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THE APPLICATION OF CONSERVED EMISSIONS OF SULPHUROUS GASES FOR IMPROVEMENT OF ALKALINE SOILS

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The aim of the study is to provide integrated solution of environmental problems by help of conservation emissions of sulphurous gases in form of sulphur or treated cement dust and their application for improvement of Alkaline Soils. New ameliorants for improvements of Alkaline soils under laboratory conditions were obtained: electro-treated mixture of sulphurous and sulphuric acids, treated cement dust containing sulphite and sulphate salts of Ca. Two electrochemical methods for production of sulphuric acid and mixture of sulphuric and hydrochloric acids from sulphurous acid were developed and the electric energy requirement for their production is calculated. The process of retention of sulphurous gases, by water solution of cement dust is studied. It is shown, that for conservation of 1 t of sulphurous gases 2 t of cement dust is required. The influence of newly-received ameliorants on physical and chemical properties of Alkaline soils during their chemical reclamation and leaching processes was studied. The most ameliorative effect, obtained in the variant, where electrochemical treated solution of the mixture of sulphurous and sulphuric acids were used.

Environmental problems – ameliorants – sulfurous and sulfuric acids – treated cement dust – reclamation

Ուսումնասիրության նպատակն էր գտնել բնապահպանական խնդիրների համապարփակ լուծում՝ մթնոլորտ արտանետվող ծծմբային գազերը ծծմբի և վերամշակված ցեմենտի փոշու կուտակման միջոցով և դրանք կիրառել ալկալի հողերի մելիորացման բնագավառում: Լաբորատոր պայմաններում ստացվել են նոր մելիորանտներ՝ ծծմբային և ծծմբական թթուների էլեկտրամշակված խառնուրդ, վերամշակված ցեմենտի փոշի, որը պարունակում է Ca-ի սուլֆիտ և սուլֆատ: Մշակվել են թթուների խառնուրդներից՝ ծծմբական և ծծմբական ու աղաթթվի խառնուրդի ստացման երկու էլեկտրաքիմիական եղանակներ: Կատարվել է ցեմենտի փոշու ջրային լուծույթով ծծմբային գազերի կլանման գործընթացի ուսումնասիրություն: Պարզաբանվել է, որ 1 տոննա ծծմբային գազերի կլանման համար պահանջվում է 2 տոննա ցեմենտի փոշի: Հետազոտվել է ալկալի հողերի ֆիզիկաքիմիական հատկությունների վրա նոր ստացված մելիորանտների ազդեցությունը դրանց քիմիական մելիորացիայի և լվացման գործընթացում: Ցույց է տրվել, որ լավագույն մելիորատիվ արդյունավետություն է դիտվել այն տարբերակում, որտեղ օգտագործվել է էլեկտրաքիմիական եղանակով վերամշակված ծծմբական և ծծմբային թթուների խառնուրդ:

Բնապահպանական խնդիրներ – մելիորանտներ – ծծմբային և ծծմբական թթուներ – վերամշակված ցեմենտի փոշի – մելիորացիա

Целью исследования является комплексное решение экологических проблем за счет консервации выбросов сернистых газов в виде серы, обработанной цементной пыли и их применения для улучшения щелочных почв. В лабораторных условиях были получены новые мелиоранты для улучшения щелочных почв: электрообработанная смесь сернистой и серной кислот, обработанная цементная пыль, содержащая сульфит и сульфат Ca. Были разработаны два электрохимических способа получения серной кислоты и смеси серной и соляной кислот из сернистой кислоты. Было проведено исследование процесса удержания сернистых газов водным раствором цементной пыли. Установлено, что для сохранения 1 т сернистых газов требуется 2 т цементной пыли. Проведено исследование влияния вновь полученных мелиорантов на физико-химические свойства щелочных почв в процессе их химической мелиорации и промывке. Наибольший мелиоративный эффект был проявлен в вариант, где использовался электрохимически обработанный раствор смеси сернистой и серной кислот.

