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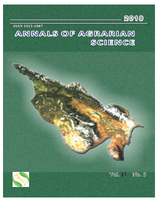

Intensified Technology of the New Type Potassium Fertilizer Production

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ABSTRACT

Soil is the important component of the ecological system on the basis of which plants grow making in their turn an important link in the food chain. In restoration of soil fertility the various fertilizers are used among which potassium fertilizers are important.

We have researched the method of potassium fertilizer production with use of wasteless, ecologically poor technology. The fertilizer is produced with the non-traditional, combined sorption and membrane method, where the Georgian natural zeolite - clinoptilolite is used as substrate and the Black sea water as a potassium ions source. Also we used electrodialysis for preliminary concentration of seawater. We have matched and developed the optimal parameters of operation of electrodialysis apparatus providing excess of potassium concentration indexes over the same for the other ions.The method is prospective for the countries of the Black sea region with deficit of potassium fertilizers and availability of the recourses of zeolites.

Keywords: Potassium fertilizer, Ion-exchange sorption, Electrodialysis concentration, Seawater, Georgian natural zeolities, Zeoponics.

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Introduction

Welfare of human society depends to a large extent on state of land resources and its fertility. Soil gradually looses the micro- and macronutrient elements, but their recourses in the oceans grow. Such growing is caused with soil erosion, as well as rivers flowing thereto and atmospheric precipitations.

One of the variants of elimination of micro- and macroelements deficit includes processing of the world ocean recourses. The scientists noticed possibility of extraction of rare metals from seawater. The rare metals contain in seawater in ionic state, what simplifies their extraction.

The Georgian and Russian scientists experimentally proved possibility of extraction of poor magnesium, potassium, sodium, bromine, lithium and the other valuable microelements [1-8].

At the same time, a new generation fertilizers attract more and more attention. It is so called meliorants – zeoponics, a kind of zeolite enriched with potassium and the other macro- and micronutrients. Their production technology is based on dependence of sorption processes on temperature [9-13].

The new type fertilizer rules out accumulation of nitrates in plants and their damage with the pathogenic microbes; its improves the biochemical processes in plants, simultaneously decreases possibility of accumulation of toxic substances in plants and further in food. Potassium-enriched products may be used separately as a full-value fertilizer or as a part of combined fertilizers. It improves also structure of soil [14-17].

A number of works covers development of sorption technology and research of physicochemical regularity [1, 3, 9, 11]. It is established that change of temperature of sorption causes sharp change of selectivity of sorbent to metal ions. The experiments prove the selectiveness series given in the writings: Cs>K>Sr=Ba>Ca>>Na>Li [1, 3, 4, 10].

The essence of the method includes use of the cheap natural sorbents with capacity of selective extraction of the ions of alkaline and alkaline-earth metals. Separation of seawater components for production of potassium-enriched solution is provided on clinoptilolite by so called dual temperature ion-exchange method. Kinetics of metal ion sorption is researched in static [4] and further in the dynamic conditions [10, 18]. The experiment proves that the process runs by the way of replace of one kind of ion by the other at change of temperature.

Specifically: at law temperature K^+ retains at clinoptilolite, while Ca^{+2} and Mg^{+2} move into filtrate and vice versa, at high temperature Ca^{+2} and Mg^{+2} retain at clinoptilolite, but the potassium ions move into filtrates.

It is known that in comparison with the other waters, in the Black sea these components including potassium are twice less. So, we have to process a great amount of seawater to receive the final product. Aiming this, we have researched combination of the sorption method with the method of electrodialysis concentration.

We modified the process of sorption of potassium on clinoptilolite: aiming intensification, we used seawater concentrate in sorption on the model electrodialysis plant and aiming to grow concentration of potassium in the concentrate, provided desorption of clinoptilolite enriched with potassium with hot sea water (60-70°C). Resulted this, we received the solution with concentration of potassium higher than the same of sodium.

Objects and methods

In the experiments we used clinoptilolite from Dzegvi mine. Its percent content is: SiO_2 -60.1%, Al_2O_3 -12.86%, Fe_2O_3 – 1.57%, MgO – 1.58%, CaO – 4.54%, Na_2O -1.68%, K_2O -1.38%, H_2O -16.3%, Si/Al -4.13%. Exchange capacity of clinoptilolite is established to be $C\sum = 1.91$ mg-eq/g

We fractionated the grained clinoptilolite according to the particles sizes running them through the screens and separated the fraction of 2.0 – 2.5 mm.

