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Interaction Features of Some Acid Ameliorants in the Process of Chemical Reclamation of Sodic Solonetz-Solonchaks

Sahakyan Samvel V.[1], Eloyan Arevik Sh.[1], Yedoyan Tatevik V.[2*], Daveyan Sevak H.[1]

[1]*Department of Amelioration of Research Centre of «Soils Science, Agrochemistry and Amelioration after Hrant Petrossyan», branch of the Armenian National Agrarian University, 24 Admiral Isakov av.,Yerevan 0004, Republic of Armenia*

[2]Faculty of Management and Technology,National University of Architecture and Construction of Armenia, 105 Teryan Street, Yerevan 0009, Republic of Armenia, yedoyantatevik@nuaca.am*

Abstract

The purpose of the study is to reveal the mechanisms of interaction of some acid ameliorants in the process of chemical reclamation of Sodic Solonetzes-Solonchaks (SSS). The experiments have been carried out within 2018-2020 under laboratory conditions using soil column techniques.13 soil samples have been collected from Ararat valley, Republic of Armenia. These soils have a high alkaline reaction (pH 9.5-10.5), a sodium exchangeable percentage (ESP 44.5-74.0%) and electrical conductivity (EC 12.4-42.2 dS cm-1).It has been shown, that in thecase of iron sulphate application the products of its hydrolysis promote soil dealkalization and improvement of soil physical properties due to creation of iron-clay complexes accumulated in the soil primarily in crystalline form (66-67 %). It has been revealed, that the penetration depth of 1% of sulphuric acid and iron sulphate solutions during the chemical reclamation is 8-12 cm, and the accumulation of gypsum in topsoil (0-12 cm) is observed. Due to thehigher solubility of magnesium sulphate in the process of acidification, soil dealkalization and the increase of filtration rate of soil solutions (10-12 cm day^{-1}) are watched. During the soil leaching process, the newly-formed gypsum plays a major role in further dealkalization process of soils and regulation of exchangeable Ca and Mg relation in optimal range. It is shown, that in the process of acidification, the pressure of the formed carbon dioxide gas (CDG) in the soil may reach up to 2.2 atm, in which the solubility of calcium and magnesium carbonate are increased, and the share of CDG in soil dealkalization process is in average 50%. The results obtained allow for the opportunity to recommend improvements of SSS chemical reclamation technology.

Keywords: soil; Ameliorants; Penetration Depth; Reclamation; Products Reaction; Carbon Dioxide Gas

1. Introduction

Soil salinization and alkalization are global problems, which have a negative impact on agricultural productivity and sustainability. As a result of these processes, the chemical and physical properties of soil are going from bad to worse. Soil salinization and alkalization are dynamic processes spread globally inover 100 countries (Shahid et al., 2018). The area of saline and alkaline soils in the world is 932.2 million ha, includingsalt-affected soils with an area of 351.2 million ha and alkaline soils with an area of 581.0 million ha (Abrol et al., 1988; Pardeep and Pradeep, 2020).Thus, the effective and

professional management of soil resources worldwide is indispensable to insure food needs and sustainable agricultural development (Aldabaa and Yousif, 2020; Zein et al., 2020; Saeed and Bedair, 2021; Elramady et al., 2022).

The area of naturallysaline-alkaline soils in Armenia's Ararat plain is approximately 24.5 thousand ha, which are not cultivated and require chemical reclamation. The irrigated areas on the Ararat plain cover around 81 thousand hectares, from which the 19.4 thousand ha of soils are secondary salt-affected and alkalized.

Depending on the soil and hydrogeological conditions, as well as thecountry's technical and economic capability, the following specialized methods of saline and alkaline soilsreclamation, agro-technical, biological, phyto-technical, electrical, and chemical, were devised and implemented(Gupta et al., 2019; Yaseen et al., 2020; Ganzour et al., 2020). The first two are mostly used for improving solonetzic soils under non-irrigated agricultural conditions, and they involve various tillage techniques ensuring the utilization of inter-soil calcium compounds for self-reclamation of soils with a subsequent sowing of relatively salt-tolerant crops-ameliorants(AbouHussien, et. al., 2020). In some countries, such soils are improved by application of manure straw, plugging with green manure crops, sanding, land reclamation((Xie et al., 2019). The following substances are extensively applied for chemical reclamation ofSodic Solonetzes-Solonchaks(SSS): gypsum, plaster, chalk, industrial wastes containing phosphogypsum, calcium chloride, defecates, etc. (Abuhashim and Abdel-Fattah, 2013;Brauen et al., 1977; Farid, 2000; Mace at al., 1999; Sharma, 1988; Temiz and Cayci, 2018). It is shown, that the application of gypsum in conditions of high content of water-soluble and exchangeable sodium is extremely slow and often ineffective(Abdel-Fattah et al, 2015; Abdel-Fattah and Merwad, 2016), which is explained by:

a) bylower solubility of gypsum (2.0 g/l, or 23 mmol L^{-1}). It has been demonstrated that in order to induce an infiltration flow over the soil profile, a calcium and magnesium concentration in soil solution of 60-80 mmol $L^{-1}$is required, which cannot be reached using gypsum,

b) bygypsuminteraction with sodium carbonates and bicarbonatesin soil solution, calcium is precipitated inthe form of calcium carbonate which reduces Ca concentration on theone hand, and precipitation occurs on the surface of gypsum particleson the other hand, covered by the carbonate film, which sharply reduces its solubility.

