

Application of Inorganic SIAL Matrix and Movable Technology in Solidification of the TRU Sludges and Sludge/Resin Mixtures

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ABSTRACT

The inorganic SIAL matrix for immobilization and solidification of radioactive waste was developed by AllDeco Company. The SIAL matrix is the product of polycondensation of inorganic compounds. Process of immobilization and solidification is running at room temperature.

The application of the SIAL matrix was performed on various types of radioactive sludges, resins and sludge/resin mixtures from NPPs. Laboratory tests on waste fixed in the SIAL matrix have shown results with compressive strengths of the final product from 20 to 25 MPa and the indexes of leachability from 9 to 18.

Different tailored mobile and remotely operated devices were designed and manufactured for the application of the SIAL matrix. Devices for the solidification are relatively small, lightweight and designed for the application on site, directly “in situ” or near localized sludges or resin occurrences.

The solidification of sludge/resin mixtures was realized into 60-liter or 200-liter drums. Also TRU radioactive sludges were solidified “in situ” in original canisters used for storage and cooling of spent fuel assemblies.

INTRODUCTION

The NPP A-1 in Jaslovske Bohunice was shut down after an accident resulting to significant contamination of primary and auxiliary circuits. In facilities, tanks and heat exchangers, there are RA-sludges and deposits. Usually it is difficult to access these sludges as they often are in closed spaces. The amount of sludges at a given place varies from 0.5 to 15 m³ as well as the composition of sludges and content of dry matter depend on history. Sludges are mostly of high activity. Gamma activity varies from 10⁷ to 10¹¹ Bq.dm⁻³ of the sludge, alpha activity is 2 - 4 order lower.

The sludges usually are viscous, paste-like, adhesive or dry. It is difficult or even impossible to transport such sludges from the place of their appearance to the place of the treatment and

conditioning (distances usually represent several hundreds meters to kilometers) by pipes which are clogged by these sludges.

TECHNOLOGY DEVELOPMENT

Since 1997, the company AllDeco Ltd. has been remarkably engaged in problems of the radioactive sludge treatment. Having managed and repeatedly realized the procedure of the removal and collection of different types of sludges, including historical sludge as well as sludge with higher specific activity coming from decommissioning of the NPP A-1 or from operational NPPs V-1, V-2 in Jaslovske Bohunice, the attention was particularly focused on a conversion of collected sludge into a safe form convenient for storage/disposal. The result of research and pilot-scale works is a new procedure of the immobilization of the collected sludge into the inorganic SIAL matrix in drums (60 dm³, 200 dm³) or in situ in canisters used originally for the temporary storage of the spent fuel. Process of the immobilization and solidification of the sludge is running at room temperature during 30 - 60 minutes of mixing. Immobilization of sludge is finished after a few hours. A polymer 3D composition of aluminosilicate chains is created during the polycondensation. This kind of reaction is known also as geopolymerisation.

The developed and tested SIAL matrix convenient for the radioactive sludge immobilization at the room temperature, with a small final volume contraction of the resulting product after drying at room temperature, is the products of the polycondensation of inorganic compounds. They have a chemical composition which is similar to a standard composition of cements. The SIAL matrix, is made up of natural inorganic raw materials where the essential compounds are oxides SiO₂, Al₂O₃, and other inorganic compounds are added. The polycondensation reaction of main compounds leads under specific reaction conditions to creation of the SIAL matrix.

In the course of the immobilization, a part of radionuclides, for example Cs-137 in liquid phase, is physico-chemically fixed on some compounds of the matrix. The remaining part of radionuclides bound or involved in undissolved sludge particles is encapsulated in the bulk of the matrix.

Laboratory tests and trials on inorganic SIAL matrix samples with immobilized non-active as well as radioactive sludge and/or resins have shown results which are better than those gained with conventional cement matrixes.

Characteristic of SIAL Matrix

The compressive strengths of the blank matrix SIAL range from 52 to 58 MPa.

