REE used in several types of catalysts, particularly in automobile catalytic converters. Alumina, $Al_2O_3$, is often chosen as a base material for converters, due to its large surface area and good thermal stability [5].

$CeO_2$ is used in automobiles to prevent an active alumina from the thermal sintering. Also, $CeO_2$ in the catalytic converter is used to complete the oxidation process for hydrocarbon (HC) and carbon monoxide (CO) and to reduce oxides of nitrogen (NOx) back to simple nitrogen and carbon dioxide ($CO_2$) [6]. Thus, in the exhaust gases, the cerium oxides can either provide oxygen for oxidation of CO and CH or remove oxygen from the gas phase for the reduction of NOx.

The purpose of the work was exploration of processes that can recycle the $CeAlO_3$ and turn it back into $CeO_2$, to be used again as a coating. Two ways of recycling were estimated.

**Stability Diagrams.** Since the catalytic converter has such elements as Ce and Al, we have created Eh-pH diagrams separately for the Al-$H_2O$ system (fig. 3), Ce-H2O (fig. 4) and a diagram for the Ce-Al-$H_2O$ system (fig. 5) which also had Ce and Al.

All possible reaction chains used in recycling of the REE were determined. The chemical equations were provided for each reaction chain. Also, the types of reaction were indicated.

The final product that we wanted to obtain from the recyclable material ($CeAlO_3$), was $CeO_2$. It can be obtained in two ways.

The first way is an oxidative acid dissolution changing $CeAlO_3$ to $CeO_2$ (process $T_1$, fig. 5).

The second way is a non-oxidative acid dissolution changing $CeAlO_3$ to $Ce^{3+}$, followed by an oxidative acid dissolution, changing $Ce^{3+}$ to $CeO_2$ (process $A_1$, fig. 5).

Eh-pH – diagrams show the thermodynamic stability areas of different species in an aqueous solution. Stability areas are presented as a function of pH and electrochemical potential scales.

The vertical axis Eh shows voltage potential in an aqueous solution. The system tends to remove electrons from the species when the potential is high (Eh>0). Such conditions may exist near the anode in the electrochemical cell. When potential is low (Eh<0), the system is able to supply electrons to the species, near the cathode electrode.

The pH of the system describes its ability to supply protons H+ to the species. In acid conditions (pH<7) the concentration of the protons is high and in alkaline conditions (pH>7) the concentration of protons is low.

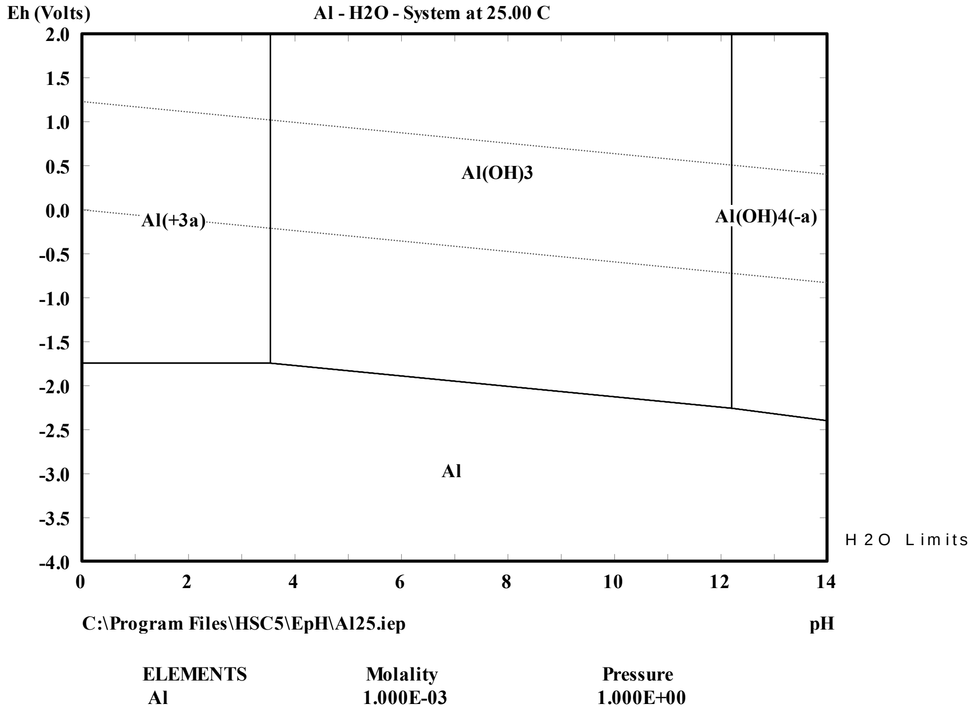

*Fig. 3. Eh-pH diagram for Al-$H_2O$ system*

The solid black lines in fig. 3 show the stability areas of the most stable species of Al on the pH and Eh-scales. The chemical stability of water is shown with dotted lines. The lines in the diagrams can also be represented with chemical reaction equations.