Экологические проблемы – мелиоранты – серная и сернистая кислоты – обработанная цементная пыль – мелиорация

The emissions of sulphurous gases in the atmosphere take place from thermal power plants, the activities of non-ferrous metallurgy and others [1], which have negative effect on the environment and on the human health. Due to the smoke of sulphur dioxide gas, the incidence of bronchitis, bronchial asthma, and emphysema of the lungs increases [5]. There are several methods of conservation the emitted sulphurous gases [4, 2]

The method for obtaining sulphuric acid from sulphurous gases. However, its storing and using in large quantities is a big problem due to the expensive technology and aggressive effect of the reagent on the environment.

The lime method. According to this method, the sulphurous gases are retained with lime milk ($Ca(OH)_2$). In result of interaction of lime milk with sulphurous gases, the salt of $CaSO_3$ and partially gypsum ($CaSO_4 \cdot 2H_2O$) are formed. The disadvantage of this method is the need for a large amount of lime.

The soda method. The essence of this method is to wash the waste of sulphurous gases with aqueous solutions of soda ash (Na_2CO_3). In this case, reactions occur to produce ($NaHSO_3$). However, it has not found widespread use due to the limited marketing of this salt.

The ammonia method. The process of conservation of sulphurous gases, by ammonia method consists in washing the gas with ammonia water (NH_4OH). In this case, a reaction occurs with formation of ammonia sulphate ($(NH_4)_2SO_4$), which is used as a fertilizer in agriculture. However, a production of large amounts of ammonia is required, which leads to increasing of the cost of technology.

The methods of reduction of sulphurous gases. A number of methods were proposed. For example, the method of obtaining the elemental sulphur (S) was offered by (Zagoruiko et al. [10]).

In our opinion, the main criteria for selecting existing methods of conservation of sulphurous gases are: how safe the conserved product for the environment, the cost of technology and the possibility of using the formed products in various fields, including the agriculture are. Coming out of these criteria, the choice has stopped on the lime method in which, the salts of $CaSO_3$ and $CaSO_4$, and the production of pure sulphur are formed. These products may be used in sphere of reclamation of Alkaline soils.

The processes of salinization and alkalization of soils are a global problem, which has a negative impact on the chemical and physical properties of soils and, as a result, the agricultural productivity is reduced. For stable development of agriculture, it is important to improve the ameliorative and the ecollogical state of Alkaline soils, by application of ameliorants [3, 6-8]. For reclamation of non-carbonate Alkaline soils, gypsum or other salts containing calcium were applied [9]. The acids or the acid salts are usually used for reclamation of Calcareous Sodic Soils. A positive result has been obtained in Armenia through the application of 1% of solution of sulphuric acid as an ameliorant for reclamation of these soils [11]. By this technology 5.5 thousand ha of Saline-Alkaline soils have been reclaimed in Ararat valley of Armenia. However, by this technology there is necessity of transportation of huge quantity of ameliorants from other countries, for which significant charges are required.

Materials and methods*. The method of production of mixture of sulphurous and sulphuric acids.*

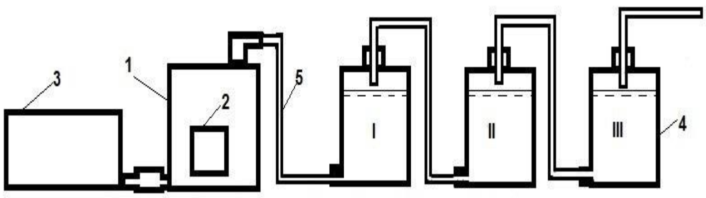

Figure 1. The scheme of experimental setup: 1 – stove for burning sulphur, 2 – door, 3 – compressor, 4 – receptacle, 5 – connecting hoses

As a result of oxidation of sulphur, the mixture of sulphurous gases passes through the connected hoses (5) into the receptacle I. A part of its volume is dissolved, and the other part passes into the receptacle II, then passes into the receptacle III and is dissolved and left in the atmosphere. The concentration of the formed solution was determined after burning 24 g sulphur on the stove and dissolving the gases in receptacles with 4.0 l of water. Because of dissolution of sulphur dioxide gases in receptacles I, II, III, a mixture of sulphurous and sulphuric acids is formed. To determine the quantitative ratio of these acids, they are shaken with calcium carbonate ($CaCO_3$), and the Ca ions were determined. The ratio of $CaCO_3$ and acids solution is 1:5. Because of the interaction between acids and calcium carbonates, the salts of calcium sulphite ($CaSO_3$), which has very lower solubility, and calcium sulphate ($CaSO_4$) are formed.

