

Investigations

# Comparative Ameliorative Efficiency of Phosphogypsum and Elemental Sulfur in Semi-Terrestrial Soda and Sulfate Moderately Halophytic Solonetz of the Light Gray Earth Subzone

Kanaibek Kubenkulov, Nurzhamal Khokhanbaeva and Askhat Naushabayev

Kazakh National Agrarian University, 050010, Kazakhstan, Almaty, Abaya Avenue, Kazakhstan

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Corresponding Author:  
Kanaibek Kubenkulov  
Kazakh National Agrarian  
University, 050010,  
Kazakhstan, Almaty, Abaya  
Avenue, Kazakhstan  
E-mail: k-kubenkulov@yandex.ru

**Abstract:** The article presents the data from field tests on determination of the relative ameliorative efficiency of equivalent dosages of phosphogypsum and elemental sulfur on the alkaline saline semi-terrestrial solonetz. Basing on the analysis data of soil water extract, higher ameliorative efficiency of elemental sulfur compared to phosphogypsum and fast amelioration of alkali-saline soils with the use of sulfur have been detected. Ten month of phosphogypsum and elemental sulfur incubation in soils significantly affected presence and contents of the salts, restructuring their ionic contents and growth of total salts. The latter required carrying out washing of the soils from the starting primary and newly formed secondary salts from root-inhabited soil layer. Washing of the soils ambiguously affected the ionic contents of the soil solution. It created more benefactor conditions on the elemental sulfur variant, to a greater degree reducing contents of all ions compared to phosphogypsum (the exception was  $\text{HCO}_3^-$ ).

**Keywords:** Alkali-Saline Soil, Fertility, Amelioration, Sulfur, Phosphogypsum

## Introduction

Alkali-saline soils are widespread in two regions of the Republic of Kazakhstan: In the grain belt among black soils and chestnut soils in the form of solonetz and saline-alkaline soils (over 25 million ha) and in the southern part, among the most fertile soils in the foothill plain of Northern Tien-Shan, sprayed meadows, meadow-brown and meadow-gray soils (7.09 million hectares) (Borovskiy, 1978). The main method of amelioration is the introduction of phosphogypsum. However, research in the recent years has shown low efficiency of traditional ameliorants like gypsum and phosphogypsum on the alkali-saline soils due to the rapid reduction of their initial efficiency due to coating of the surface of crystals with insoluble film of calcium carbonate, which isolates them from the environment (Feofarova, 1950; Chawla and Abrol, 1982).

Among of all chemical ameliorants, sulfur had the lowest efficiency. Therefore, it had been almost never used and the problem of increasing its ameliorative

efficiency was not paid attention to. However, the recent rapid growth of the volume of oil and gas production in the country has resulted in a sharp increase in the volume of their processing and accumulation of its by-product, elemental sulfur, the amount of which in the Republic exceeded 8 million tons. The country has become the largest (second to Iran only) sulfur storage in the world (SDPT, 2011), hence increasing the value of the problem of its disposal. Our research in 2009 and 2012 showed that in the first year, only 25% of introduced sulfur was transferred into its oxide forms, forming sulfuric acid, therefore, in order to obtain a full ameliorative effect from it four years were required (Tazabekov and Bespalova, 1988).

Thus, the above-mentioned circumstances in place in the Republic, i.e., the presence of considerable areas with alkaline saline soils in the zone of intensive agriculture, the low economic efficiency of the currently used ameliorant, phosphogypsum and the huge amount of accumulated sulfur require developing technologies of

ameliorating alkaline saline soils with the use of sulfur. In our opinion, this problem may be solved by speeding up oxidation of elemental sulfur, which is possible with high dispersion capacity of its particles.

## Program and Methods

The studies were performed in 2015 and 2016 on the territory of LLC "Amiran" in the Talgar district of the Almaty region.

