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# Isolation of Sodium Chloride from the Human Exometabolite Mineralization Solutions and Vegetable Wastes as Applied to Closed Ecosystems

A. G. BELOBABA<sup>1</sup>, A. I. MASLIY<sup>1</sup>, A. A. GUSEV<sup>1</sup>, A. A. TIKHOMIROV<sup>2</sup>, YU. A. KUDENKO<sup>2</sup> and S. V. TRIFONOV<sup>2</sup>

<sup>1</sup>*Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Kutateladze 18, Novosibirsk 630128 (Russia)*

*E-mail: belobaba@ngs.ru*

<sup>2</sup>*Institute of Biophysics, Siberian Branch of the Russian Academy of Sciences, Akademgorodok, Build. 50, Krasnoyarsk 660036 (Russia)*

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## Abstract

There were investigated two variants of NaCl isolation from the solutions of human exometabolite mineralization and plant wastes, based on the fractional crystallization of salts *via* evaporation and the low solubility of NaCl in concentrated HCl, respectively. It has been established that owing to preferential dissolution of the impurities in the concentrated HCl, from the mineralized solutions one could recover 99 % of NaCl contained therein, whose purity of which is not worse with respect to the standard food grade salt. The methods for proposed processing the mineralized solutions allow one to involve NaCl and H<sub>2</sub>O into the mass exchange within closed environments.

**Key words:** life-support systems, intersystem mass exchange, sodium chloride, fractional crystallization, evaporation, electro dialysis

## INTRODUCTION

In order to perform the Martian or Lunar mission those should be connected with an enduring human presence on the mentioned planet's surface, it is necessary to develop a closed bioengineering life support system (BELSS). The Institute of Biophysics of the SB RAS (Krasnoyarsk) demonstrated the BELSS to be promising based on the regeneration of the environment due to the cultivation of higher plants integrated with the oxidation of human exometabolites and plant wastes in the medium of H<sub>2</sub>O<sub>2</sub> activated by an alternating electric field [1, 2]. In the course of conveyor growing the crops within the framework of the BELSS [3] with the use of irremovable nutrient solution prepared basing on human exometabolites, there arises a problem of increasing the NaCl

concentration in the mentioned solution, which negatively affects the productivity of plants, resulting in the death thereof at sufficiently high concentrations of NaCl. In order to solve this problem, one could propose two alternative approaches.

The first approach is based on the isolation of NaCl from the solution of mineralized wastes or from plant nutrient environment in order to avoid exceeding the maximum permissible concentration of the salt for the plants. In this case, the level of extraction and purity of the resultant NaCl are not of fundamental importance, since the solutions of sodium chloride mixed with other salts could be used for intra-system growing halophytes such as, for example, *Salicornia* that can be used in human food [4, 5]. Thus, there can be achieved involving the NaCl in the intra-system turnover.

The aim of the second approach consists not only in decreasing the concentration of sodium chloride in mineralized solutions, but also in obtaining food grade salt that could be consumed by the BELSS crew, which also allows involving the NaCl into the intra-system mass exchange. In this case, it is necessary to develop a method that allows performing the most complete and pure isolation of NaCl from the solution for direct human use.

The aim of this work consisted in developing the mentioned approaches for the isolation of NaCl from the solutions obtained in the course of the mineralization of organic wastes, as well as for subsequent involving all the elements in the turnover process.

## EXPERIMENTAL

The isolation of NaCl from the mineralized solution can be accompanied by the loss of the elements necessary for growing higher plants within the system. In particular, there is a problem of maintaining the potassium content in the solution, since the ions of this metal exhibit almost the same activity as  $\text{Na}^+$ . It is therefore necessary to develop a method that would allow not only reducing the NaCl concentration in the solution, but also eliminating the high losses other mineral elements. For separate (fractionated) recovering the NaCl and other salts, one could use the process of solution evaporation because the salts exhibit different water solubility level at different temperature values [6, 7]. For example, at 90 °C the ratio between the solubility values NaCl/KCl is equal to 0.72, therefore, upon evaporation there should be mainly NaCl precipitated [7, p. 1129].

