Production of bentonite and humus natural organic substances from fluoride compounds

Bakhron Boynazarov[1], *Tolib* Berdiyev[2], *Uktam* Temirov[3], *Pirnazar* Ganiev [4], and *Najimuddin* Usanbaev[5*]

[1]Tashkent State Agrarian University, 111218 . University str., 2, Uzbekistan
[2]Research Institute of Soil Science and Agrochemistry, 100179, Tashkent, Almazar district, str. Qamarniso 3, Uzbekistan
[3] Navoi State Mining and Technology University, 210100 Galaba Str. 27, Uzbekistan
[4]Tashkent State Technical University named after Islam Karimov, University str., 2, 100095 Tashkent, Uzbekistan
[5]Institute of General and Inorganic Chemistry, 77a Mirzo Ulugbek, 100170 Tashkent, Uzbekistan

Abstract. In this paper, scientific research has been conducted on the production of fluoride disinfectants based on local raw materials in order to neutralize fluorine-contaminated soils in the vicinity of industrial enterprises. At the same time, the processes of fluoride ion binding of environmentally safe, biologically active drugs obtained on the basis of various bentonites, humic substances and chemically and physically modified bentonites were carried out in 0.1 normal sodium fluoride solution. Interaction of fluoride ion in fluoride solution with bentonite samples, oxidized charcoal, humic acid extracted from oxidized charcoal and humic calcium was studied in a wide range (100: 1 to 100:10) of the ratios of fluoride solution and the mentioned drugs.

1. Introduction

Protection of the country from pests and fertilizers in excess of the norm in order to increase the number of industrial enterprises, increase the yield of agricultural crops, as well as reduce the size of irrigated arable land per capita due to population growth, water scarcity, large-scale construction of industry and housing. Due to the use of fertilizers, there is an increase in the amount of substances in the soil that adversely affect the development of plants in the soil, as well as human health. These substances are primarily physical, chemical, biological of the soil. and ultimately has a detrimental effect on productivity.

The main sources of soil contamination with fluorine-containing compounds are aluminum, steel, ceramics, phosphorus fertilizers, glass, cement and brick plants. Phosphorus fertilizers are also a source of damage to soils and agricultural crops, as more than 50% of fluoride in phosphorus is retained in the form of slightly soluble salts in fertilizers. The entry of fluorine into the agroeco system is mainly due to the release of industrial wastes into the atmosphere. The radius of influence of aluminum giant enterprises is extremely large, exceeding 50 km. Significant fluoride contamination of the soil leads to a decrease in its fertility and quality of agricultural products. It is therefore recommended that the amount of fluoride in the soil and plants be monitored regularly. In experiments carried out on low-yielding soils, soil leaching was observed as a result of the application of sodium fluoride to the soil. The high level of damage (1000 mg of fluoride per 1 kg of soil) led to a significant change in the soil, its structure was disrupted and signs of alkalinity appeared. The high level of damage altered the structure of the humus substances. A water-soluble layer of organic matter was formed on the surface of the soil [1].

It is known that plants grown near fluoride-contaminated sources receive it in large quantities, which leads to the accumulation of the element in food products. Studies have shown that the amount of fluoride in wheat, potatoes, rice does not exceed 0.5 - 1 mg / kg of dry mass. When the amount of phosphorus and complex fertilizers is increased, as well as when crops are grown near sources contaminated with fluorides, their fluoride content increases several times (2-10 mg / kg). Fluoride can enter plants not only in the form of complex anions, but also in appearance.

---

*Corresponding author: najim70@mail.ru

Gaseous fluoride is absorbed by plants through the leaves or through the cuticle. Currently, fluoride is the most dangerous and most phytotoxic micropolyutant among other harmful substances such as SO, SO_2, No.