Positive results have been achieved in Armenia by sulphuric acid (waste of oil production) usage as an ameliorant for reclamation of SSS soils (Rafaelyan, 1959; Petrossyan et al., 1983; Manukyan, 1977; Sahakyan, 1994). In addition to the neutralization of alkaline reaction of soil solution, acidic solutions decompose calcium and magnesium carbonate compounds and promote the formation calcium and magnesium active forms, which also replace the exchangeable sodium in theCation Exchangeable Capacity (CEC) (FAOSoils Bulletin, 1976) (Reactions 1.).

$H_2SO_4+ CaCO_3 \rightarrow CaSO_4+CO_2+H_2O$
$H_2SO_4+ MgCO_3 \rightarrow MgSO_4+CO_2+H_2O$
$CaSO_4 + CEC^{Na} \rightarrow Na_2SO_4 + CEC^{Ca,}$
$MgSO_4+ CEC^{Na} \rightarrow Na_2SO_4+ CEC^{Mg}$
$H_2SO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + CO_2 + H_2O/1/.$
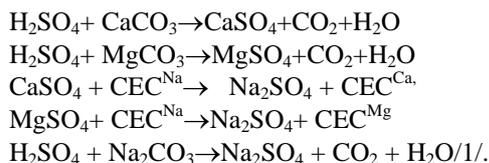
Calcium and magnesium cations increase in CEC is accompanied by coagulation of hydrophilic colloids and decreases the soil disparity, enhancing the water permeability and filtering rate in soils, as well as, improving other physical and chemical properties of soils. The ameliorative effect of iron sulphate (green vitriol), which is the waste of titanium production, is based on its ability to form sulphuric acid and ferrous hydroxide (Reaction 2) in the course of acid hydrolyses(FAO Soils Bulletin, 1976).

$FeSO_4 + 2H_2O \rightarrow Fe(OH)_2 + H_2SO_4/2/.$

The interaction of the formed sulphuric acid with alkaline soils is described above. Ferrous hydroxide increases the coagulation process of soil colloids and improves the physical properties of soil. The technology of SSS reclamation by application of chemical ameliorants: sulphuric acid and iron sulphate was developed by the Research Centre of Soil Science, Agrochemistry and Amelioration of the Armenian National Agrarian University (Manual, 2002).

The technology includes the following stages:
-   Construction of drainage and irrigation systems,
-   Capital levelling of lands and their preparation for application of ameliorants,
-   Ridging of leaching checks,
-   Chemical reclamation and leaching,
-   Agricultural development.

Depending on the hydrogeological conditions and water permeability of the ground, closed horizontal or vertical drainage is used. The groundwater level is lowered to 3.0-3.5 m using collector drainage systems, allowing not only to remove toxic salts from the reclaimed land but also to protect the soil from secondary salinization during the agricultural development.

In the process of chemical reclamation,alkaline reaction is complexly neutralized, the total amount of salts in the layer (0-100 cm) of soil decreases to 0.2-0.3 %, and the content of exchangeable sodium drops

to 3-4 cmol$_c$ kg^{-1} of soil (Petrossyan, et al, 1983;Manual, 2002).

This technology aided in the restoration of the Ararat Plain's SSS soils, bringing 5.5 thousand ha of land back into cultivation. Despite the significant practical work being carried out, some mechanisms of interaction of acid ameliorants in the process of the chemical reclamation of SSS soils have not been fully revealed until now.

The objectiveof this paper is to reveal the features of these acid ameliorants interaction with soilby revealing the role of iron, the penetration depth of 1% solution of sulphuric acid, and the dealkalization influence of the magnesium ions, in addition to the role of carbon dioxide gas in the process of SSS chemical reclamation targeting the chemical reclamation technology improvement of these soils.

2. Material and Methods

The laboratory experiments were conducted to reveal the role of iron in the process of chemical reclamation of SSS with application of iron sulphate, as well as the mechanism of interaction of 1.0% sulphuric acid during the chemical reclamation of SSS. The concentration of sulfuric acid was taken 1%, as several experiments conducted in Armenia, especially by professor Aghababyan, showed, that it is an optimal concentration for chemical reclamation of solonchaks(Aghababyan, 1967).

The first experiments were carried out underlaboratory conditionsduring 2018-2019, using soil columns of one meter in height and15.5 cm in diameter. The soils for the experimentswere selected from area of distribution of typical SSS located in the Arevik community of the Ararat Valley, Armenia (Fig. 1). The location coordinates are: 44.1044 longitude, 40.10782 latitude WGS 84 EPSG:4326.

Samples from three soil layers were taken: 0-33, 33-66 and 66-100 cm. Soil samples were air-dried, crushed and sieved through a 2 mm sieve.
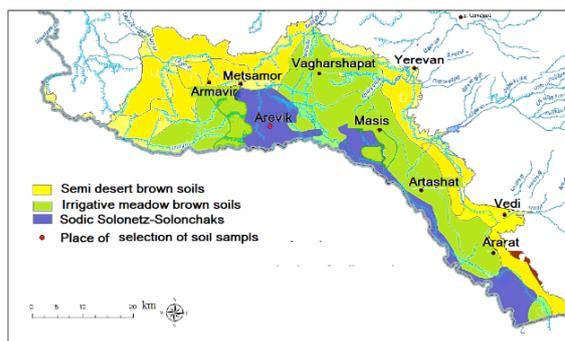

Fig. 1. Soil typesin Ararat valley, Armenia

The samples were transferred layer by layer into the soil columns and slightly compacted, maintaining it density at 1.0-1.1 g cm^{-1}.