The experiments concerning the isolation of NaCl from the solutions by means of fractionation were carried out using a laboratory-scale setup that consisted of a thermostat and a measuring glass reservoir for evaporation with dial graduations. The precipitate of the salts was isolated from the solution using a grid collector located in the bottom of the vessel (Fig. 1).

In the course of the experiments, we measured changing the volume of the solution and took the precipitate crystals collected on the grid for the analysis of ions  $\text{Na}^+$ ,  $\text{K}^+$ , and others.

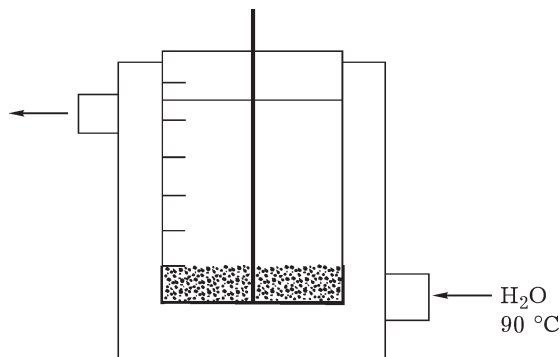


Fig. 1. Schematic diagram of the unit for fractional separation of the salts.

Choosing the specific temperature values (90 °C) was caused by a high evaporation rate and by prevailing the precipitation of NaCl under these conditions. The phase composition of the precipitates was determined using a DRON-3 diffractometer; the mass of precipitate was measured with the use of a CAUX 220 electronic balance. The concentrations of K, Na, Ca, Mg, Fe and P were determined by means of atomic absorption technique. We determined  $\text{NH}_4^+$  and  $\text{NO}_3^-$  with the help of ion-selective electrodes,  $\text{Cl}^-$  with the help of titration technique,  $\text{SO}_4^{2-}$  gravimetrically.

The experiments on the extraction of NaCl from mixed solutions were carried out with the use of the model and real human exometabolite and plant waste mineralization solutions. As the model solutions we used two-salt (184 g/L NaCl + 108 g/L KCl) and three-salt (184 g/L NaCl + 108 g/L KCl + 82 g/L  $(\text{NH}_4)_2\text{SO}_4$ ) systems. The salt content in these solutions is close to the solubility level thereof at a room temperature. Real human exometabolite and vegetable waste mineralization solutions exhibited the following ionic composition (g/L):  $\text{K}^+$  1.5,  $\text{Na}^+$  1.9,  $\text{NH}_4^+$  1.4,  $\text{Cl}^-$  3.3,  $\text{SO}_4^{2-}$  1.5,  $\text{NO}_3^-$  1.3,  $\text{Ca}^{2+}$  0.01,  $\text{Mg}^{2+}$  0.0005, Fe 0.001, P 0.3.

In order to isolate NaCl from precipitates obtained in the course of the complete evaporation of the solutions, we used a method based on the difference in the solubility level of the salts in concentrated hydrochloric acid [5, p. 542]. The composition of the saturated solution of HCl–NaCl–KCl– $\text{H}_2\text{O}$  system at 25 °C was as it follows (mass %): HCl 32.78, NaCl 0.18, KCl 1.27,  $\text{H}_2\text{O}$  65.77.

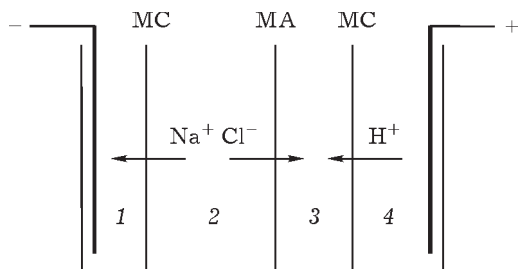


Fig. 2. Schematic diagram of arranging the chambers in the electrodiolysis unit: 1 – cathode chamber, 0.1 M NaOH solution; 2 – desalination chamber; 3 – chamber for concentration, 0.1 M HCl solution; 4 – anode chamber, 0.1 M HNO<sub>3</sub> solution; indices “+” – platinum cathode and anode, respectively; MC and MA – cation-exchange (MC-40) and anion-exchange (MA-40) membranes, respectively (geometric area  $S = 37 \text{ cm}^2$ ).