There are no data on the phytotoxicity of fluoride in root absorption, but according to the data of various authors, the total concentration of fluoride on the surface of the soil layer in the range of 200 to 1000 mg / kg is relative to the calculated phytotoxicity. Fluoride affects plant metabolism and slows the rate of oxygen absorption, disrupts respiratory function, reduces nutrient absorption, reduces chlorophyll levels, kills starch synthesis, disrupts DNA and RNA, and more inhibits a number of processes. It has a stopping effect on the hydrolysis of hexadisiphosphoric acid and is an inhibitor for the formation of lactic acid. There are reports that fluorides inhibit enzymes such as enolza, phosphoglucomutase, phosphatase. The activity of phosphoglucomutase and acid phosphatase decreases even at small concentrations. When plants are well supplied with nutrients, their resistance to fluoride increases. Fluorine has antagonistic properties in plants to calcium, magnesium, potassium, nitrogen. A synergistic effect on phosphorus has been identified. The reaction of plants to fluoride contamination is characterized by a weakening of the growth rate and a decrease in productivity until some symptoms appear. A synergistic effect on phosphorus has been identified. The reaction of plants to fluoride contamination is evident from the weakening of the growth rate, the decrease in yield, until some symptoms appear. However, the most dangerous consequence of fluoride damage is its accumulation in forage plants. Accumulation of fluoride in plant products used by humans is considered dangerous. Many fluorine organic substances also interact with iron and manganese, which are dangerous in their composition, and the complex forms enzymes and compounds that are vital for plants, leading to the breakdown of catalysts. Fluoride, first radiated from calcium and then from chlorophyll, also precipitates magnesium and magnesium-activated enzymes, forming a number of harmful phosphorus-fluoride-magnesium complex compounds. converts into substances. Organic compounds of fluorine extracted from soybeans have been found to be 500 times more toxic than inorganic compounds present in water and air. mg / kg dry mass. Plants have different resistance to high levels of fluoride [2].

Among them, the most resistant to sarsabil concentrations are beans, cabbage, carrots, willow, sensitive to barley, corn, gladiolus, apricots, pine. There is a difference in the accumulation of fluoride between varieties and genotypes of some species. The need for fluoride in plant life activities has not been proven, but fluoride has been identified in all plant species. The amount of fluoride in sorghum, beet leaves in ferns 139, 134 and 85 mg / g of dry matter, respectively, in legumes, carrots, potatoes k a 2,3,6; 30 mg / g mg / g of dry matter.

The results of the analysis of the state of fluorine in the environment show that in recent years there has been an increase in the negative impact of fluorine-containing compounds on the agro-ecosystem. Sources of fluoride in plants can be different: man-made, agrogen, aerogen, etc. It should not be overlooked that no part of the biosphere is contaminated with fluoride, because they are closely related in nature. For example, atmospheric contamination of the soil layer with fluoride causes its natural water to leach into water bodies, rivers or groundwater. Under irrigation conditions, the toxic element vapor eventually returns to the soil, resulting in exposure to both human-consumed products and animal feed. In all cases, human health suffers as a result of increased damage along the trophic chain. Given the high toxicity of fluorine, there is a great risk of contamination of the natural environment with this element. Even local pollution around large industrial enterprises poses a threat to the health of the population of this region [3].

In such cases, nature is an open system with toxins, all its joints are interconnected. Atmospheric and Pollution Open Systems Fluorine can spread through the hydrosphere for tens and hundreds of kilometers to the extent that it threatens the agroeco system. Great attention is paid to the use of agrochemicals (fertilizers and ameliorants) in the consideration of methods of polluting the environment.

In the total amount of fluoride contamination of agricultural lands, they occupy an insignificant amount. Local pollution of the natural environment with harmful elements, including fluoride, by chemical plants producing mineral fertilizers has a negative impact on the environment. Mankind must change its attitude towards nature before it is too late for the soil cover that provides food to more than 90% of the world's population.

Attempts to replace environmentally friendly mineral fertilizers in local agriculture with various wastes of industry, utilities, energy facilities (composts from household waste, sewage sludge, cement dust, slag waste, etc.) pose a serious threat. All of them, as a rule, contain large amounts of fluoride and other contaminants. Due to their low percentage of useful biogenic elements, it is necessary to use them in high doses to meet the needs of agriculture in fertilizers and chemical ameliorants. This leads to contamination of the soil, as well as other parts of the ecological chain with various toxic substances, including fluorine. Knowing the sources of soil contamination with fluoride and other toxic elements, it is important to imagine that they will enter agroeco systems. For example, man-made pollution of the biosphere can be reduced by converting various industrial facilities to modern low-waste or non-waste technologies. have outdated technologies, especially if the environment cannot be reconstructed, they should be closed. Non-traditional types of fertilizers and chemical ameliorants are possible only if their environmental