The decrease of compressive strengths of the tested blank matrix samples by 16 - 39 % up to the values of 33 - 48 MPa was found out after the irradiation of these matrixes by the total dose of 1.027 MGy using Co-60 emitter with dose rate of 2.5 kGy.h⁻¹.

Other very good properties of SIAL matrix are:

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- incombustibility
- thermal stability (cold resistance)
- non-toxicity
- microbiological stability
- minimum volume contraction
- setting even under water

Characteristics of Final Product

The compressive strengths in different real samples with the immobilized radioactive sludge from four different NPPs (A-1, V-2, Temelin and Dukovany) have reached the values from 20 to 25 MPa. These values significantly exceed the minimal value 5 MPa required for the cemented products with fixed radioactive wastes.

The indexes of leachability (L_i) which were determined according the ANSI/ANS-16.1-1986 Standards using the real samples of the immobilized sludge have reached following values:

- for Cs-137 $L_i = 9 - 14$
 - for Am, Pu nuclides $L_i = 12 - 18$
 - for Sr-90 $L_i = 12 - 14$
- after the shortened 5-days test as well as after the long-termed 90-days test.
These values are significantly higher than the required minimal value of 6.

Irradiation and laboratory tests for leachability and compressive strength measurements were performed with solidification of 20 weight percent of the dry sludge or resin content in the SIAL matrix samples. No decrease of good properties was found, the presence of the sludge even increased the compressive strength.

Long term tests of the SIAL matrix stability in dry, wet and cold conditions have been being conducted for a period of several years with very satisfactory results. Very good results were obtained up to 20 weight percent of the sludge, sludge/resin mixtures or resin content in the SIAL matrix for L_i (over 10), compressive strength (≥ 15), physical stability and water resistance.

The SIAL matrix is an approved waste package for disposal in the Slovak Republic. The approval was issued by the Nuclear Regulatory Authority. The approval process with the SIAL matrix is also in its final phase in the Czech Republic.

Sludges, mainly old historical sludges, have according to their origin different composition, variable content of organic matter or organic liquids (oils, solvents etc.).

Technology of application of the SIAL matrix is always laboratory tested on real samples of each specific sludge, sludge/resin mixture. Then, appropriate mixture of aluminosilicate composition and other inorganic compounds is defined for a given solidification application. Also other requirements are taken into account like maximal dose rate on the drum with solidified product, mass, volume or activity of alpha radionuclide contents in the product, need for a dewatering of sludges or resins before solidification, dry matter content of sludge or resin in the solidification product.

Similar situation of appearance of sludges, sludge/ionex mixtures or ionexes is present also at operated NPP units with VVER 440. Because of these reasons, in the past the attention was paid to development and verification of the flexible SIAL matrix for solidification of these kinds of waste.

Various goals were considered in developing and testing of the SIAL matrix, solidification technology and equipment. Firstly, the aim was to convert the quasi-liquid sludges into the safe form for transportation, temporary storage or for disposal in radioactive waste repository. Second aim was to perform the solidification quickly and with consideration of properties and parameters of sludges in the place of their appearance. Use of long transfer paths and transfer containers was recognized as ineffective, not safe and often not realizable considering the properties of sludges and accessibility of places of their occurrence.

TECHNOLOGY APPLICATION

Various mobile and remotely operated devices were designed and manufactured for the implementation and application of the developed SIAL matrix. The aim was immobilization and solidification of the radioactive sludge “in situ” or near to existing position without problematic transport of sticky, tight sludges through long pipes.

A flexible technology for solidification of sludges with different composition and also with the ion-exchange resin content was verified. For implementation of this solidification technology, the movable remotely operated devices were designed and manufactured. Sludge is removed from the bottom of tanks by remotely operated devices or vehicles with special suction heads. Sludge is transported through plastic or metal housing connection up to distance 10 - 30 meters from the tank into drums where it is solidified by adding of the SIAL matrix components into the drum during mixing. Very often a disintegrating of the sludge or dewatering is also performed in the drum before solidification. Devices for the solidification are relatively small, lightweight and designed for the specific application on site, directly "in situ" or near the localized sludges/resins. Devices are manufactured with strong respect for the safety and effectivity of the solidification process in specific conditions for each implementation of the SIAL matrix.

