Immobilization of liquid low-level waste from Kozloduy NPP by drying and subsequent sintering with inorganic additives

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The Evaporator Concentrate (EC):

Waste to be conditioned:	Evaporator Concentrate from Kozloduy NPP
EC composition:	Water solution of different Sodium and Potassium salts (nitrates, borates, citrates, oxalates, etc.)
Waste load:	About 350 g/l (dry basis)
Recent treatment of the EC:	Cementation with slag blended cement

The Cementitious Waste Form:

Advantages of the cementation technique	***Advantages of the cementitious waste form***	***Disadvantages of the cementitious waste form***
➢ Mature ➢ Simple and robust equipment ➢ Low temperature - low secondary contamination ➢ Cheap raw materials ➢ Low energy demand	➢ Good compressive strength ➢ Good leach resistance ➢ Good resistance to freeze/thaw treatment ➢ Proved behavior at aging (for up to 50 years)	➢ Low waste loading – about 150 $kg.m^{-3}$ EC (dry basis) ➢ Large volume – high disposal costs ➢ Problems with processing of historical wastes ➢ Unknown behavior for long-term storage periods (for centuries)

The Project:

Recent solution:	The cementation of the EC is a mature, reliable and viable technique which, however, has some limitations.
The Project goals:	To search for a supplementary waste form for stabilization/solidification of EC with ***higher waste loading*** and better acceptance of ECs with ***variable compositions.***

The candidates:

Low Temperature Waste Forms (Bitumen, Geopolymers, Ceramicrete)
High Temperature Waste Forms (Glasses, Glass ceramics, Ceramics)
Moderate Temperature Waste Forms (Clay-based ceramics, Sintered composites)

A. Low Temperature Waste Forms

Waste form	*Composition*	*Processing Temperature*	*Advantages*	*Disadvantages*
Bitumen	Organic	90 - 150°C	Simple; low operating cost, leach resistant	Flammable; poor performance with salts; thick even when molten; require extrusion
Geopolymers	Alkali (Lime) - Alumosilicate	Room temperature	Low temperature, fire resistant, pore water less alkaline than cements	Formulations are waste specific; batches are thick and require extrusion
Ceramicrete	Magnesium-Potassium Phosphate Hydrate	20 - 80°C	High waste loading (8 to 23 wt% on a dry basis), leach resistant, low temperature	Needs set retarder, waste specific, develops cracks at aging

Summary: *The non cementitious low temperature waste forms can not meet all requirements for the new waste form.*

B. High Temperature Waste Forms

Wasteform	*Composition*	*Processing Temperature*	*Advantages*	*Disadvantages*
Glasses	Borosilicate, Alumo-phosphate, Iron Phosphate	1200 - 1450°C	Preferred for HLW	Too expensive for LLW
Glass ceramics	Silicate, Borosilicate, Phosphate	1200 - 1450°C	Actinides can be securely confined in the crystalline phase	Too expensive for LLW
Ceramics Synroc - C	Ba, Al, Ca, Zr Titanates	1280 - 1380°C	The titanate minerals can incorporate into their crystal structures nearly all of the elements present in a radwaste.	Too expensive for LLW
Synroc – Glass Composites	Borosilicate glass + Synroc	1150 - 1400°C	50 wt% waste loading of HLW and ILW	Too expensive for LLW

Summary: *The highest waste loadings are reached at Synroc – Glass Composites. The preparation method, however, is too expensive and with too low capacity for LLW immobilization.*

C. Moderate Temperature Waste Forms

Wasteform	*Composition*	*Processing Temperature*	*Advantages*	*Disadvantages*
Clay-based Ceramics (FBSR)	Alkali - Alumosilicate	700 - 800°C	Can process a wide variety of solid and liquid streams including wastes containing organics, high waste loadings	Large volume of steam and off-gases to be conditioned, operationally complicated
Clay-based Ceramics (sintered)	Alkali - Alumosilicate	700 - 800°C	Same as by FBSR	Insufficient leaching resistance for some EC compositions
Glass Composite Materials (GCM)	Silicate, Borosilicate and Phosphate Glasses	600 - 1200°C	High waste loadings, moderate temperatures are possible, leach resistant	Not directly applicable for liquid waste streams

Summary: *None of the known waste forms can satisfy all requirements of the project. The sintered Clay-based Ceramics, however, as well as the Glass Composite Materials, sintered at moderate temperatures are promising.*

Start of the Project

The Project was started in the year 2012 at the University of Chemical Technology and Metallurgy ***(I. Gugov, I. Mitev, D. Ilieva)*** in collaboration with the Institute of Physical Chemistry – BAS, BG ***(E. Karamanova, A. Karamanov)***. The experiments started with ***sinter - encapsulation*** of simulated non-active EC compositions with CRT panel glass powders. The EC simulates was calcined previously at 800°C and ball-milled.