Horizontal lines on fig. 3 represent reactions that are involved with electrons, but are independent of pH. Neither $H^+$-ions nor $OH^-$-ions participate into these reactions.

Diagonal lines represent reactions that are involved with both electrons and $H^+$-ions and $OH^-$-ions. Vertical lines represent reactions that are involved ether with $H^+$ or $OH^-$ -ions, but are independent of Eh. In other words, electrons do not participate in these reactions.

Fig. 4 shows the thermodynamic stability areas for Ce-$H_2O$ system, and fig. 5 same for Ce-Al-$H_2O$ system.

In fig. 5 we can see that the transition from the $CeAlO_3$ to $CeO_2$ is possible in two ways. The first ($T_1$) transition is possible from the $CeAlO_3$ to $CeO_2$. The second transition is possible from the $CeAlO_3$ to Ce $^{+3}$ ($A_2$), and further from the $Ce^{+3}$ to $CeO_2$. Chemical reactions, which are representing recycling CeO2 from $CeAlO_3$ are presented in the tabl.

For each dissolution scheme, corresponding flow diagrams were provided (fig. 6).

Comparing the flow diagrams in fig. 6, we san see that costs in process 1 will be spent only on water, but in the process of 2 they will be spent on water and HCl (to go from $CeAlO_3$ to $Ce^{+3}$(A2)). We have selected the following chemical reaction $CeAlO_3 + 3HCl = Ce^{3+} + Al(OH)_3 + 3Cl^-$, which makes the process 2 more expensive than the first one.