To identify the relative ameliorative efficiency of phosphogypsum and elemental sulfur on the alkali-saline soils, a plot with the area of 0.5 hectares was chosen. The soil of the field was the soda and sulfate moderately halophytic semi-terrestrial high-sodium moderate solonetz. The field experiment was laid by using calculated equivalent dosages of ameliorants. Calculation of gypsum dosages (g) was carried out according to the Agayev's formula (1966) (following from 100%  $\text{CaSO}_4 \times 2\text{H}_2\text{O}$ ):

$$G = 0.086x(\text{Na}^+ - 0.1T) + [(\text{CO}_3^{2-} + \text{HCO}_3^-) - 1,0]xN \times SD, t / ha$$

Where:

- $\text{Na}^+$  = The contents of exchange sodium, mg-eq per 100 g soil  
 $N$  = The thickness of ameliorated layer, cm  
 $SD$  = The soil density, g/cm<sup>3</sup>  
 $E$  = The adsorption capacity, mg-eq per 100 g soil  
 0.086 = The calcium to gypsum transition coefficient  
 0.1 = The coefficient allowing maintaining of 10% exchange sodium in PPK of the alkali soils  
 $(\text{CO}_3^{2-} + \text{HCO}_3^-)$  = The contents of these ions in water extract, mg-eq per 100 g soil  
 1.0 = The amount  $(\text{CO}_3^{2-} + \text{HCO}_3^-)$  in water extract which was not damaging to plants, mg-eq per 100 g soil

To transform the gypsum percentage to phosphogypsum and elemental sulfur the gypsum doses were multiplied correspondingly by 1.10 and 0.19 coefficients.

Phosphogypsum from the Tarazphosphate fertilizer plant and micronized sulfur from the Atyrau oil refinery (1966) were used as ameliorants (MILPC, 1981). The scheme of the field experiment was the following:

No.	Variants of the experiment	Dosages of ameliorant, t/ha
1	Reference	-
2	Phosphogypsum	27
3	Elemental sulfur	5

The plot area was  $(3 \times 5)$  15 m<sup>2</sup>, the experiment was repeated 3 times. Covering of ameliorants into the soil was carried out by plowing to the depth of 29 cm with subsequent disking. Samples of soil were taken in the spring before the introduction of ameliorants (26.06.2015), in the autumn after 4.5 month of ameliorants' incubation (07.11.2015), in the spring and the summer of the next year before (26.03.2016) and after (28.04.2016) washing. The depth of sampling was 0-20, 20-40 and 40-60 cm. Ion contents of water extract were determined in them, obtained by filtering the soil suspension with soil to water ratio of 1:5. The field experiment was performed according to the standard methods (Dospekhov, 1985; Coyne and Thompson, 2006).

To remove secondary salts that had formed due to the interaction of phosphogypsum and elemental sulfur as well as sodium salts displaced from the adsorbed complex, in 2016 washing of the soil was carried out. Feeding of the calculated washing water amount was supplied to the plot in 2 stages (6.04 and 14.04.2016) in the amount of 6,900 l, or 4,600 m<sup>3</sup>/ha. During the entire amelioration period the optimal soil humidity was maintained within the ranges of 70% of its least water capacity.

## Results and Discussion

Data for the analysis of the water extract from the starting contents of the soil salts in the experiment variants indicate their soda and sulphaticity and average salinity level (sum of salts is 0.5-0.7%) (Sokolov, 1985) (Table 1).

In the soil solution, ions are present in the quantities that affect growth and development of plants. However, the greatest harm is registered from alkalinity. The alkali salinity of the site is indicated by presence of  $\text{HCO}_3^-$ , in amounts exceeding its threshold concentration, which is 0.8 mg-eq (number of milligrams of the ion equal to its equivalent) per 100 g of the soil. Its content usually increases with the depth reaching 1.7-2 mg-eq per 100 g soil. Presence of  $\text{CO}_3^{2-}$ , is only indicated at depths of 40 to 60 cm in an amount also exceeding its threshold concentration (0.03 mg-eq per 100 g soil), in connection with which the lower soil horizons have higher alkalinity (pH is 8.2 to 8.5).

The contents and distribution of chloride-ion by the profile of soil is uniform (0.60-0.75 mg-eq per 100 g of soil) in the amounts twice exceeding its threshold toxicity (0.35 mg-eq per 100 g of soil). This distribution of chlorine-ion is the evidence of the absence of both leaching and exudative water regimes in the soil profile. Of ions, the highest concentration is characteristic of the sulfate-ion (7-8 mg-eq per 100 g soil) exceeding its threshold concentration (1.7 mg-eq per 100 g soil) more than 4-fold. Its content decreases with the depth down to 4 to 5 mg-eq per 100 g of soil.

