

Production of Potassium-Enriched Fertilizer Using the Complex Sorption and Membrane Technology

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ABSTRACT

The production of potassium-containing fertilizer using improved, complex method was researched. Cheapness and availability of the raw material (the natural zeolite, clinoptilolite from Dzegvi and Tedzami mines is used as a substrate and seawater – as a source of potassium ions) make this method very interesting and prospective for the countries with clinoptilolite stocks, located in the seaside regions and engaged in agrarian industry (Georgia, Greece, Romania, Bulgaria). It includes two technological processes: sorption and membranes ones. At the first stage, for intensification purpose electrodialysis was used for concentration of sea water. The optimal parameters for concentration of sea water were matched using the electrodialysis apparatus produced in the Institute workshop. In the produced concentrate of sea water, the index of potassium-ion concentration exceeds 4, being twice higher than the sodium-ion concentration index. At the second stage, selection of sea water ions was provided on the natural zeolite by so called dual-temperature ion exchange method: during sorption of potassium by clinoptilolite at low temperature the other ions pass into filtrate. The received potassium-enriched zeolite is a new type fertilizer: potassium containing therein passes into soil “as needed”, when soil is impoverished.

Keywords: potassium enriched clinoptilolite, ion-exchange sorption, electrodialysis, seawater concentration.

INTRODUCTION

In the last decades, the scientists' attention has been focused on the new technologies, as well as the use of non-traditional raw materials for production of potassium products, which is caused by the deficiency of potassium mineral fertilizers [Fao, 2019]. In the countries with the developed agrarian production and reserves of the natural clinoptilolite, one of the variants of deficiency elimination is sorption extraction of potassium ions from sea water using the natural zeolites. In Georgia, this situation determines the viability of production of a new type of fertilizer – potassium-enriched zeolites [Okudjava et al., 2008, Beruashvili et al., 2008].

Natural zeolites are the micro-porous framework aluminosilicate minerals of crystal-structure.

Due to the strictly determined dimensions of pores and inner cavities, they are good adsorbents for many inorganic and organic substances [Mumpton, 1999]. They have the unique physicochemical properties and comparatively low cost, which provides the potentiality of using zeolites in the technological processes designed for solving of some tasks of nature protection [Shimzu et al., 2007, Vilcek et al., 2013, Girijaveni, 2018, Rasyid et al., 2021].

There are many scientists' works [Tikhonov et al., 1998, Ivanov et al., 2003, Khamizov et al., 2010] covering development of technologies and research of physicochemical regularities of the process. The essence of the work includes use of cheap natural sorbent for processing of sea water for selective extraction of alkaline and alkaline-earth ions [Khamizov et al., 1995]. The writings

contain the selectiveness raw for alkaline and alkaline-earth ions: Cs>K>Sr=Ba>Ca>>Na>Li [Vilcek et al., 2013].

In sea water, rare metals occur in dissolved (ionic) state, which makes their extraction easier. Possibility of extraction of pure magnesium, potassium, sodium, bromine, lithium and the other valuable microelements from sea water is experimentally proved by the scientists [Khamizov et al., 1998, Kozhevnikova et al., 2008, Krachak et al., 2008, Nishihama et al., 2011, Dampilova & Zonkhoeva, 2013].

The reactant-less dual-temperature method of potassium concentration was proposed for sorption of potassium ions from sea water for effective use of natural clinoptilolites. It is based on dependence of sorption processes on temperature. Sorption kinetics was researched under static and then dynamic conditions [Okudjava et al., 2008, Gotsiridze et al., 2009].

Researchers [Tikhonov et al., 1997, Ivanov et al., 2003] reported that a change of sorption temperature causes a sharp change of selectiveness of sorbent to metal ions. The experiments result show that when temperature changes, the ions are replaced with other ones at clinoptilolite. Namely, at low temperature clinoptilolite sorbs K^+ , but Ca^{+2} and Mg^{+2} pass into filtrate and vice versa; at high temperature clinoptilolite sorbs Ca^{+2} and Mg^{+2} , but K^+ ions pass into filtrate.

