Vitrification of Iron-phosphate sludge

Joint ICTP-IAEA International School on Nuclear Waste Vitrification

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Framework of Ansaldo Vitrification

Previous experience on Decommissioning phase of NPPs

The PHADEC Process (Phosphoric Acid Decontamination Process) was designed for decontamination of steel scrap with phosphoric acid and has been installed in Caorso NPP (PC) at the end of 2008.

The decontamination of steel parts (scrap parts) works by removing the surface oxides containing radioactive contaminants by means of 40%-phosphoric acid (with or without electropolishing): The saturated solution is then recycled. The main product of the PHADEC process is dry iron oxide powder, which can be easily conditioned in concrete for final storage.

Framework of Ansaldo Vitrification

Under development process

1. Decontamination (acid pickling)
2. Acid solution recycling
3. Vitrification
4. Glass in Final Waste Packages

Framework of Ansaldo Vitrification

Sludge to be vitrified

The starting point is a solution of Phosphoric acid and iron coming from pickling of contaminated metals (as for PHADEC process).

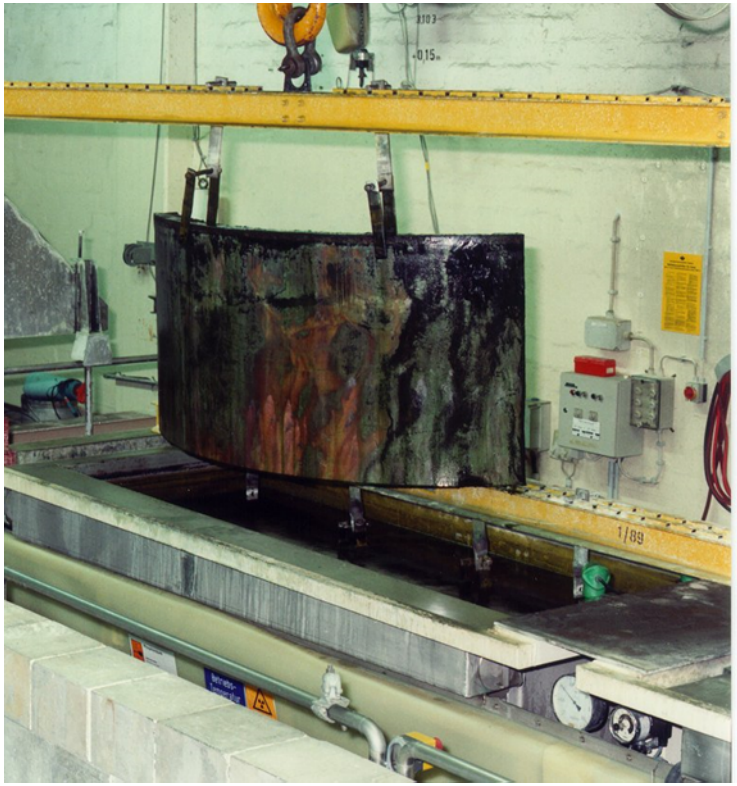
A series of unit phases allow a mixture of iron phosphates to precipitate together with radionuclides (Cs, Ni, Co , etc.).

<u>Properties of sludge.</u>

The **Loss On Drying** (LOD_{120}) depends mostly from the starting content of water in sludge.

TGA-EGA analysis, instead, demonstrated that hydration and crystallographic water does not vary so much, and it can be completely removed at a temperature T of about 600°C.

The **Loss On DeHydration** is averagely ($LODH_{625}$) equal to **16%**$_{wt}$.



Framework of Ansaldo Vitrification

Sludge to be vitrified

Most of sludge samples produced show a chemical composition in the following ranges (ICP-AES and XRF analysis):

P_2O_5	48 ÷ 53 $\%_{wt}$
Fe_2O_3	30 ÷ 34 $\%_{wt}$
H_2O	15 ÷ 18 $\%_{wt.}$

The resulting average composition is the following:

	As it is	DeHydrated
P_2O_5	50,7 $\%_{wt}$	60,4 $\%_{wt}$
Fe_2O_3	33,3 $\%_{wt}$	39,6 $\%_{wt}$
H_2O	16,0 $\%_{wt}$	-

