Prevention of radioactive and other contaminant leaching into soil by high temperature synthesis fixing

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A new method, based on Self-propagating High-Temperature Synthesis (SHS), has been developed for fixing radioactive and other harmful compounds originating from human actions or ecological catastrophies. The SHS method is based on combustion processes and synthesis of high-melting minerals, analogous in structure and phase composition to natural minerals, with high mechanical strength and chemical stability. Due to agglomeration and phase recrystallisation, it is possible to render harmless very large quantities of radioactive and other harmful materials. The new technology is characterized by ease of application and autonomy and its application does not depend on any energy source. It can thus be applied used in-situ to remediate environmentally polluted areas.

Keywords: SHS, contaminants, radioactive

1. Introduction

The origination of the new branch of geo-ecology and protection of geological media from negative influence of industrial and domestic wastes is connected with the reality of contemporaneousness: pollution of surrounding medium by harmful substances and prevention of radioactive isotopes, distributed in large soil volumes, diffusion to atmosphere and water medium. Contaminations are generally chemically unstable systems, lead to irreversible destruction of geological medium and their migration negatively influence various biosphere processes. The development of methods of prevention of migration and accumulation in geological medium of eco-toxic compounds worldwide is attempted via different routes. The main route is first of all isolation, i.e. accumulation of harmful substances, e.g. radioactive wastes in hermetic containers for temporary storage [1]. Secondly, generally for low activity wastes, dispersal is used, i.e. decreasing the concentration of harmful substances up to a safe level for biosphere [2]. Thirdly, fixation is carried out, by mixing and fixing harmful wastes in a mineral structure, similar to natural [3-4], useful since, in nature, harmful substances are in chemical stable form in balance with surrounded medium. The third route is the most universal and promising as it can be used for different types and concentrations of contaminants.

In the USA, France, Germany and Russia vitrification fixing is generally used for radioactive wastes. Other fixing forms are natural-like artificial minerals, as they can exist in natural conditions during extended periods without structural changes or any deterioration. Among material requirements of such fixing forms, the most important ones are mechanical strength, stability to atmospheric influence, in particular to the humidity and long presence in water and also to acid and alkaline media. In order to obtain such properties to the matrix materials, which may hold internally isotopes and conglomerates of harmful substances, their synthesis conditions have to be as close to natural as possible, especially high synthesis temperature.

Worldwide, thermal, chemical and physico-chemical methods are used for utilization of nuclear and chemically dangerous wastes and decontamination of polluted materials. Thermal methods include combustion, gasification and pyrolysis. Combustion is the most conventional and widely used method. This method is realized at temperatures not less than 1200°C in different types of furnaces equipped with special heaters and high cost refractory materials. However, the possibility of fixing harmful substances within mineral matrixes similar to natural materials remains a challenge.

Contaminated soil is not just unsuitable for processing it is also a source of pollution for the whole local ecosystem. So there is a great need for new technologies of immobilization of dangerous components of polluted soils. Such technologies should be based on the proposed method of immobilization of radio nuclides and other dangerous chemical substances.

2. SHS fixing

To approach the problem it is assumed that soil agglomeration into separate complexes and its further caking under natural conditions (without a furnace) would enable the decontamination of greater volumes of polluted soils. This has become the basis for the development of the new method for decontamination of dangerous soil components. It allows fixing radio nuclides or chemically harmful substances in soil and prevent their migration in the soil and to adjacent ambiences (atmosphere and hydrosphere)

Immobilization of soil radioactive components may be carried out by agglomeration of powder material and fixing it in a chemically resistant metallo-ceramic matrix, such as a metallo-ceramic material, produced by self propagating high-temperature synthesis (SHS) [5-6]. The elaborated method is based on forming mechanically stable agglomerates (particles of soil bonded in the shape of spheres or blocks), pouring and packing them into natural reactors (pits, trenches) filling the empty spaces between them with the SHS charge of the bonding mixture (combustible mixture composed of metal oxides and a reducer, for example, powdered aluminum) and finally initiating combustion in a wave regime. As a result of this process, which is a form of self-propagating high-temperature synthesis (SHS), a cermet is formed that bonds separate agglomerates into a single block. The structure of these agglomerates under the influence of high temperatures undergoes changes via sintering and is a process similar to ceramic firing. The parameters of the combustion process of such a bonded mixture determines the depth of heating of the agglomerates as well as the final phase composition of the matrix of the composite material obtained. Consequently, the mechanical and chemical properties of the prepared block also depend on temperature and kinetics of the combustion wave.