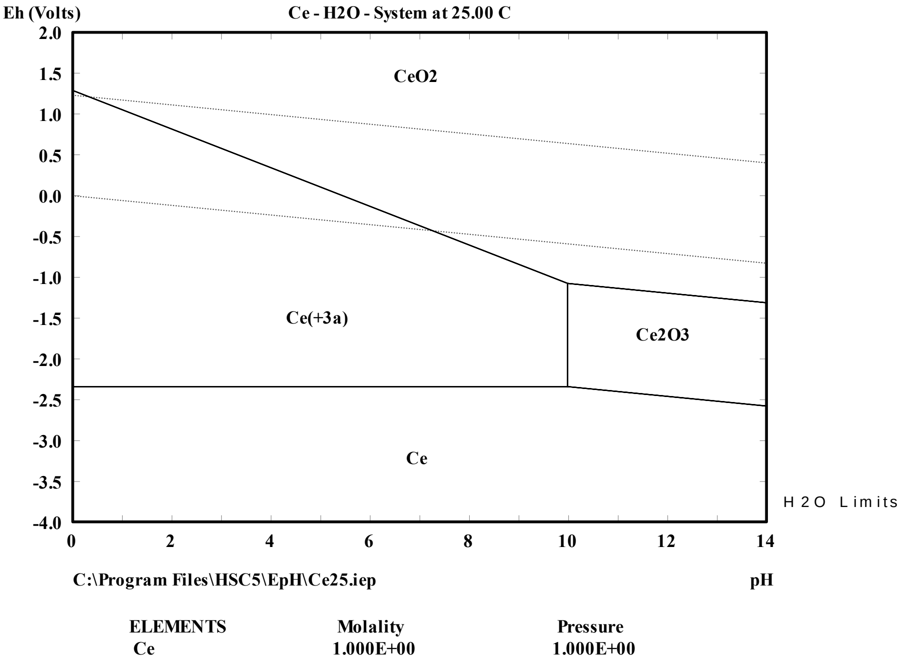

*Fig. 4. Eh-pH diagram for Ce-$H_2O$ system*

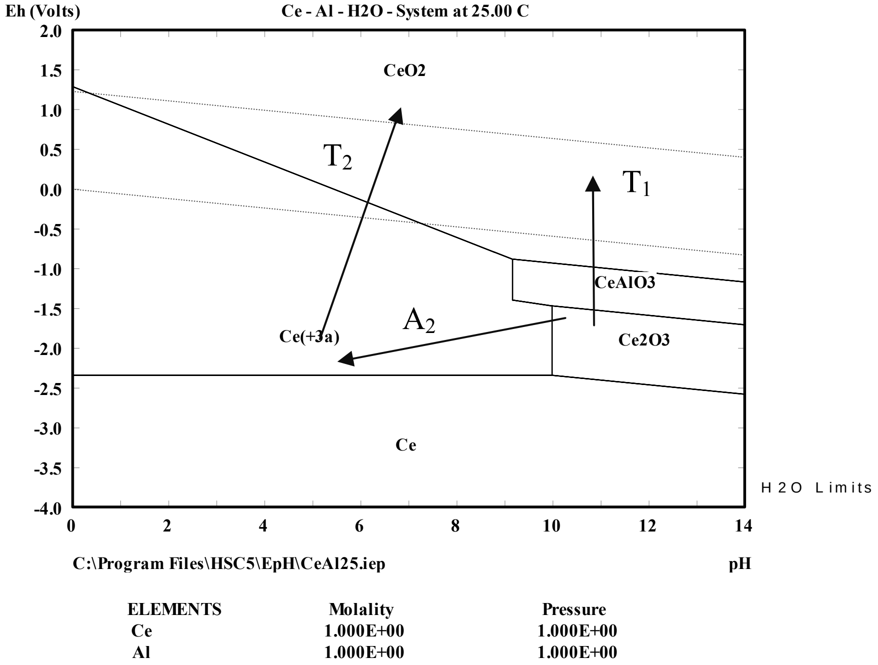

*Fig. 5. Eh-pH diagram for Ce-Al-$H_2O$ system*

*Table*

Characteristic of Ce-Al-$H_2O$ system

| Name | Path | Chemical reaction | Reaction type |
|---|---|---|---|
| $T_1$ | $CeAlO_3$ to $CeO_2$ | $CeAlO_3+3H_2O=CeO_2+Al(OH)_4^-+2H^++e^-$ | oxidative acid dissolution |
| $A_2$ | $CeAlO_3$ to $Ce^{3+}$ | $CeAlO_3+3H^+=Ce^{3+}+Al(OH)_3$ | non-oxidative acid dissolution |
| $T_2$ | $Ce^{3+}$ to $CeO_2$ | $Ce^{3+}+2H_2O= CeO_2+4H^++e^-$ | oxidative acid precipitation |

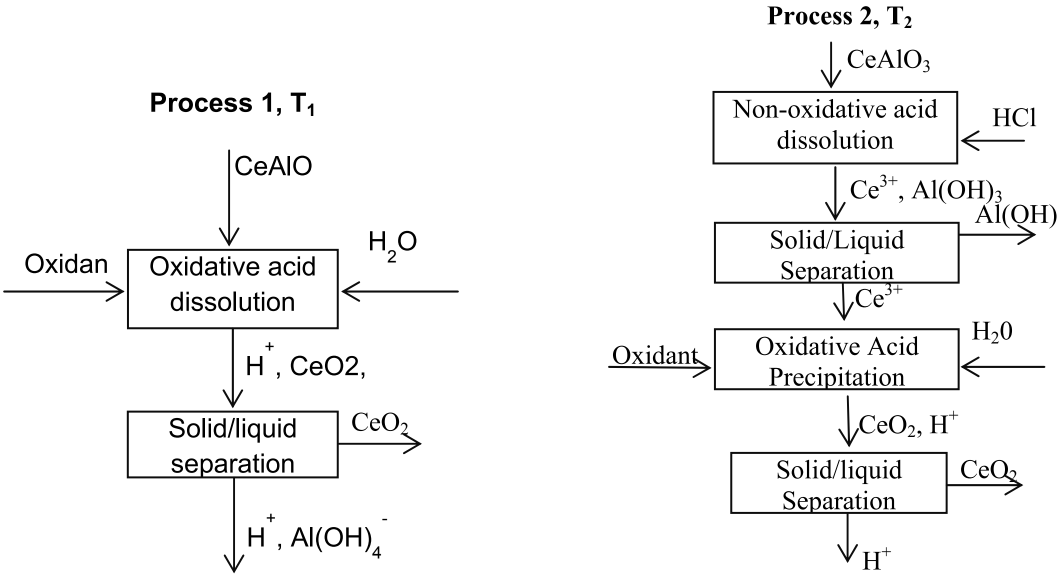

*Fig. 6. Block diagrams for Ce-Al-$H_2O$ system*

**Redox Windows.** Redox windows (areas) were calculated to show for which values of Eh and pH redox reactions are occurring in the process 1 and 2. The areas were calculated based on the relative values of log (K). For $CeO_2$ oxidation, the value of log (K) was calculated at a temperature of 1000°C [7]. Thermodynamic data needed to construct Eh-pH diagrams were found using the HSC 5.1. Thus, the redox window for CeAlO3/CeO2 ($T_1$ process) is presented in fig. 7.