Composition of the dry EC simulate (wt%)

KNO_3	$NaNO_3$	$NaNO_2$	$NaHCO_3$	$NaCl$	H_3BO_3
23.6	20	20	18.2	4.6	13.6

Composition of the EC simulate, calcined at 800°C

K_2O	Na_2O	$NaCl$	B_2O_3
24.98 wt%	52.14 wt%	5.46 wt%	17.42 wt%

Composition of the CRT panel glass used (wt%)

SiO_2	Al_2O_3	Na_2O	K_2O	BaO	SrO
61.0	2.7	8.4	5.6	10.0	9.0

Result:

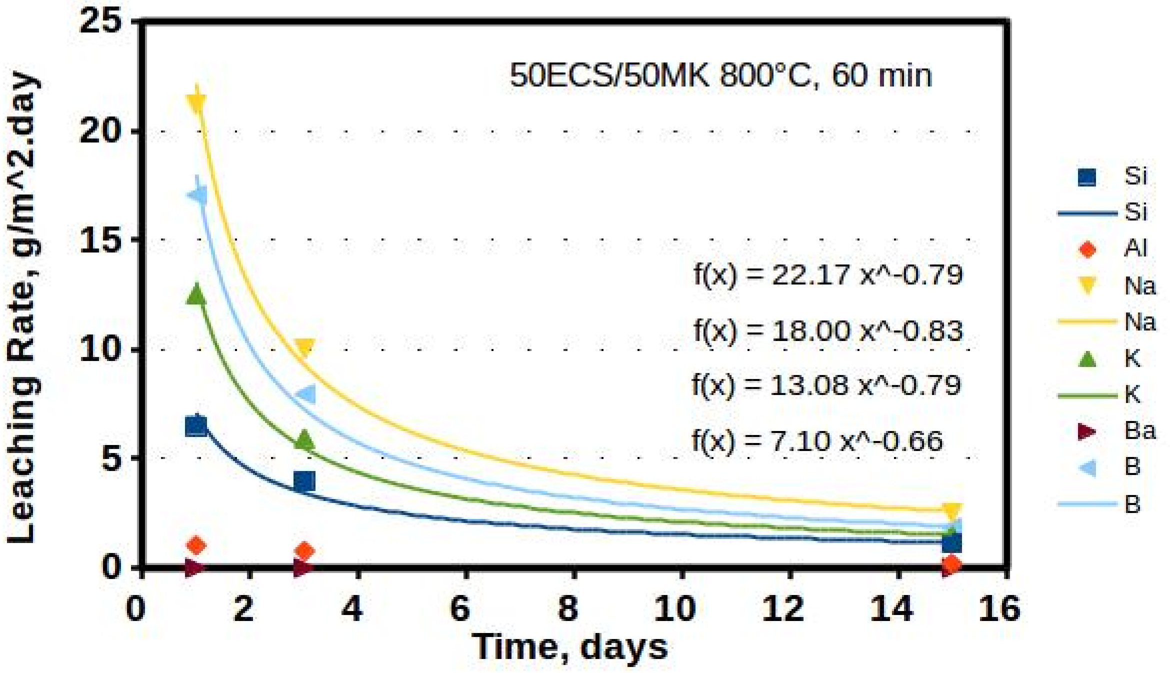
Fumed glass/waste composites with high porosity and insufficient leaching resistance.

Next step:

Preparation of sintered clay-based ceramics: The dry EC simulate was mixed with powdered metakaolin (50:50 wt parts) and calcined at 800°C; The calcinate was ball-milled and subsequently sintered at temperatures 750-800°C. Uniaxial cold pressing was used to obtain cylindrical samples.