We used seawater taken from Batumi harborage. Its Chemical content shown in the table below:

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

Initial Sea Water	Na^+	Mg^{+2}	Ca^{+2}	K^+	Cl^-	SO_4^{-2}
Sea Water 1	5,7	0,729	0,200	0,23	11, 224	2,1
Sea Water 2	6,8	0,608	0,240	0,31	9, 184	1,9
Sea Water 3	8,7	0,630	0,340	0,20	9, 999	1,47

We performed seawater concentration experiment on the model electrodialysis plant which hydraulic scheme is given on Fig. 1

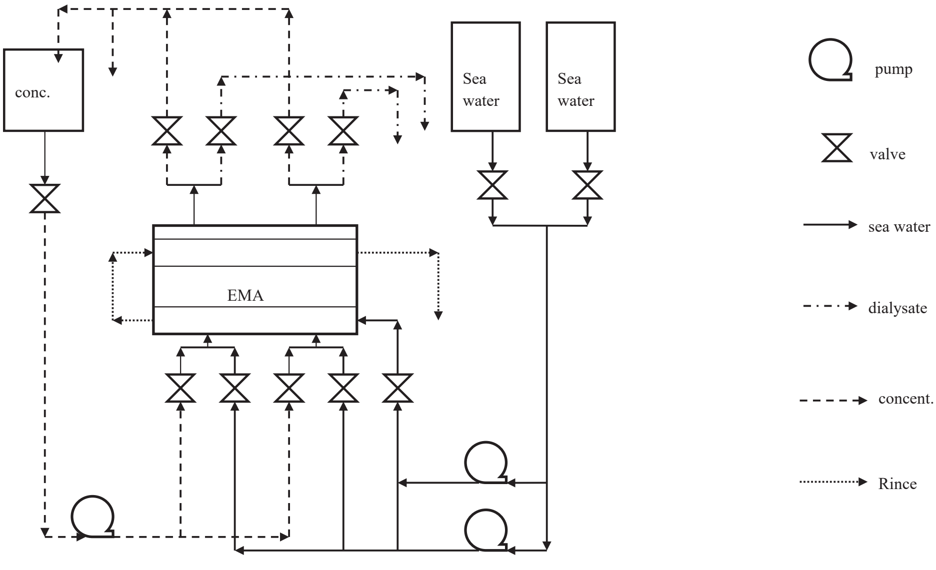

Fig. 1. *Hydraulic scheme of the model electrodialysis plant (Remark: EMA – electromembrane apparatus).*

Operational package of the model electrodialysis plant includes 30 dialysates and 30 concentration chambers with parallel-serial scheme and 7 sections.

Electrodialysis plant complex includes:

- two platinum-covered titanium electrodes;

-polypropylene frames – 61 pieces

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 we changed polarity and hydraulic stream direction on the electrodes in the operational chamber of electrodialysis plant aiming to avoid deposition on electrolytes and 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/m^2 h. for concentrate. Power consumption for concentration process was 5.3W per liter of concentrate.

We researched sorption of potassium ions from seawater concentrate in dynamic conditions in the thermostatic glass columns containing 200g of clinoptilolite (S=130 cm^2, h=30cm). First we ran it through the first column clinoptilolite at T_1 temperature (T_1=13-15°C), until content of K+ in filtrate gets equal to the initial content.

On the 2nd stage (desorption of potassium) we used natural seawater. This time, considerable amount of sodium retained on clinoptilolite. We ran hot seawater at T_2 temperature (T_2= 80-85° C) through the column. After that we cooled the concentrate received from the column down to temperature T_1 and ran it through clinoptilolite contained in the 2nd column, where we received the potassium-enriched product.

In research of sorption-desorption processes we determined content of K^+ and Na^+ by the flame-ionization photometry (we used Jenwey flame-ionization photometer, model PFP7), but content of Ca^{+2} and Mg^{+2} – by titrimetric method.