The choice of such density is due to the fact that in the reclaimed field, before acidification, soil loosening is carried out, in which the soildensityvaries approximately in this range.

The experiments were performed in three variants, including the following mechanical composition:

I. Light loam, II. Heavy loam, III. Medium clay

Soil texture analysisis done by determining the percentage of sand and clay in the soil samples (Table 1).

Depending on the mechanical composition, the features of the interaction of iron with the soil, as well as changes of water-physical properties, have been studied. The chemical composition of soluble salts,sodium exchangeable percentage(ESP) and CEC of the experimental soils are presented in Table 2 and Table 3.

The initial soils of the columns are typical SSS. The salt content of 0-100 cm of soil layer varied from 0.758 to 2.808 % (EC-13.0-40.8 dScm^{-1}),pH - 10.0-10.5, the content of water-soluble Na - 8.77-38.08, Ca-0.30-0.50, Mg- 0.08-0.16 cmol$_c$ kg^{-1} of soil, ESP is 44.5-74.0%. The norm of iron sulphate for three variants was 551.3, 645.6, 857.0 g/column, the norm of leaching water was 41.6, 50.0, 70.0 l/column accordingly.

The norm of ameliorants is calculatedbyEquation 1 (Manual, 2002).

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$$S = K(M - d) \quad (1),$$

where S is the norm of ameliorant (in t ha^{-1}), M is the sum of total alkalinity(HCO$_3$) and exchangeable Na (in cmol$_c$ kg^{-1} of soil), d is the permissible amount of exchangeable sodium (3cmol$_c$kg^{-1}), K is the conversion coefficient of the norm of ameliorant required for neutralization of 1 cmol$_c$ kg^{-1} of soil, the amount of exchange and total alkalinity in the 1m layer of 1 ha of the plot. K is 6.62 t ha^{-1} in case of sulphuric acid application, and K is 18.77 t ha^{-1} when iron sulphate is used.

TABLE 1. The mechanical composition of experimental soils, %: *I experiment*

Vari-ants	Depth, cm	Fractions, mm						Physical clay, %	Sand, %
		1-0.25	0.25-0.05	0.05-0.01	0.01-0.005	0.005-0.001	<0.001		
I	0-33	0.09	58.8	24.21	2.7	6.83	7.37	16.9	83.10
	33-66	0.21	58.9	23.71	2.68	6.68	7.82	17.18	82.82
	66-100	0.28	61.07	23.24	2.77	6.91	5.73	15.41	84.59
II	0-33	0.30	13.94	46.16	8.97	15.27	15.36	39.60	60.4
	33-66	0.09	9.71	50.74	8.63	14.97	15.86	39.41	60.59
	66-100	0.12	24.34	36.74	8.55	16.53	13.72	38.80	61.20
III	0-33	0.23	12.45	40.08	13.13	16.79	17.32	47.24	52.76
	33-66	0.20	11.96	42.21	13.04	16.51	16.08	45.63	54.37
	66-100	0.27	20.02	29.68	13.8	16.35	19.88	50.03	49.97

TABLE2. The contents of soluble salts in SSS before the chemical reclamation: *I experiment*

Variants	Depth, cm	pH	EC dS cm^{-1}	Total salts, %	cmol$_c$ kg^{-1} of soil						
					CO$_3^{2-}$	HCO$_3^-$	Cl$^-$	SO$_4^{2-}$	Ca^{2+}	Mg^{2+}	Na$^+$
I	0-33	10.3	28.1	1.938	3.27	4.03	15.44	8.48	0.50	0.16	27.29
	33-66	10.2	13.0	0.898	2.73	3.97	4.79	2.89	0.40	0.16	11.09
	66-100	10.3	10.9	0.758	3.13	4.08	3.44	1.71	0.30	0.16	8.77
II	0-33	10.5	40.8	2.808	5.10	9.89	19.75	7.36	0.40	0.08	36.52
	33-66	10.2	37.4	2.571	4.10	4.58	24.25	9.01	0.40	0.02	37.42
	66-100	10.0	37,2	2.559	3.33	4.36	37.36	7.03	0.35	0.03	38.08
III	0-33	10.4	35,8	2.460	5.83	6.34	16.94	10.50	0.55	0.16	33.07
	33-66	10.5	38,7	2.663	6.08	9.97	16.28	8.46	0.50	0.16	34.05

TABLE 3. The contents of exchangeable cationsin SSS before the chemical reclamation

Vari-ants	Depth, cm	Cmol$_c$ kg^{-1} of soil				% of CEC		
		Ca^{2+}	Mg^{2+}	Na^{+*}	CEC*	Ca^{2+}	Mg^{2+}	Na^{+*} (ESP)
	0-33	5.6	4.0	12.9	22.5	24.9	7.6	67.5
	33-66	6.6	3.4	12.9	22.9	28.8	14.8	56.4
I	66-100	8.4	4.2	10.1	22.7	37.0	18.5	44.5
	0-33	6.4	2.5	15.7	24.6	26.0	13.4	60.6
	33-66	6.4	2.2	16.4	25.0	25.6	13.5	60.9
II	66-100	7.1	3.5	15.8	26.4	26.9	13.6	59.5
	0-33	6.9	3.4	22.8	33.1	20.8	10.3	68.9
	33-66	6.8	4.5	22.2	33.5	20.3	13.5	66.2
III	66-100	5.8	2.3	23.0	31.1	18.6	7.4	74.0

* The content of K is small (1-5 %) andis included in the contents of Na

The second laboratory experiment was carried outduring 2019-2020 in three repetitions to disclose the depth of sulphuric acid penetration into the soil, the quantitative change of calcium and magnesium carbonates, the ratio of water-soluble calcium and magnesium in the soil solution, and their interaction with the soil.

