Geopolymer Solidification Technology Approved by Czech / Slovak Nuclear Authority to Immobilise NPP Resins and Sludge Waste – 15555

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ABSTRACT

This paper presents the features and performance record of the geopolymer solidification technology, SIAL®, licensed for use by both the Slovakian (ÚJD SR) and Czech Nuclear (SUJB) regulators. An overview of its performance at Bohunice in Slovakia, where it has been used to successfully treat resins and sludge wasteforms will be provided along with references to other plants where it has been used. More recently, geopolymers have been noted as an immobilization technology which shows potential for resins produced by treatment of radioactive contaminated water resulting from the clean-up of the Fukushima Daiichi Plant.

The Nuclear Power Plant A-1 located in Jaslovske Bohunice was completed in 1972 and operated for 5 years until two accidents in 1976 and 1977. After the second accident in February 1977 (INES level 4) the Nuclear Power Plant was permanently shut down for decommissioning. Fuel assemblies and fuel cladding damaged in the accidents led to significant Sr-90, Cs-137 and transuranic contamination. As a consequence of the long-term corrosion of the barrier's material, highly contaminated sludge accumulated which could not be effectively immobilized using conventional methods such as cementation or bitumen treatment due to adverse physical-chemical properties and high specific activity of the waste (Cs-137). This challenge led to AMEC developing and licensing the geopolymer, SIAL®. Today, this geopolymer is one of the most proven and widely used for on-site solidification of radioactive materials such as sludge, resins, sorbents and organic liquids.

There are numerous benefits to using this geopolymer for waste immobilisation. It can be used at room temperature and can incorporate up to approximately four times as much waste (sludge, resin) as a Portland cement matrix equivalent depending on the waste being treated. In addition, it is characterized by excellent mechanical and physical properties, compared with the earlier generation techniques. This includes higher mechanical strength, lower leachability, low volatility, posing a low fire risk and excellent physical stability in the presence of frost and water (no distortion or cracking).

Dedicated facilities to receive and encapsulate waste from different locations can be created but this geopolymer can also provide efficient and practical on-site treatment of radioactive waste streams. This is achievable because the equipment used to encapsulate waste using SIAL® is also modular, flexible and versatile. At Bohunice, the facility for encapsulation was designed to occupy existing areas of the plant in close proximity to the tanks where the waste was being stored. This allowed for the removal of the waste using Remote Operated Vehicles (ROVs) and for the waste to be immediately treated on site without the need for transportation saving both time and resource. To achieve this, some of the rooms and areas of the building were assessed and modified to ensure that the waste package flow was suitable whilst ensuring that appropriate safety measures were in place such as adequate shielding to reduce or entirely eliminate dose uptake of workers.

To date, SIAL® has been used to successfully immobilize approximately 500 tons of waste which includes sludge and resin from Bohunice, Slovakia and approximately 250 m^3 of spent ion exchange resins from tanks on site at the Dukovany nuclear plant, Czech Republic. It now has a track record of over 15 years which includes on-going research and development. The International missions WANO and OSART evaluated the SIAL® matrix technology at NPP Dukovany as an example of good practice.

INTRODUCTION

Today, as Nuclear Power Plants (NPPs) seek life extensions or are approaching decommissioning, a particularly important focus is the problem of effective treatment, conditioning and disposal of sludge and spent resins that have accumulated in on-site storage tanks. Other nuclear facilities such as research reactors also have non-standard waste streams that require treatment.

Cementation and bituminisation which were originally designed for these purposes are being replaced by solidification into geopolymers-aluminosilicate matrix. This technology enables users to readily retrieve spent resins and sludge and to treat them on-site under room temperature conditions. Solidification to a geopolymer matrix also enables a higher load of waste to matrix ratio than alternative materials, and effective use of the disposal capacity allowing continued encapsulation facility use. Moreover, it avoids the significant problems associated with long distance transfer of untreated wasteforms such as sedimentation of mixed wastes in the pipes resulting in a complicated radiation situation.