Concentration of the components on sorbent in ion-exchange phase was calculated by the formula:

$$\bar{C}i = \frac{Co,i(Vn - Vo) - \sum_{i=1}^{i=n} CiVi}{m}$$

where Co, i – initial concentration of solution, mg.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, Ci – concentration of i- fraction, m – mass of sorbent (g).

After processing of the results we drew up the tables and the made drawings completely reflecting our results.

Results and Discussions

The results clearly show specificity of change of concentration of the various elements in seawater in the process of electrodialysis. According to the data, concentration coefficient β = C conc/C initial equals to: in the first example (cycle N1) – β=4.35 for potassium, β=2.59 for sodium; in the second example (cycle N2) – β=4.4 for potassium, β=2.87 for sodium; in the third example (cycle N7) – β=3.48 for potassium, β=2.6 for sodium. Concentration coefficient for sulphate ion is 1.9.

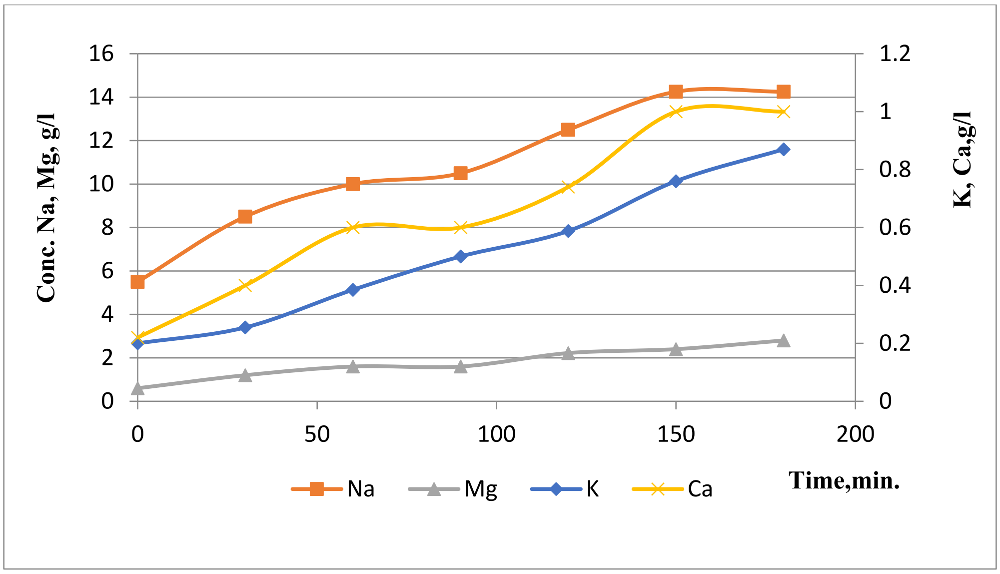

Fig. 2. *Electrolysis Concentration of Seawater, cycle N1.*

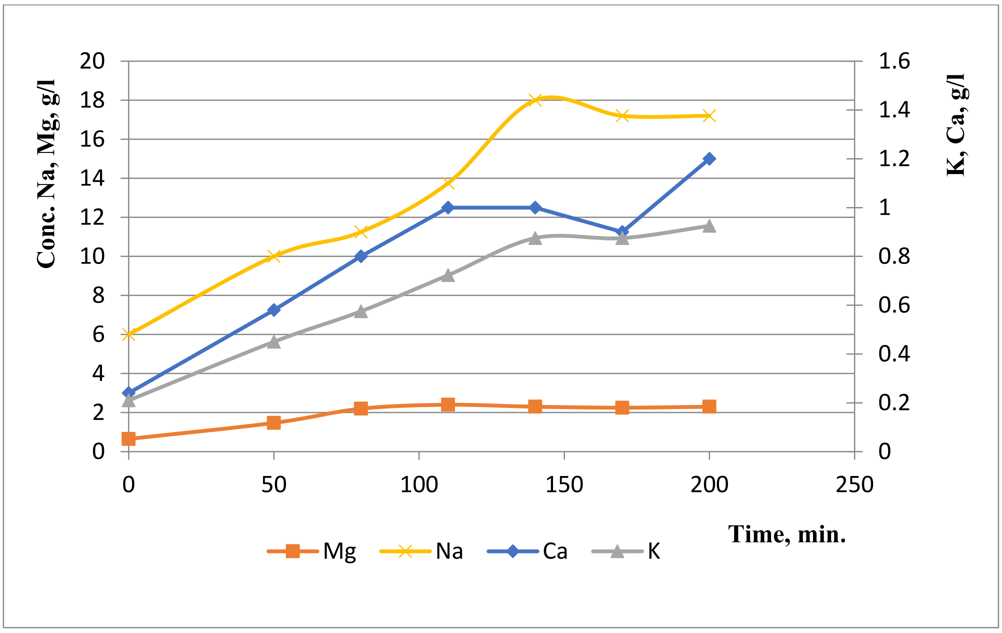

Fig. 3. *Electrolysis Concentration of Seawater, cycle N2*

The experiment proved irregularity of the indexes received for concentration of sulphate ions.

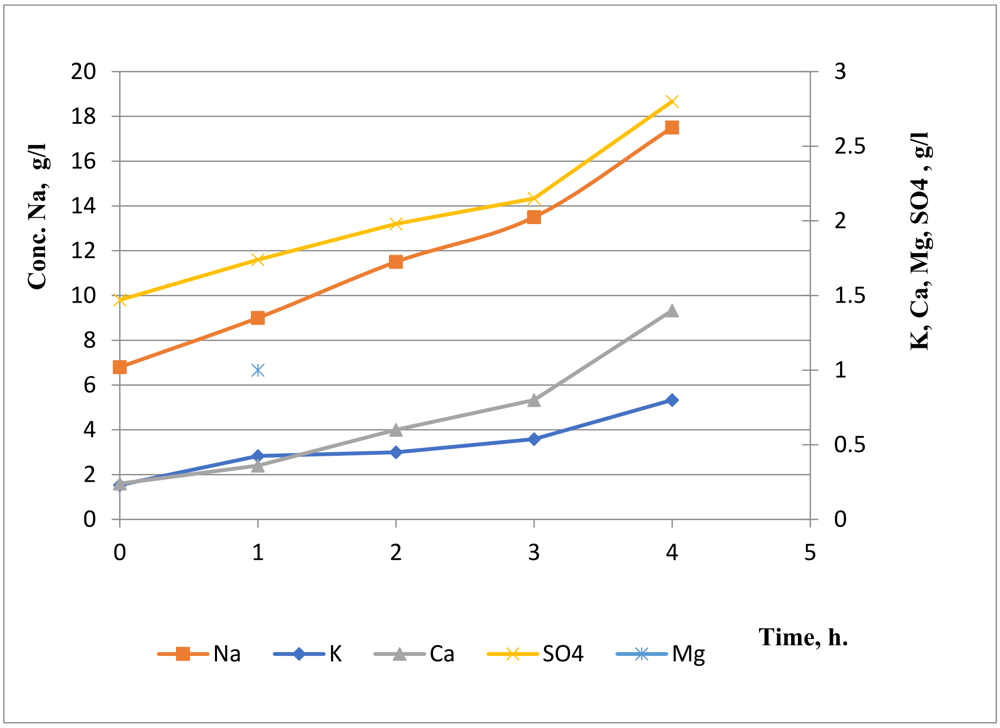

Fig. 4. *Electrolysis Concentration of Seawater, cycle N7*

In the course of the both concentration cycles $\beta=C_{conc}/C_{initial}$ 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. Fig. 5 shows change of quantity of potassium (mg) retained on clinoptilolite together with change of potassium ions concentration (mg/l) in filtrate in the process of sorption from electrodialysis concentrate