For process 1, the line of transition from $CeAlO_3$ to $CeO_2$ was built using the values of log (K) = -32.94, obtained by means of software HSC 5.1. Lines 1 and 2 in fig. 7 show higher and lower stability limit of water respectively. Data for the vertical axis Eh were calculated using the Nernst equation

$$Eh = E^0 - \frac{0.0592}{n} \cdot \log\frac{[C]^c[D]^d}{[A]^a[B]^b}, \qquad (1)$$

when $E^o$ is the standard cell potential at the temperature of interest; n is the number of moles of electrons transferred in the cell reaction, $\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$ is oxidative and reluctant activity forms of matter. For line 1 on fig. 7 $Eh = 1.23 - 0.0592pH$, for line 2 $Eh = -0.0592pH$. The upper stability limit of water on fig. 7 (from $O_2$ to $H_2O$) corresponds to the process of oxygen (at higher potentials oxidation of water to oxygen is possible), and the lower line (from $H_2O$ to $H_2$) corresponds to the release of hydrogen (at lower potentials recovery of hydrogen from water is possible). For process 2, the same plot was constructed (fig. 8) showing the area where the oxidation-reduction reactions take place. The value of log (K) = 47 was obtained by means of HSC 5.1, and was applied to construct the transition line from $Ce^{3+}$ to $CeO_2$. To build the lower stability limit of water and hydrogen $Eh = -0.0592pH$ was used.