From the anion compositions stated above, it follows that the soils of experimental site have been represented by alkaline sulfate type of salinization.

The cation composition of the water extract of soils is characterized by high content of calcium and sodium and less content of magnesium. The increased concentration of sodium may be explained by significant soil salinity.

Thus, the initial state of ameliorated soil is characterized by moderate alkalinity due to the increased content of bicarbonate iron along the entire profile and the presence of normal carbonates in its bottom part, as well as high content of sulfate ion, which, with increased content of  $Ca^{2+}$  and  $Na^+$ , form toxic salts with the predominance of sodium salts ( $NaHCO_3$ ,  $Na_2SO_4$ ).

**Table 1:** Initial composition of aqueous extract of alkali and sulfate moderately alkaline high sodium semi-terrestrialsolonetz,

Variants	Depth (cm)	$\left(\frac{mg - eq}{\%}\right)$							Sum of salts (%)	pH
		$HCO_3^-$	$CO_3^{2-}$	$Cl^-$	$SO_4^{2-}$	$Ca^{2+}$	$Mg^{2+}$	$Na^+ + K^+$		
1 Reference	0-20	1.440	None	0.650	8.25	4.370	2.500	3.340	0.692	8.0
		0.087	None	0.022	0.39	0.087	0.030	0.076		
	20-40	1.620	None	0.550	8.38	4.750	2.750	3.050	0.715	8.2
		0.098	None	0.019	0.40	0.095	0.030	0.070		
2 Phosphogypsum	0-20	1.700	0.370	0.600	8.88	5.000	2.880	3.700	0.774	8.2
		0.103	0.011	0.021	0.42	0.100	0.034	0.085		
	20-40	1.120	None	0.750	8.63	4.250	2.880	3.370	0.777	8.1
		0.068	None	0.026	0.41	0.085	0.034	0.077		
3 Sulfur	0-20	1.560	None	0.700	4.25	1.750	1.380	3.690	0.454	8.2
		0.095	None	0.024	0.20	0.035	0.016	0.084		
	20-40	1.640	0.480	0.600	4.13	2.250	1.500	3.100	0.459	8.3
		0.100	0.014	0.021	0.19	0.045	0.018	0.071		
3 Sulfur	0-20	1.480	None	0.650	7.75	4.000	2.880	2.750	0.659	8.1
		0.090	None	0.022	0.37	0.080	0.034	0.063		
	20-40	1.920	None	0.750	5.38	2.500	1.750	2.290	0.516	8.2
		0.117	None	0.026	0.25	0.050	0.021	0.052		
40-60	2.320	0.600	0.750	4.38	2.000	1.250	4.800	0.56	8.5	
	0.141	0.018	0.026	0.21	0.040	0.015	0.110			

**Table 2:** The influence of equivalent dosages of phosphogypsum and elemental sulfur on the composition of aqueous extract of the moderately alkaline-sulfate high sodium semi-terrestrialsolonetz in the subzone of light gray earth  $\left(\frac{mg - eq}{\%}\right)$

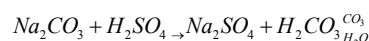
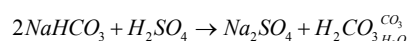
Variants	Depth (cm)	$\left(\frac{mg - eq}{\%}\right)$							Sum of salts (%)	pH
		$HCO_3^-$	$CO_3^{2-}$	$Cl^-$	$SO_4^{2-}$	$Ca^{2+}$	$Mg^{2+}$	$Na^+ + K^+$		
Reference	0-20	1.520	Traces	0.600	6.500	3.50	2.500	2.620	0.583	8.3
		0.092	Traces	0.021	0.310	0.07	0.030	0.060		
	20-40	2.360	Traces	0.400	5.000	1.63	0.860	5.060	0.553	8.5
		0.143	Traces	0.014	0.240	0.03	0.010	0.116		
Phosphogypsum	0-20	2.560	Traces	0.400	3.630	1.50	0.750	3.700	0.739	8.6
		0.156	Traces	0.019	0.170	0.03	0.009	0.085		
	20-40	1.560	None	0.550	7.130	3.63	2.380	2.240	0.603	8.2
		0.095	None	0.019	0.340	0.07	0.028	0.051		
Sulfur	0-20	1.560	0.120	0.500	8.750	1.75	1.250	7.920	0.772	8.5
		0.095	0.003	0.017	0.420	0.03	0.025	0.182		
	20-40	2.560	0.240	0.600	8.000	1.88	1.130	8.400	0.804	8.8
		0.156	0.007	0.021	0.380	0.03	0.013	0.193		
Sulfur	0-20	0.800	None	0.600	13.25	5.00	2.880	6.630	0.995	7.4
		0.048	None	0.021	0.636	0.10	0.034	0.156		
	20-40	1.000	None	0.600	13.00	4.00	2.500	8.100	0.998	7.4
		0.061	None	0.021	0.620	0.08	0.030	0.186		
40-60	1.140	None	0.600	8.750	4.00	2.630	3.870	0.71	7.4	
	0.069	None	0.021	0.420	0.08	0.031	0.089			