1. 2. The method of oxidation of sulphurous acid and production of sulphuric and mixture of sulphuric and hydrochloric acids

To increase the ameliorative effectiveness of the sulphurous acid, electrochemical methods were developed. The obtained mixture of acids was processed in the electrolyser in positive and negative electrode chambers. The solution was processed in 1-2 hours. The obtained mixture of acids was filled into the chambers of positive and the negative electrode, which were separated by a membrane. The following electrochemical reactions around the positive electrode took place (1):

$$H_2O = 1/2O_2 + 2H^+ + 2e, \textbf{(1).}$$
$$2H_2SO_3 + O_2 = 2H_2SO_4$$

To obtain the mixture of sulphuric and hydrochloric acids, the chamber of negative electrode was filled with the solution of sodium chloride and the chamber of positive electrode was filled with the formed mixture of acids. The positive and negative chambers were separated by a membrane. The following electrochemical reactions around the positive electrode took place (2):

$$2Cl^- = Cl_2 + e, \quad \textbf{(2).}$$
$$H_2SO_3 + Cl_2 + H_2O = H_2SO_4 + 2HCl$$

As a result of the above mentioned processes, every 0.5 hour during the electrochemical treatment, the sample of solution was taken observing the process of sulphurous acid oxidation. Formed mixture of acids was shaken with calcium carbonate (by ratio of 1:5) and the concentration of Ca^{2+} was determined in the filtered solution. Based on the result of concentrations of acids and Ca^{2+}, the percentage of sulphurous and sulphuric acids was calculated in the mixture. The solution was processed during 1-2 hours. The electrodes with 5 V voltages and 0.61-0.93 A current were supplied.

3.The retention method of sulphurous gases by water solution of cement dust

Cement dust contains in 43.26% CaO, 1.26% MgO, and 10% of lime. The laboratory experiments were carried out to determine the possibility of adsorption of sulphurous gases using the aqueous solution of cement dust, in the experimental setup described in Figure 1. The receptacle I with 4 l of water and 100 g of cement dust was filled, and the receptacles II and III were filled with 4 l of water in each. In the stove 25 g of sulphur was burnt and air was supplied by compressor. The concentration of formed solutions was determined in three vessels. The experiment was repeated with different contents of cement dust in the I receptacle.

4.The method of laboratory experiment to study the influence of newly-received ameliorants for chemical reclamation of Saline-Alkaline soils

The experiments were made under laboratory conditions using the polyethylene pipes (diameter 10 cm, height of 120 cm), as a soil column. Each pipe was filled with 9 kg saline-alkaline soils in the column with the height of 100 cm, preserving their natural profile of distribution of salt contents and their mechanical composition. The experiment was carried out in 4 variants with 3 repetitions.

1. Chemical reclamation of saline-alkaline soils using a mixture of sulphuric and sulphurous acids and leaching by water.
2. Chemical reclamation of Saline-Alkaline Soils using electrochemically treated by solution of mixture of sulphuric and sulphurous acids and leaching by water.
3. Chemical reclamation of Saline-Alkaline Soils using 1% of sulphuric acid solution and leaching by water (control).
4. Chemical reclamation of Saline-Alkaline Soils using cement dust treated by solution of a mixture of sulphuric and sulphurous acids and leaching by water.

