PowerPlants2016 IOP Publishing
IOP Conf. Series: Materials Science and Engineering **135** (2016) 012001 doi:10.1088/1757-899X/135/1/012001

Lithium and magnesium isotopes fractionation by zone melting

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Abstract. The process of changing isotopic composition of the lithium and magnesium salts was studied by using the process of zone melting. It was founded in the paper that the process of separation of the lithium isotopes is more effective than for magnesium isotopes when the conditions of process were the same. The coefficients of isotopes separation were calculated and have the next value: $\alpha = 1.006$ for ^{26}Mg isotope and $\alpha = 1.0022$ for ^{6}Li isotope.

1. Introduction

Naturally occurring lithium is composed of two stable isotopes ^{6}Li (7.589 %) and ^{7}Li (92.411 %) [1]. Each of them is very important for nuclear energetics. The isotope of ^{7}Li is used as additive in the coolant of the first loop pressurized water reactor and also for production chemical reagents for nuclear energetics [2].

Naturally occurring magnesium is composed of tree stable isotopes ^{24}Mg (78.992 %), ^{25}Mg (10.003 %) and ^{24}Mg (11.005 %) [3]. The isotope of ^{24}Mg is used for production radioisotope ^{22}Na [4]. Other isotopes ^{25}Mg and ^{26}Mg are used for biological labeling during the process of study the absorption and metabolism of magnesium in the human body.

Isotopes of lithium and magnesium are nonvolatile compounds. For this reason for separation of these isotopes we use the next methods: electromagnetic [5-6], crown ethers extraction [7-11], ion exchange [12-14], vacuum distillation [15], amalgam-lithium and amalgam-magnesium systems [16, 17] during precipitation from aqueous solutions [18, 19].

The process of zone melting is widely used for deep cleaning the different substances and for their production in single crystal form [20-23]. Also, this process can be used for separation isotopes such as H_2O and D_2O [24-26], the isotopes of boron, zinc, magnesium, lead and tin [27-32].

The purpose of this work is to investigate the process of changing isotope composition of lithium and magnesium during the process of zone melting of their salts.

2. Experimental part

2.1. Reagents

$MgCl_2{\cdot}6H_2O$ (analytical grade), $LiClO_4{\cdot}3H_2O$ and $LiClO_4$ were used. $LiOH{\cdot}H_2O$ (pure) and $HClO_4$ (pure) were used for synthesis $LiClO_4{\cdot}3H_2O$. The anhydrous lithium perchlorate $LiClO_4$ was obtained by dehydration of the $LiClO_4{\cdot}3H_2O$ at 200 °C for 3 hours. According to the results of X-ray diffraction analysis, the obtained salts were correspond to $LiClO_4{\cdot}3H_2O$ (PDF 00-008-0156) and $LiClO_4$ (PDF 30-0751).

2.2. Instrumentation
Investigations were conducted on samples with a length of 100 mm and a diameter of 3 mm. For preparing samples $MgCl_2 \cdot 6H_2O$, $LiClO_4 \cdot 3H_2O$ or $LiClO_4$ were heated until salt melted. After that a part of the melt was placed into a glass tube which was sealed at one end. When the process of zone melting was done, the glass tube was cut into samples, 10 mm in length. Then the samples were removed and dissolved in distilled water. After this, in the obtained solutions the isotope composition of the lithium or magnesium was determined. The analysis of isotope compositions was carried out on the mass spectrometer MX-1301T.

2.3. The process of zone melting
All experiments were carried out on the installation, which has five heating elements and five cooling elements (Figure 1). The main part of the installation was a platform with the heating elements placed at equal distance in the form of a ring, the inner diameter of which corresponds to the outer diameter of the glass tube. Power supply GW INSTEK PSH -10100 was used for regulating the temperature of the heating elements. Temperature was measured by using a chromel-alumel thermocouple. The cooling elements were installed between the heating elements.

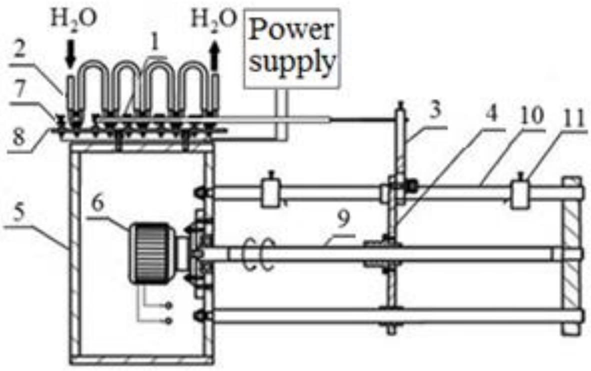

Figure 1. Installation for zone recrystallization (1 – mixture of REEs; 2 – cooling element; 3 – rod; 4 – carriage; 5 – housing; 6 – stepper motor; 7 – heating element; 8 – platform; 9 – shaft; 10 – guides; 11 – sensor).