Results of analysis of the water extract from the soil samples (Table 2), sampled 4.5 months after starting the experiment from the control variant, demonstrate presence of significant changes in concentrations both in contents of anions: Increase of  $\text{HCO}_3^-$  in the lower 20-40 and 40-60 layers from 1.65 to 2.45 mg-eq, decrease in  $\text{SO}_4^{2-}$  from 8.0 to 4.00 mg-eq and cations: Drastic decrease in  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in lower layers, correspondingly, from 4.9 to 1.55 mg-eq and from 2.8 to 0.80 mg-eq, some increase in concentrations of  $\text{Na}^+$  in subsurface horizon (20-40 cm) from 3.05 mg-eq to 5.06 mg-eq per 100 g soil.

These changes in the concentration of ions in the liquid phase of soil in the reference variant determine increased concentrations of the most toxic salts of sodium in the composition of the solution ( $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$ ) and decreased share of less toxic (especially  $\text{Na}_2\text{SO}_4$ ) and non-toxic ( $\text{CaSO}_4$ ,  $\text{Ca}(\text{HCO}_3)_2$ ) salts. The ion composition stated above is manifested in intervals in the pH values, significantly increasing it from 8.1 to 8.3.

Introduction of phosphogypsum significantly increased content of  $\text{SO}_4^{2-}$  in 0-40 cm soil layer from 6.56 to 7.94 mg-eq per 100 g soil and insignificantly lowered their concentrations and increased content of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in 0-20 cm layer. Increase in sulfate ion concentration occurs due to release of  $\text{SO}_4^{2-}$  contained in phosphogypsum into the solution and increased content of sodium is due to its displacement from the soil adsorption complex by calcium ions in phosphogypsum. Thus, the 4.5 months incubation of phosphogypsum in the alkali-saline semi-terrestrial solonchak had significant influence on the ionic composition of the aqueous extract by increasing the content of sulphate and sodium ions in it, without substantial changes in the content of other ions.

Moreover, in contrast to phosphogypsum, sulfur more significantly affected the contents of water extract, which was associated with formation of sulfuric acid as a result of sulfur oxidation with sulfur-oxidizing bacteria according to the scheme:  $\text{S} \rightarrow \text{SO}_2 \rightarrow \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ . The most significant changes were manifested in the content of ion  $\text{HCO}_3^-$ , where its initial content in layers 0-20, 20-40 and 40-60 cm equal to 1.48, 1.92 and 2.32 mg-eq per 100 g soil decreased to 0.80, 1.00 and 1.14 mg-eq, respectively. Moreover, the content of  $\text{CO}_3^{2-}$  observed in the initial soil (of 0.60 mg-eq per 100 g of soil) disappeared. The noted aspects signify higher efficiency of elemental sulfur for reducing high alkalinity of alkali-salinized soils, compared to phosphogypsum. They are explained by the neutralization reactions, which occur according to the following scheme:



The occurrence of the reaction above is confirmed by growing concentrations of sulfate ion. So, while before the introduction of elemental sulfur, the content of  $\text{SO}_4^{2-}$  in the layers 0-20, 20-40, 40-60 cm was 7.75, 5.38 and 4.38 mg-eq per 100 g soil, respectively and after 4.5 months of elemental sulfur incubation in soil, its content increased to 13.25, 13.00 and 8.75 mg-eq per 100 g soil, or 171, 242, 200%, respectively.