The object of this study was the Saline-Alkaline soils of Ararat valley in Armenia. The total salts vary from 0.86% to 2.216% in the 0-100 cm layer of soils and the EC indicator from 12.4 to 32.2 mS/cm. The soils have a high alkaline reaction (pH-8.4-10.2) due to the presence of soda -3.4-8.6 mmol/100 g. The contents of water-soluble sodium in the 0-100 cm layer of soil makes 12.03-31.38 mmol/100 g. The contents of soluble Ca^{2+} and Mg^{2+} is not higher than 0.1 mmol/100 g. The soils are strongly alkalized, and the exchangeable sodium percentage (ESP) varies 31.39% to 72.56% in the 0-100 cm layer of soil.

The mechanical composition of soils in the 0-100 cm layer of soil has from medium to heavy loamy mechanical composition.

Results and Discussion. *1. Electrochemical oxidation of sulphurous acid*

As a result of electrochemical process (method 1) of the mixture of sulphuric (H_2SO_4) and sulphurous (H_2SO_3) acids the content of sulphuric acid increased from 35.6% up to 100% and the content of sulphurous acid decreased from 64.4% up to 0%. It means that the whole content of H_2SO_3 was oxidized (fig.2).

The data on fig. 3 show that the mixture of solution contains 42% of sulphuric acid and 58% of sulphurous acid. After 2 hours of electro-treating (method 2.), sulphurous acid was oxidized as a result of it 66.7% of sulphuric and 29.3% of hydrochloric acids were formed.

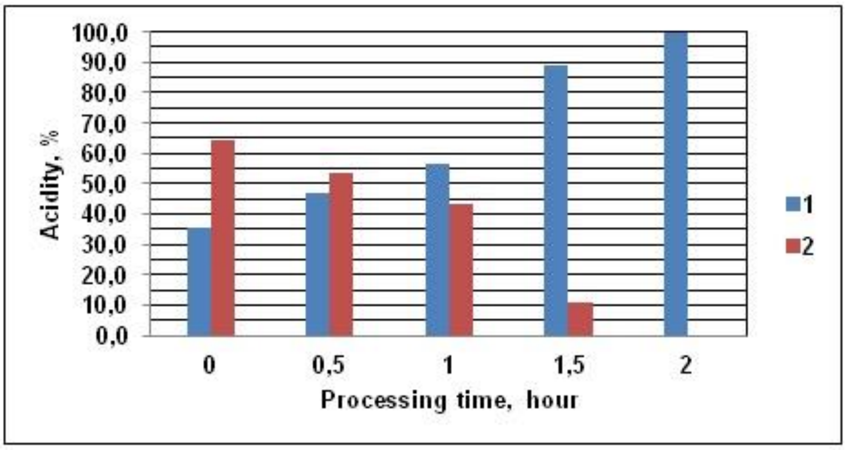

Figure 2. The process of electrochemical oxidation of sulphurous acid and formation of sulphuric and hydrochloric acids. 1-H_2SO_4, 2-H_2SO_3

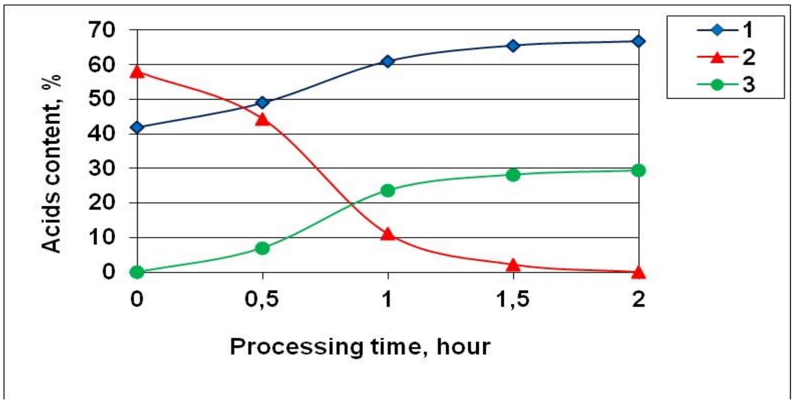

Figure 3. The process of electrochemical oxidation of sulphurous acid and formation of sulphuric acid. 1-H_2SO_4, 2-H_2SO_3, 3-HCl