The proposed method of radionuclide fixing is universally applicable, as it is suitable for many different kinds of polluted soils of different chemical composition and physical properties. The methodology has been tested on clay and sand soil samples in laboratory conditions. In the framework of the project to develop radioactive immobilization methods, soils from the Semipalatinsk region of Kazakhstan, similar to the soils of Semipalatinsk “nuclear polygon” were also used.

Polluted soils to be immobilized may have a range of physical and chemical properties. For instance, the soil samples taken from the Semipalatinsk region of Kazakhstan had the composition shown in Table 1.

The qualitative composition of the tests remains constant. There are differences in quantitative relation of the phases. Beside the main compounds (quartz, albite and limestone) there is $Al_2(Si,Al)_4O_{10}(OH)_2$, chamozit $(Fe,Mg,Mn,Al)_6(Si,Al)_4O_{10}$ and others in smaller amounts. The rest of it is an X-ray amorphous phase – a finely dispersed clay fraction with organic inclusions.

The proposed method is also universally applicable since water is the binder for formation agglomerates

Table 1. Main components of the soil samples taken in the Semipalatinsk region of Kazakhstan (wt%)

Samples	**$CaCO_3$**	**SiO_2**	**Albite $Na_2AlSi_3O_8$**
I	6.0	35.0	10.0
II	10.5	27.3	7.0
III	1.9	29.1	17.2
IV	1.0	23.0	26.0
V	0.8	32.1	24.0

from soil, prior to SHS agglomeration. Apart from other advantages, water aids settling of dust containing radio nuclides and other chemically dangerous materials. This is a very important ecological aspect and one of the advantages of the proposed technology, because, during extraction of top layer, dust generation always takes place.

Water as a binder were also used two water solutions (10-% solution of four-water sodium tetraborate ($Na_2B_2O_4 \cdot 4H_2O$) and 10-% solution of sodium tetraborate with nine-water sodium monosilicate ($Na_2B_2O_4 \cdot 4H_2O + Na_2SiO_3 \cdot 9H_2O$) were used as a binding agent.

The form and strength of agglomerates themselves must provide the possibility of placing a bonding SHS-mixture between them. If the form of soil agglomerates is a spheroid one, the volume of separate cells filled in with a bonding mixture is limited by the contacting spheres and depends on their diameter and the packing density. The space factor of the reactor, the size of which considerably exceed the diameter of the spherical agglomerate, approaches the value of 0.74, which corresponds to the dense packing of equal diameter spheres. In this case, the volume of the cell filled in with a SHS bonding mixture depends on one parameter ¬– the diameter of the spheres and can be calculated, so it can be used as an initial parameter for regulation of the combustion process in the system.

As with all processes of combustion, self-propagating high-temperature synthesis has its own limits – there is a critical size of a packed-powder sample above which propagation of combustion front is impossible. The combustion in a limited volume, i.e. the space between spherical agglomerates, proceeds under conditions of intensive heat feeding from the hot zone. Dissipation of heat evolving from the reaction center occurs through the surface of the contact of the bonding mixture with surrounding medium, i.e. with the soil material. The amount of heat loss significantly depends on the area of the surface through which it is removed, i.e. the diameter of the spheres.

For strong compacting agglomerates into a block, cohesion of their surfaces with the product of the SHS bonding mixture, combustion is necessary. Most safely it occurs by phase recrystallisation in the surface layer of the agglomerate – partial melting of the soil components followed by its sintering or melting of the soil followed by its solidification. Concentration and pre-heating conditions of these processes can be determined with high degree of accuracy by a triple diagram of the corresponding system if the phase composition of the soil is known.

For a density of the agglomerate material ρa and thermal conduction Ca, recrystallisation of the surface layer with thickness h and mass mph recurred the amount heat equal to Q_{ph}. If the amount of heat evolved by the combustion of the bonding SHS mixture is $Q << Q_{ph}$, caking of agglomerates into a block might not be sufficiently strong due to low cohesion of solid phase product of the SHS-mixture combustion with the agglomerate surface which is in a solid state too. If $Q >> Q_{ph}$ separation of the combustion product into a ceramic phase (a slag) and a reduced metal. This circumstance will lower the chemical stability of the block material.