Under the conditions of closed ecosystem, the reserves of consumable materials are limited, so we tested the possibility of obtaining the hydrochloric acid from the mineralized solution by means of electrodiolysis. For this purpose, we used a four-chamber laboratory-scale apparatus that simultaneously provided both desalination of the initial solution and the procedure of HCl (Fig. 2).

Desalting the solutions those simulate the solutions of mineralization with respect to main components (4.8 g/L of NaCl, 2.8 g/L of KCl and 10.3 g/L of NH<sub>4</sub>Cl) was carried out in a galvanostatic mode at a current strength ranging within 0.28–0.84 A. The volumes of dialysate and concentrate were equal to 0.5 L each, the flow-through rate being equal to 6.6 L/h.

In order to produce table salt from the solutions of mineralization it is required for the most complete and pure isolation of NaCl. With this purpose we proposed and tested a method that involves the evaporation of the starting solution up to obtaining dry solid residue, the calcination for to remove the organic residue with further extracting NaCl therefrom with the use of concentrated HCl. The dry solid residue was

obtained *via* the evaporation of 3 L of real mineralization solution, whose composition is presented above. The residue was dried for to obtain constant mass at 100–110 °C with further calcinations in a PVK-1,4-8 electric furnace in a flow of air at the temperature ranging within 400–700 °C to remove organic impurities. The duration of heat treatment was equal to 75 min, temperature accuracy amounted to 5 °C, and the heating rate was equal to 20 °C/min. The efficiency of heat treatment was evaluated according to such parameters as the total organic carbon content, phase composition, the content of NaCl and KCl, the mass of the sample. The total organic carbon content (TOC) was determined by means Pregl technique [8].

## RESULTS AND DISCUSSION

### *Isolation of NaCl by means of fractional crystallization*

The studies on the fractional isolation of salts from the model and real solutions of mineralized human exometabolites demonstrated that the treatment of the model two-salt pure chloride solution results in the precipitation of mainly NaCl (according to XRD, more than 99 %), the ratio of K<sup>+</sup>/Na<sup>+</sup> therein almost does not depend on the degree of evaporation being equal to 0.1 (Table 1).

The evaporation of a more complicated three-salt chloride-sulphate solution is accompanied by the formation of two types of precipitates. At a low degree of evaporation (about 20 %), the precipitate is enriched in potassium. In the course of the further evaporation of the solution, the proportion of potassium in the precipitate is reduced, and at the degree of evaporation amounting to 50–60 % the ratio of K<sup>+</sup>/Na<sup>+</sup> remained at the level of 0.3. The main components of the precipitate, according to the XRD data, are presented by NaCl

TABLE 1

K<sup>+</sup>/Na<sup>+</sup> ratio in the precipitates obtained by the evaporation of model solutions

Starting solutions	K <sup>+</sup> /Na <sup>+</sup> ratio in precipitate (%) at a degree of evaporation				
	20	25	40	50	60
184 g/L NaCl + 108 g/L KCl	0.12	–	0.093	0.085	–
184 g/L NaCl + 108 g/L KCl + 82 g/L (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1.17	1.02	0.54	0.33	0.30

(60 mass %),  $K_3Na(SO_4)_2$  (36 mass %) and KCl (4 mass %) [9].

Real mineralization solutions were previously evaporated about by 40 times, that is until a state close to saturation at a room temperature. In the course of the further evaporation thereof at 90 °C the precipitates are formed those are close to the precipitates of model three-salt solutions in the composition and  $K^+/Na^+$  ratio equal to (0.25–0.35). According to XRD data, the precipitate crystallizing from the real mineral solution at 60 % degree of evaporation, has the following composition (mass %): NaCl 59,  $K_3Na(SO_4)_2$  37, KCl 4. This indicates an almost identical composition of the precipitates obtained from the model and real mineralization solutions.

