Efficiency of chemical ameliorants for reclamation of bore mud and solonetzic soils of Siberia and Ural

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Abstract. The problem of solonetzic soils fertility is still one of the most important in the country. The areas of Siberia and Ural make up about 10 million hectares. To improve chemical properties of solonetz, chemical method of amelioration is applied. It’s possible to use this method on the bore muds. Number of mud storage pits only in Khanty-Mansisk is about three thousand. On Yamal the situation is the same. As ameliorants-coagulants in the conditions of Siberia and Ural their natural reserves, wastes of mining and chemical industry can be used. The method of tubes was used for the comparative analysis of the studied ameliorants. Equal soil and bore mud samples with increasing doses of coagulants allow to assess maximal filterability of solonetz, bore mud and reveal their optimal dose. The studies have shown that choice of ameliorant-coagulant is mostly determined by the chemism of soil and bore mud salinization, and also content of exchangeable sodium in soil adsorption complex. As promising ameliorants-coagulants we should consider the wastes of chemical industry – phosphogypsum, and as raw material of mining industry – gypsum, carnallite, calcium chloride.

1.  Introduction

The saline soil including solonetz-like soils are widely spread in numerous countries. According to V.A. Kovda, their area in the world is about 950 million hectares. Within Russia Federation they occupy about 30 million hectares, including 10 million hectares in Western Siberia. The scientists of Russia and Western Siberia in particular have accumulated rich experience on amelioration of these soils [1-4].

The difficulty in mastering of solonetzic soils is connected with the variety of their properties within the limits of each soil and climatic zone. The designing of solonetz amelioration depends on hydrological condition, chemism and degree of salinization, depth of water-soluble salts occurrence, exchangeable sodium content in solonetz horizon, availability of gypsum and carbonates in the layer of 0-40 cm, power of humus horizon etc.

During the amelioration of solonetzic soils it's recommended to apply two main methods: chemical and self-amelioration. Chemical amelioration is based on the process when chemical substances, ameliorants, are added to soil and after the interaction with solonetz the fundamental changes of its chemical and physical properties take place. Gypsum, phosphogypsum, sulphuric acid, acid wastes of industry, green vitriol etc. can be such ameliorants. Under their influence an alkalinity is neutralized, sodium is removed from soil and soil material transfers into aggregate state. Solonetz becomes mellow, it is able to absorb and let precipitation wetness and meltwater through into deep horizons, its efficiency is able to increase up to the level of zonal soils [5-7].

2.  Materials and methods
The obligatory condition of chemical amelioration is availability of materials, corresponding characteristics of solonetzic soils properties for every filed massif. The scientists of Siberia and Ural have accumulated experience of amelioration of solonetz with gypsum, phosphogypsum, sulphuric acid, green vitriol, artificial aggregate stabilizer etc.

It's important to note that in conditions of Western Siberia and Ural there are all potential possibilities to actively master these lands. Thus, Altai Territory possesses local reserves of gypsum (about 20 deposits), its large reserves in Ural are located in Perm Territory (Kungur town), reserves of carnallite are in Salikamsk, diatomite – in Kamyshev (Sverdlovskiy region) and northern districts of Tyumen region. In conditions of Polar Ural there is zeolite deposit. This region uses as ameliorants-coagulants wastes of chemical industry in form of phosphogypsum (Revdan town), wastes of paint and coatings industry in form of green vitriol (Chelyabinsk region), carbonic calcium gypsum (industrial waste, Ekaterinburg town), muds of surface and artesian waters cleaning (Tyumen etc). Mining of calcium, magnesium and iron-bearing materials are often used in building sphere and their wastes can be utilized on scientific basis for the ameliorative mastering [8-12].

Taking into account properties of salinized soils even within the limits of one land-user, efficiency of different coagulants will be different. In connection with this, we have carried out comparative study of influence of different ameliorants-coagulants, represented by the wastes of chemical and mining industry.

Goal and objectives of the studies – to determine comparative efficiency of different ameliorants-coagulants on chemical and physical properties of solonetz and bore mud.

The object of study is meadow solonetz. In the first case the studied solonetz refer to multisodium, even its surface can contain up to 40% of exchange capacity and solonetz and sub-solonetz horizons – up to 56-72%. Degree of soil salinization of tested plot is very high. Maximum of salts refers to solonetz and sub-solonetz horizons (table 1).

