RADIOACTIVE CONTAMINATION OF JAPANESE SOILS AND POSSIBLE WAYS OF THEIR REHABILITATION

L. Maskalchuk, A. Baklay, T. Leontieva, D. Strelenko
SSI «Joint Institute for Power and Nuclear Research – Sosny» National Academy of Sciences of Belarus, Minsk, The Republic of Belarus
leonmosk@tut.by, L.Maskalchuk@sosny.bas-net.by

1. Background and Goal of the present work

It was established that after the accident at the "Fukushima" NPP (level 7 on the scale INES) there is an excess of the maximum level of ^{137}Cs concentration on soils surface in several prefectures in Japan. The area of the radioactive contamination consists of about 13 782 km2, concentration of ^{137}Cs varies from 800 to 230000 Bq/kg. At the present time the radionuclides availability in milk, meat and other agricultural products in the Fukushima and others Prefectures were identified.

The results of the long-term research that were carried out by the Remediation Techno Polluted Territories Laboratory of the SSI "JIPNR – Sosny" of NAS of Belarus within the framework of the national programs for rehabilitation of the radioactively contaminated soils in Belarus, as well as the results of the ISTC project #3189, indicate that the use of the amendments based on the natural raw materials (sapropels) and clay-salt slimes will be a very promising method for rehabilitation of radioactively contaminated soils.

2. *Theoretical aspects of ^{137}Cs behavior in soils*

One of the main factors governing the redistribution of ^{137}Cs and ^{90}Sr in ecosystems is the mobility of radionuclides in soil on the contaminated areas. The physicochemical conditions and migration properties of the radionuclides impact seriously the radioecological situation of an ecosystem as a whole. The most important role in the process of migration of the radionuclides through a soil profile plays the soil solution, composition and physicochemical characteristics on which the level of the radionuclides migration in a soil-plant system depends. The mobility of ^{137}Cs strongly depends on the concentration of cations K^+ and NH_4^+, competing for sorption centers.

In general the triply charged cations are adsorbed by soils more efficiently than the singly charged ones, and the doubly charged cations occupied the intermediate position. However, this rule is not true for the singly charged cations such as K^+, Cs^+, Rb^+, NH_4^+, which exhibit the ability to be specifically adsorbed, and to be particularly strongly kept by soils. The specific sorption of the caesium trace amounts occurs in the mineral soils, as the desorption curves of the soils treated with hydrogen peroxide in order to remove organic matter, turned to be homogeneous with desorption curves of the untreated soils. Special properties towards such cations are directly related with the availability of minerals of certain groups in the soils, primarily of the clay and mica minerals, and energy heterogeneity of the binding sites which are single type with these cations.

Three types of binding sites in increasing order of the selective sorption of the singly charged cations are usually distinguished:

1) the **Regular Edge Sites (RES)**, located on the flat outer faces on the surface of minerals and micromolecules of the humus substances;

2) the **Frayed Edge Sites (FES)**, which are located on the edges and the extended boundary (wedge) zone of the layered structure of minerals;

3) the **Highly Affinitive Sites (HAS)**, which are located deep in the inter-packet space of the crystal lattices of minerals.

Energetic heterogeneity of binding sites explains the specificity of ^{137}Cs sorption. Only ^{137}Cs which was sorbed at RES retains the ability to exchange easily for other cations in soil solution. The sites (FES and HAS) are quite heterogeneous in themselves and are responsible for solid sorption and fixation of ^{137}Cs. Exchange of ^{137}Cs in the cations Ca^{2+}, Mg^{2+} and Na^+ is hampered when placed on FES.

It can be concluded from the above that the specific sorption of ^{137}Cs in different types of soils is driven by clay minerals with the crystal lattice of type 2:1, which are present in a particular soil type in different quantity. Thus, features of the ^{137}Cs behavior in each type of soil will be determined by the special characteristics of its mineralogical composition.

3. Objects of investigation and obtained results

Within the framework of the ISTC project #3189 the complex of research on the properties and characteristics of natural raw materials, industrial wastes, and different types of soils in Belarus has been executed. As a result of its implementation, amendments on the basis of sapropels and industrial waste (clay-salt slimes) have been developed intended for the rehabilitation of radioactively contaminated soils.

3.1. Sapropels

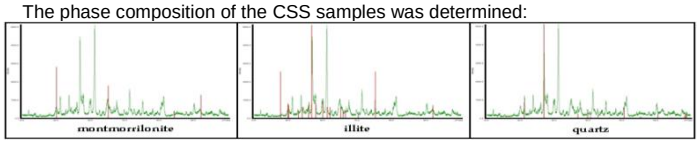
Sapropels are the substances of biogenic origin, which are formed by animal and vegetable remains at the bottom of freshwater lakes where there is a lack of oxygen. There are four types of sapropels in the Republic of Belarus: organic, siliceous, carbonate and mixed. As for determination of sapropel types, the main feature is the content of organic matter. Besides, colloidal structure of sapropel, the big specific surface and considerable cation exchange capacity allow to use sapropel as an effective sorbent of radionuclides.