In order to isolate a pure NaCl from the precipitates obtained *via* fractional crystallization it is necessary to remove  $K_3Na(SO_4)_2$  and KCl impurities. For this purpose, we used a method based on differences in the solubility of the salts in concentrated HCl. It was established that the hydrochloric acid treatment of dry solid residues obtained *via* fractional crystallization in the course of the evaporation of model and real mineralization solutions, the double sulphate  $K_3Na(SO_4)_2$  and KCl are almost completely removed therefrom. According to XRD data, the purified precipitate contains almost pure NaCl ( $\geq 99$  %) (Table 2), whereby the resulting salt could be used in human food.

Thus, by means of the fractional crystallization of the salts from the real mineralization solutions one could obtain the NaCl that is similar in the composition to food grade salt (State Standard GOST R 58574–2000) after purifying in hydrochloric acid [10]. The disadvantages of this method of producing food grade salt con-

sist in a relatively low yield of solid products at the stage of fractional crystallization (almost 16 % of total mass) because of a high solubility of the salts at 90 °C. This means that the real yield of NaCl inherent in the fractional crystallization method is equal to approximately 10 % of the original content thereof in the solution of mineralized human exometabolites and plant wastes. For this reason, this method is appropriate for using only for reducing the concentration of NaCl in a mineralized solution. Such solutions (with a high content of NaCl or other salts) could be used for plant nutrition, for example, *Salicornia* those could be further used in human food.

Heating the precipitate and the supernatant and capturing the vapours [11], one could recover HCl to re-use it in the next cycle of NaCl extraction. Owing to the limited potentialities to create large-scale reserves of supplies, including reagents in closed ecosystems, we investigated the possibility of obtaining HCl from the mineralized solutions by means of electrodi-  
alysis. Figure 3 demonstrates the dynamics of

TABLE 2

Phase composition of f salt precipitates before and after treatment in HCl (flow rate 20 mL per 1 g of salt)

Solutions	Residue	Mass fraction, %		
		NaCl	KCl	$K_3Na(SO_4)_2$
Model	Original	60	4	36
	After treatment	$\geq 99$	$\leq 1$	abs.
Real	Original	67	6	27
	After treatment	$\geq 99$	$\leq 1$	abs.

Note. Here and in Table 3: abs. denotes “absent”.

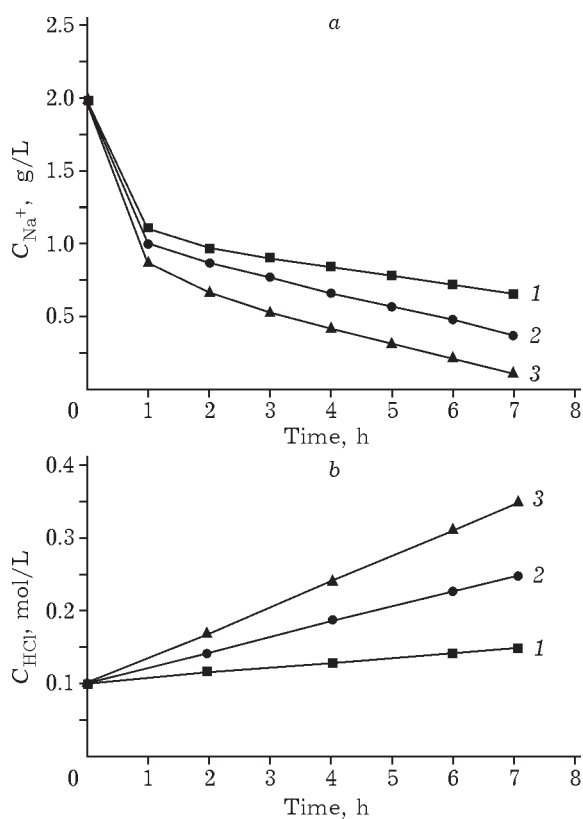


Fig. 3. Dynamics of sodium ions extraction from the dialysate (a) and of HCl accumulation in concentrate (b) depending on the current strength (A): 0.28 (1), 0.56 (2), 0.84 (3).

extracting the  $\text{Na}^+$  ions and of HCl accumulation in the course of electro dialysis; it follows therefrom that it is possible to obtain simultaneously both concentrated HCl (0.35 M), and a considerably desalted solution (50 mg/L of  $\text{Na}^+$  and 20–30 mg/L of  $\text{K}^+$  and  $\text{NH}_4^+$ ). A higher level of salt extraction is impractical due to an abrupt increase in the voltage and hence increasing the power consumption of the electro dialysis procedure (about 2.5 times). The desalted solution (pH  $\approx$  2) after the neutralization thereof, for example, by the catholyte obtained (pH  $\approx$  13), could be used for watering the plants, whereas one could use the solution of HCl after additional concentration for the final purification of sodium chloride prepared from mineralized solutions.