It is known that in comparison with the ocean waters, the content of potassium ions in the Black sea is halved, so great amounts of sea water should be processed to obtain the final product. For this purpose, a combination of sorption and electromembrane methods was researched.

At the initial stage, the concentration of ions containing in sea water was provided with electromembrane apparatus (EDA) produced in the Institute workshop. EDA was supplied with the MK-40 and MA-40 membranes (Ltd „Innovative Enterprise Shchekinoazot», Russia). The membranes were previously investigated for the sea water concentration and for the removal of metal ions from aqueous solutions [Gotsiridze et al., 2018, Mkheidze et al., 2021].

As a result of passing this concentrate through a clinoptilolite sorption column, the concentration of potassium ions retained on the sorbent grew.

For the purpose of increasing the concentration of potassium in filtrate, desorption from potassium-enriched zeolite with hot (60-70°C) sea water was provided. The solution produced as a

result had much higher concentration of potassium than sodium. After running such concentrate through a clinoptilolite column, the fertilizer having high content of potassium ions was produced.

The developed process, compared to the dual-temperature scheme of rough seawater processing, allows more effective collection of target component within one step of sorption treatment. Prospectively, the process can be applied for production of artificial soils saturated with potassium nutrient.

The new form of potassium-containing fertilizer proposed by us is so-called “zeoponic”. Zeoponic is a zeolite enriched with the various macro- and micro nutrients (zeolite + potassium, zeolite + amino acid) [Allen et al., 1995, Gruener et al., 2003, Pisanu et al., 2012]. On the basis of the ion exchange process, zeolite matrix may be enriched with a single type cation. The potassium fertilizer produced and proposed by us contains potassium ions in easily assimilable form which has some positive effects on soil and supplies various needs of plants: it improves the water-physical conditions and agrochemical properties both of greenhouse grounds and soil increasing the moisture content and air ingress, creating favorable conditions for rhizosphere of plant rootage [Andronikashvili et al., 2006, Abdi et al., 2008, Szatanik-Kloc et al., 2021].

The Zeoponics system enhances the retention of nutritive substances, decreases losses and need of fertilizers, providing well-balanced supply of nutrients into rootage zone [ZeoponiX. Inc].

In ionite substrates, the nutrients are chemically bound with the carrier (zeolite) and may be absorbed by plants roots in exchange for metabolite ions only. Such metabolites include mainly hydrogen ions, hydrocarbonate and carbonate-ions synthesized by plant itself from carbon dioxide and water. These ions are exchanged for nutritive elements of substrate and absorbed by roots. This mechanism provides plants with those nutritive elements and in the quantities which are actually needed. Therefore, the substrate formula adjusts as per “requests” of concrete plants realizing the principle “take whatever and as much as you need”.

MATERIAL AND METHODS

In the experiments, the clinoptilolite from Dzegvi mine was used. Its percent content is: SiO_2 – 60.1%, Al_2O_3 – 12.86%, Fe_2O_3 – 1.57%,

MgO – 1.58%, CaO – 4.54%, Na₂O – 1.68%, K₂O – 1.38%, H₂O – 16.3%, Si/Al – 4.13%. The exchange capacity of clinoptilolite is established to be $C_{\Sigma} = 1.91$ mg-eq/g.

The grained clinoptilolite according to the particles sizes running them through the screens was fractionated and the fraction of 2.0–2.5 mm was separated. Seawater was taken from Batumi harborage. Its chemical content is shown in the Table 1:

The seawater concentration experiment was performed on the model electro dialysis plant, the hydraulic scheme of which is given in Figure 1.

Operational package of the model electro dialysis plant includes 30 dialysates and 30

concentration chambers with parallel-serial scheme and 7 sections. The electro dialysis plant complex includes: two platinum-covered titanium electrodes; polypropylene frames – 61 pieces; MK-40 and MA-40 membranes. Current strength $I = 3.8–6.2A$ (according to temperature), voltage 1 V. On this model, plant specific output (μ) was 4.9 l/m² h. for concentrate. The power consumption for the concentration process was 5.3W per liter of concentrate.