Theoretical and applied research carried out during 1988-2010 (Belgium, Belarus) has shown that sapropels have high sorption properties both in terms of radiocaesium and radiostrontium, and depending on a type of sapropel the extent of sorption of radionuclides differs significantly. It is indicated that organic sapropels, which are characterized by high values of cation exchange capacity (CEC), are more effective for the sorption of radiostrontium. While the silica, which have the highest Radiocaesium Interception Potential (RIP) values will be the most effective for the sorption of radiocaesium.

3.2 Clay-salt slimes (CSS)

Clay-salt slimes are the waste of chemical industry, resulting from the sylvinite ore processing. As for material constitution, clay-salt slimes are complex entities.

The phase composition of the CSS samples was determined:



The phase composition of the CSS samples

The diffraction peaks are identified, the corresponding structure of montmorillonite, illite and quartz. The remaining mineral phases (biotite, K-feldspar, sericite) are subordinate. Main CSS components are calcium and magnesium carbonates, sulfates, calcium, alumosilicates, chlorides, sodium and potassium.

Clay-salt slimes have several important properties such as hydrophilicity, swelling, high dispersion (the slimes contain 60-70% of particles smaller than 0.05 mm). Clay-salt slimes are characterized by high specific surface area (40-45 m^2/g) and a significant degree of defectiveness of the crystal structure that stimulates their high sorption capacity. Cation exchange capacity CSS is 7-12 meqv/100g and is determined only by the content of alumosilicates in them. The use of clay-salt slimes as sorbents of radionuclides is reasonable because of their content of KCl up to 15%, biologically active trace elements (Mn, Cu, Mg) and the presence of alumosilicates.

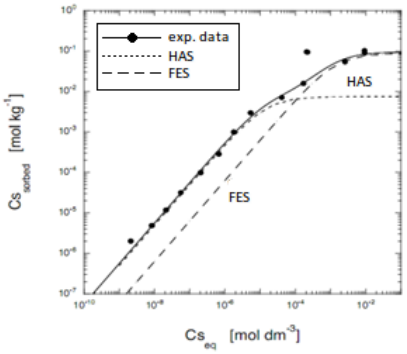
CSS are characterized by highly selective sorption with respect of ^{137}Cs:

Samples	^{137}Cs RIP(K), mg-eq/kg
Soddy-podzolic soils	35-2500
Sapropel (silica)	590-990
Clay-salt slimes	3000-6000

The Radiocaesium Interception Potential (RIP(K)) for different samples (Belarus)

Use of CSS as a mineral additive to sapropels will increase their sorption properties and significantly increase fixation of radiocaesium during the rehabilitation of the contaminated soils. For this means, clay-salt slimes are applied as perspective inorganic additives to the amendments, intended for carrying out of rehabilitation of radioactive contaminated soils.

The results of the laboratory experiments on ^{137}Cs sorption by the CSS samples can be displayed via sorption isotherm:



Sorption isotherm of ^{137}Cs on CSS samples (in 0.1 M $NaClO_4$ background electrolyte)

As can be seen from the sorption isotherm, the curve can be divided into two parts, described by the linear form of the Langmuir equation. The first part describes sorption on the Frayed Edge Sites (FES), the second – on the Highly Affinitive Sites (HAS). Availability of these specified sorption sites explains the high capacity for selective sorption in relation to ^{137}Cs, observed in the CSS samples.

4. Results and discussion

In the course of the long-term research that was carried out by the Laboratory staff within the framework of the national programs for rehabilitation of the radioactively contaminated soils in Belarus, as well as the results of the ISTC projects #859 and #3189, the following results were obtained:

1) Analysis of physicochemical, agrochemical and sorption properties of soils, sapropels (organic; silicon; carbonate), hydrolyzed lignin (acid, neutralized), clay-salt slimes and organomineral amendments (OMA) on their basis was carried out.

2) Sorption-desorption kinetics of ^{137}Cs and ^{90}Sr was determined by soils, sapropel, hydrolyzed lignin, clay-salt slimes.

3) The effect of the OMA application on the soils contaminated by radionuclides was studied: a) physicochemical properties of soils and amendments; b) essential dependence on the quantitative parameters which describe behavior of radionuclides in soils and amendments. Amendments containing CSS are the most perspective for protection of ^{137}Cs and ^{90}Sr migration from soils into plants.

4) A methodology of purposeful search of substances and materials as a sorbent of radionuclides of ^{137}Cs and ^{90}Sr was developed with use of the following parameters: a) the content of exchange forms of radionuclides; b) cation exchange capacity (CEC); c) Radiocaesium Interception Potential (RIP).

5) A technical specification draft on amendments composition was prepared.

6) The Technology Implementation Plan for amendments production on the basis of the natural raw material and industrial waste and their testing on the radioactive contaminated soils in Belarus and other countries was developed, two patents of the Republic of Belarus have been received.

5. Conclusions and Acknowledgements

- The obtained results indicate high sorption properties of the amendments based on sapropels and clay-salt slimes and the prospects of their use for rehabilitation of radioactively contaminated soils.
- The given approach could be used in Japan for rehabilitation of radioactively contaminated as a result of the nuclear accident at Fukushima soils, and in other countries for minimization of the consequences of a possible radiation accident.
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