#### Isolation of NaCl from the total salt precipitate

For a more complete use of salts contained in the mineralization solutions and to increase the yield of NaCl we proposed and tested method comprising the evaporation of the starting solution to obtain dry solid residue, the calcination to remove organic matter and the treatment of the residue in concentrated HCl for the isolation of NaCl.

According to XRD phase analysis, the original dry residue contained 65.8 vol. % of NaCl, 5.4 vol. % of KCl and 28.7 vol. % of sodium-potassium sulphate double salt with variable composition from  $\text{K}_3\text{Na}(\text{SO}_4)_2$  to  $\text{KNaSO}_4$  (Fig. 4).

The content of organic matter in the original precipitate of salts, characterized by the value of total organic carbon (TOC) was equal to 1.8 mass %. In the course of the thermal processing of the salts at different temperature values, we observed a modest (10–15 %) decrease in the sample mass, changing the phase composition (see Fig. 4) and an abrupt decrease in the total organic carbon. So, at 20 °C, it was 1.8 mass % at 400 °C – 0.39 mass % and at 500 °C no carbon was detected.

It was found that at the temperature of 400 °C the original sample exhibits the formation solid NaCl–KCl solutions, changing the composition and an abrupt decrease of the amount of sulphate-containing phase to begin. In particular, there appears a phase having the com-

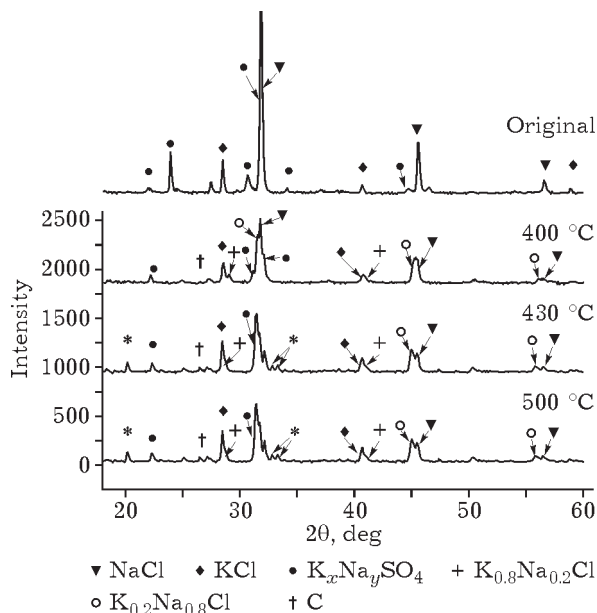


Fig. 4. XRD profiles for the original dry solid remainder of salts and for that after heat treatment at different temperature values. An asterisk denotes an unidentified phase.

position close to the composition  $\text{K}_{0.67}\text{Na}_{1.33}\text{SO}_4$ . With increasing the heating temperature, this phase becomes well-crystallized, whereas its amount further remains almost unchanged, since the amount is, to all appearance, limited by the original content of sulphate. On the contrary, the content of NaCl and KCl phases in the precipitate exhibits decreases with increasing the temperature as the result of the interaction between them, and of the formation of solid solutions with varying composition.