safety is carefully confirmed by Ra. and its application under sanitary-hygienic control is agrochemical and It is necessary in the toxic determination of the degree of soil contamination of all agricultural lands and the differential approach to their use. If the amount of substances in the soil-plant system Down system is acceptable, they can be used to grow food crops. At the same time, it is necessary to: optimize the nutritional conditions of crops grown using organic and mineral fertilizers, which often significantly reduce the penetration of toxic elements into cultivated plants; selection of field and vegetable crops that, due to their genetic nature, absorb less toxic substances from the soil and do not respond to the presence in the soil to certain value chemical reclamation of soil (plastering of acidic saline soils), which has a certain positive effect even when the soil is contaminated with fluoride; Systematic monitoring of the amount of pollutants in agro-ecosystems[4-7].

In the following study [8], the results of field studies of fluorine and if of arable soils located in the zone of man-made wastes of the cryolite plant, al agrochemical indicators depending on the distance to the source, the degree of contamination and the aggregation of soil aggregation were determined.

Experiments on soils and the amount of fluoride in them, in the field and on small plots, studied the effect of fluoride contamination on plant productivity, tested the background of protection against fluoride contamination. Under the toxic effects of fluoride, abnormalities in the anatomical structure and formation of generative cells have been identified. Fluorine is present in the environment mainly as hydrogen fluoride, metal fluorides and fluorine gas. The second is a yellow-green gas with a pungent odor. Chemically, it combines with metals to form fluorides, particularly sodium fluoride or calcium fluoride. The first, unlike the second, is easily soluble in water. Hydrogen fluoride is a colorless gas formed by the reaction of fluorine with hydrogen, which is readily soluble in water to form a corresponding acid [9].

In the following work [10], field experiments have shown that phytoremedia phytoremediation of soils contaminated with fluorides of aluminum production of field crops widely used in agriculture is not equal. The value of the surface mass of plants grown in contaminated soil was determined by their resistance to polyutantic effects.

The accumulation of fluoride in it depended more on the type of field crop than on the damage to the soil. Decreases in the efficiency of bioaccumulation of water-soluble fluorides from contaminated soil were observed in the following order: oily radish yellow donnik topinambur> corn> shark goat. The results allow us to see yellow donnik and oily radish as promising species to improve fluoride-contaminated crop soils.

In this study [11], the qualitative composition of two samples of vermicompost from different batches of the same producer and the effect on the state of humus in agro-gray soils contaminated with aluminum fluorides were studied. It has been shown that vermicompost, which is characterized by a large amount of organic matter and low mobility fractions, helped to enhance the wetting process and ensured the stable state of humus in the affected soil. The introduction of less humus vermicompost, which contains mobile fractions of sediments, in contrast, activated mineralization processes, which increased the risk of degradation of contaminated soils.

The following [12] study presents the results of determining the direction of change under the influence of soil humus contamination. Naturally, regardless of heavy metals or fluorides, changes in humus status were associated with an increase in the amount of carbon in the labile pool and a decrease in stability. Negative changes in the ratio of ponds indicate that the stability of the humus system in contaminated soils is compromised.

2. Materials and Methods

Most of them are characterized by low humus resource, which significantly increases the risk of degradation under conditions of ongoing man-made damage. Rational use of contaminated soils in agriculture requires the implementation of measures aimed at maintaining the optimal ratio between its labile and sustainable components to improve the quality of humus.

Excessive levels of harmful substances in the soil lead to damage to plants, deterioration of the quality of agricultural products, which adversely affects the health of animals and humans. The synthesis and application of environmentally safe drugs for the implementation of modern agro-technical measures in the decontamination of contaminated areas where agricultural products are grown and increasing soil fertility is one of the urgent tasks today.

From the above, it is clear that the decontamination of soils contaminated with fluoride is very important, in this regard, it is advisable to use local raw materials, to increase soil fertility, as well as substances that have harmful properties.

Based on the above, bentonite clays from the Azkamar and Navboxor deposits, dried in normal weather conditions and ground to a size of 0.1 mm in a grinding mill, were used in this work. Their chemical composition is given in Table 1.