10 cycles of seawater concentration were performed. In the course of the process, dialysate flowed directly, but the concentrate was run by circulation. After each cycle of concentration, polarity and the hydraulic stream direction on the

Table 1. Chemical content (g/l) of seawater used in the experiment

Initial sea water	Na ⁺	Mg ⁺²	Ca ⁺²	K ⁺	Cl ⁻	SO ₄ ⁻²
Examble 1	5.7	0.729	0.200	0.23	11.224	2.1
Examble 2	6.8	0.608	0.240	0.31	9.184	1.9
Examble 3	8.7	0.630	0.340	0.20	9.999	1.47

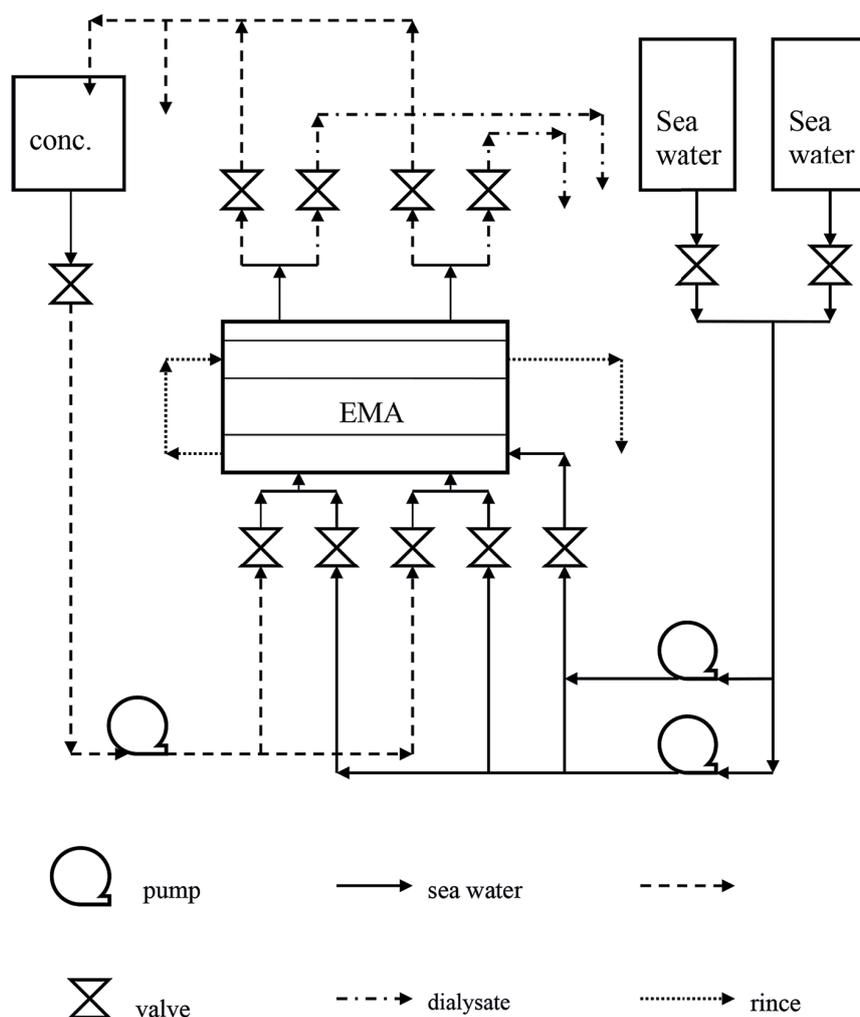


Fig. 1. Hydraulic scheme of the model electro dialysis plant (EMA – electromembrane apparatus)

electrodes in the operational chamber of electro-dialysis plant were changed aiming to avoid de-position on electrolytes and membranes.

Sorption of potassium ions from seawater concentrate was researched under dynamic conditions in the thermostatic glass columns containing 200 g of clinoptilolite ($S = 130 \text{ cm}^2$, $h = 30 \text{ cm}$). First, it was run through the first column clinoptilolite at T_1 temperature ($T_1 = 15\text{--}17 \text{ }^\circ\text{C}$), until the content of K^+ in filtrate became equal to the initial content.