Optimum geometric sizes of spherical agglomerates were calculated. Sphere diameters were determined from equation:

$$da = \frac{2h}{1-\left[1-\frac{q \cdot \rho \cdot (1\ k)}{k \cdot \rho \cdot C \left(T - t\right)}\right]^{1/3}}$$

Analysis of this equation shows that the higher the density of bonding mixture and greater its specific heat generation, the smaller may be the agglomerates prepared from the polluted soil. Conversely, if the soil has large-fragment structure, the bonding mixture may have lower thermo-physical characteristics. This also indirectly concerns the critical diameter of combustion front propagation.

Experimental verification of such calculations was carried out on bonding mixtures for two systems:

1) - (Fe_2O_3 + Al) + (chromite concentrate + Al)

2) - (Fe_3O_4 + Al) + (chromite concentrate + Al).

The concentrations of the main components of the SHS bonding mixture are stoichiometric correlations of iron oxides with aluminum (75 % Fe_2O_3 + 25 % Al) and (76 % Fe_3O_4 + 24 % Al).

The agglomerate size was chosen from the above analytical expression. Initiation of the combustion process in bonding mixtures was initiated in two different ways, electric, using an electric impulse and chemical, by means of an easily inflammable mixture and powdered metallic magnesium. The direction of the combustion wave propagation (downwards) was chosen taking into account the workability of the process and reaching maximum temperature values on agglomerate surfaces for improvement of the conditions of soil caking.

Comparing the results of chemical and phase analyses of polluted soils with the phase diagrams of CaO-Al_2O_3-SiO_2 the corresponding sintering temperature does not exceed 1300-1540^{0}C. The maximum temperature reached in the combustion wave front was found to be about 1950 ^{0}C. The bulk density of the SHS-mixture on the basis of Fe_3O_4 is about 2 g/cm^3. These conditions provided reliable caking of agglomerates into a block (Figure 1).

Figure 1. Agglomerates of soil caked into a block by the SHS-method using a composition on the basis of Fe_3O_4 and chromite concentrate.

Introduction of chrome-containing component to the composition of initial SHS bonding mixture for caking of agglomerates, improves the chemical properties of both the ceramic phases and metallic phases of the final product. Mixtures of reduced iron and chromium form over an unlimited range of solid solutions, characterized by good anticorrosion stability (similar to chromium-treated steel). In a ceramic phase of the given composition, at temperatures higher than 1500 ^{0}C, the processes of i nteraction of oxides are activated resulting in the formation of the spinels $FeAl_2O_4$, $FeCr_2O_4$ and of more complex variable composition, which is a category of mechanically strong, stable and chemically resistant materials. Figures 2 and 3 present the data on the loss of mass of samples of caked agglomerates and the block matrix, respectively, under the long-term effect of corrosive liquids.

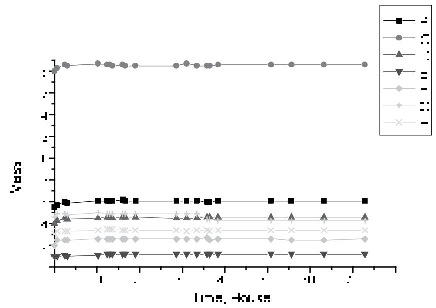

Figure 2. Water-stability of caked agglomerates of soil with different bonding mixtures and space factor of the reactor (from 0.5 to 0.7):

B - Fe_3O_4+Al (k = 0.5); C - Fe_3O_4+Al (k = 0.6); D - Fe3O4+Al (k = 0.7); E - Fe2O3+Al (k = 0.5); F - chromite concentrate +Fe_2O_3+Al (k = 0.5);G - chromite concentrate +Fe_2O_3+Al (k = 0.6);H - chromite concentrate +Fe_2O_3+Al (k = 0.7).

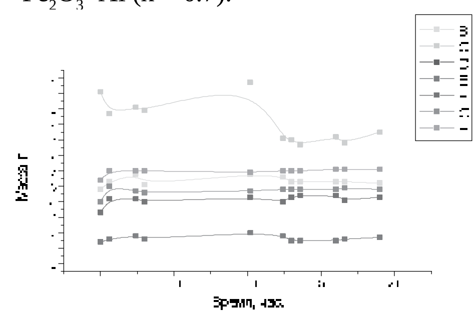

Figure 3. Change of mass of matrix sample under the long-term influence of 30% nitric acid:

B - Fe_3O_4+Al (k = 0.5); C - Fe_3O_4+Al (k = 0.6); D - Fe_3O_4+Al (k = 0.7); E – Fe_2O_3+Al (k = 0.5); F – chromite concentrate +Fe_2O_3+Al (k = 0.5); G - chromite concentrate +Fe_2O_3+Al (k = 0.6); H - chromite concentrate +Fe_2O_3+Al (k = 0.7).