Bibliographic review

Iron-phosphate glasses

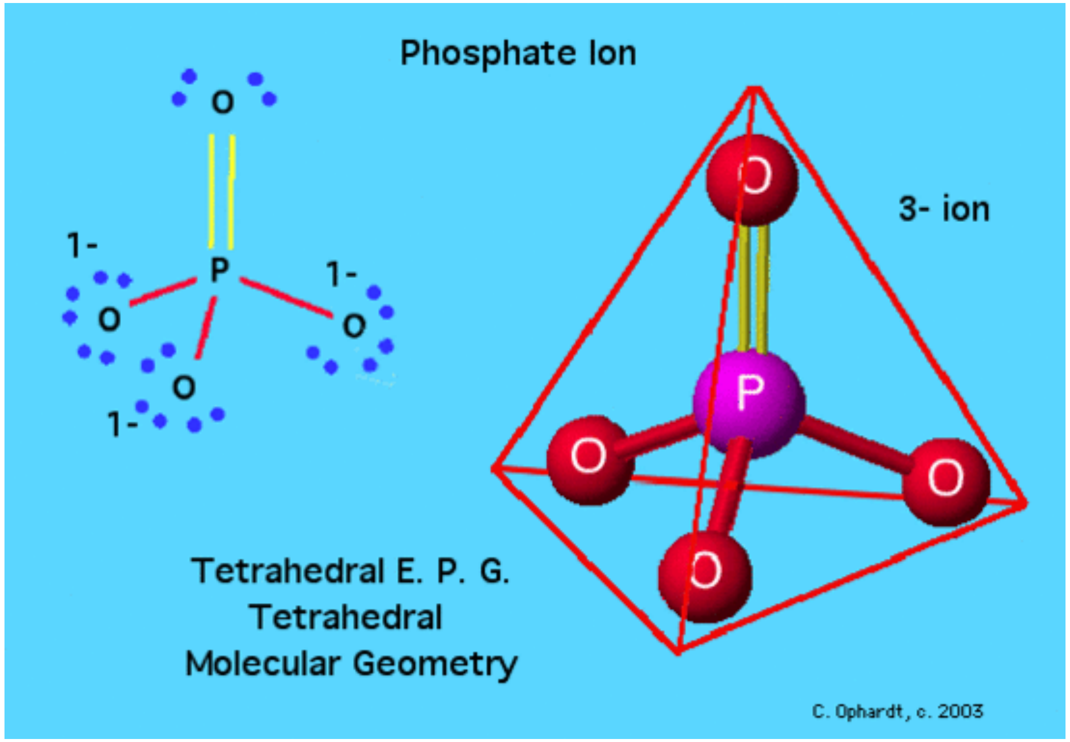
Bibliographic review

Iron-phosphate glasses - Structure

- Glass phosphate properties usually depends mostly upon the additives used in the melting process (formers and modifiers).

- Commonly used additives are:
  - rare earths, for optics and photonics;
  - Zn phosphates, for medical applications;
  - Pb and Na phosphates, because of their low glass transition temperature (<300°C).

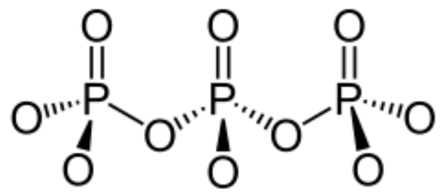
Basic structure unit of phosphate glasses network is the ortho-phosphate $[PO_4]^{3-}$ tetrahedron.

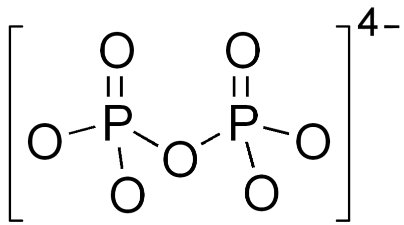


Bibliographic review

Iron-phosphate glasses - Structure

- Several types of network could be formed, dependently on the basic unit organization and other oxide abundancy presence; possible structures could be:
  - Meta-phosphates = long linear polymeric chains of tetrahedrons (PO_4) linked by -P-O-P- bonds; other oxides inserts in this chain form the network.
  - Pyro-phosphates = the basic structure is the dimer of two phosphates tetrahedrons with a single P-O-P bridge,
  - Orto-phosphates = their structure is based on isolated PO_4 tetrahedra