Oxidized coal and its humic calcium and humic calcium synthesized on the basis of humic acids and humic acid, which play an important role in increasing soil fertility, were also studied to determine the possibility of converting fluorine in fluorine briquettes into a form that cannot be assimilated by plants. To obtain oxidized coal, it was dried under normal air conditions and ground in a grinding mill to a size of 0.25 mm and had the following composition (heavy.%): Moisture 15.66; kuli 14.90; organic 69.44; relative to the organic mass, a sample of Angren brown coal with humic acid 3.82 and fulvic acid 0.91 was used.

Oxidation processes were carried out at a concentration and mass ratio of 10 to 30% solution of hydrogen peroxide and coal (organic part): H_2O_2: 1: 0.1 to 1: 0.6. The experiments were carried out as follows, a solution of hydrogen peroxide was added to a pre-poured tubular reactor while the coal was added and oxidized for two hours. In all experiments, after the process was completed, the reaction mass was dried in air and the moisture, ash, organic matter, humic acids, fulvic acid and residual coal were determined. When the oxidation of coal was carried out in the ratio of 10% hydrogen peroxide and coal: $H_2O_2 = 1: 0.6$ mass, the maximum amount of humic acid was obtained 63.75%. Under optimal conditions, ie 20% hydrogen peroxide, coal (organic part): $H_2O_2 = 1: 0.2$ mass ratio, the amount of humic acid increased from 3.98% to 53.69% when coal was oxidized for two hours at a temperature of 700C. Under optimal conditions, oxidized coal has the following composition (weight.%): Humidity 48.2; kuli 10.35; organic matter 41.45; humic acid relative to total organic matter 53.64.

As noted, humic acids were isolated from oxidized coal to determine fluorine binding from fluorine briquettes. We separated humic acids from oxidized coal as follows. After the oxidation process was complete, we separated the solid phase from the liquid phase by centrifugation. We then washed it with distilled water from water-soluble acids to a neutral medium. The resulting solid phase was treated with an aqueous solution of 1% NaOH, then the liquid phase was separated from the solid phase. To precipitate the humic acids, we treated the filtrate with a 5% NSl solution.

The precipitate obtained was purified from chloride ions using distilled water (qualitative reaction) and dried to a constant mass at 70 ^{0}C. The composition of humic acids isolated from oxidized coal is as follows (relative to the organic part) (%.): Moisture content 3.83; ash 6.63; carbon 51.11; hydrogen 3.26; nitrogen 3.76; oxygen and sulfur 41.87; functional groups; -COOH 5.02 mg-eq / g, -OH 4.64 mg-eq / g.

It should be noted that their structure has a significant impact on the agronomic properties and fertility of soils. Structural soils will have optimal conditions for moisture, air, heat and nutrient regime. Gumat calcium is a highly effective soil structurer. Its molecular mass can range from 1,000 to 100,000, depending on the amount of hydrocarbon radicals.

When humate calcium is applied, the capillary and total moisture capacity of the soil increases, water permeability, moisture resistance of the structure and soil aggregates improves, air exchange and water retention properties in the root developing layer of the soil increase. Calcium humic ameliorant-humate was obtained on the basis of oxidized coal and its fluorine-damaging properties were determined.

To do this, the coal was oxidized with hydrogen peroxide under the above conditions. Unquenched lime was added to the oxidized coal at a pH of 6-6.5 while constantly stirred. After the lime was added, it was stirred for another 30 minutes. It was then dried at a temperature of 75-80ºC. The resulting product was obtained in the form of particles of various shapes, from dark red to black in color, with the following composition (weight.%): Organic matter 65.6; nitrogen total 2.17; free humic acids 3.69; gumat calcium 45.5.

Table 1. Chemical composition of bentonites

Bentonite cones	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	MnO	CaO	Na_2O	K_2O	P_2O_5	SO_3	H_2O	CO_2
Azkamar (Navoi)	50.34	0.73	15.21	5.67	2.3	0.03	4.76	2.31	2.36	0.13	1.48	5.42	3.41
Navbaxor	46.06	0.39	8.78	3	4.33	0.27	12.2	0.75	1.05	0.77	1.39	6	9.35

Before determining the binding of bentonite clays to fluorine in fluorine briquettes, bentonite clays were heat treated at temperatures of 150, 200, 250, 300, 400 and 500 0S. To do this, the bentonite samples were kept in the muffle furnace at the recorded temperatures for 2 h and then cooled in a desiccator.