SIAL®, is the internationally proven geopolymer and technology for the safe solidification of radioactive waste streams developed by AMEC Nuclear Slovakia. It allows the on-site treatment of various special radioactive waste streams (sludge, resins, sludge/resins, Cs-137, Sr- 90, C-14, contaminated soils etc.) at room temperature within a 30 - 60 minute timeframe. On-site treatment and solidification of waste involves the process of waste retrieval from tanks or various contaminated areas and/or facilities using remotely operated manipulators. This is followed by transportation to the on-site waste treatment facility, where waste separation from free water is performed before the waste is placed into 200 litre drums and solidified into the SIAL® matrix. Depending on the amount of waste and site characteristics (e.g. multiple reactors and/or sparsely spaced tanks), waste can be either processed using the mobile equipment in situ, or a dedicated centralized facility can be installed to service multiple locations. It can encapsulate waste quicker than cementation and will also set under water. Combined with the excellent mechanical and physical properties mentioned earlier, this shows the SIAL® matrix to be an effective technology for a range of radioactive wastes.

CHEMICAL PRINCIPLE OF THE TECHNOLOGY

The SIAL® geopolymer technology is based on the polycondensation of waste with inorganic matrix compounds, mainly SiO_2 and Al_2O_3 and other natural inorganic raw materials containing CaO, MgO, Na_2O, K_2O, Fe_2O_3, and TiO_2. In the course of immobilization, the radionuclides in soluble form are physically and chemically fixed on various compounds of the matrix. The remaining radionuclides present in insoluble or liquid phases of the sludge are encapsulated in 3D structures in the bulk of the matrix.

In contrast, cement matrix encapsulation of waste is only into 2D (planar) structures. The SIAL® matrix has been shown to be predominantly amorphous whiles Portland cement matrices exhibit strong crystalline properties.

The SIAL® technology is deployed at room temperature. The polycondensation process during curing is a slightly exothermic reaction with the maximal temperature reached in the middle of a 200 litre drum being approximately 55 °C as illustrated in Figure 1 below. This temperature is the maximum temperature observed to date for the solidification of more than 500 tonnes of actual NNP waste.