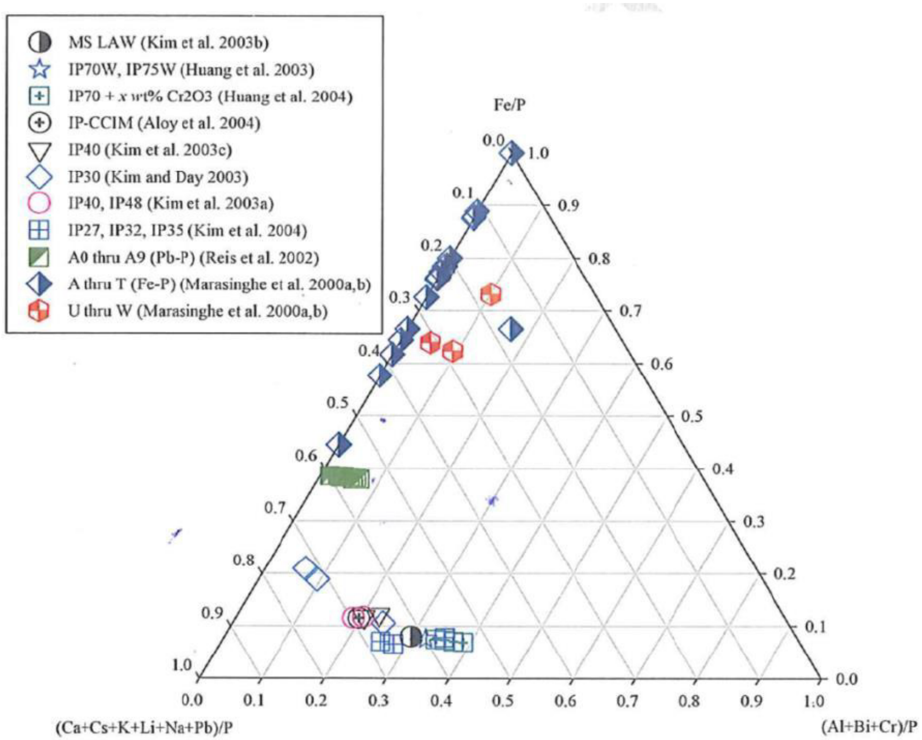


- By adding adequate amount of M_2O_3 oxides to phosphate glasses, resistance to leaching significantly improve:
  - This is the case of iron phosphate glasses having the system $P_2O_5 – Fe_2O_3$

Bibliographic review

Iron-phosphate glasses - Literature

- At Rolla University, Missouri, various systems such as $M_2O-P_2O_5$, $MO-P_2O_5$, ternaries, quaternaries, etc, have been studied since 70s;
- First researches on phosphate glasses as a matrix for radioactive waste conditioning were conducted by URSS, both for civil and military waste:
  - Mainly phosphate glasses with Na e Al (with few Fe); till today is the unique industrial scale production made in Mayak of some thousands tonns of waste, melting was obtained electrically with Mo electrodes.
- Lead Iron Phosphates (LIP) have been studied and patented by Sales and Boatner, Oak Ridge National Laboratory.
- Iron phosphates was deeply studied at Battelle laboratories (Pacific Northwest, Lawrence Livermore, Idaho National, etc).



Bibliographic review

Iron-phosphate glasses - Literature

- D. E. Day group studied the iron-phosphates glass capacity of incorporate different amounts of radioactive waste, and with different composition, comprehending Cs_2O, UO_2, Na_2O, Bi_2O_3, SrO, SO_3, CsCl, SrF_2, and testing their glass properties with DR90, leaching, PCT.
  - Base glass had a composition 40%mol Fe_2O_3 – 60%mol P_2O_5 (similar to ECIR-ANN).
  - Studied demonstrated that this kind of glass matrixes can be loaded till 40%wt without affecting chemical durability.
  - This result double classical borosilicate glasses (15% max), mostly for waste rich in Na_2O (affecting durability) and SO_3 (low solubility).

Bibliographic review

Iron-phosphate glasses – Glass Networks

- The network made by Fe-O-P bridges , Results in more stable bonds respect to P-O-P.

- Moreover coordination polyhedra of Fe and pyro-phosphate dimers leave empty interstitial void that can be filled with other ions (including big ones like U), without significant alteration or depolymerization of the network.