The soil sampling place, the method of soil preparations and distribution in soil columns are the same as in the first experiment.The soil columns were of one meter height and 20 cm in diameter. Holes with a diameter of 30 mm were drilled at depths of 0-4, 4-8, and 8-12 cm, and ceramic filters were installed for soil solution collection. The total weight of the soil in each column was 38 kg. The norm of sulphuric acid is 350 g, or in the form of 1.0 % solution is 35 l. During the experiment, the dynamics of filtration rate, the pH and concentration of soil solution were investigated.

Following the calculation of the ameliorant norm, soil samples were selected based on depth: 0-25, 25-50, 50-75, 75-100 cm of soil, and the contents of carbonates, gypsum and magnesium sulphate were determined.The soils in the columns have a medium loamy mechanical composition texture, a high carbonate (18.6 %) and salt content (0.799-1.523 %,

EC-11.5-22.1 dS cm^{-1}), high alkaline reaction (pH-9.5-9.9) and alkalization (ESP-53.0-66.6 %) (Table 4).

Chemical reclamation of SSS by sulphuric acid and iron sulphate is accompanied by active release of CDG, the effect of which in the process of desalination and dealkalization needs to beresearched.The role of CO_2 gas was investigated under laboratory conditions in accordance with the study of interaction mechanism of 1% sulphuric acid.

The partial pressure of CDG in the columns was measured by the general gas equation (Moran and Shapiro, 2000) (Eq. 2).

TABLE 4. Soluble salts and ESP content in SSS before chemical reclamation: II experiment

Depth, cm	pH	EC mScm^{-1}	Total salts, %	CO$_3^{2-}$	HCO$_3^-$	Cl$^-$	SO$_4^{2-}$	Ca^{2+}	Mg^{2+}	Na$^+$	ESP, %
						cmol$_c$ kg^{-1}of soil					
0-25	9.5	22,1	1.523	1.60	2.36	17.52	4.24	0.20	0.08	23.84	66.6
25-50	9.9	16,2	1.119	2.33	3.39	12.52	1.45	0.10	0.16	17.10	57.5
50-76	9.8	12,3	0.850	2.40	3.53	8.16	1.12	0.10	0.24	12.47	54.1
75-100	9.5	11,5	0.799	1.94	2.63	8.68	0.83	0.10	0.32	11.89	53.0

where p is the partial pressure in atm, n is the molar parts of CO_2 gas in the solution, R is the universal gas constant (in latm/K), T is the temperature of the solution (in ^oK), V is the volume of the solution (in litres).

The volumetric approach was used to determine the amount of CO_2 gas released from the soil (Arinushkina, 1970).

3. Results and Ddiscussion

3.1 Identifying the role of iron in the chemical reclamation process

The dynamics of oxidized forms of iron, their change, and removal from the soil were examined during the experiment. Laboratory investigations ofthe reclamation process show that by end of the leaching period (after being supplied 41.6, 50.0, and 70.0 l/column of leaching water), the amount of divalent iron reduces from 120 to 0.3 cmol$_c$ kg^{-1}of soil. The intensive oxidation of divalent iron into trivalent iron takes place in the interval of leaching, when 19-38 l/column of water was given, its concentration in the 0-25 cm layer of soil reaches a maximum value of 5-7 cmol$_c$ kg^{-1}. Withcontinuation

of leaching, the decrease of $Fe^{3+}$is watched andat the end of leaching its content varies in 0.1-0.5 3cmol$_c$ kg^{-1} of soil.

Several kinds of iron and their elimination from the soil during the SSS reclamation have been investigated: silicate - $Fe_{esil} = Fe_{gr} - Fe_j$, crystalline - $Fe_{cris} = Fe_j - Fe_a$, amorphous - Fe_a, where Fe_{gr} is the gross iron, determined by classical method (Vodyanitskii et al., 2007), Fe_j is the iron determined by Mehra Jackson method (1960), Fe_a is the iron determined by the Tamm method (1953). The balance of these elements is given in Table 5.

It was revealed that when the calculated amount of iron sulphate is applied, 1.36-1.80% increase in gross iron is observed. At the same time, the iron removal from 0-100 cm soil layer makes 20.4-28.9 % (from the given iron). The iron accumulated in the soil isin three forms: silicate (4.40-8.80%), crystalline (66.1-67.1%), and amorphous (3.66-5.60%).

Thus, the main part of the penetrated iron into the soil is accumulated in crystallized form, which indicates the accumulation of iron in the soil in the form of iron (II) hydroxide. This assertion is justified by the fact that the iron (II) hydroxide particles are

crystalline, and the iron (III) hydroxides are mostly discharged in amorphous form (Panov and Bykova, 1968; Bernhard et al., 2021). The iron (II) hydroxide supplies the hydration of hydrophilic colloidal soil particles, their coagulation and the formation of micro-aggregates (Nikolidze, 1987). After chemical reclamation in SSS the process of micro-aggregation of soil particles is observed due to thereduction of clayparticles with a diameter of <0.001 mm from 11.2 to 1.1 and 2.2% of the soil fraction and after chemical reclamation 0.005-0.001 mm, from 24.1 up to 8.2 and 2.0%, respectively, when using sulphuric acid and ferrous sulphate. At the same time, the contents of the 0.25-0.05 mm fraction from 5.3 to 24.1 and 22.8% and the 0.05-0.01 mm fraction from

48.4 to 55.5 and 66.0% increases significantly (Fig. 2).