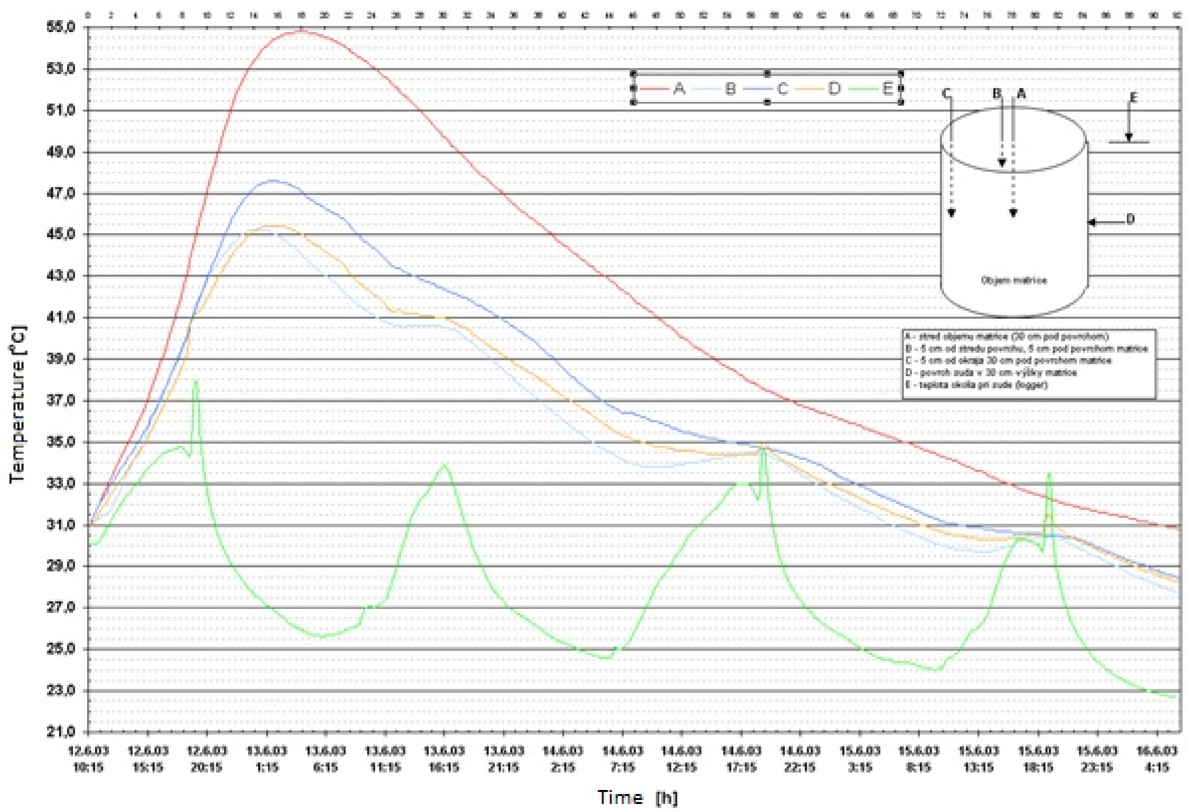

Fig. 1. Increasing of the temperature in SIAL® matrix during solidification (200 L drum**)**

The water in SIAL® (and other geopolymers) is present in two forms:

Evaporable – this water is physically absorbed and bounded only by hydrogen bounds on aluminosilicate surfaces in the pores of matrix. This water is gradually evaporated by room temperature. It is released up to temperatures of 180-200°C, (Differential Thermal Analysis (DTA) measurement). The process of water evaporation is controlled by very simple and easy technological measurements (slow evaporation).

Nonevaporable – "chemically bound". This water is in the form of hydroxyl groups fixed on silicon and aluminium atoms (Si-OH and Al-OH) in an aluminosilicate three-dimensional amorphous geopolymer structure.

THE PROCESS OF LICENSING SIAL®

The SIAL® matrix and technology was licensed by the Czech State Office for Nuclear Safety (SUJB) in 2006 and the Nuclear Regulatory Authority of the Slovak Republic (ÚJD) in 2003. The approvals were received on the basis of suitable properties of final solidification products reported by AMEC from laboratory tests up to full-scale experiments including industrial applications.

The following basic and additional parameters were investigated and tested for real waste solidified into this matrix: compressive strength, leachability, diffusion coefficients, radiation stability, biodegradability of matrix, distribution and partition coefficients, influence of frost and water presence to the product stability including long term physical stability in the water, dustiness, time dependence of compressive strength and water reduction. These tests were provided by independent laboratories.

Fig. 2. View of the homogeneous structure of SIAL® matrix with resins

Compressive strength was measured by independent methods which included both the destructive approach in accordance with guidance EN 12 398 by Form+Test and the non-destructive test using DIGI SCHMIDT 2N for standard measurements of concrete in accordance with guidance EN 12 398.

Leachability tests were performed in accordance with the guidance ANSI/ANS-16.1-1986 in shorted 5 days way – leachability index L_i (7), or in full 90 days way – leachability index L_i (10). This index is a non-dimensional number, which expresses, through the theory of mass transfer, the level of leachability by diffusion processes. Simplified, it is common logarithm of reciprocal effective diffusivity [$cm^2.s^{-1}$] calculated from the measured activity increasing in time in the water containing the sample with known volume and surface. For cases where individual radionuclides are not listed, the leachability was calculated from the total activity measurement.

The values of compressive strength were always significantly higher than the limit value 5 MPa (valid for repository Mochovce in Slovak Republic) and 10 MPa (valid for repository Dukovany in Czech Republic). Leachibility index L_i was never below 8.5 (limit required for repository Dukovany) and it was significantly higher than the value of 6 (required for repository Mochovce).

The destruction of polymer bonds due to irradiation can lead to the changes of strength or leachability. Therefore the influence of ionising irradiation was investigated (dose of 10^6 Gy which approximates the irradiation dose uptake in the repository for a 300 year period). Products (sludge and resin in SIAL® matrix) were irradiated by a Co-60 source (dose rate ~2.5 kGy/hour) for total dose 1,027 MGy. No reduction of compressive strength or increase of leachability values were found.

Biodegradability tests were performed in accordance with ISO 10707. Tested samples are evaluated as stable if the chemical consumption of oxygen ($CHSK_{Cr}$) after 28 days remains lower than 10%. The value observed for matrix SIAL® after 28 days was 3.58% $CHSK_{Cr,}$ from which it can be concluded that the matrix is biologically stable.

Flammability and explosivity were tested in accordance with Proc. A.10, resp. A.14, guidance 92/69/EHS. The matrix was found to be non-explosive and non-flammable.