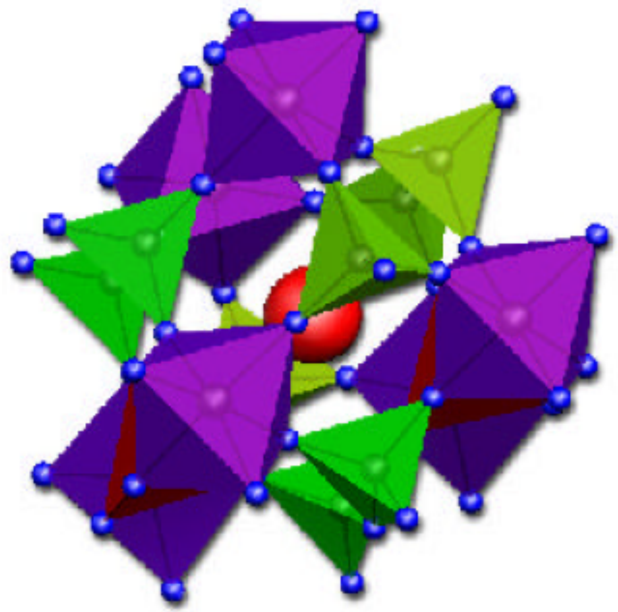


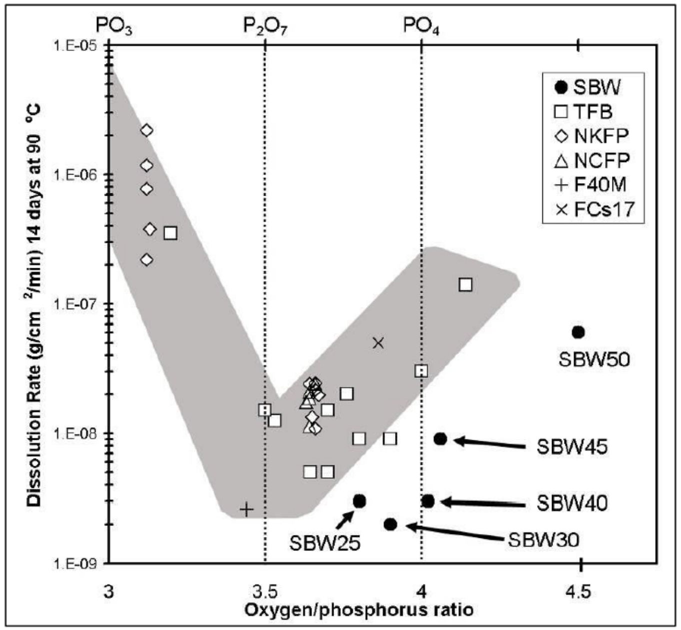
Fig. 14. A computer generated model of a uranium ion (red) encapsulated among the PO_4 tetrahedra (green) and FeO_n (n ~ 5-6) polyhedra (purple).

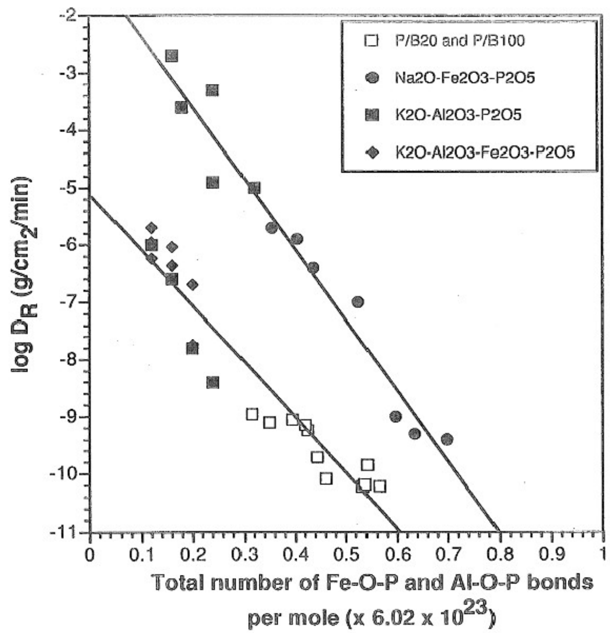
Bibliographic review

Iron-phosphate glasses – P/O and Fe/P optimal ratio

- Binary glasses $Fe_2O_3 - P_2O_5$ have the best chemical resistance with the following parameters:
  - Molar ratio O/P ≈ 3.5
  - Molar ratio Fe/P ≈ 0.67

- If other elements are added tolerance ranges continue to be wide enough for an industrial process (i.e. O/P ≈ 3.25 ÷ 3.70; (Fe+Al)/P ≈ 0.45 ÷ 0.70).