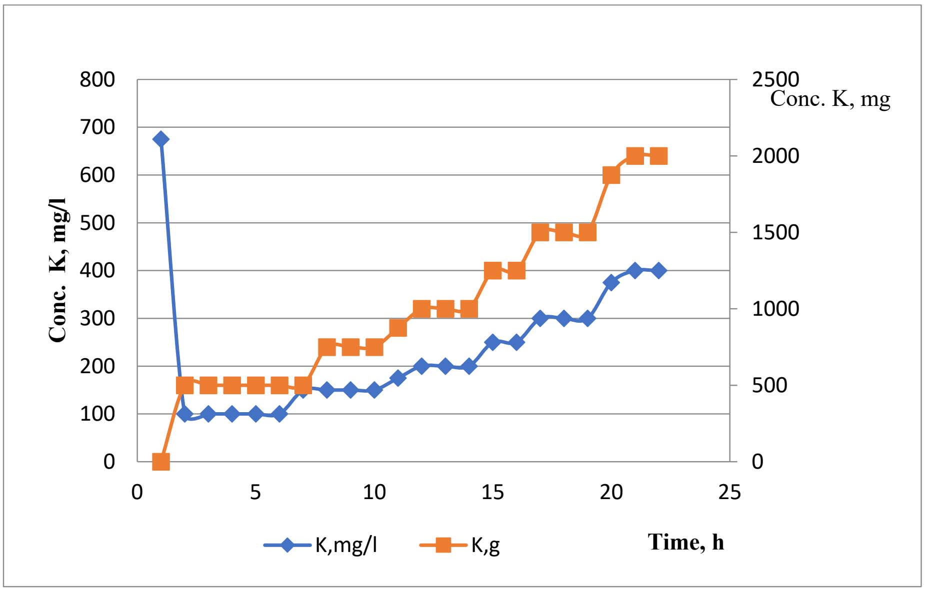

Fig. 5. *Change of potassium ions concentration (mg/l) in the process of sorption from electrodialysis concentrate.*

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 clinoptilolote allowed ions separation with twentyfold volume hot seawater. In case of seawater general salinity 17g/l we received the concentrate with potassium concentration of 0.6 g/l and calcium concentration of 0.1g/l what triply exceeds the results of the last research. According to the practical considerations, continuation of the process up to constant meaning of potassium ions concentration is not purposeful. Maximum concentration of retained potassium on clinoptilolite in the balanced condition equals to 4%.

The experiment was performed both in the laboratorial conditions and with the experimental model with production of the sample of zeolite fertilizer.

Conclusion

Thus, on the basis of the natural zeolite (clinoptilolite) we produced the potassium –enriched fertilizer as nitrate-free, ecologically poor product. It has prolonged action, i.e. capacity of long-time regulation of ion-exchange processes.

We have matched electrodialysis membranes (MK-40 and MA-40), determined the parameters of

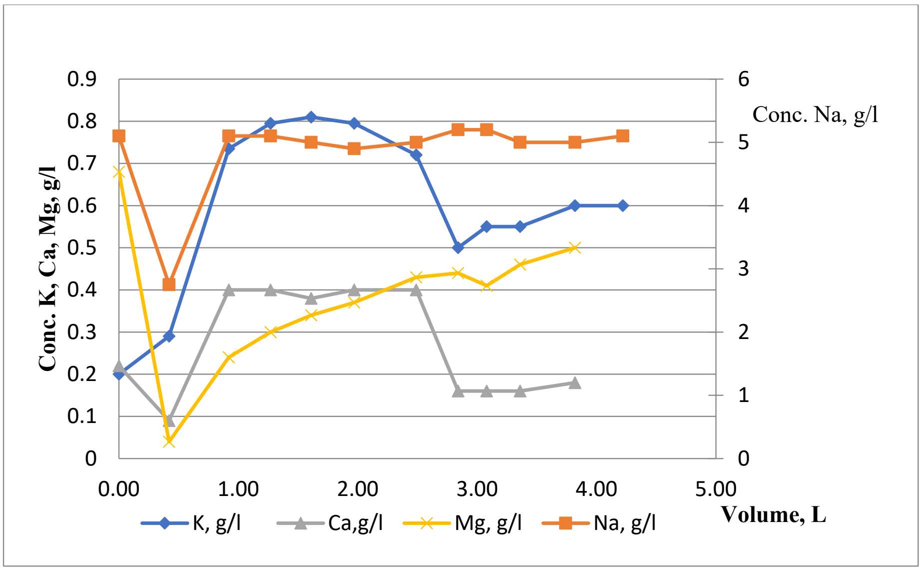

Fig. 6. *Change of ions concentration in desorption with hot seawater*

technological process providing excess of concentration indexes of potassium ions over the other ions concentration indexes in seawater concentrate. Use of electrodialysis in the process allowed to make concentration of potassium ions in seawater 4 times more, resulting intensification of the process.

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).

This products may be consumed by small or large scale factory-farm enterprises or private farms.

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