From the results, SHS charge compositions on the basis of two iron oxides and chromite concentrate can be considered to be the most promising materials for bonding mixtures to produce bonded agglomerates.

Optimization of fixing of radioactive soil components fixing using this SHS-bonding technology in mechanically strong blocks with chemically stable spinel matrices is possible by preparation of spherical soil agglomerates in 2 sizes. This approach allows for reduced quantity of bonding composition and increased volume of soil to be treated. This leads to lower cost of added material and reduces the whole technology.

Optimization of the technology is also possible by replacing the reducer, the expensive aluminum powder with a cheaper component. Silicon and its alloys (for example Al-Si alloy, silumin) can also be used as the reducer in such metallo-thermic processes.

The silumin application in the SHS process for immobilization of radioactive soil components is very promising because of the following reasons.

First of all, the thermal effect of the silicon reaction with iron oxide is sufficiently high. For the reaction:

$$3Si + 2Fe_2O_3 \rightarrow 4Fe + 3SiO_2$$

the Gibbs free energy is - 2462 J/g or 980,2 kJ/mol

Secondly, silumin wastes are abundant (e.g. car pistons) and therefore a cheap raw material.

Thirdly, the main silumin phase is aluminium; silicon content is about 3% or more. Abundant waste silumin pistons contain about 11-13% of silicon.

Considering the thermo-physical parameters of the SHS process using silumin, it is shown that there occurs phase recrystallization of soil agglomerate surface layer in the reactor and formation of minerals (quartz, corundum, albite, hercynite) as a result of layer combustion. From such tests, this composition showed satisfactory results, especially regarding mechanical and chemical resistance requirements.

3. Conclusion

The SHS-bonding method presented herein, to immobilize radioactive and chemically dangerous components present in soils uses the peculiarities of self-propagating high-temperature synthesis (SHS) combined with agglomeration of polluted materials. SHS is based on processes of combustion and allows to obtain refractory minerals which are similar to natural ones both in structure and phase composition, and having high mechanical strength and high chemical stability. This provides secure radio-nuclide fixation and elimination of their further migration in ecosystem. Agglomeration provides the possibility for treatment and decontamination of greater volumes of polluted soils with considerably less consumption of bonding SHS-mixture including it's most expensive component, powdered aluminum. There is a possibility of proposed technology optimization by increasing the reactor soil filling coefficient and by replacing the most expensive component of the SHS bonding charge with Al-Si (silumin) wastes. The proposed technology provides a high degree of mechanization which is very important when working with harmful substances.

REFERENCES

1. Belkov B.M., 2000, " Technology methods and carbon containing industrial and solid civil wastes utilization conception", Chemical industry, n.11.
2. Arhipenko A.I., Vovchanov V.V., Gusarov E.E., 2001, "Industrial and civil wastes as potential resource and as pollutants – Directions of utilization technical progress and possibility of ecological danger reduction ", Life and security, issue.1-2, p. 377 – 386.
3. Knatko V.M., Sherbakova E.V.,Maslennikova I.S.,2005, Mineral-matrix technologies of rendering harmless and wastes utilisation - new directions in geological medium defence problem solution, Geo-ecology, issue 4, p.326 – 337.
4. Radioactive Waste Management. The report of URANIUM INFORMATION CENTRE Ltd., 2006, Melbourne, Australia.
5. Ksandopulo G.I., Baydeldinova A.N., Bayrakova O.S., Gassan N.V., Kartkuzhakov S.S.,2007, Application of the self-propagating high temperature synthesis for the ecological tusks solution, Bulletin of National Academy of Science. Chemical series , issue 4, p. 51-57
6. G. Ksandopulo, A.Baideldinova, O.Bairakova, N.Gassan, G.Xanthopoulou, S.Kartkuzhakov, 2007, "Method of Self-propagating high temperature synthesis in Immobilization Radioactive Components in Soil" , 9th International Symposium on SHS, Dijon, France, p217-218.