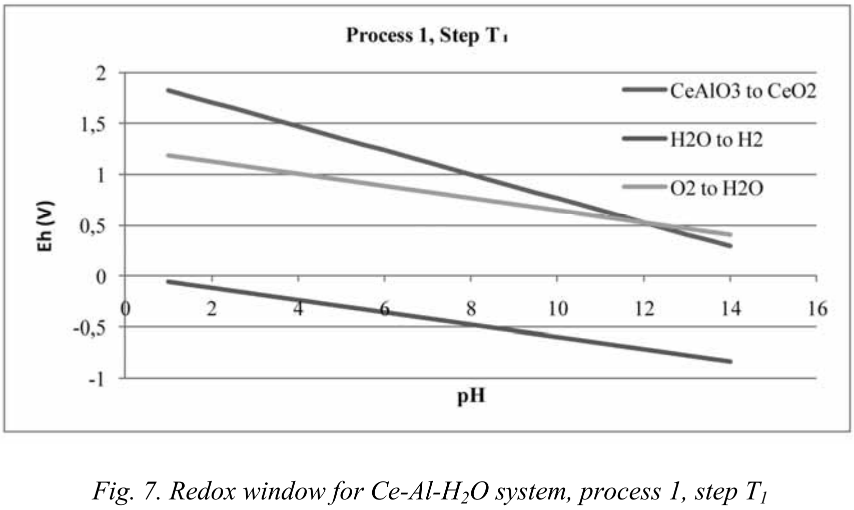

*Fig. 7. Redox window for Ce-Al-$H_2O$ system, process 1, step $T_1$*

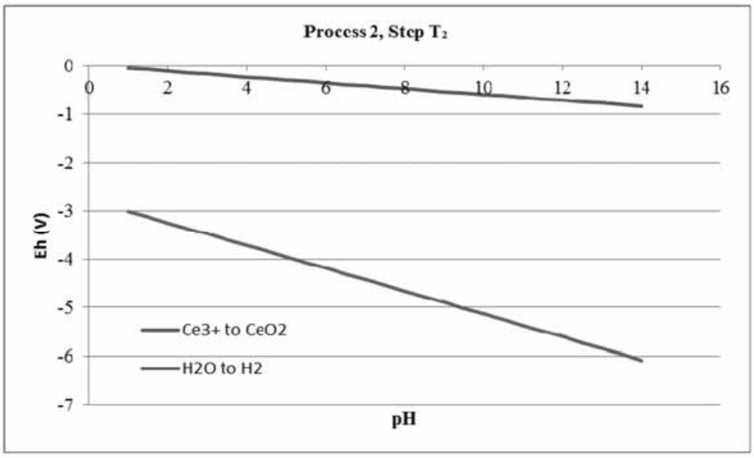

*Fig. 8. Redox window for Ce-Al-$H_2O$ system, process 2, step $T_2$*

In the redox window for Process 1, lines for $CeO_2$ and $CeAlO_3$ coexist, which makes sense because the $O_2$ is used to oxidize the $CeAlO_3$. In the Process 2 redox window, $H_2$ and $CeO_2$ coexist. Fig. 7 and fig. 8 give us better understanding of chemical processes which took places in process 1 and 2.

**Conclusion of Selected REE: Cerium.** Process 1 for cerium production from secondary sources was selected among the two alternatives. Process 1 is simpler than process 2 and contains fewer transactions. Also, the cost for process 2 is higher, as it involved HCl. Therefore, process 1 is preferred for recycling $CeAlO_3$.

**Список літератури / References**

**1.** Haxel. G. and Hedrick, J. (2002), Rare Earth Elements – critcal resources for high technology, Greta Orris. U.S Geological Survey.

**2.** Tech, Rare earth. “Rare earth elements”. Rare earth Tech., awailable at: www.rare-earth-tech.com.

**3.** Rose, E.R. (1960), “Rare Earths of Grenville Sub-Province Ontario and Quebec”, Otawa: Geological Survey of Canada Department of Mines and Technical Surveys.

**4.** China’s Rare Earth Dominance., awailable at: www.wikipedia.com.

**5.** Kaspar, J. (2003), “Automotive catalytic converters: current status and some perspectives”, Elsvier Science, Vol. 77.

**6.** Piras, A. Udine (2000), “Remarkable stabilization of transition alumina operated ceria under reducing and redox conditions”, Italy: Elsvier, Vol. 28.

**7.** Langer, A. (1995), Method of making a quartz glass tube having a reduced ultraviolet radiation transmissivity, Germany, Nov. 7.

Метою даної статті є аналіз використання та технології вилучення рідкоземельних металів. У статті наведено приклади впливу цих металів на світову економіку та політику. Також розглянуті деякі аспекти впливу гірничовидобувної промисловості на довкілля та питання забезпеченості вторинною сировиною країн світу. У статті представлено результати отримання церію із вторинної сировини. Кінцевим продуктом, який ми хотіли отримати із ($CeAlO_3$), був $CeO_2$. Його можна було отримати двома способами. Для кожного способу були визначені відповідні шляхи реакцій з їх хімічними формулами та типами. Також були побудовані Eh-pH діаграми для системи Ce-Al-$H_2O$ (Al-$H_2O$, Ce-$H_2O$, Ce-Al-$H_2O$). Для кожної реакції, при відповідних температурах з використанням значення log(K), було розраховано вікна окислювально-відновлювальних реакцій. Було зроблено аналіз виробництва / споживання для двох можливих процесів. Згідно з аналізом та відповідними діаграмами, процес 1 обрано як найкращий поміж двох можливих. Моделювання здійснювалось за допомогою програми HSC 5.1.

**Ключові слова:** *рідкоземельні метали, церій, каталіз, конвертер, розчинення, осадження*

Целью данной статьи является анализ использования и технологии получения редкоземельных металлов. В статье представлены примеры влияния этих металлов на мировую экономику и политику. Также рассмотрены некоторые аспекты влияния горной промышленности на окружающую среду и вопросы обеспечения стран вторичным сырьем. В статье также представлены результаты получения церия из вторичного сырья. Конечным продуктом, который мы хотели получить из ($CeAlO_3$), был $CeO_2$. Его можно было получить двумя способами. Для каждого способа были определены соответствующие пути реакций с их химическими формулами и типами. Также были построены Eh-pH диаграммы для системы Ce-Al-$H_2O$ (Al-$H_2O$, Ce-$H_2O$, Ce-Al-$H_2O$). Для каждой реакции, при соответствующих температурах с использованием значения log(K), были рассчитаны окна окислительно-восстановительных реакций. Был произведен анализ производства / потребления для двух возможных процессов. Согласно анализу и соответствующим диаграммам, процесс 1 был выбран как наилучший среди двух возможных. Моделирование выполнялось с использованием программы HSC 5.1.

**Ключевые слова:** *редкоземельные металлы, церий, конвертор, растворение, осаждение*

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