Result:

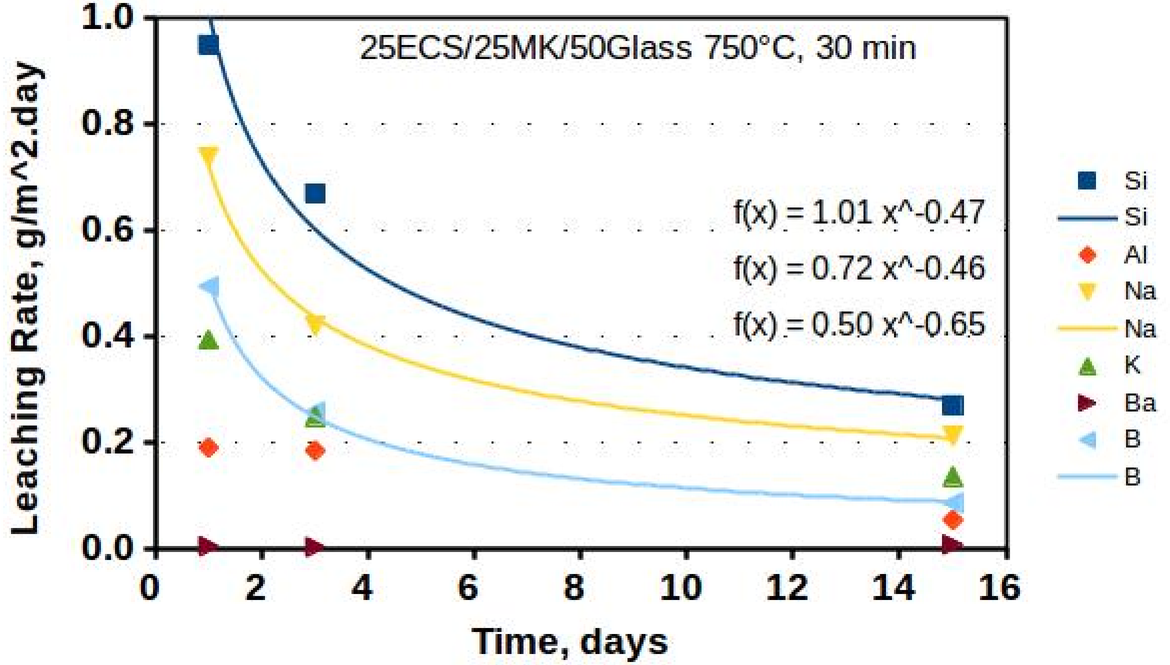
Sintered clay-based ceramics with apparent density of 1.9 g/cm^3, waste loading of 50 wt% (dry basis) and ***too high leaching rate*** of Sodium, Boron, Potassium and Silicon.



Remark: The allowed Leaching Rate for Sodium is ***1 g.m^{-2}.day^{-1}***

A Better Solution:

Sinter – encapsulation of EC/MK calcinate with a CRT glass powder: The powdered EC/MK calcinate was mixed with powdered CRT panel glass (50:50 wt parts). The mixture was homogenized, uniaxially pressed and sintered at 750°C. The obtained composite glass – ceramics has an apparent density of 2.1 g/cm^3, waste loading of 500 kg.m^{-3} and Sodium Leaching Rate lower than the allowed 1 g.m^{-2}.day^{-1}.



Final Results from the experiments with EC simulates:

The dry EC simulate can be chemically stabilized by calcination with metakaolin. A successive encapsulation of the EC/MK calcinate by sintering with CRT panel glass produces a chemically and mechanically stable waste form with waste loading of 500 $kg.m^{-3}$ on dry basis.

Questions:

1. Is it possible to treat real EC from NPP Kozloduy with the new technique?
2. How can the glass-ceramic composite to be immobilized?
3. Is it possible to complete the different technological steps within the highest standards for radiological and environmental safety?

Current development of the Project

The Project was developed further in a collaboration between the State Enterprise "Radioactive Waste" ***(A. Malakova, K. Ivanova, G. Georgiev)***, the University of Chemical Technology and Metallurgy ***(I. Gugov)*** and the "Besttechnika" Ltd. Co. ***(M. Kleitman)***.

Experiments with real EC were performed in Kozloduy. The real EC compositions were similar (on oxide basis) to the composition of the EC simulate. In addition to the radioactivity, the main difference is that part of the alkaline salts in the real EC have organic nature – oxalates and citrates. At the calcination step at 800°C, however, the organic salts decompose to alkali oxides, H_2O and CO_2 and do not affect the final products.

It should be mentioned, that at the calcination step the inorganic salts like nitrates and nitrites decompose as well, producing a relatively large amount of ***off-gases*** which are potentially radioactive. Future development of the Project should address this issue.