“In situ” solidification of alpha bearing (TRU) sludges resulting from the damaged spent fuel in 9 meter high (diameter 150 mm) original canisters was performed at the NPP A-1 [1]. High contaminated inorganic sludges (Cs-137 over 100 MBq.g^{-1} and TRU radionuclides over 1 MBq.g^{-1}) were fixed at the bottom of 73 pieces of canisters with the rest of inorganic coolant and in 5 canisters with the rest of organic coolant.

Highly contaminated sludge from previous history is accumulated on the bottom of the fuel storage pool at the NPP A-1. This sludge contains insoluble inorganic compounds in a mixture of inorganic liquid (water solution) and organic liquid (biphenyl and biphenyl-dioxide). The sludge is pumped by a remotely operated vehicle equipped with a special pump and TV camera from depth of 10 meters from the bottom of the pool. The complex sludge is transported into

shielded 60-liter drum positioned over the pool. Water phase (activity 10^6 Bq.dm^{-3}), organic phase (activity $10^5 - 10^6 \text{ Bq.dm}^{-3}$) and inorganic solid components (mass gamma activity is over 10^7 Bq.g^{-1} of dry matter) are separated from the sludge using additives. After removal and separation of liquid phases the solidification of the sludge is realized directly in the collecting 60-liter drum.

The process scheme and used devices are presented on Fig. 1 and Fig. 2.

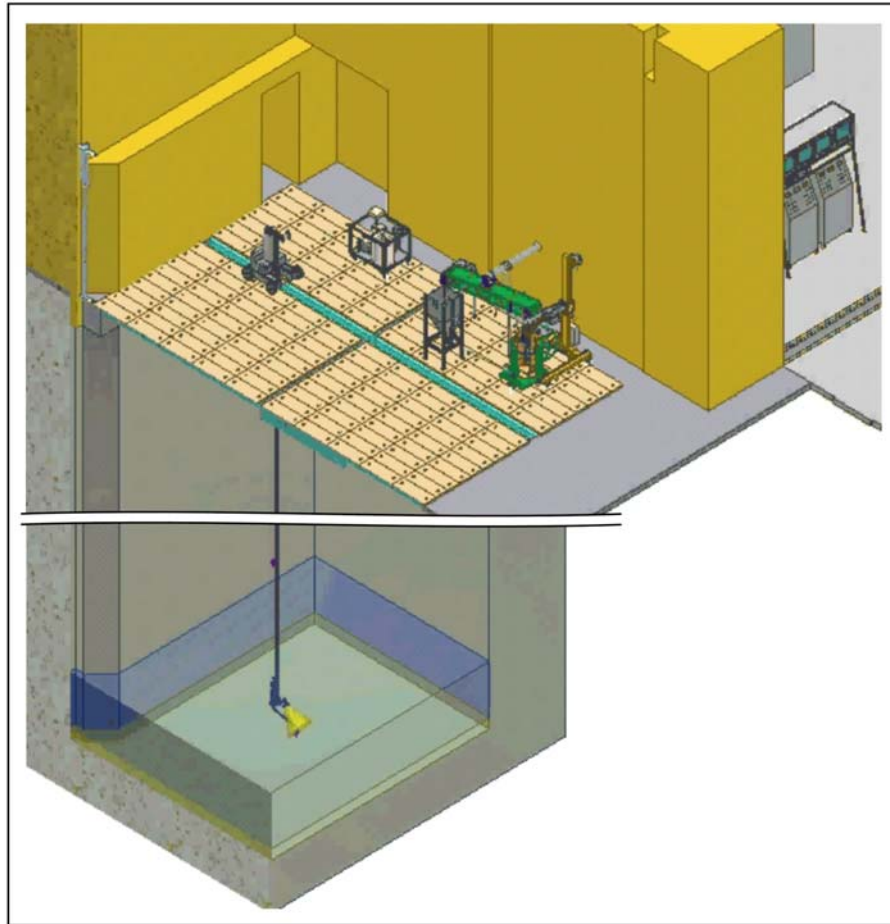


Fig. 1. Scheme of the sludge removal from the bottom of the fuel storage pool and its solidification