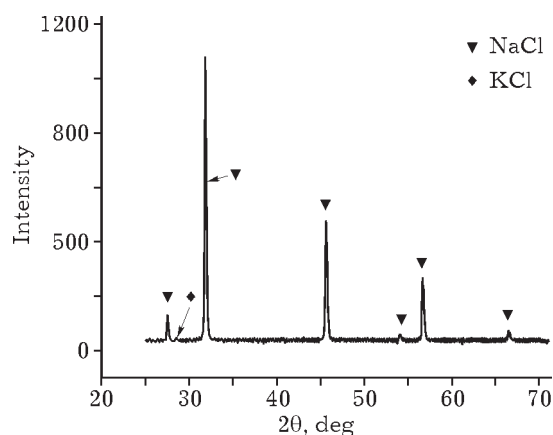


Fig. 5. XRD profile for a sample purified from organic matter, sulphates and potassium chloride. For NaCl and KCl, the position of reflex [200] is presented with the intensity of 100 %.

TABLE 3

Chemical composition of the standard food table salt and prophylactic salt, as well as of precipitates obtained from mineralization solutions *via* fractional crystallization and evaporation, before and after treating in HCl, mass %

Components	Salt from mineralization solutions				Food grade salt	
	Fractional crystallization		Evaporation and heat treatment		Table salt	Prophylactic salt
	Original	After treatment	Original	After treatment		
NaCl	67	≥99	77.0	≥99	97	65
KCl	6	≤1	23.0	≤1	0.38	30
K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub>	27	abs.	21.7	abs.	–	–

Note. For designations, see Table 2.

After annealing at 430 °C (see Fig. 4) the XRD patterns distinctly exhibit to identify hexagonal modification carbon, whose reflex at 400 °C is commensurable with respect to the background level. The amount of this phase also almost does not change with increasing the annealing temperature, and only after annealing at 700 °C one could observe a significant decrease in its amount. At this temperature, a melt is partially formed that reacts with the material of mullite crucible to forms a compound with variable composition with respect to sodium and potassium such as K<sub>0.65</sub>Na<sub>0.35</sub>AlSi<sub>3</sub>O<sub>8</sub>, wherein there are almost no pure NaCl, KCl present.

Dissolving the precipitate annealed at 400 °C, the filtering and re-evaporation of the solution result in the fact that carbon is completely removed from the sample, with remaining a four-phase system consisting of NaCl, KCl, solid solution of potassium chloride in sodium chloride, and double sulphate K<sub>0.67</sub>Na<sub>1.33</sub>SO<sub>4</sub>. In this case, the amount of sulphate phase is equal to about 21.7 %, that of NaCl and KCl being of 70, and 8.3 vol. %, respectively.

In order to obtain pure NaCl from this precipitate one should remove and both double sulphate and KCl, therefore the concentrated HCl was used, too (20 mL per 1 g of salt). After the acidic treatment according to the XRD data, in the sediment there remained almost pure sodium chloride, KCl content being less than 1 vol. %, whereas the phase of double K, Na sulphate was not detected (see Fig. 5). The resultant purified salt is close to the food table

salt according to in its composition (State Standard GOST R 58574–2000) (Table 3).

Thus, the method of a complete evaporation of human exometabolite mineralization solutions with subsequent thermal treatment of the precipitate and selective treatment thereof in HCl allows one to isolate almost all the NaCl with the purity being not worse than the purity of table salt. As the result, one could attain an almost complete integration of the method of the mineralizing the organic waste into a closed life-support system. The sodium chloride could be recycled for use in human food, whereas the remaining elements of the mineralized products could be sent to the nutrient solution for higher plants. The gases those are formed during the calcination of the precipitate could be purified from organic impurities by means of a catalytic setup used in the experiments with BIOS-3 [12].

## CONCLUSION

Two variants of processing the solutions of human exometabolite mineralization and vegetable wastes were considered, those provide different level of NaCl extraction therefrom. According to the first variant based on the fractional crystallization of salts via evaporating the solution, there can be isolated about 16 % of NaCl, whereas the solution treated can be used for growing halophytes within the system, such as *Salicornia* that could be used for human food. The second variant of the treatment based on a low solubility of NaCl in concentrated HCl allows one to extract 99 % of NaCl, whose

purity is not worse with respect to the standard food grade salt. The treatment products obtained (NaCl and H<sub>2</sub>O) could be involved in the intra-system mass exchange in closed life-support systems. Efficiency is demonstrated concerning the method of electro dialysis for producing HCl required for the final purification of NaCl.

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