The preparation route:

- ***Drying the EC to constant wight***
- ***Ball-milling the dry EC***
- ***Mixing 50 EC / 50 metakaolin wt%***
- ***Homogenization***
- ***Calcination at 800°C for 60 min***
- ***Ball-milling the calcine***
- ***Mixing 50 calcine / 50 CRT glass***
- ***Homogenization***
- ***Optional uniaxial pressing***
- ***Sintering at 750°C for 60 min***
- ***Slow cooling***
- ***Immobilization in concrete***

Result:

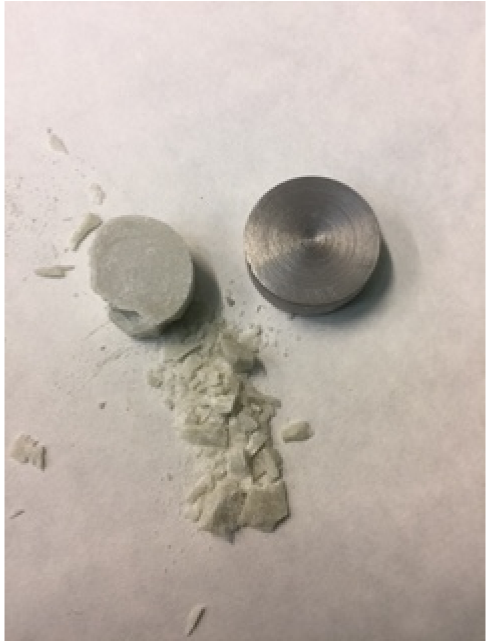
Sintered glass-ceramic composite with apparent density ***ρ = 2.3 ± 0.1 g.cm^{-3}***, waste loading of ***500 kg.m^{-3}*** (dry basis), compressive strength ***15 MPa*** and good leaching resistance.

Pressed and unpressed samples in furnace

Pressed samples after sintering

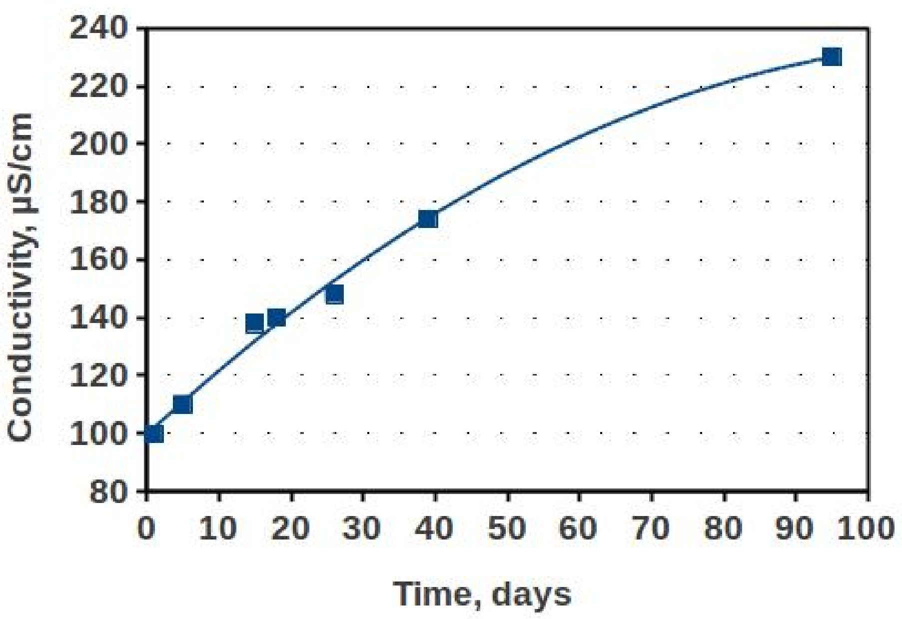
Shrinking of the pressed samples after sintering