Bibliographic review

Iron-phosphate glasses – Melting and Long-term behaviour

Melting

- Most of literature reports melting experiences of iron-phosphates with other oxides around 1100 – 1150°C, and a residence time of 1-3 hrs.
- Commonly used borosilicate glasses for HLW has melting temperature about 150°C higher, with residence time of about 24 hrs.
- Since temperature and residence time are lower, retention of elements such as Cs is improved for iron-phosphate and make them candidate for immobilization of LILW.
- Mayak plant in Russia produced glasses with composition: P_2O_5 55%wt – (Al_2O_3+Fe_2O_3) 24% – Na_2O 21%, for HLW, over 6 years.

- Most of melting experiences was made on laboratory scale melting from ≈ 100 g to semi-pilot scale of about 30 kg per single melting (MO-SCI corp.).
- Some significant experiences in continuous melting were made at Savannah River with a crucible heated by Joule effect (JHM, electrodes were in Inconel 693, refractories Monofrax K3 in Cr_2O_3–Al_2O_3); while Idaho National Lab and KRI (Russia) successfully tested Cold Crucible Induction Melter technique.

Long-term behaviour

- While borosilicate glasses for nuclear application have been widely studied (e.g. in France by CEA) and consequently some studies have been studied over some decades. These studies are not available for iron-phosphate glasses.

Laboratory production of glass (by SSV)

Steps in nuclear glass world

Laboratory production of glass (by SSV)

First step - Glass from sludge as it is

Samples of iron-phosphates mixtures had been melted at temperature of 1150°C for 2 - 3 hrs in a crucible in silico-aluminous material, and the resulting melts was poured on a steel plate and than annealed at 485°C for about 1 hr, and left at environmental temperature.

Resulting glass was homogeneous, black, without evidence of devitrification effects (result confirmed by XRD) or significant residual stresses.

Fusion: 2 ÷ 3 hrs at 1150°C

Annealing: 1 hr at 485°C

Laboratory production of glass (by SSV)

First step - Glass from sludge as it is –Glass composition

Glass had the following chemical composition:

P_2O_5: 57,7 %wt

Fe_2O_3: 42,1 %wt

Relative enrichment in Fe_2O_3 due to small amount of P_2O_5 volatilization during melting.

Other melting tests with 5 iron-phosphate sludge mixed with non-radioactive contaminants spikes (~2000 ppm) of Cs, Ni e Co showed retentions levels averagely higher than 95% after melting at 1150°C per 3 hrs.

Laboratory production of glass (by SSV)

First step - Glass from sludge as it is – Glass durability

Preliminary assessment

- Specimen were immersed in de-ionized water for 48 hrs at 30°C, resulting in dissolution rate having log(DR30)= -8.14, this value is similar to the window glasses (float soda-lime glass: log(DR30) = -8.10).
- Leaching tests according to ANSI/ANS 16.1-2003 gave no results by using «cold» contaminants (Cs, Ni, Co, Sb): lower then the detection limits of ICP-AES instrument.
- The Italian norm UNI 11193 foresees also compression tests, so a test was conducted on small cylindrical specimen, the results were largely higher than the prescribed limit of 5 MPa (min ≈ 36 MPa, MAX > 90 MPa).

Laboratory production of glass (by SSV)

Next step - Lower the melting temperature

Based on literature review the activities are focused on lower the melting temperature by adding adequate additives (max 10%wt) in the sludge; candidates are the following:

- BaO and ZnO
- Na_2O
- PbO
- B_2O_3
- Bi_2O_3

Realisation of the Pilot Plant

The scope of on-going R&D activities is the development of the process to immobilize radioactive contaminants in a stable glass matrix and to safely allow its final storage.

Sezione di vetrificazione

Produzione del vetro finale

WHY?

- The sludge can be directly vitrified at 1100°C (“low” temperatures if compared with conventional silica glasses 1600°C).