Fig. 2. Devices and control board used for the remote operated works in the fuel storage pool

After adding of the SIAL matrix components and mixing, the solidified product is transported into the storage. Dose rate on the drum (between $10 - 20 \text{ mSv.h}^{-1}$) and contents of alpha radionuclides (below 400 Bq.g^{-1}) as well as other nuclide content enabling to fulfill requirements for disposal are controlled. Also index of leachability in chosen controlled samples and compressive strength of each drum are checked. 90 drums of the solidified sludge were prepared till 2005. The evaluated year production rate is about 300 pieces of 60-liter drums. Assumed total amount of 60-liter drums with solidified product is 800 - 1000 pieces.

Different sludges and deposits from decontamination of fuel storage cooling system were immobilized in more than 100 pieces of 60-liter drums also at the NPP A-1 in years 2004 - 2005. Immobilization of sludges with higher specific gamma activity is preferred into 60-liter drums because of better shielding of the drum during treatment and conditioning .

Sludges in NPPs are very often mixtures of inorganic matter, some organics and ion exchanger resins. At operating NPP V-2 over the 15 m^3 of the wet sludge (about 4700 kg of the sludge dry matter) with ion exchanger resin were solidified into 130 pieces of 200-liter drums in years 2003 - 2004. From operating “RW” tanks the sludge (with content of 1 - 5 % of ion exchanger resin) was removed by a remote operated vehicle with TV camera and special exchangeable suction heads. Removed sludge was transported into 200-liter drums. Process of the sludge removal is illustrated on the Fig. 3.



Fig. 3. Removal of the sludge from the "TR" tank by a remote operated vehicle and the sludge collected in the drum

After dewatering, the sludge was solidified into the SIAL matrix near the "RW" tank. The process is finished by issuing of quality protocols on solidified product and transportation of drums to the repository. Shots of a small solidification device and solidified product in drums are in Fig. 4.



Fig. 4. Solidification of sludges from the "TR" tank into the SIAL matrix by the remote operated device and the solidified product in drums

Monitored and evaluated volumes of contaminated sludge, sludge/resin or resins for one NPP of the VVER type may vary from 50 up to 500 cubic meters (tons) after 20 - 25 years of operation. These volumes of radioactive sludge, sludge/resin matters were thoroughly radiologically and physically monitored in storage tanks at the NPP in Dukovany and NPP V-1 in Jaslovske Bohunice.

CONCLUSION

The SIAL matrix is a new inorganic aluminosilicate composition very favorable for the immobilization of different sludges and/or ion exchanger resin mixtures.

This approach allows fast, safe and relatively cheap immobilization and transformation of dangerous radioactive waste as sludges and resins into the solid form which is suitable for long term storage or disposal.

Implementation of the SIAL matrix solidification and technology is realized by small tailor-made remote operated devices. These devices are transportable and working very close to the places of occurrence of RA-sludges, resins, in specific rooms or tanks.

Solidification of sludge, sludge/resin mixtures or resins is successful and verified up to 20 percent of dry matter content in the SIAL matrix.

Developed and verified inorganic SIAL matrix together with appropriate mobile devices allow a very fast and safe solidification of sludges, ion-exchange resins or their mixtures without large facility investment.

REFERENCES

1. Majersky D., Sekely S., Katrlík J.: "Characterization and Treatment Experience of TRU Sludges During NPP A-1 Decommissioning in Slovak Republic", ICEM '03, September 21 - 25, 2003, Oxford, England