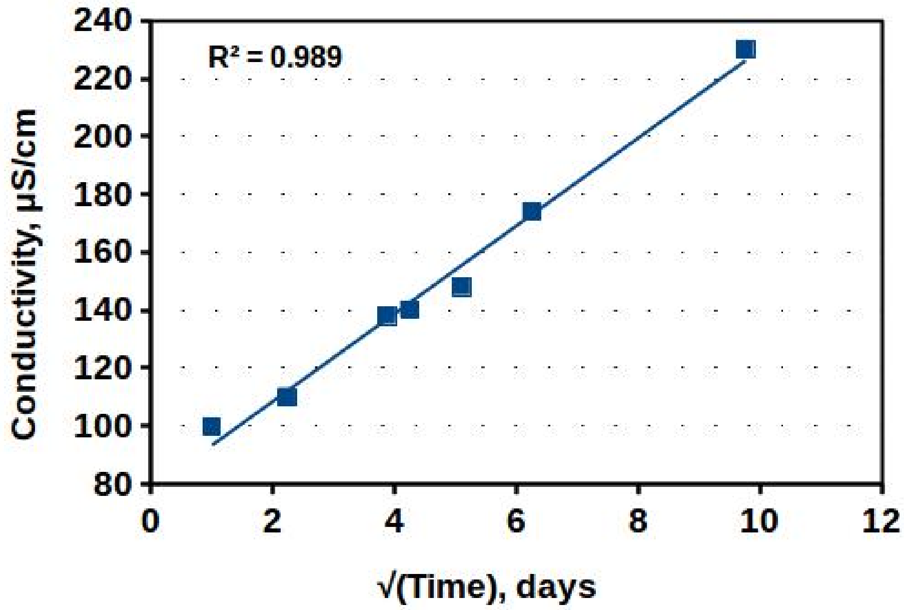
Shrinking of the unpressed samples after sintering



Pressed sample after the compressive strength test. The steel cylinder from the press form illustrates the diameter of the sample before sintering. After testing, the samples were additionally crushed in order to collect material for cementation

Preliminary leaching test of the Glass-Ceramic Composite:

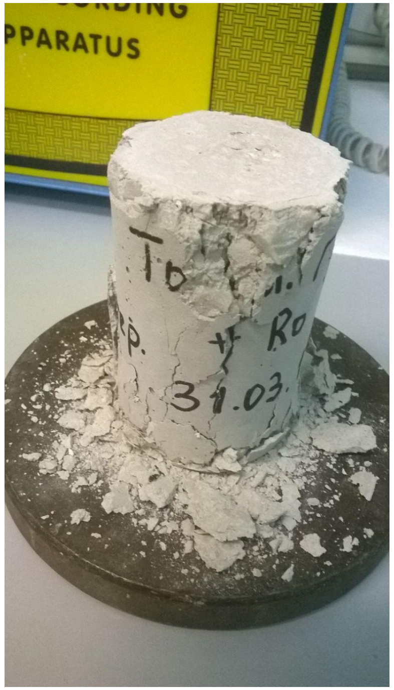




The specific conductivity is proportional to the concentration of ions in the leachate. After an initial jump, the conductivity grows proportional to the square root of time. This is typical for a leaching process governed by diffusion of ions from the sample's surface. In such a way, the mobile ions are depleted from the surface and the leaching rate decreases. For the whole period, the conductivity rise rate is as low as 2.5 µS.cm^{-1}.day^{-1}, compared to the conductivity of the deionized water of 2.5 µS.cm^{-1}.

Preparation of Concrete Waste Form with the Glass-Ceramic Composite

The particles from the crushed Glass-Ceramic Composite were mixed with slag cement and water. The Composite content in concrete is 70 wt% and the waste loading (dry basis) is ***350 kg.m^{-3}***. A standard cylindrical sample was prepared. The compressive strength of this sample was measured to be ***11.8 MPa*** after a 28 day period of curing. This is considerably higher than the required minimum of 3.5 MPa.



View of the cemented sample after the compressive strength test.

Final remarks and look to the future:

A new composite waste form was developed and applied for immobilization of real evaporator concentrate from NPP Kozloduy.

A large mass- and volume reduction can be achieved by full drying of the EC. The obtained soluble alkali salts can be chemically stabilized by mixing with metakaolin and heating at 800°C for 60 minutes.

The resulting clay-based ceramics do not have acceptable leaching resistance. This ceramics, however, can be further encapsulated by sintering with glass powder at 750°C. It is proven that the panel glass from old CRTs is suitable for this purpose.

The obtained glass-ceramic composite has waste load of 500 $kg.m^{-3}$, apparent density 2300 $kg.m^{-3}$, compressive strength 15 MPa and leaching rate of Na less than 1 $g.m^{-2}.day^{-1}$.

This composite can be used further as chemically inert concrete filler. Waste loading in this concrete is as high as 350 $kg.m^{-3}$ at 70 wt% filler loading. This is twice as high as the loading of the cement paste. The compressive strength of the concrete is 11.8 MPa.

The glass-ceramic composite immobilized in concrete can be stored in the same way as the recently used cement paste.

There are many questions which remain open at the present stage of the Project. A lot of work has to be done concerning the waste form as well as the immobilization technique.

Thank you for your attention!