Using the data of processing, the requirements for producing 1 tons of sulphuric acid are calculated. In the given regime of electrochemical processing, 6.3-8.5 mmol/l of sulphuric acid was formed in case of spending on 1 w–hour of electric energy. For producing 1 t of sulphuric acid 2900-4000 Kw-hour electric energy was required. In order to reduce the cost a solar panel station may be used

2.The study of the possibility of retention of sulphurous gases by water solution of cement dust

The results are shown in tab. 1. The data of the table give ground to assert, that the use of cement dust allows to absorb sulphur gases mostly in the vessel I, where the concentration of acidity makes 135-160 mmol/l (method 3). The concentration of the acid solution was 3-15 mmol/l in the vessel II, which corresponds only to 0.5-2.5% of the formed gas. Thus, the application of 100 g of cement dust absorbed 50 g of sulphur dioxide gas. To absorb 1 t of SO_2 gas, 2 t of cement dust were required.

Table 1. The concentration of acidity in receptacles during the absorption of sulphur gases under different contents of cement dust in the I receptacle

N_o of the receptacles	The contents of cement dust in the I receptacle, g			
	100	200	400	500
The concentration of acidity, mmol/l				
I	160	155	150	135
II	15	10	3	5
III	0	0	0	0

3. Study the influence of newly-received ameliorants (method 4.) for chemical reclamation of Saline-Alkaline soils during their chemical reclamation and leaching processes

In the I variant, both the infiltration and the filtration rates were low during the chemical reclamation and leaching and their values ranged from 1.5-1.6 cm/day. In the II variant, the infiltration rate was higher, than the I variant of it and it is 7.0 cm/day. But the filtration rate was low; it was 1.7 cm/day. In the III variant, the infiltration rate was 9 cm/day, the filtration rate was 4.5 cm/day. In the IV variant, the infiltration rate was 3.7 cm/day and the filtration rate was 1 cm/day. Thus, the filtration rate was higher in the II and the III variants, and in the other variants was much lower.

Variant I.

The content of the exchangeable Ca in 0-25 cm of soil's layer after the chemical reclamation and leaching makes -51.3 % and decreases by depth, and in the 75-100 cm layer of soil it makes 27.8 % of the sum of exchangeable cations. The content of the exchangeable Mg in 0-100 cm layer varies in the range of 32.9-49.4% (table 2.). The exchangeable sodium percentage [ESP] indicator in 0-50 cm layer of soil makes 8,6-14.5 %, which is permissible. In the layer of 50-100 cm, the ESP indicator is a little higher and makes 20.6-23.1% (the permissible ESP is 15%).

The exchangeable K content makes 1,9-2,4% of the sum of exchangeable complex. Thus, in the case of variant I, the norm of the ameliorant was not enough for complete soil reclamation. It is necessary to increase the norm of ameliorant, taking into account, that the ions of SO_3 can form insoluble salt with the Ca and they precipitate in the form of $CaSO_{3.}$

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Variant II.

Discussing the data, brought on the table 2, may be concluded that ESP of the 0-75 cm layer of soil vary in the range of 6.1-13.4%, and only 75-100 cm layer of soil ESP some high and makes 22.2 %. Thus under the influence of the ameliorant, which is used after electrochemical processing of the mixture of acid solution give an opportunity to improve the soil physical and the chemical properties and may be used as a ameliorant for reclamation of carbonate Alkaline soils.

Table 2. The chemical compositions of exchangeable cations of experimental soils before and after the chemical reclamation and leaching (average of 3 repetitions)