It follows from the outlined scheme (Kubenkulov *et al.*, 2013) that due to interaction with sulfuric acid the calcium and partially magnesium carbonates as well are destroyed, which results in the appearance of their newly formed bicarbonates. They are captured during the analysis of the water extract, data of which demonstrate growth in concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in layers 20-40 and 40-60 cm, respectively, amounting to 160, 200% and 143, 210%, compared to their values before the introduction of elemental sulfur. The introduction of sulfur even more increases the sodium contents compared to phosphogypsum which can be explained due to higher displacement of the sodium ion from the soil adsorbent complex. It is manifested in layers 0-20 and 20-40 cm. While prior to sulfur introduction, the content of sodium in aqueous extract amounted respectively to 2.75 and 2.29 mg-eq, after 4.5 months of incubation, its contents increased to 6.63 and 8.10 mg-eq per 100 g of soil, or 241 and 354%. Hence, elemental sulfur, along with a higher neutralization of alkaline salts, is also more actively involved in desalinization of soil, compared to phosphogypsum.

To determine the effect of autumn and winter climatic conditions of 2015-2016 on ameliorative soil state of experiment variants in the early spring of the next year (6.03.2016), we have examined the state of experimental sites. It turned out that the surface of the soil with ameliorants was puffier and the plough horizon was looser than in control variants. A bit later (26.03.2016), soil samples were taken for determining the influence of autumn and early-spring climatic conditions on the salt composition of soils in the variants of the experiment and water extract contents therein were determined (Table 3).

It follows from the data of Table 3 that climatic conditions had no significant influence on the salt composition of soils in the reference variant, while in the variants with ameliorants, the 1.5 times decreased concentration of  $\text{NaSO}_3^-$  was observed in layer 0-40 cm in the variant with phosphogypsum (from 1.65 mg-eq to 1.13 mg-eq) and 2 times (from 1.65 mg-eq to 0.82 mg-eq) in the variant with sulfur.

**Table 3:** The influence of autumn –winter and early-spring climatic conditions on the salt composition of soils in the variants of the experiment,  $\left(\frac{mg - eq}{\%}\right)$

Variants	Sample depth (cm)	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	Sum of salts (%)	pH
Reference	0-20	1.700	none	0.500	4.250	3.150	0.800	2.600	0.457	8.1
		0.104		0.018	0.204	0.063	0.059	0.059		
	20-40	1.600	none	0.500	4.750	3.250	0.900	2.700		
Phosphogypsum	40-60	0.098		0.018	0.228	0.065	0.011	0.062	0.482	8.1
		0.520	none	0.400	5.000	1.500	0.300	4.120	0.421	7.8
		0.032		0.014	0.246	0.030	0.004	0.095		
	0-20	0.880	none	0.300	6.000	5.080	0.830	1.260	0.495	7.8
		0.054		0.011	0.288	0.102	0.011	0.029	0.558	8.1
	20-40	1.380	traces	0.230	6.250	2.920	0.530	4.420		
Sulfur	40-60	0.084		0.008	0.300	0.058	0.006	0.102	0.585	8.2
		1.260	0.56	0.330	6.250	2.830	0.560	4.720	0.472	7.2
		0.077	0.59	0.019	0.300	0.057	0.007	0.109		
	0-20	0.730	none	0.230	5.920	4.250	0.960	1.660	0.472	7.2
		0.045		0.008	0.284	0.085	0.012	0.038	0.582	7.6
	20-40	0.900	none	0.270	7.170	3.250	0.830	4.250		
40-60	0.055		0.009	0.344	0.065	0.011	0.098	0.647	7.8	
	1.770	0.56	0.260	6.670	3.500	0.700	5.060			
	0.108	0.59	0.009	0.320	0.070	0.008	0.116			