The processes of binding of the mentioned substances, bentonite samples, oxidized coal, humic acids extracted from oxidized coal, and calcium humate obtained on the basis of oxidized coal and slaked lime, to fluoride ions were determined as follows. 0.1 normal sodium fluoride solution was used as the fluoride solution.

We studied the interaction of fluoride ions in fluoride solution with bentonite samples, oxidized coal, humic acid extracted from oxidized coal, and humic calcium in a wide range of ratios of fluoride solution and recorded drugs (100: 1 to 100:10).

We studied the interaction of fluorine ions in a fluorine solution with the above-mentioned compounds as follows. Place the ingredients in a porcelain bowl and grind for 30 minutes until they are the same size. They were then transferred to a 250 ml flask and 100 ml of fluoride solution was poured over them. Setting the flasks on a rotating apparatus, we mixed the mixtures for 6 h and kept them at 25 ° C for 24 h. The solutions were then kept at normal air temperature for 15 to 30 days. The amount of fluoride ions was determined using a selective electrode in accordance with GOST 24596.7-81.

The amount of water-soluble fluoride ion in the filtrate was then determined by filtering the solutions. The precipitates were returned to the flask with a filter, dissolved in 0.2 M Trilon B solution, and a fluorine ion in the form of an absorbent was detected. The results of the experiment are presented in Tables 2-4.

3. Results and Discussion

The results of the experiment showed that the more bentonite was obtained for sodium fluoride balancing and the higher the temperature at which bentonite clay was processed, the less water-soluble fluoride in the system, for example, 100 ml of 0.1 normal fluoride solution in 100: 1 ratio at 150 0C The amount of fluorine in the soluble form decreased by 66.24%, and the amount of soluble fluorine decreased by 44.48%. The fluoride ion in the form decreased by 52.83%, about 50% of the active fluorine was converted into a form that could not be assimilated by plants.

Experiments have also shown that fluoride ions in water-soluble and absorbable form change over time. It can be seen from the table that over time, a decrease in active fluoride ions was observed, for example, in 100 ml of 0.1 normal fluoride solution in a ratio of 100: 2 with the addition of recycled bentonite clay at a temperature of 500 ^{0}C in water for 1 day.

The amount of soluble fluorine decreased by 59.68%, while the amount of soluble fluoride ion decreased by 67.38%, and after 30 days the amount of soluble fluorine in water decreased by 41.37%, and the amount of soluble fluoride ion decreased by 31.45% (Table 2).

In the results of the experiment with Navbakhor bentonites, adding bentonite clay processed at 250 ^{0}C in a ratio of 100:2 to 100 ml of 0.1 normal fluorine solution reduced the amount of water-soluble fluorine by 48.90%, and the absorbable fluorine ion by 56.23%. When bentonite clay processed at 400 ^{0}C was added to 100 ml of 0.1 normal fluorine solution in the ratio of 100: 6, it was found that the amount of fluorine soluble in water decreased by 34.84%, and the absorbable fluorine ion decreased by 41.23%. As it can be seen from the table, a reduction of fluoride ions in the active state was observed over time, for example, when bentonite clay processed at a temperature of 300 ^{0}C was added to 100 ml of a 0.1 normal fluoride solution in a ratio of 100: 1, after 1 day, the amount of fluoride soluble in water decreased by 51.61%, the absorbable fluorine ion decreased by 59.08%. After 30 days, the amount of fluorine soluble in water decreased to 40.41%, and the absorbable fluorine ion decreased to 46.27% (Table 3).

It should be noted that there are more than 200 deposits of concrete in the country, in which two types of bentonite were used (Table 1). It is important not to rush to the conclusion that this work should be studied in soil conditions.

Positive results were also obtained in the study of oxidized coal, humic acid and humic calcium. For example, in 100 ml of 0.1 normal fluoride solution in the ratio of 100: 1 with the addition of humic calcium, oxidized coal, humic acid, the amount of water-soluble fluorine is reduced by 47.27, 44.39, 41.80%. , 09, decreased by 48.71%, and when added to 100 ml of 0.1 normal fluorine solution in a ratio of 100:10, the amount of water-soluble fluorine decreased by 34.01, 31.94, 30.07%, and the amount of fluoride ion in the absorbable form decreased by 39.49, 37. , 29, decreased by 35.55%.