It was shown, that when the iron sulphate was used instead of sulphuric acid, a larger degree of micro aggregation, especially in soil fractions of 0.05-0.01 mmwas recognized. For example, using sulphuric acid as an alternativeincreases the content of this fraction to 55.5%, and using iron vitriol its content increases by66 %(Fig. 2). It is shown that, in comparison tothe original soil, the filtration rate increases by15-40 times depending on the mechanical componentsof the soil, whereas the filtration rate is by 40% greater when the iron sulphate is used than in the variant when sulphuric acid was used(Sahakyan, 1994).

TABLE 5. Balance forms of iron in 0-100 cm layer of SSS, during the chemical reclamation by iron sulphate

Iron balance items	Light loam				Medium clay			
	Fe_{gr}	Fe_{sil}	Fe_{crys}	Fe_{am}	Fe_{gr}	Fe_{sil}	Fe_{crys}	Fe_{am}
Have been in the soil before reclamation, %	5.68	5.10	0.35	0.23	6.45	5.89	0.33	0.23
Entered into the soil with the ameliorant, %	1.36	-	-	1.36	1.80	-	-	1.80
Total	*7.04*	*5.10*	*0.35*	*1.59*	*8.25*	*5.89*	*0.33*	*2.03*
Stay in soil after reclamation, %	6.76	5.22	1.26	0.28	7.22	4.42	1.52	0.33
Accumulated in the soil, % of the entered	79.6	8.84	67.1	3.66	76.1	4.4	66.1	5.60
Removed from 0-100 cm of the soil layer, % of entered	20.4	-	-	-	28,9	-	-	-
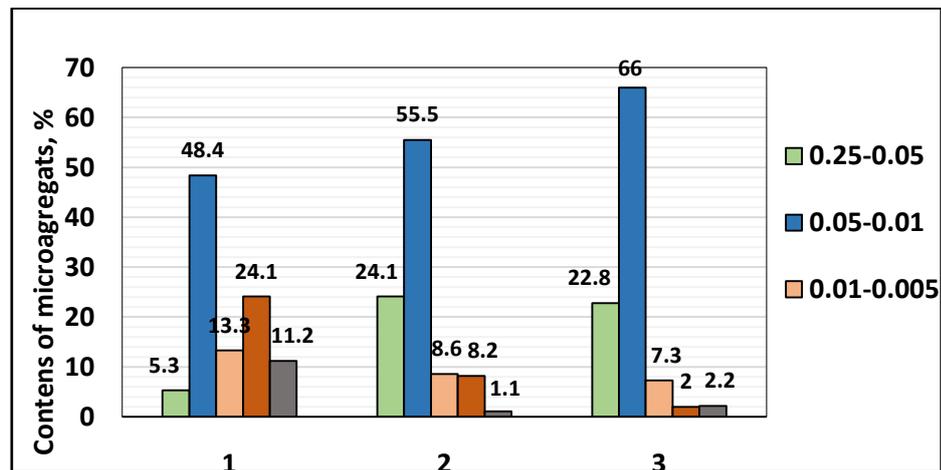
Fig. 2. The changes of micro-aggregate composition in the SSS: without ameliorants (1) during the chemical reclamation by sulphuric acid (2) and iron sulphate (3)

The products of iron sulphate hydrolysis have a good influence on the physical and chemical characteristics of SSS, helping to neutralize the alkaline reaction and keeping hazardous salts below

allowed limits (Luo et al., 2015).

3.2 Sulphuric acid interaction characteristics with SSS

The depth of sulphuric acid penetration into the soil, the quantitative change of carbonates, the kinetics of dissolution of newly generated calcium and magnesium sulphates, and their interaction with the soil-exchangeable complex are all studied.

Filtration rates increaseclearly demonstrate the change in soil physical and physicochemical characteristics during the acidification process (Fig.3A). It steadily rises from near zero to 15-16 cm/day after being givenupto 20-25 litres of 1% sulphuric acid solution. The filtration rate is reduced significantly at the end of acidification and reaches 10-12 cm/day as a result of compaction and repacking of soil particles. Such filtration rate dynamics is typical to SSS chemical reclamation process. The relevant researchesconducted in Armenia by Rafayelyan and Petrossyan confirms this fact (Rafayelyan, 1959, Petrosyan et al, 1983).

According to the variation of pH of soil solution at different depths of the soil, we came to the conclusion, that during the acidification of soils, the maximum penetration of sulphuric acid into the soil does not exceed 8-12 cm from the surface of soil (Fig.3B). Below this depth, the sulphuric acid is completely neutralized and the soilsolutionhas only an alkaline reaction.