The aforementioned changes indicate continuing chemical and physical and chemical processes in the soils with degradation products of the dissolved part of phosphogypsum (Ca<sup>2+</sup> и SO<sub>4</sub><sup>2-</sup>) and with formed sulfuric acid. They are manifested in a noticeable increase in the content of SO<sub>4</sub><sup>2-</sup>, compared to the reference variant. Thus, while in the reference variant its content in the 0-40 cm layer of soil was 4.50 mg-eq, in the variants with phosphogypsum and elemental sulfur it was 6.55 mg-eq and 6.13 mg-eq per 100 g of soil, respectively. The increase in the content of Ca<sup>2+</sup> to 4.0 mg-eq compared to the reference (3.20 mg-eq) in the variant with phosphogypsum, should be related to the calcium part of phosphogypsum released into the solution and its growth to 3.75 mg-eq in the variant with elemental sulfur - to the calcium in its carbonate released into the liquid phase of the soil as a result of its decomposition by sulfuric acid. One should also note higher concentrations of Mg<sup>2+</sup> (0.90 mg-eq per 100 g of soil) in the option with sulfur, compared to phosphogypsum (of 0.68 mg-eq), which can be explained only by the magnesium of its carbonate that is also released into the solution as a result of its decomposition by sulfuric acid.

The content of sodium ion in the aqueous extract of soil by the spring deadline in the reference variant is slightly less, compared to the autumn one, which may be explained by its leaching with autumn and early spring rainfall.

Thus, the ten-month incubation (26.06.2015 to 26.03.2016) of phosphogypsum and elemental sulfur in the semi-terrestrial alkali-sulfate moderately saline high-sodium medium solonetz from the area of light

gray earth had significant influence on the content and composition of salts, by altering their ionic composition, increasing the amount of salts and reducing pH in soil. Some increase of the sum of salts due to secondary salts, especially in the variant with sulfur, requires performing the next phase of soil amelioration–washing of the salts from the root-inhabited layer of the soil.

Before leaching, soil was plowed to the depth of 25 cm. Soils in the reference variant were not leached due to their extremely low permeability, but were moistened with 1,000 liters of water per plot, or 667 m<sup>3</sup>/ha. Soil was leached with ameliorants in two stages (6.04.2016 and 14.04.2016) by feeding calculated amounts of flushing water in four cycles (two per each stage). The total amount of flush water supplied to the plots was 6,900 l or 4,600 m<sup>3</sup>/ha. The water supplied in the last fourth cycle (1,500 l) to the plots with phosphogypsum, due to low permeability of soil, was absorbed much slower (5 days) compared to the variants with elemental sulfur (2 days). The marked ones indicated weak ameliorative efficiency of phosphogypsum on the soil permeability.

To establish the efficiency of leaching the soil after two weeks (28.04.2016), soil samples were taken and ionic composition, totals and pH of the aqueous extract were determined (Table 4).

From the analysis of the aqueous extract it follows that irrigation and leaching soils contributed to a sharp increase in the content of ions HCO<sub>3</sub><sup>-</sup> and appearance of CO<sub>3</sub><sup>2-</sup> and, as a consequence, increase in alkalinity, especially in the reference and in the variant with phosphogypsum.

**Table 4:** The results of analyzing water extract of soil samples taken after leaching,  $\left(\frac{mg-eq}{\%}\right)$

Variants	Sample depth (cm)	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	Sum of salts (%)	pH
Reference	0-20	3.040	0.750	0.250	3.170	1.750	0.330	5.400	0.738	8.6
		0.185	0.022	0.009	0.152	0.035	0.004	0.124		
	20-40	3.040	0.640	0.360	3.420	1.580	0.330	5.550	0.545	8.6
		0.185	0.019	0.013	0.164	0.032	0.004	0.128		
	40-60	2.370	0.430	0.500	3.660	1.420	0.260	5.280	0.503	8.6
		0.145	0.012	0.018	0.176	0.028	0.003	0.121		
Phosphogypsum	0-20	5.730	0.320	0.350	2.750	1.500	0.300	3.500	0.617	8.5
		0.349	0.009	0.012	0.132	0.030	0.004	0.081		
	20-40	3.000	0.400	0.350	2.750	1.920	0.330	3.830	0.469	8.4
		0.183	0.012	0.012	0.132	0.038	0.004	0.088		
	40-60	2.310	0.240	0.300	3.370	1.750	0.400	4.070	0.455	8.3
		0.141	0.007	0.011	0.168	0.035	0.005	0.094		
Sulfur	0-20	1.980	0.400	0.300	1.750	2.370	0.300	1.600	0.315	8.2
		0.121	0.012	0.011	0.084	0.047	0.003	0.037		
	20-40	2.010	0.360	0.200	3.330	3.620	0.630	0.550	0.393	8.2
		0.123	0.011	0.007	0.159	0.072	0.008	0.013		
	40-60	2.820	0.350	0.250	2.660	2.330	0.570	4.220	0.471	8.3
		0.172	0.011	0.009	0.128	0.047	0.007	0.097		