Over time, changes in fluoride ions in water-soluble and absorbable form have been identified. The table shows that over time, a decrease in active fluoride ions was observed, for example, in 100 ml of 0.1 normal fluoride solution in a ratio of 100: 2 with the addition of humic calcium, oxidized coal, humic acid, the amount of water-soluble fluoride after 1 day was 42.59, 39, The amount of fluorine ion in the form of absorption decreased by 99.37.66%, 48.96,

46.24, 44.08%, and after 30 days the amount of water-soluble fluoride decreased by 33.35, 31.32, 29.50%. fluoride ions in the absorbed form decreased by 38.34, 36.21, 34.52% (Table 4).

Table 2. Interaction and kinetics of interaction of Azkamar deposit bentonite clays treated with sodium fluoride at different temperatures

Activation temperature of bentonite	The relative ratios of the starting materials and the degree of binding of fluoride ions,%									
	100 : 1		100 : 2		100 : 4		100 : 6		100 : 10	
	water soluble F	assimilation 0.2 M Tr. B F.	water soluble F	assimilation 0.2 M Tr. B F.	water soluble F	assimilation 0.2 M Tr. B F..	water soluble F	assimilation 0.2 M Tr. B F.	water soluble F	assimilation 0.2 M Tr. B F..
After 1 day										
150^0C	66,24	74,46	59,68	67,38	53,85	61,53	50,57	57,72	47,66	54,35
200^0C	62,69	70,60	56,48	63,89	50,97	58,35	47,86	54,73	45,10	51,53
250^0C	59,17	67,47	53,30	61,06	48,10	55,76	45,17	52,30	42,57	49,25
300^0C	56,25	64,16	50,68	58,06	45,73	53,03	42,94	49,74	40,47	46,83
350^0C	52,83	60,59	47,59	54,83	42,95	50,07	40,33	46,97	38,01	44,23
400^0C	49,74	57,77	44,81	52,28	40,44	47,74	37,97	44,78	35,79	42,16
450^0C	47,05	55,31	42,39	50,06	38,25	45,71	35,92	42,88	33,85	40,37
500^0C	44,58	52,83	40,16	47,81	36,24	43,66	34,03	40,95	32,07	38,56
After 15 day										
150^0C	58,62	65,89	52,81	59,63	47,66	54,45	44,75	51,08	42,17	48,09
200^0C	55,48	62,48	49,98	56,54	45,11	51,64	42,35	48,43	39,91	45,61
250^0C	52,36	59,71	47,17	54,04	42,57	49,35	39,97	46,29	37,67	43,58
300^0C	49,78	56,78	44,85	51,38	40,47	46,93	38,00	44,02	35,81	41,45
350^0C	46,75	53,62	42,12	48,52	38,01	44,31	35,69	41,57	33,63	39,14
400^0C	44,02	51,12	39,66	46,26	35,79	42,25	33,60	39,63	31,67	37,31
450^0C	41,64	48,95	37,51	44,30	33,85	40,45	31,79	37,95	29,96	35,73
500^0C	39,45	46,75	35,54	42,31	32,07	38,64	30,11	36,24	28,38	34,12
After 30 day										
150^0C	51,88	58,31	46,74	52,77	42,18	48,19	39,60	45,20	37,32	42,56
200^0C	49,10	55,29	44,23	50,04	39,92	45,70	37,48	42,86	35,32	40,36
250^0C	46,34	52,84	41,74	47,82	37,67	43,67	35,37	40,96	33,34	38,57
300^0C	44,05	50,25	39,69	45,47	35,82	41,53	33,63	38,95	31,69	36,68
350^0C	41,37	47,45	37,27	42,94	33,64	39,22	31,58	36,78	29,76	34,64
400^0C	38,96	45,24	35,10	40,94	31,67	37,39	29,74	35,07	28,03	33,02
450^0C	36,85	43,32	33,20	39,20	29,96	35,80	28,13	33,58	26,51	31,62
500^0C	34,91	41,37	31,45	37,44	28,38	34,19	26,65	32,07	25,12	30,20

Table 3. Interaction and kinetics of Navbahor bentonite clays treated with sodium fluoride at different temperatures