The alkaline reaction of the soil solutionvaries especially strongly in the upper 0-4 cm layer, where given norm of sulphuric acid is neutralized. It depends on the filtration rate.
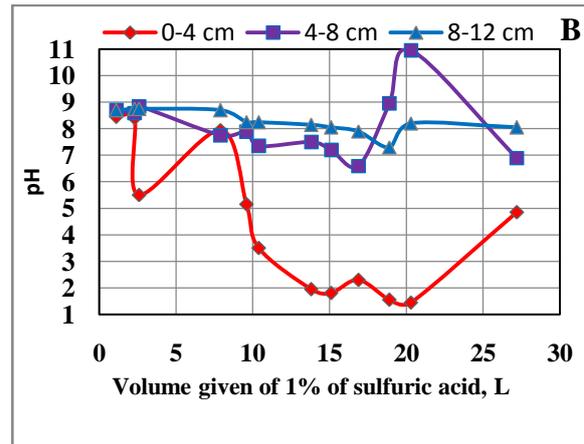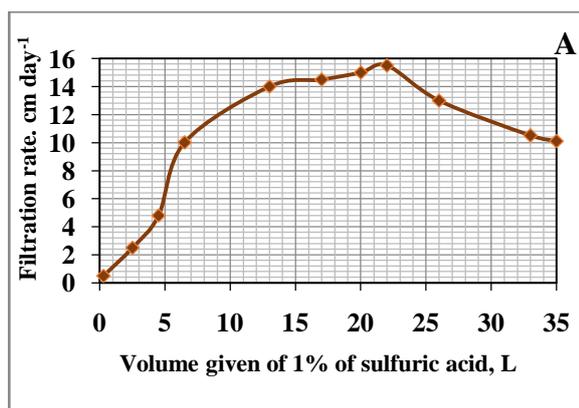

Fig. 3. The dynamic of filtration rate (A) and pH of soil solution (B) in the process of chemical reclamation of SSS with the use of sulphuric acid. Soil layers

As the filtration rate increases, the interaction period of the acid with the soil carbonates reduces, and the pH of the soil solution lowers appropriately, reaching a minimum value of 1.5-2.0 in the 0-4 cm layer after being provided by 15-20 litres of 1% of solution. The pH value increases to 4.5 at the end of acidification (after filtration of 20-27 litres). The pH variation in the soil layer of 8-12 cm is 7.2-8.8, indicating that the soil solution reaction is neutral or alkaline. The dynamics of Ca, Mg, and Na ions clearly shows their quantitative changes in the soil solution during the acidification of SSS (Fig.4). It is known that the solubility of gypsum at does not exceed in 2 g/l, or on average 23 mmol L^{-1}, but in soil solution its concentration usually does not exceed in 10-15 mmol L^{-1}.

The data in Figure 4clearly show, that the Ca^{2+} concentration at the beginning of acidification (2.6 l/column) reaches 30.5-45.3 mmol L^{-1}, exceeding the limit value(26.3mmol L^{-1}), at the first stage of acidification, it is obviously due to the presence of other salts, which increases its concentration. With continued acidification, the calcium concentration remains relativelyhigh, and it isleftin the interval of 20-25 mmol L^{-1}. In the first period of acidification (before the applicationof 10 l/column), the concentration of Mg ions is low- 5-20 mmol L^{-1}. However, when 1% of sulphuric acid solution is applied upto 10-28 l/column, its concentration increases to 100-125 mmol L^{-1}, due to which an active displacement of sodium ions from the CEC and creation of the filtration flow through the soil column are observed.

Due to the active action of the reaction products of acid solutions, the concentration of sodium ions in the interval after havingbeengiven 10-28 l/column of acid solution, it rapidly decreases from 10.9 to 1.3 mmol L^{-1}.

According to balance calculations, 1.1% of calcium sulphate and 3.4% of magnesium sulphate or 11.3 and 73.9% of formatting amounts of the corresponding products are removed along the soil column from the 0-12 cm layer, during the acidification process (Table 6).

Thus, in the acidification process Mg ions play the main role in the exchangeable sodium replacement from CEC, which is favourable for the soil filtration rate increase.Therefore, the acid ameliorants' ability to restore acidity should be significantly diminished when SSS' do not contain magnesium carbonates (Abdul Qadir at al., 2022).

The amount of newly formed gypsum after acidification is basically accumulated in the 0-4 cm layer (13.7%) of soil.
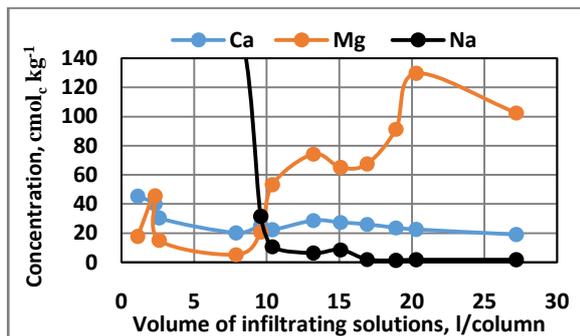

Fig. 4. The dynamics of concentration of Ca, Mg, Na ions at the output of 0-12 cm layer of the SSS in the process of acidification with 1% sulphuric acid solution

By depth, its content decreases and in the 8-12 cm layer of soilis 2.9%. A similar regularity is observed in the decomposition of carbonates in the soil.

The most intensive decomposition occurs to the upper 0-4 cm layer (12% $CaCO_3$ and 2.5% $MgCO_3$). The process of decomposition of carbonates decreases by depth and in the layer of 8-12 cm makes 1.0% of $CaCO_3$ and 0.98% of $MgCO_3$(Table 6).

The amount of formed gypsum is spent during the leaching process, where the dealkalization process has been carried out. Due to lower solubility of gypsum the norms of leaching water, depending on the mechanical composition of soils, ranging from 40 to 90 thousand m^3ha^{-1}, and the leaching period is prolonged up to 6 months. For decreasing the leaching norms and the duration of leaching period the low frequency mechanical oscillations may be used, by vibrator application (Sahakyan, 2011).