By anion content, solonetz refers to sulphate-sodic, by cation content – to magnesium-sodium, by the occurrence depth of upper border of water-soluble salts it's saline. Response of soil solution of crusted solonetz changes from alkaline (layer 0-10 cm) to strongly alkaline in the soil stratum of 10-60 cm.

| Depth, cm | Salts sum, % | HCO₃⁻ | Cl⁻ | SO₄²⁻ | Ca²⁺ | Mg²⁺ | Na⁺ |
|----------|--------------|-------|-----|-------|------|------|-----|
| 0-10     | 0.284        | 0.138 | 0.007 | 0.029 | 0.006 | 0.003 | 0.0058 |
| 10-20    | 0.389        | 0.26  | 0.2  | 0.06  | 0.3  | 0.24 | 2.58 |
| 20-40    | 0.416        | 0.246 | 0.007 | 0.029 | 0.008 | 0.004 | 0.025 |
| 40-60    | 0.373        | 4.04  | 0.2  | 0.6   | 0.4  | 0.3  | 4.14 |
| 60-80    | 0.341        | 0.253 | 0.008 | 0.038 | 0.003 | 0.002 | 0.112 |
| 80-120   | 0.333        | 3.98  | 0.24 | 0.19  | 0.014 | 0.003 | 0.001 |

The second object of studies was presented by meadow solonetz which refers to chloride-sulphate (neutral) type of salinization. By cation composition it's sodium or sodium-calcium one (Table 2). Content of water-soluble salts in horizons A₅₉ (0-22 cm) and B₂ (22-41 cm) is 0,385; 0,492%,
correspondingly. Ca$^{2+}$ and Mg$^{2+}$ prevail in the content of absorbed cations. Exchange capacity in the layer 0-30 cm is 33.7-35.5 mg-eq/100 g of soil.

Table 2. Analysis of water extract of meadow neutral solonetz of Tyumen region.

| Layer depth, cm | Salts sum, % | HCO$_3$- | Cl$^-$ | Mg-eq/100 g of soil | SO$_4^{2-}$ | Ca$^{2+}$ | Mg$^{2+}$ | Na$^+$ |
|----------------|--------------|----------|-------|---------------------|-----------|---------|---------|-------|
| 0-10           | 0.362        | 0.012    | 0.082 | 0.149               | 0.034     | 0.006   | 0.079   | 3.42  |
| 10-20          | 0.408        | 0.20     | 2.34  | 3.10                | 1.72      | 0.50    | 4.18    |       |
| 20-40          | 0.492        | 0.048    | 0.118 | 0.110               | 0.023     | 0.015   | 0.096   |       |
| 40-60          | 0.572        | 0.78     | 3.38  | 2.30                | 1.04      | 1.24    | 4.18    |       |
| 60-80          | 0.626        | 0.38     | 4.72  | 2.90                | 0.92      | 1.44    | 5.64    |       |
| 80-100         | 0.519        | 0.034    | 0.158 | 0.226               | 0.023     | 0.017   | 0.130   |       |

As the third ameliorative object there are bore muds of northern district of Tyumen region. Chlorides and hydrocarbonates prevail in the composition of their water extract. Samples of the bore mud have as a rule chloride-sodic salinization by anion composition and calcium-sodium salinization by cation composition. The source of chlorides is sea sedimentary deposits. The source of soda is caustic and soda salt which is added to the content of bore mud to facilitate the drilling process (table 3.).

Table 3. Results of water extracts of the bore mud, 2006.

| BM samples | Water extract | | | | | | | |
|------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
|            | potassium K$^+$ | sodium Na$^+$ | calcium Ca$^{2+}$ | magnesium Mg$^{2+}$ | chloride Cl$^-$ | sulphates SO$_4^{2-}$ | carbonates CO$_3^{2-}$ | bicarbonates HCO$_3^{-}$ | Dry remains, % |
| 1          | 0.002         | 0.052         | 0.02          | 0.006         | 0.071         | 0.0001        | 0.006         | 0.079         | 0.21          |
| 2          | 0.061         | 2.244         | 0.499         | 0.251         | 2.00          | 0.0011        | 0.100         | 1.200         | 0.26          |
| 3          | 0.003         | 0.076         | 0.01          | 0.003         | 0.107         | 0.00008       | 0.006         | 0.085         | 0.17          |
| 4          | 0.077         | 3.319         | 0.249         | 0.126         | 3.00          | 0.00085       | 0.100         | 1.400         | 0.26          |
| 5          | 0.004         | 0.047         | 0.02          | 0.006         | 0.053         | 0.00007       | 0.0           | 0.061         | 0.17          |
| 6          | 0.130         | 3.819         | 0.499         | 0.251         | 1.00          | 0.00029       | 0.0           | 0.120         | 0.20          |
| 7          | 0.096         | 2.036         | 0.499         | 0.251         | 1.500         | 0.00075       | 0.0           | 1.00          | 0.20          |
| 8          | 0.005         | 0.088         | 0.02          | 0.006         | 0.036         | 0.00028       | 0.0           | 0.073         | 2.42          |

The content of exchangeable sodium in the bore mud varies from low to medium sodium. Considering that the chemical and physical properties of bore mud are identical to saline soils, and the number of mud storage pit in Khanty-Mansiisk autonomous district reaches only about three thousand, the situation is similar in the YNAO, this suggests similar approaches to their remediation. A number of coagulant ameliorants used on solonetz according to the results of our research can be used on the bore muds.