WASTE TREATMENT PROCESS

The common approach to the waste treatment process is based on three steps – waste characterisation, waste pretreatment and solidification of pretreated waste.

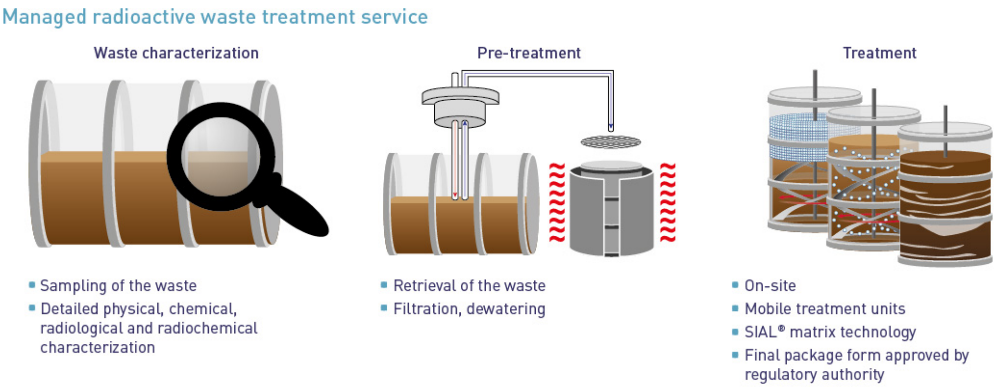

Fig. 3. Outline of SIAL® process

Sludge and resin wastes in NPPs are commonly stored in large tanks which usually results in layers of wasteform which are several metres thick. The character and properties of the stored resins can change in the both the vertical and horizontal directions as no mixing system is usually installed. To better understand this waste, standard characterisation procedures are undertaken at various locations. This involves measurement of dose rates in contact with tanks, video inspection of tank internals, representative sampling of waste, radiochemical analyses, chemical analyses and physical-chemical analyses.

The removal of radioactive sludge/resins from the tanks is considered to be ranked among the most difficult operational stages of wasteform solidification. This is due to the remote nature of the work and the confined space and restricted access points which were not necessarily considered during plant commissioning. There are two basic approaches to removing sludge/resin from tanks:

1. Mix or suspend waste in a liquid so that slurry can be flushed to a fixed location where a pump then removes it from the tank. It is necessary to place the pump or the suction piping as low as possible and to install a flushing system if this approach is used.

2. Remove the waste using a movable tool/vehicle operating at the waste surface.

The solidification process is modified for individual radioactive streams with different composition especially at the stages of retrieval and pre-treatment.

SIAL® has been used to successfully immobilize approximately 500 tons of sludge and resin waste from Jaslovske Bohunice, Slovakia and approximately 250 m^3 of spent ion exchange resins from tanks on site at the Dukovany nuclear plant, Czech Republic. The technology has a track record of over 15 years which includes on-going research and development and over 10 years of actual nuclear on site usage.

TREATMENT OF SLUDGE AT NPP A1 JASLOVSKE BOHUNICE, SLOVAK REPUBLIC

The NPP A-1 located in Jaslovske Bohunice was built in the 1950s as the pilot project for the development of the generation of CO_2 cooled, and heavy water moderated reactors with natural metallic uranium as the fuel, 150 MWe. It was operated in the period from 1972 to 1977 with two accidents occurring in 1976 and 1977. After the second accident (INES level 4) the NPP was permanently shut down for decommissioning. Fuel assemblies and fuel cladding damaged in the accidents led to significant Sr-90, Cs-137 and long lived alpha nuclides contamination. Radioactive substances are spread widely in the primary and secondary circuit and also in many collecting equipment. A lot of the “historic” waste are thixotropic, sticky and dense with high sedimentation rate. Dry matter content of the sludge varies from 15 to 50 % (see Figure 4). As a consequence of the long-term corrosion of the barrier’s material, highly contaminated sludge accumulated which could not be effectively immobilized using conventional methods such as cementation or bitumen treatment due to adverse physical-chemical properties and high specific activity of the waste (Cs-137).