Depth, cm	The contents, mmoll/100 g of soil					The contents,%			
	Ca^+	Mg^+	Na^+	K^+	Total	Ca^+	Mg^+	Na^+	K^+
Before the chemical reclamation									
0-25	4.8	1.76	21.2	1.45	29.21	16.4	6.0	72.6	5.0
25-50	5.3	3.26	21.7	1.45	31.71	16.7	10.3	68.4	4.6
50-75	13.8	8.87	11.2	1.41	35.28	39.1	25.1	31.7	4.0
75-100	16.7	7.42	11.7	1.43	37.25	44.8	19.9	31.4	3,8
After the chemical reclamation and leaching									
Variant I									
0-25	19.9	14.84	3.35	0.73	38.82	51.3	38.2	8.6	1.9
25-50	14.85	10.84	4.48	0.73	30.9	48.1	35.1	14.5	2.4
50-75	13.8	10.84	7.61	0.74	32.99	41.8	32.9	23.1	2.2
75-100	9.85	17.49	7.3	0.75	35.39	27.8	49.4	20.6	2.1
Variant II									
0-25	24.55	6.94	2.95	1.47	35.91	68.4	19.3	8.2	4.1
25-50	19.7	14.66	2.29	0.68	37.33	52.8	39.3	6.1	1.8
50-75	12.3	17.34	4.67	0.67	34.98	35.2	49.6	13.4	1.9
75-100	12.3	12.34	7.08	0.18	31.9	38.6	38.7	22.2	0.6
Variant III									
0-25	39.4	13.5	1.04	0.3	54.24	72.6	24.9	1.9	0.6
25-50	42	16.1	1.04	0.3	59.44	70.7	27.1	1.7	0.5
50-75	19.5	21.02	2.29	0.33	43.14	45.2	48.7	5.3	0.8
75-100	16.1	20.76	2.61	0.72	40.19	40.1	51.7	6.5	1.8
Variant IV									
0-25	27.3	10.9	3.74	0.26	42.2	64.7	25.8	8.9	0.6
25-50	12.3	6.34	9.89	0.54	29.07	42.3	21.8	34.0	1.9
50-75	9.35	10.02	10.49	0.59	30.45	30.7	32.9	34.4	1.9
75-100	9.75	9.76	10.11	0.28	29.9	32.6	32.6	33.8	0.9

Variant III.

Discussing the process of improvement of soils may be concluded, that the soils are fully ameliorated. The toxic salts are completely leached. The contents of exchangeable cations (tab. 2) show, that in case of application of 1% of sulphuric acid solution, soil is completely dealkalined and ESP in 0-100 cm layer of soil makes 1.9-6.5%.

Variant IV.

ESP of the 0-25 cm layer of soil makes 8.9%. So, 25- 75 cm layer of soil is not fully reclaimed and the ESP indicator varies in the range of 33.8-34.4%. Although the salts content is significantly reduced, it makes 0.251-0.456%, and the EC rate is 3.5-6.5 mS/cm, so the soils remained weakly salined and alkalined, and need a further improvement of their physical and chemical properties. Particularly, in the variant IV of experiments, it is necessary to increase the norm of ameliorant, considering the fact, that during the reaction between the ameliorants and soils, the hard dissolving salt of $CaSO_3$ is formed, which is not enable to improve the soil chemical properties. The treated cement dust may be successfully used for improvement of the chemical and physical properties of weakly and middle Alkaline soils.

CONCLUSION

1. New ameliorants for improvements of Alkaline soils under the laboratory conditions were obtained: electro-treated mixture of sulphurous and sulphuric acids, treated cement dust containing sulphite and sulphate salts of Ca.
2. Two electrochemical methods for production of sulphuric acid and mixture of sulphuric and hydrochloric acids from sulphurous acid were developed and the electric energy requirement for their production is calculated. It will give an opportunity to increase the ameliorative affections of sulphur and use it for reclamation of Calcareous-Sodic soils.
3. The process of retention of sulphurous gases, by water solution of cement dust is studied. It is shown for conservation of 1 t of sulphurous gases, 2 t of cement dust is required. The treated cement dust may be successfully used for improvement of chemical and physical properties of weakly and middle Alkaline soils.
4. The influence of the newly- received ameliorants on the physical and chemical properties of Alkaline soils during their chemical reclamation and leaching processes were studied. The most ameliorative effect obtained in the variants, where 1% of sulphuric acid solution and electrochemical treated solution of the mixture of sulphurous and sulphuric acids were used.

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