Methodology of studies. We determined the effectiveness of coagulants in laboratory conditions by tube method. Combination of similar samples in the tests with neutral and sulphate-sodic solonetz under the increasing samples of different ameliorants with equal gradation and following water filling with
constant norm provided demonstration of different filterability. This is stipulated by the activity of coagulation and displacement of exchangeable sodium from the soil absorbing complex. Comparative action of all tested ameliorants was assessed according to the water filtration. As a standard we used traditional coagulant – gypsum, maximal amount of filtrate was taken as one. Analogous dose was compared with all other ameliorants, including bore muds.

Preliminary analysis of water extract was carried out according to the following methods: alkalinity, from the soluble carbonates (CO\textsubscript{3}) - by potentiometry, by chloride-ions argentometry according to Mohr, sulphate-ions in the presence of indicator nithromazo – according to Aidinyan, calcium and magnesium – by chelatometry, potassium – by difference or by flame-photometry.

| Ameliorants, including industrial wastes | Sulphate-sodic solonetz | Neutral solonetz | Bore mud |
|----------------------------------------|-------------------------|------------------|---------|
| Without ameliorant (control)           | 0                       | 0                | 0       |
| Gypsum (CaSO\textsubscript{4}·2H\textsubscript{2}O)(st) | 1.00                    | 1.00             | 1.00    |
| Calcium chloride (CaCl\textsubscript{2}·2H\textsubscript{2}O) | 1.20                    | 1.10             | 1.10    |
| Quick lime                            | 0.97                    | -                | 1.00    |
| Slack lime                            | -                       | -                | 0.20    |
| Ferric sulphate (FeSO\textsubscript{4}·7H\textsubscript{2}O) | 0.84                    | 1.10             | 1.70    |
| Aluminum sulphate (Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}·18H\textsubscript{2}O) | 0.97                    | 1.10             | 1.10    |
| Diatomite                             | -                       | -                | 0.08    |
| Carnallite                            | 0.20                    | 1.10             | 0.80    |
| Mud of artesian waters cleaning (heat-treated) | -                       | -                | 0.02    |
| Mud of surface waters cleaning (heat-treated) | -                       | -                | 0.02    |
| Phosphogypsum                         | 1.10                    | 0.80             | 1.20    |

Note: maximal filtration on solonetz of sulphate-sodic salinization made up 75 ml/day by the gypsum, 80 ml/day on neutral and 10 ml/day – on the bore mud.

The data of table 4 shows that the main part of studied minerals and their wastes after the mining and chemical industry are able to fundamentally change physical properties of saline soils and bore mud. It's important to note that without their introduction, there was almost no filterability of these soils and bore muds. This indicates the impossibility of fundamental improvement of these objects without chemical amelioration. The studies have proved the main provision that the ameliorant dose on solonetzic soils depends on the content of exchangeable sodium in them. Neutral solonetz with low level of sodium required 2 times less amount of ameliorant for maximal filtration then high-sodium solonetz of sulphate-sodic salinization.

Preliminary studies have demonstrated wide possibility to use mining and chemical industry wastes for amelioration of solonetz of sulphate-sodic salinization. Filterability varied within 0.84 – 1.20 in relation to the gypsum effect (taken as unit). Influence of carnallite wastes was very weak, under the index 0.2 in relation to gypsum. The range of use of ameliorants on neutral solonetzic could be compared with influence of the standard (gypsum). Range of use of ameliorants on neutral solonetzic soils was wider. All studied ameliorants can be used to master them.

Reclamation of the bore muds in conditions of northern regions of Tyumen region is connected with bad hydrophysical and chemical properties, such as: ash structure, crust formation, high hydrophilic nature, very weak water permeability, alkalinity, toxicity etc. Application of coagulants fundamentally illuminates the series of their negative properties.

It's reasonable to use presented ameliorants, excluding slack lime, on the stage of biological reclamation of the bore muds.
3. Conclusion.
To master the saline soils of different chemism together with traditional ameliorant – gypsum, we should actively use wastes of mining and chemical industry in a form of calcium chloride, ferric sulphate and aluminum, phosphogypsum and quick lime. Carnallite wastes proved themselves well on low-level sodium solonetze soils of neutral salinization and the bore muds.

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