Fig. 4. Presence of the sludge on the bottom of different tanks

The following radioactive waste was solidified in SIAL® at NPP A1:

- Sludge from the bottom of casings at the long term spent fuel storage – sludge in inorganic (Chrompik) and organic (Dowtherm) coolant
- Sludge from the bottom of long term spent fuel pool
- Sludge from decontamination of Dowtherm
- Sludge from decontamination of special sewage

Treatment of High Radioactive Sludge on the Bottoms of Spent Fuel Casings

The long-term storage (DS) at the NPP A-1 was designated as a pool for temporary storage of the spent fuel during operation. Fuel elements were inserted into vertically positioned carbon steel casings (internal diameter 160 mm, height 9500 mm).

A specially designed columnar equipment, MEZA (external diameter 120 mm, height 11500 mm) for remotely operated monitoring (video, dose rate) and sampling of sludge from the bottom of casings was designed, manufactured and installed and representative samples of sludge from casings were taken using this equipment. These samples of sludge were of different colors, densities, viscosities and radionuclide content.

TABLE 1: Characterisation of sludge from long term storage casings

Contents of radionuclides					**Content of dry matter in sludge [%]**	**Fuel burnup (MW/t)**
^{241}Am [Bq/g]	**$^{239, 240}$Pu [Bq/g.]**	**^{238}Pu [Bq/g.]**	**^{90}Sr [Bq/g.]**	**^{137}Cs [Bq/g.]**		
$6{,}01 - 3{,}42.10^{6}$	$97{,}0 - 1{,}95.10^{6}$	$9{,}80 - 3{,}55.10^{5}$	$2{,}74.10^{5} - 6{,}36.10^{7}$	$9{,}93.10^{7} - 4{,}28.10^{8}$	6,1 - 23,9	871 - 5024

After monitoring, sludge was treated directly from the casings at the treatment facility. Following this process, which treated the bulk of the sludge, it was necessary to treat the remaining residual high radioactive sludge at the bottom of the casings. The SIAL® components were added directly to the casings and mixed together with sludge. After solidification of waste the lower parts of casings containing the solidified product were cut and put into shielded drums for disposal.

The Dowtherm was separated into two separate constituents that required different treatments. Firstly, low level burnable waste was separated, stored in tanks before being transported to an incineration facility for final treatment. The second constituent was the medium level liquid waste (parts of Dowtherm and sludge - incombustible). This waste was transported in to the fixation facility (developed, manufactured, and operated by AMEC) and incorporated into the SIAL® matrix (60 L drums).

Removal and Treatment of Sludge Collecting Tanks of Drainage System

In the past, cooling liquid (chrompik) from short term storage were put into the drainage system with sludge which was collected at the bottom of horizontal collecting tanks (diameter 1600 mm, length 4500 mm). Measured dose rates were up to 120 - 150 $mGy.h^{-1}$ at the bottoms of the tanks. The 300 mm thick layer of dense sludge was removed using high-pressure-water jetting and ejector pumping. A volume of ~ 1.5 m^3 of sludge was removed from each tank. The removed sludge was collected in 60-litre drums and prepared for the solidification into the SIAL® matrix directly in those drums.

The average mass activity of collected wet sludge was:

- 10^6 - 10^8 $Bq.kg^{-1}$ for Sr-90
- 10^8 - 10^9 $Bq.kg^{-1}$ for Cs-137
- 10^5 - 10^6 $Bq.kg^{-1}$ for alpha nuclides

Throughout the operations all the necessary verifications were performed in line with the licensing requirements and AMEC's own verification and auditing procedures to ensure quality of product. A selection of the observations are shown below:

- The values of compressive strength of the fixed packages were found to be between 9.5 to 32 MPa.
- The leachability coefficients for these products were from 9.3 to 9.5 for Cs-137, from 13.4 to 14.8 for Sr-90 and from 11.7 to 16.2 for TRU radionuclides (Am-241, Pu-238, Pu-239, Pu-240).

- All tests confirmed that the product met or exceeded the licensing standards agreed with the regulator.

SOLIDIFICATION OF SPENT ION EXCHANGE RESINS INTO THE SIAL® MATRIX AT THE DUKOVANY NPP, CZECH REPUBLIC

Based on the decision of the State Office for Nuclear Safety, the Dukovany NPP has been obliged to secure the efficient capacity for the disposal of spent ion exchange resins. Therefore, in September 2010, pumping and treatment of ion exchange resins began which came from the storage tank 0TW30B02, situated at the auxiliary building.