Nichrome wire was used as the heating element. In Table 1 the temperatures of the heating elements for different work substances are presented. The length of the melt of the ingot was from 7 to 8 mm.

Table 1. The melting point of the work substances.

The work substance	The melting point, °C	Temperature of the heating elements, °C
$LiClO_4$	236	285±15
$LiClO_4 \cdot 3H_2O$	95	115±5
$MgCl_2 \cdot 6H_2O$	120	140±5

3. Results and discussions
In the experiments with lithium the parameters of the process of zone melting were the following: the speed of the tube was 3 cm/h, the number of zone processes was equal to 30. The results of isotopic

analysis show that the isotopic composition of lithium in the work substances has change. The process of isotopes fractionation is more effective if we use $LiClO_4 \cdot 3H_2O$ as the work substance. The results of isotopic analysis of the lithium isotopes after the process of zone melting are shown in the Table 2.The coefficients of separation of the lithium isotopes are shown in Table 3.

Table 2. The isotopic composition of $MgCl_2 \cdot 6H_2O$ in the initial zone of crystallization.

The work substances	The isotope content, %			
	^{6}Li		^{7}Li	
	the original composition	after the process of zone melting	the original composition	after the process of zone melting
$LiClO_4$	6.950±0.01	7.32±0.03	93.045±0.01	92.68±0.04
$LiClO_4 \cdot 3H_2O$	6.955±0.01	7.15±0.02	93.050±0.02	92.85±0.03

Table 3. The coefficients of separation of the lithium isotopes.

The work substances	The coefficients of separation	
	$\alpha(^{6}Li)$	$\alpha(^{7}Li)$
$LiClO_4$	1.0019	0.9981
$LiClO_4 \cdot 3H_2O$	1.0022	0.9978

The parameters of the process of zone melting of $MgCl_2 \cdot 6H_2O$ were the same. The results of isotopic analysis of the magnesium isotopes after the process of zone melting are shown in the Table 4.

Table 4. The isotopic composition of $MgCl_2 \cdot 6H_2O$ in the initial zone of crystallization.

The isotope content, %					
^{24}Mg		^{25}Mg		^{26}Mg	
the original composition	after the process of zone melting	the original composition	after the process of zone melting	the original composition	after the process of zone melting
79.58±0.03	79.35±0.04	9.8±0.02	9.87±0.04	10.62±0.02	10.78±0.04

The data obtained from the Table 4 shows that the isotopes ^{25}Mg and ^{26}Mg concentrate in the initial zone of crystallization and, also, the isotope ^{24}Mg moves with the melt zone and concentrates in the end of zone crystallization. The coefficients of separation of the magnesium isotopes are presented in Table 5.

Table 5. The coefficients of separation of the magnesium isotopes.

The coefficients of separation		
$\alpha(^{24}Mg)$	$\alpha(^{25}Mg)$	$\alpha(^{26}Mg)$
0.9995	1.0002	1.0006

These results can be explained as follows. Burton, Prim and Slichter obtained the formula for the effective distribution coefficient [33]:

$$K = \frac{1}{1+\left[\left(\frac{1}{K_0}\right)-1\right]e^{-f\delta/D}}, \tag{1}$$

where K_0 – the equilibrium distribution coefficient, f – the crystal growth rate, δ – the thickness of the diffusion layer in front of the crystallization front, D – the diffusion coefficient.

From this equation we can conclude that differences between the effective distribution coefficient K and the equilibrium distribution coefficient K_0 will be more significant if the value of the diffusion coefficient D is higher and the thickness of the diffusion layer in front of the crystallization front is smaller.

4. Conclusion

The distribution of lithium and magnesium isotopes was studied during the process of zone melting of their salts. During the process of zone melting the isotopes ^{25}Mg and ^{26}Mg concentrate in the initial zone of crystallization and, also, the isotope ^{24}Mg moves with the melt zone and concentrates in the end of zone crystallization. The coefficients of isotopes separation were calculated and have the next value: $\alpha = 1.006$ for ^{26}Mg isotope and $\alpha = 1.0022$ for ^{6}Li isotope. In the next work effectiveness of separation isotopes during the process of zone melting can be changed by using the other work substances, such as $LiClO_4 \cdot H_2O$ [34].

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