In the 2nd stage (desorption of potassium), natural seawater was used. This time, a considerable amount of sodium was retained on clinoptilolite. Hot seawater at T_2 temperature ($T_2 = 80\text{--}85 \text{ }^\circ\text{C}$) was ran through the column. After that, the concentrate received from the column was cooled down to temperature T_1 and was run through clinoptilolite contained in the 2nd column, where the potassium-enriched product was received.

In the research of the sorption-desorption processes, the content of K^+ and Na^+ was determined by the flame-ionization photometry (flame-ionization photometer, model PFP7, Jenway), but the content of Ca^{+2} and Mg^{+2} – via the titrimetric method. The concentration of the components on sorbent in ion-exchange phase was calculated by the formula:

$$\bar{c}_i = \frac{C_{o,i}(Vn - V_0) - \sum_{i=1}^n C_i V_i}{m} \quad (1)$$

where: $C_{o,i}$ – initial concentration of solution, $\text{mg}\cdot\text{eq./ml}$, Vn – volume of solution passed through the column before coming of n fraction (ml), V_0 – free volume in the column determining by solution under sorbent layer in the porous space of the layer, C_i – concentration of i -fraction, m – mass of sorbent (g).

RESULTS AND DISCUSSIONS

The results clearly show specificity of change of concentration of the various elements in seawater in the process of electro-dialysis. According to the data, concentration coefficient $\beta = C_{\text{conc}}/C_{\text{initial}}$ equals to: in the first example (cycle N1) – $\beta = 4.35$ for potassium, $\beta = 2.59$ for sodium; in the second example (cycle N2) – $\beta = 4.4$ for potassium, $\beta = 2.87$ for sodium; in the third example (cycle N7) – $\beta = 3.48$ for potassium, $\beta = 2.6$ for sodium. Concentration coefficient for sulfate ion is 1.9.

In the course of the both concentration cycles $\beta = C_{\text{conc}}/C_{\text{initial}}$ was 3.8–4.4 for potassium ions and 1.87–2.87 for sodium ions, i.e. potassium ions concentration index was twice more than sodium ions concentration index.

The sorption-desorption dual temperature ion-exchange mode of ions separation showed the regularity according to which, the process of potassium ions sorption was accompanied with desorption of calcium ions, light desorption of magnesium ions, but sodium ions concentration practically remained unchanged. Figure 5 shows the change of quantity of potassium (mg) retained on clinoptilolite, together with the change of potassium ions concentration (mg/l) in filtrate in the process of sorption from electro-dialysis concentrate.

A difference was revealed also in the process of desorption with hot seawater: potassium desorption was accompanied with the bivalent ions sorption, but sodium concentration remained unchanged (Fig. 6).

Processing of potassium-enriched clinoptilolite allowed ions separation with twenty-fold volume hot sea water. In the case of seawater with general salinity 17 g/l, the concentrate with potassium concentration of 0.6g/l and calcium concentration