On-site treatment and solidification of spent ion exchange resins at Dukovany NPP involved process of resin removal from tank using remotely operated manipulator, resin transportation, resin separation from free water (see Figures 5,6), resin filling into 200L drums and solidification into SIAL® matrix. The final product was observed for compressive strength, leachability, radionuclide composition, dose rate, solids and total weight. After meeting the requirements for final disposal and consolidation, the drums were transported for final disposal to the repository at Dukovany site.

During the 3 month of trial operation in 2010, and the subsequent operation to December 2012, around 200 tons of dewatered resins have been treated into 2006 drums (200L), with total activity higher than 600 GBq.

The average weight of resins in the drum ranged from 89 – 106 kg and compressive strength limit (10 MPa) was achieved after 24 hours of fixation. The final measured strength values ranged from 19.0 - 34.7 MPa and real leachability values ranged from 0.03 – 0.65%, far below the 4% limit value.

Fig.5. Pretreatment facility

Fig. 6. Control room

The whole project was successfully finished in 31 months - 3 years before original client target date. The international missions WANO and OSART evaluated it as an example of best practice.

TREATMENT OF HISTORICAL WASTE – SLUDGE AND SORBENTS AT NPP V1, JASLOVSKE BOHUNICE, SLOVAK REPUBLIC

The Slovak Republic is committed to the adoption of Government Resolution no. 801/1999 of 14 September 1999, the definitive closure of Units 1 and 2 of the V1 NPP in Jaslovske Bohunice in a staged manner.

In order to obtain a licence for the 2^{nd} stage of decommissioning, the Nuclear Regulator requires the removal and/or treatment the operational (historical) Radioactive Waste (RAW) in the V1 NPP.

About 650 m^3 of radioactive waste (spent resins, sludge and borates with crystalline-sediment) was stored in 14 tanks situated in an auxiliary building of V1 Bohunice NPP.

There are two categories of waste:

Category A Waste – Spent Resins

These were stored in four tanks (ZT20N-1,2, 3, 4)) in the auxiliary building. They comprised wet sorption materials from spent filters such as organic ion exchange resins and other sorbents (ceramsite, anthracite and charcoal) and admixtures. These materials were stored as mixtures and they contained other impurities. Tanks ZT20N-2 and ZT20N-4 contained a mixture of sorbents, crystalline sediments and sludge. The total amount of waste in tanks ZT20N-1, 2, 3, 4 was estimated at 439 m^3 (158 t of dry matter). More than 20% of resins were made up of sludge fractions. Gamma activity of the resins from V1 NPP reached up to $2x10^7$ $Bq.kg^{-1}$ for wet resins.

Category B Waste – Crystalline Sediments and Sludge_

These were stored in tanks ZT10N-1, 2, 3, 4, 5, 6, 7, 8, 9, 10 in the Auxiliary Building. They comprised crystalline sediment (Figure 7) from alkaline saturated solutions (liquid radioactive concentrate) with a total volume of 211 m^3 (140 tons of dry matter). Almost half of B waste category (about 100 m^3) was constituted of fine sludge fractions. Gamma activity of crystalline sediments and sludge ranged from 10^6 to 10^7 $Bq.kg^{-1}$. Dominant radionuclides were Co-60 and Cs-137.

The main tasks to be completed by AMEC within 35 months (May 2015) are:

- to provide licensing documentation and management of licensing process for Environmental Impact Assessment according to Act No. 24/2006 Coll. as amended, and approval process according to Act No. 541/2004 Coll. on the peaceful use of nuclear energy, as amended, and Act No. 355/2007 Coll. on the protection, support and development of public health, as amended, and if necessary documentation for approval process according to Act No. 50/1976 Coll. on Land-use Planning and Building Order (the Building Act), as amended,
- to provide and install the required equipment for the removal and processing of spent radioactive resins and crystalline sediments and sludge within building No. 801:V1 (Auxiliary Building),