Thus, while in the soils in the reference variant before irrigations the average content of HCO<sub>3</sub><sup>-</sup> in the 0-40 cm soil layer was 1.65 mg-eq and CO<sub>3</sub><sup>2-</sup> was absent, after the irrigation the content of HCO<sub>3</sub><sup>-</sup> increased to 3.04 mg-eq and CO<sub>3</sub><sup>2-</sup> appeared in significant amount (0.70 mg-eq). Soil irrigation in the reference variant resulted in a marked decrease in the concentration of sulfate ion (from 4.50 to 3.30 mg-eq), calcium (from 3.20 to 1.67 mg-eq), magnesium (from 0.85 to 0.33 mg-eq) and drastic sodium increase (from 2.65 to 5.47 mg-eq), which eventually resulted in a considerable increase in the amount of salts (from 0.467 to 0.642%) and alkalinity (pH from 8.1 to 8.6).

The results of the washing the salts of variants with ameliorants were ambiguous. While soil leaching in the variant with phosphogypsum resulted in considerable increase in the content of HCO<sub>3</sub><sup>-</sup> from 1.13 to 4.36 mg-eq and CO<sub>3</sub><sup>2-</sup> to 0.37 mg-eq per 100 g soil (absent before leaching), then in the elemental sulfur variant it led to increase in contents of the HCO<sub>3</sub><sup>-</sup>, correspondingly, from 0.81 to 2.00 and CO<sub>3</sub><sup>2-</sup> from 0.00 to 0.38 mg-eq, i.e., at the latter one more benefactor soil conditions for plants were provided.

Soil flushing also had positive effect on the content of SO<sub>4</sub><sup>2-</sup> in the soil, significantly reducing its concentrations from 6.13 to 2.75 mg-eq in the variant with phosphogypsum and from 6.55 to 2.54 mg-eq in the variant with sulfur. The influence of leaching on the content of Ca<sup>2+</sup> in the soil solution was manifested in a considerable decrease from 4.00 to 1.71 mg-eq per 100 g soil in the variant with phosphogypsum and a slight decrease from 3.75 to 3.00 mg-eq in the variant with elemental sulfur. The same behavior was observed in the

content of Mg<sup>2+</sup>, although its concentration was much lower than Ca<sup>2+</sup>. Leaching resulted in a decrease in Mg<sup>2+</sup> from 0.68 to 0.32 mg-eq per 100 g soil in the variant with phosphogypsum and from 0.90 to 0.46 mg-eq per 100 g soil in the variant with elemental sulfur.

The influence of leaching on the content of Na<sup>+</sup> in the soil in the variants of the experiments also proved controversial. In the variant with phosphogypsum, an increase from 2.84 mg-eq to 3.66 mg-eq was observed, whereas in the variant with elemental sulfur, a considerable decrease was observed (from 2.96 to 1.08 mg-eq per 100 g. of soil), which was explained by high water permeability of the soil in the latter.

The results of quantitative changes in the ionic composition of the liquid phase of soil from the introduced ameliorants and soil flushing had unambiguous effect on total salts. So, while the introduction of ameliorants resulted in increased amounts of salts in variants both with phosphogypsum and elemental sulfur (with some advantage in the latter), leaching had little effect on salt removal (only 0.032%) in the variant with phosphogypsum from 0.527 to 0.543% and in the variant with elemental sulfur to higher desalination, where the salt content decreased from 0.527 to 0.354%. Moreover, after flushing salts in the variants with phosphogypsum became more toxic due to the "peak" of alkalinity.

## Conclusion

The aforesaid factual materials obtained on the basis of the field experiment for determining the comparative efficiency of amelioration of

phosphogypsum and elemental sulfur on the moderately alkali-sulphate saline high-sodium semi-terrestrial solonchaks in the subzone of light gray soils indicate the significant advantage of elemental sulfur over phosphogypsum, which allows reducing the duration of the amelioration period down to one year.

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## Author's Contributions

All authors equally contributed in this work.

## Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and there are no ethical issues involved.

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