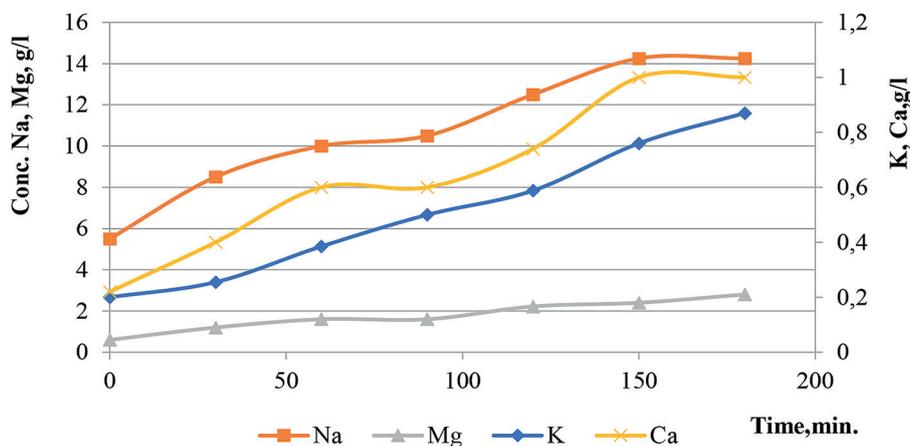


Fig. 2. Sea water concentration with electromembrane apparatus, cycle N1

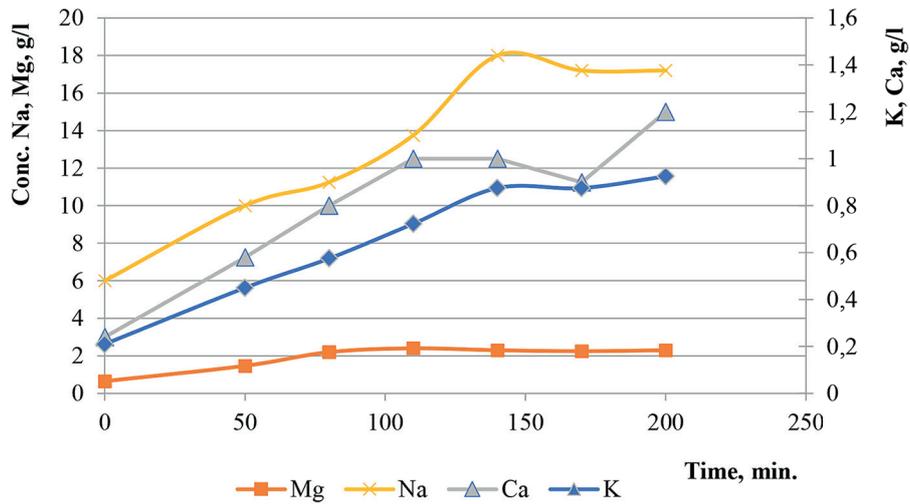


Fig. 3. Sea water concentration with electromembrane apparatus, cycle N2
The experiment proved irregularity of the indices received for concentration of sulfate ions.