3.3 The role of carbon dioxide gas in the process of chemical reclamation

To determine the amount of carbon dioxide gas,which was formed in the process of the chemical reaction of carbonates, with 1% of solution of sulphuric acid, formula *3* is used. The reaction of sulphuric acid neutralization occurs in0-8 cm soil layer. To calculate the partial pressure of carbon dioxide gas, the volume of soil, having 1 m^2 area with the height of 0.08 m was chosen, the volume of which is 0.08 m^3 or 80 litres.If the soil porosity is 50%, the pore space volume is 40 litres. If each litre of 1.0% of sulphuric acid solution contains 10 g of acid, then 40 litres ofit contain 400 g of sulphuricacid.By ratio of the chemical reaction, we determine the amount of carbon dioxide gas:
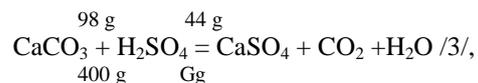
$$\underset{400\text{ g}}{\overset{98\text{ g}}{CaCO_3}} + H_2SO_4 = CaSO_4 + \underset{Gg}{\overset{44\text{ g}}{CO_2}} + H_2O \;/3/,$$

TABLE 6. The change of products of chemical reactions and their balance in 0-12 cm layer of soil in the process of acidification of SSS

Layers, cm	Before the reclamation, %				After acidification, %			
	$CaCO_3$	$MgCO_3$	$CaSO_4$	$MgSO_4$	$CaCO_3$	$MgCO_3$	$CaSO_4$	$MgSO_4$
0-4	16.0	2.6	0.3	0	4.0	0.1	13.7	2.5
4-8	16.0	2.6	0.3	0	11.0	0.6	7.5	0.8
8-12	16.0	2.6	0.3	0	15.0	1.6	2.0	0.3
Products	**Has been In the soil, %**	**Format-ted, %**	**Accumu-lated, %**	**Removes, %**	**Removes, % at the formatted**			
$CaSO_4$	0.3	9.4	8.6	1.1	11.3			
$MgSO_4$	0	4.6	1.2	3.4	73.9			

Gco$_2$ = (44x400)/98=176g. By experimental data only 10% of gas is released into the atmosphere: Gco$_2$ = 179 – (179x10)/100 =179-17,9=161.1g.The partial pressure of CO$_2$ gas is determined by the formula 1.

Let us assume that the soil temperature is 20^oC,then T = 273 + 20 = 293, V= 40 l, R gas constant is 0.082 l.atm/K, n = Gco$_2$/44 = 161.1/44 = 3.66 mol.

The partial pressure of CO$_2$ gas will be: P$_{CO_2}$ = (3.66 x 0.082 x 293)/40 = 2.2 atm.

The dependence of the solubility of calcium and magnesium bicarbonates (Fig. 5.) on the pressure of carbon dioxide gas shows, that at the pressure of 2.2 atm, the solubility of calcium bicarbonate is29.0 mmol L^{-1}, and magnesium bicarbonate is 34.0 mmol L^{-1}. The reaction of calcium and magnesium bicarbonates with CEC may be represented (Reactions 4).

$Ca(HCO_3)_2 + CEC^{Na} = NaHCO_3 + CEC^{Ca}$
$Mg(HCO_3)_2 + CEC^{Na} = NaHCO_3 + CEC^{Mg}/4/.$
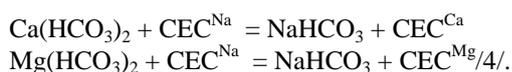
The ion-exchange interactions of calcium and magnesium bicarbonates with the CEC produce NaHCO$_3$, which is leached out of the soil's 0-100 cm layer, while Ca and Mg ions are being absorbedinto the CEC. This regularity is also confirmed by the balance data of gypsum and carbonates (Table 7). From the Table data shows, that the use of chemical ameliorants actually contributes to the consumption of only a part of the resulting fine gypsum, which, respectively, for light, medium and heavy soils in terms of mechanical composition makes 40.0, 63.8, and 65.0%, or an average of 56.0%.

The Table 7shows,thatthe carbonates in the soil were decomposed significantly more than they were theoreticallycalculated. According to the Table 7, 66.0, 57.0, and 32.0 %of carbonates arealso additionally decomposed inthe soil, or on average 51.7 %. This regularity is observed both with the use of iron sulphate and with sulphuric acid.
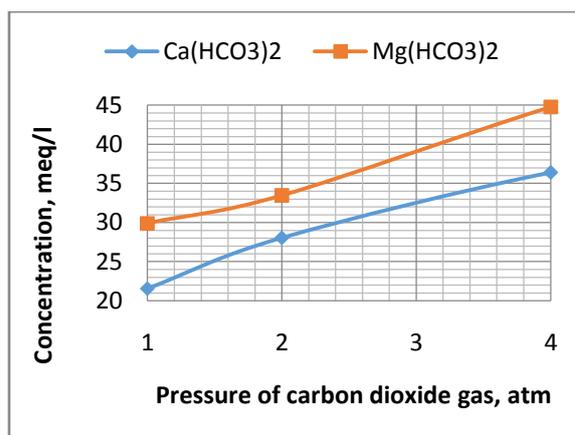

Fig. 5. The dependenceof solubility of calcium and magnesium bicarbonates on the pressure of carbon dioxide gas in the soil

The change of the contents of water-soluble salts at the outlet of 0-100 cm layer of soil columns, is shown in the Table 8. Summarizing the results, we conclude that in the process of acidification, at the outlet of 0-100 cm layer, soil solutions have a strongly alkaline reaction (pH-9.2-9.6), with the sodic content, the total alkalinity decreases during acidification from 460 to 30 mmol L^{-1}. The concentrations of Ca and Mg ions are insignificant, and they make in averages 2.0-2.2 mmol L^{-1}. Thus, the removal of salts takes place mainly in the form of sulphates and sodium bicarbonates.