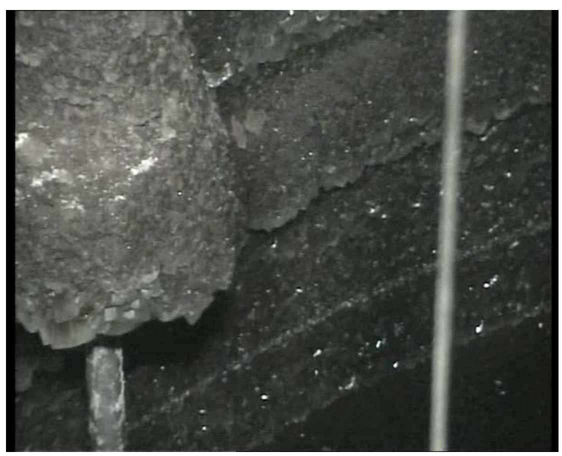

Fig. 7. Crystalline sediments on the walls of the tank N. ZT10N-8

- to empty the tanks in building No. 801:V1 containing stored RAW and to clean the tanks afterwards,
- to process that RAW into a solidified form by means of the new installed process facilities that are capable of meeting the acceptance requirements of Mochovce National Radwaste Repository (NRR) and compatible with the list of approved packaged forms.

All radioactive waste of category “A” from tanks ZT20N-2, ZT20N-3 and ZT20N-4 have been completely retrieved and processed. After the cleaning out, these tanks were handed-in to the client by a protocol. Together with spent sorbents, a part of dissolved crystalline sediments are being treated. They are added to de-watered sorbents within allowed limits into the drum and by this method two distinct waste steams can be treated simultaneously.

Technological scheme and process chemistry for treatment of alkaline saturated solutions (liquid radioactive concentrate) with a total volume of 211 m^3 (140 tons of dry matter) and with specific gamma activity in range of 10^6 to 10^7 $Bq.kg^{-1}$ were optimised in order to achieve maximum yield of the non-active borates product (< 300 Bq/kg) and minimum additions of reagents into the active concentrate with real possibility of its further volume reduction. The procedure involves:

- Dissolution of borate crystalline sediments in tanks
- Separation of liquid borates from non-soluble waste
- Onsite pre-treatment of liquid borates: (1) simple filling into drums with radwaste of category “A”, (2) concentrating and filling into drums or (3) cleaning by removal of radionuclides
- Retrieving the non-soluble radwaste from storing tanks and final cleaning of storage tanks
- On-site solidification of waste in drums using SIAL®
- Final treatment into fibre-concrete containers.

The total amount of waste treated are shown in Table 2.

TABLE 2. Data from the treatment progress

Summary of historical radwaste treatment till October 31, 2014	Weight [t]	Volume [m^3]	Dry matter [t]
Sorbents	384.40	321.39	174.27
Sludge	207.40	144.65	105.27
Dissolved crystalline sediments	126.55	104.27	30.51
In total	**718.36**	**570.31**	**310.04**
Total number of drums with retrieved waste		**4286**	
Total number of drums with solidified waste		**4132**	

APPLICABILITY TO THE JAPANESE MARKET

SIAL® has been proven to successfully treat wastes deemed to be difficult using alternative matrices due to factors such as radionuclide content and/or physical and chemical incompatibility. In addition, it has been shown to be just as successful in treating wastes from non-standard routes such as accidents (Jaslovske Bohunice)

This is directly applicable to the conditions at Fukushima Daiichi (as well as other Japanese NPPs) where the waste streams are not well understood. Therefore, AMEC have been engaged to carry out a research and development program which will consider particular waste streams in Japan. AMEC has already successfully solidified a resin produced through normal operations from a Japanese NNP which and is planning a program to explore the possible hydrogen performance of SIAL® encapsulated high level waste. This work is ongoing and will be reported elsewhere when complete

CONCLUSIONS

Developed and tested over the last 20 years, SIAL® is a new generation waste solidification technology that offers a safe and cost-effective alternative conditioning technology that solidifies radioactive waste streams.

AMEC has significantly tested and approved this method. The technology has been successfully licensed and has been adopted at two nuclear power stations in Central Europe as an alternative to cement and bitumen treatment. Its proven track record, offering significant benefits to these sites has established SIAL® as a practical and valuable immobilization and waste treatment technology. SIAL® benefits include:

- Saving time and cost by treating waste much quicker than alternative technologies.
- On average there is a 75% reduction of immobilized wasteform packages than other treatments, reducing transportation, storage and disposal costs.
- SIAL® can be applied on site, avoiding the need to transport dangerous active waste to another site for treatment; eliminating the cost of disposing contaminated transport materials, and negating the need for costly off site treatment facilities.