Activation temperature of bentonite	The relative ratios of the starting materials and the degree of binding of fluoride ions,%									
	100 : 1		100 : 2		100 : 4		100 : 6		100 : 10	
	water soluble F	assimilation 0.2 M Tr. B F.	water soluble F	assimilation 0.2 M Tr. B F.	water soluble F	water soluble F	assimilation 0.2 M Tr. B F.	water soluble F	assimilation 0.2 M Tr. B F.	water soluble F
After 1 day										
150^{0}C	60.77	68.56	54.75	62.05	49.41	56.66	46.39	53.15	43.72	50.04
200^{0}C	57.52	65.01	51.82	58.83	46.76	53.73	43.91	50.40	41.38	47.45
250^{0}C	54.28	62.13	48.90	56.23	44.13	51.35	41.44	48.16	39.05	45.35
300^{0}C	51.61	59.08	46.50	53.47	41.96	48.83	39.40	45.80	37.13	43.12
350^{0}C	48.47	55.79	43.67	50.49	39.41	46.11	37.00	43.25	34.87	40.72
400^{0}C	45.64	53.19	41.12	48.14	37.11	43.96	34.84	41.23	32.83	38.82
450^{0}C	43.17	50.93	38.89	46.09	35.10	42.09	32.95	39.48	31.06	37.18
500^{0}C	40.90	48.64	36.85	44.02	33.25	40.20	31.22	37.71	29.42	35.50
After 15 day										
150^{0}C	53.78	60.67	48.45	54.90	43.72	50.14	41.05	47.03	38.69	44.28
200^{0}C	50.90	57.53	45.86	52.06	41.38	47.55	38.85	44.60	36.62	41.99
250^{0}C	48.04	54.98	43.28	49.76	39.06	45.44	36.67	42.62	34.56	40.13
300^{0}C	45.67	52.28	41.14	47.31	37.13	43.21	34.86	40.53	32.86	38.16
350^{0}C	42.89	49.37	38.64	44.68	34.87	40.80	32.74	38.27	30.86	36.04
400^{0}C	40.39	47.07	36.39	42.60	32.84	38.90	30.83	36.49	29.06	34.36
450^{0}C	38.20	45.07	34.41	40.79	31.06	37.25	29.16	34.94	27.48	32.90
500^{0}C	36.19	43.05	32.60	38.96	29.42	35.58	27.63	33.37	26.04	31.42
After 1 day										
150^{0}C	47.60	53.69	42.88	48.59	38.70	44.37	36.34	41.62	34.24	39.19
200^{0}C	45.05	50.91	40.59	46.07	36.63	42.07	34.39	39.47	32.41	37.16
250^{0}C	42.51	48.66	38.30	44.04	34.56	40.21	32.45	37.72	30.58	35.52
300^{0}C	40.41	46.27	36.41	41.87	32.85	38.24	30.85	35.87	29.07	33.77
350^{0}C	37.95	43.69	34.19	39.54	30.85	36.11	28.97	33.87	27.30	31.89
400^{0}C	35.74	41.66	32.20	37.70	29.06	34.43	27.28	32.29	25.71	30.41
450^{0}C	33.81	39.89	30.46	36.10	27.49	32.97	25.81	30.92	24.32	29.12
500^{0}C	32.03	38.09	28.86	34.47	26.04	31.48	24.45	29.53	23.04	27.80

Table 4. Kinetics of interaction of oxidized coal in sodium peroxide with hydrogen peroxide, pure humic acid extracted from oxidized coal and humic calcium obtained on the basis of a mixture of humic acid and calcium hydroxide

Activation temperature of bentonite	The relative ratios of the starting materials and the degree of binding of fluoride ions,%									
	100 : 1		100 : 2		100 : 4		100 : 6		100 : 10	
	water soluble F	assimilation 0.2 M Tr. B F.	water soluble F	assimilation 0.2 M Tr. B F.	water soluble F	water soluble F	assimilation 0.2 M Tr. B F.	water soluble F	assimilation 0.2 M Tr. B F.	water soluble F
After 1 day										
Gumat Ca	47,27	54,10	42,59	48,96	38,43	44,71	36,08	41,94	34,01	39,49
Oxidized coal	44,39	51,09	39,99	46,24	36,09	42,22	33,89	39,60	31,94	37,29
Humic acid	41,80	48,71	37,66	44,08	33,98	40,26	31,91	37,76	30,07	35,55
After 15 day										
Gumat Ca	41,83	47,88	37,68	43,33	34,01	39,57	31,93	37,12	30,09	34,95
Oxidized coal	39,29	45,21	35,40	40,91	31,94	37,36	29,99	35,05	28,27	33,00
Humic acid	36,99	43,10	33,32	39,00	30,07	35,62	28,24	33,41	26,61	31,46
After 30 day										
Gumat Ca	37,02	42,37	33,35	38,34	30,10	35,02	28,26	32,84	26,63	30,93
Oxidized coal	34,76	40,01	31,32	36,21	28,26	33,07	26,53	31,02	25,01	29,20
Humic acid	32,74	38,15	29,50	34,52	26,62	31,53	24,99	29,57	23,55	27,85