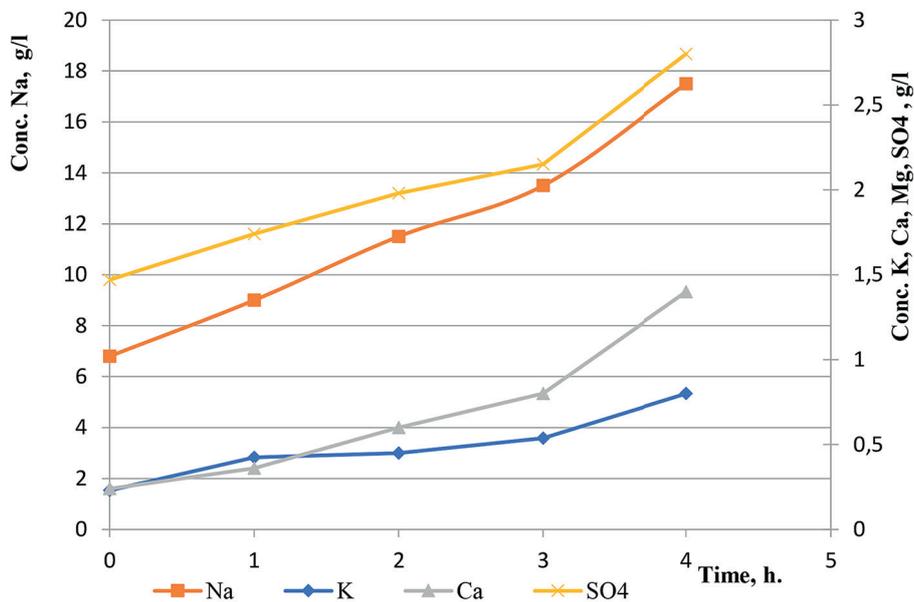


Fig. 4. Sea water concentration with electromembrane apparatus, cycle N7

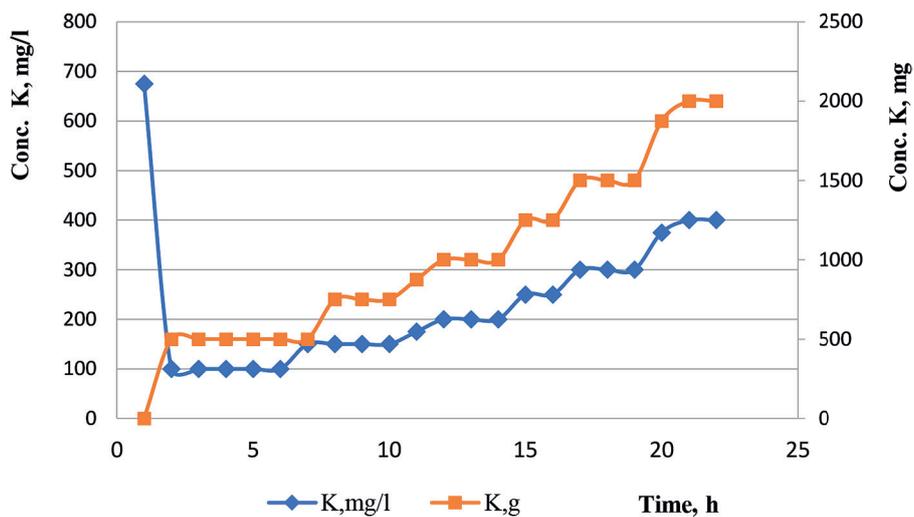


Fig. 5. Change of K^+ ions concentration (mg/l) in the process of sorption from electro dialysis concentrate

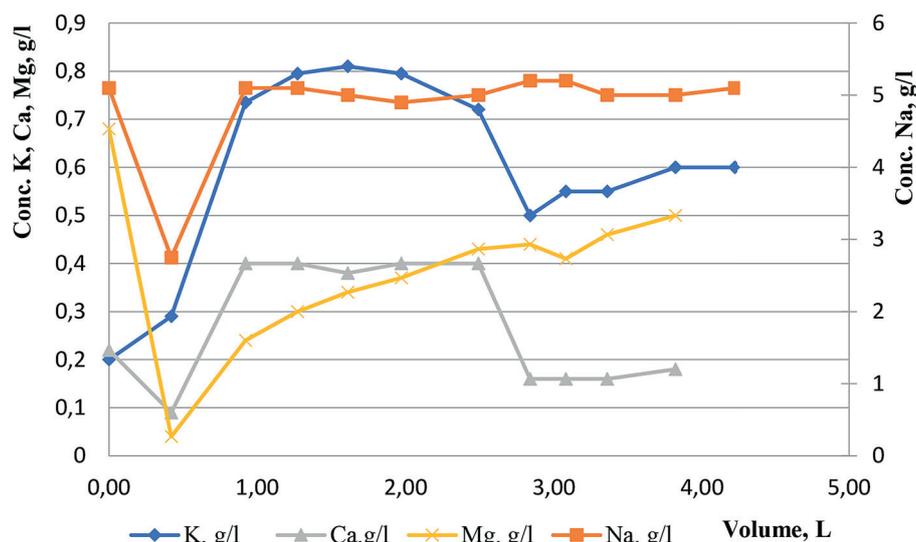


Fig. 6. Change of ions concentration in desorption with hot seawater

of 0.1 g/l was obtained, which exceeds the results of the last research by a factor of 3. According to the practical considerations, continuation of the process up to constant meaning of potassium ions concentration is not purposeful. The maximum concentration of retained potassium on clinoptilolite in the balanced condition equals 4%.

The experiment was performed both under the laboratory conditions and with the experimental model involving the production of a zeolite fertilizer sample.

CONCLUSIONS

On the basis of the natural zeolite (clinoptilolite) the potassium fertilizer was produced as nitrate-free, ecologically pure product. The potassium-enriched fertilizer has prolonged action, i.e. capacity of long-time regulation of ion-exchange processes.

The chosen electro dialysis membranes (MK-40 and MA-40) and the determined parameters of technological process provided excess of concentration indices of potassium ions over the other ions concentration indices in seawater concentrate. The use of electro dialysis in the process allowed achieving 4 times greater concentration of potassium ions in seawater, resulting in intensification of the process.

The selected technology is reactant-less, energy-saving, ecologically pure and cheap, as the required raw materials include the natural zeolite widespread in Georgia (Dzegvi and Tedzami clinoptilolite deposits) and the Black sea water (as a

source of potassium ions). The obtained products may be consumed by small or large scale factory-farm enterprises or private farms.

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