Table 9 shows the chemical composition of exchangeable ions after chemical reclamation and leaching. Summarizing the data, we can conclude that the soil was completely desalinized and the EC in the 0-100 cmlayer of soil ranging from 0.46 to0.79 dS cm^{-1}.

TABLE 7. Balance of gypsum and total carbonates in 0-100 cm layer of SSS after chemical reclamation

Mechanical composition of soils	Contents of gypsum, g/column					Used, % of the formed
	Before reclamation	Was formed	Total	Left after reclamation	Spent	
Light loam	66,5	329,0	395,5	264,0	132,5	40,0
Heavy loam	67,2	372,9	440,1	202,0	238,1	63,8
Medium clay	70,7	532,8	603,5	256,0	347,5	65,0
					Average	56,3

Contents of carbonates, determined by volume of CO_2, %

Mechanical composition of of soils	Before reclamation	Stay after reclamation	Actual decomposed	Decomposed theoretical	Difference between actual and theoretical	Additionally decomposed, % of theoretical
Light loam	16,31	14,31	2,00	1,20	0,80	66,0
Heavy loam	19,31	17,10	2,21	1,41	0,80	57,0
Medium clay	17,96	15,47	2,49	1,88	0,61	32,0
					Average	51,7

TABLE 8. Removal of water-soluble salts from 0-100 cm layer of SSS in the process of acidification with 1% of sulphuric acid solution

Volume of removed solutions, l/column	pH	mmol L^{-1}					
		HCO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+
0.3	9.2	460	2644	955	8	8	4043
3.9	9.6	130	3.2	89	0.8	0.6	220.8
7.5	9.4	68	3.1	64	0.8	0.3	134
20.2	9.3	67	2.9	85	0.6	0.4	153.9
33	9.4	30	3.2	80	1.6	1.5	110.1

The ESP in the 0-100 cm layer of soil is 6.3-2.3%, which is acceptable. The content of exchangeable Ca and Mg is respectively 69.2-84.9 and 12.1-24.5%.

Summarizing the results obtained, we can conclude that the 50% of calculated norm of the ameliorant is sufficient for chemical reclamation of SSS. This cancelation is confirmed also by experimental studies by Oganesyan, 1988, which proved that when applying 50% and 75% of the calculated norm of ameliorant has the same effect on 0-100 cm layer of soil, as 100% norm.

TABLE 9. EC and the contents of exchangeable cationsof SSS after chemical reclamation and leaching

Depth, cm	EC, dS cm^{-1}	cmolc kg^{-1} of soil				% of CEC		
		Ca^{2+}	Mg^{2+}	Na^+	Total (CEC)	Ca	Mg	Na (ESP)
0-25	0.46	11.0	3.9	1.0	15.9	69.2	24.5	6.3
25-50	0.48	18.0	1.5	1.7	21.2	84.9	7.1	8.0
50-75	0.56	17.0	2.5	1.2	20.7	82.1	12.1	5.8
75-100	0.76	16.0	2.6	2.6	21.2	75.5	12.3	12.3

4. Conclusion

During the chemical reclamation of SSS with iron sulphate, the products of its hydrolysis - sulphuric acid and the iron hydroxide promote the intensification of soil dealkalization process, improvement of soil physical properties due to creation of iron-clay complexes which areaccumulated in the soil primarily in crystalline form (66-67 %).

The penetration depth of acid solutions during the chemical reclamation with sulphuric acid and iron sulphate is 8-12 cm. Under low solubility of newly formed gypsum (2.0 g/l) it is accumulated in the upper 0-12 cm layer of soil.

Due to higher solubility of magnesium sulphate during the acidification process, the soil dealkalization and the increase of the filtration rate of soil solutions are observed. If the SSS contains no magnesium carbonates the reclamation effect of the acid ameliorants should be greatly diminished. During the soil leaching process, the new-formed gypsum plays a major role in further dealkalization process of soils and in the regulation of optimal composition of ions in cation exchangeable complex. Gypsum is less soluble than other minerals, so leaching standards ranging from 40 to 90 thousand m3 ha^{-1}, and the process can take up to six months. By applying a vibrator, low frequency mechanical oscillations can be used to reduce leaching standards and the length of the leaching period.

It has been discovered that CDG, which was formed when acid ameliorants interacted with the carbonates in the soil, has a reclamation function. Moreover, it has been demonstrated that during the acidification process, the pressure of CDG in the soil can reach 2.2 atm, at which calcium bicarbonate solubility can reach 29 and magnesium bicarbonate solubility can reach 34 mmol L^{-1}.

The balance calculations of the content of gypsum and carbonates before and after chemical reclamation show that in the process of soil dealkalizationthe share of CDG is in average 50%.is inaverage around50%.

5. Conflicts of interest
The authors declare no conflict of interest.

6. Formatting of funding sources

None

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