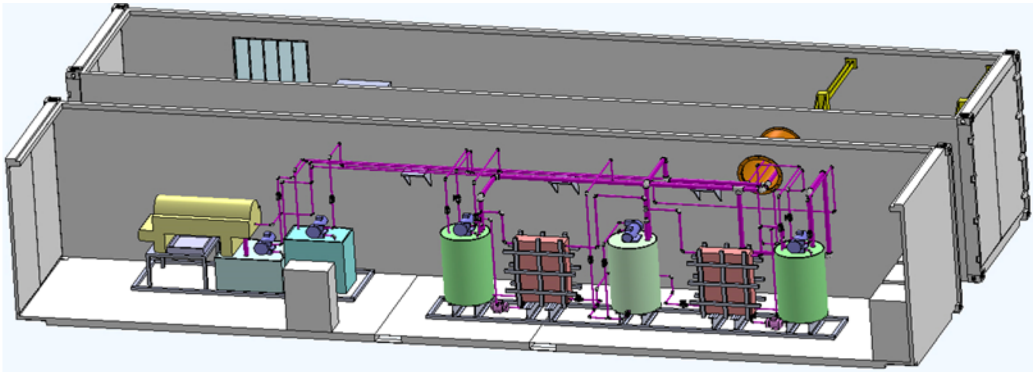
- No additives are required but their use could lower the melting temperature.

- Iron-phosphate glasses, based on available literature data, present high chemical stability, with dissolution rates (DR) higher than the ones shown by boron-silicate glasses:
  - DR = $1{,}5 \times 10^{-9}$ g/cm^2 min. vs 10^{-8}

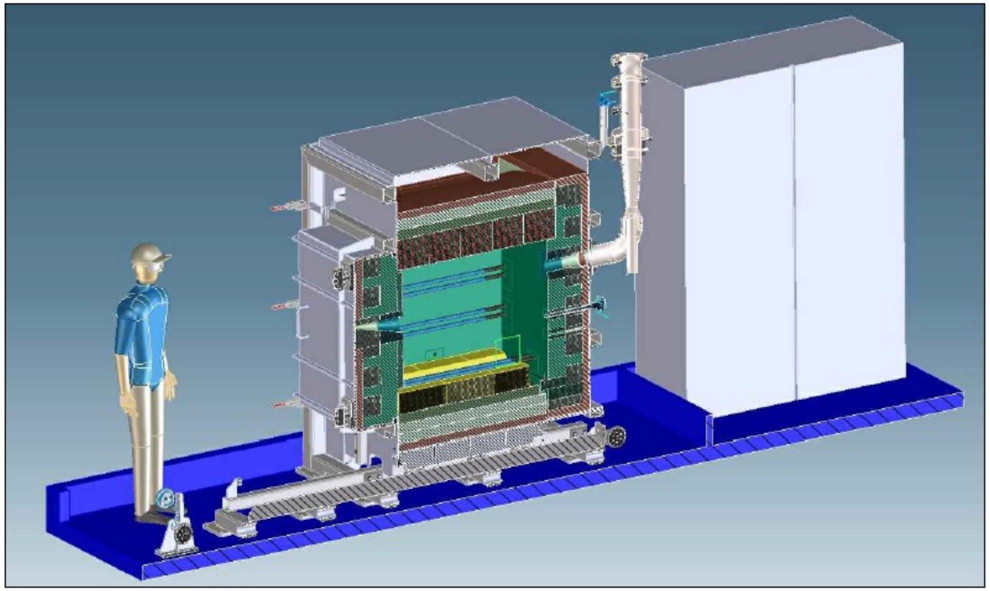
Sezione di vetrificazione

Produzione del vetro finale

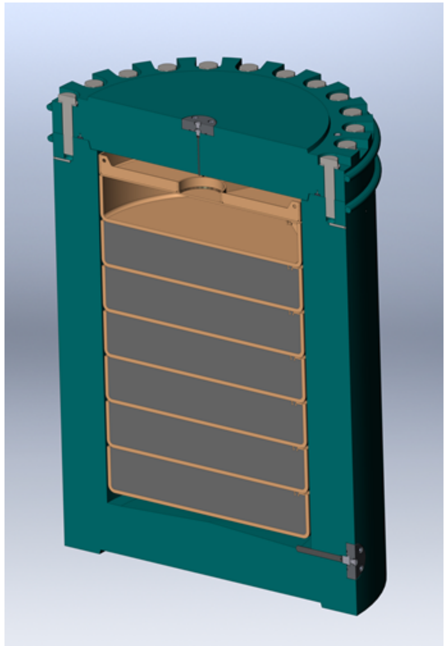
Decontamination section



Vitrification section



FWP in HIC



Thank you for your attention

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Aknowledgements:

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