4. Conclusions

The results show that the use of bentonite clays and humic acid and humic calcium not only increases soil fertility but also protects the soil from harmful substances.

Based on the research, it was found that the conversion of fluoride ions in water-soluble fluorine substances into water-soluble and not assimilated by plants can be achieved using local agro-ores Nabakhor and Azkamar bentonites, oxidized coal, humic acid and calcium humate. The transition of the fluorine ion to the bound state was found to depend on the thermal activation of the bentonite, the mutual mass ratio, and the time. Also, oxidized coal in hydrogen peroxide, humic acid pure from oxidized coal, and humate calcium fluoride ion obtained on the basis of oxidized coal and slaked lime, the fluoride ion is bound to the bound state depending on the amount and time of oxidized coal, humic acid and humic calcium.

The starting materials are bentonites of Azkamar and Nabakhor deposits, thermally treated at a temperature of 400 ^{0}C, oxidized coal, humic acid and calcium humate, 63, 25.01, 23.55% to reduce the fluoride ion in the absorbable form to 33.02, 30.41, 30.93, 29.20, 27.85%. The results show that local agro-ores and organic and organomineral fertilizers containing humic acids can be used to fluoridate contaminated soils.

References

1. Yu.P. Tandelov, Fluorine in the soil-plant system. 2nd ed., Krasnoyarsk (2012)
2. V.I. Gladushko, Introduction of fluorine into soils with fertilizers, *Chemization of agriculture* **1**, 17–21 (1992)
3. V.I. Golov, N.M. Kamenshchikova, Fluorine in the main components of landscapes subject to industrial emissions, Trace elements in anthropogenic landscapes of the Far East, DVNTs AN SSSR, Vladivostok (1985)
4. B.N. Golovkin, Migration of herbaceous perennials to the Polar North, Leningrad (1973)
5. V.M. Grishko, Changes in the agrochemical properties of soils contaminated with fluorides, *Agrochemistry* **1**, 85–93 (1996)

6. I. Bozorov, M. Iskandarova, A. Mamataliyev, N. Usanbayev, U. Temirov, Production of humic superphosphates based on central kizilkum phosphorites, *AIP Conference Proceedings* **2432**, 050062 (2022)
7. P. Ganiyev, Sh. Namazov, N. Usanbaev, Humic Superphosphates Based On Phosphorites And Oxidized Local Coal, *International Journal of Advanced Science and Technology* **29**, 2042-2052 (2020)
8. Yu.L. Baikin, L.B. Karengina, A.A. Belichev, A.N. Fedorov, Ecological state of soils and plants in the zone of influence of fluoride emissions from the Cryolite Plant and agrochemical methods of protection against the consequences of pollution, *Bulletin of Biotechnology* **18**, 2-7 (2019)
9. V.I. Polonsky, D.E. Polonskaya, Fluoride contamination of soil and phytoremediation, *Agricultural Biology* **18**, 3-14 (2013)
10. L.G. Sokolova, S.Yu. Zorina, Study of the potential of field crops for the purposes of phytoremediation of soils contaminated with fluorides of aluminum production, *Applied Chemistry and Biotechnology* **14**, 61-68 (2015)
11. S.Yu. Zorina, L.G. Sokolova, Problems and prospects of using vermicompost as a remediant of fluoride-contaminated soils, *Applied Chemistry and Biotechnology* **14**, 74-79 (2015)
12. S.Yu. Zorina, L.G. Sokolova, The state of humus in agro-gray soils of the forest-steppe of the Baikal region under conditions of technogenic pollution, *Proceedings of the Samara Scientific Center of the Russian Academy of Sciences* **6**, 81-84 (2014)