



07.87.14

REPO - 22

GERENCIA DE PROTECCION RADIOLOGICA Y SEGURIDAD

REPO-22

07.87.14
CNEA-NT 18/87

ANALYSIS OF DIFFERENT VITREOUS
MATRICES OF THE BOROSILICATE
TYPE FOR SOLIDIFICATION OF HIGH-
LEVEL RADIOACTIVE WASTE

Varani, J.L.; Pasquali, R.C.;
Petratis, E.; Nollmann, C.E.



COMISION NACIONAL DE ENERGIA ATOMICA
BUENOS AIRES - ARGENTINA

1987

REPUBLICA ARGENTINA
COMISION NACIONAL DE ENERGIA ATOMICA
Dependiente de la Presidencia de la Nación
GERENCIA DE PROTECCION RADIOLOGICA Y SEGURIDAD

REPO-22

07.87.44
CNEA-NT 18/87

ANALYSIS OF DIFFERENT VITREOUS
MATRICES OF THE BOROSILICATE
TYPE FOR SOLIDIFICATION OF HIGH-
LEVEL RADIOACTIVE WASTE

Varani, J.L.; Pasquali, R.C.;
Petraitis, E.; Nollmann, C.E.

Este trabajo fue presentado en el "6 th. International Congress of the
International Radiation Protection Association", realizado en Berlín,
Rep. Fed. de Alemania, del 7 al 12 de mayo de 1984.

BUENOS AIRES
1987

INIS CLASSIFICATION AND KEYWORDS

E52.00

BOROSILICATE GLASS
HIGH-LEVEL RADIOACTIVE WASTES
MATRIX MATERIALS
RADIOACTIVE WASTE DISPOSAL
REPOSITORIES (*)
SOLIDIFICATION
UNDERGROUND DISPOSAL
VITRIFICATION

(*) Not Show in INIS Thesaurus 1985.

ANALYSIS OF DIFFERENT VITREOUS MATRICES OF THE BOROSILICATE TYPE FOR SOLIDIFICATION OF HIGH-LEVEL RADIOACTIVE WASTES

J.L.VARANI, R.C.PASQUALI, E.PETRAITIS, and C.E. NOLLMANN

1. INTRODUCTION

Presently, the Argentine Nuclear Plan (1) contemplates the installation of four nuclear power plants, in addition to Atucha I and Embalse, which are already in operation, before the end of the present century.

These six NPPs will involve an installed capacity of 3.5 GWe. The programme is based on natural uranium reactors and includes an industrial plant for the production of heavy water, whose construction is already well-advanced, as well as all the necessary installations aimed at completing the fuel cycle, including plutonium recycling.

Advanced studies are also being performed concerning the construction of a repository for the disposal of high-activity radioactive wastes in a granitic rock formation, with the objective of avoiding the occurrence of non-stochastic effects and of limiting the probability of occurrence of stochastic effects, while collective detriment is reduced as far as it is reasonable (2).

In order to reach these goals, the eliminated wastes must be kept isolated from mankind for as long as it is necessary for the original radioactivity to decay sufficiently.

Considering that, in order to limit the individual risk, the container of these vitrified wastes must allow for an isolation of an order of 1,000 years, while disregarding other engineering barriers, several studies were performed concerning the capacity of some vitreous matrices to retain a simulated composition of high level wastes. Additionally, an analysis was made of the glass properties by means of evaluation techniques.

2. EXPERIMENTAL WORK PERFORMED

2.1. PREPARATION OF GLASS CONTAINING SIMULATED WASTES

In a first step, the parent glasses were made; for their employment as frit in the final formulae. They were designed on the basis of three prototype compositions and the final formula was then analyzed after frit-

ting. The various compositions are shown in Table 1. These vitreous matrices, after their grinding and sieving through a 120-mesh screen, were added 10% in weight of simulated wastes. The composition of the latter is shown in Table 2. This is a mixture of oxides that was obtained by denitration with formaldehyde and later drying and calcination at 700°C of a 6N nitric solution of the various elements. The simulated waste glasses (further on "waste glasses") were elaborated in a muffle furnace at 1100°C for 8 hours inside ceramic crucibles.

Table I

Composition of the parent glasses
(in weight percentages)

Type	SiO ₂	B ₂ O ₃	Al ₂ O ₃	CaO	Na ₂ O	TiO ₂	Fe ₂ O ₃
A	42.2	20.0	14.43	0.73	14.49	0.10	1.20
B	39.4	22.0	14.90	8.67	8.58	0.10	0.22
C	49.7	12.4	2.23	3.62	25.72	4.70	0.30

Table II

Composition of the simulated waste oxides
(in weight percentages)

RuO ₂	6.89	La ₂ O ₃	22.68	SrO	2.45	Cr ₂ O ₃	0.71
BaO	4.42	MnO ₂	2.00	TeO ₂	1.82	NiO	0.71
CeO ₂	7.95	MoO ₃	13.39	ZrO ₂	13.18	P ₂ O ₅	6.46
Cs ₂ O	6.39	Rb ₂ O	0.99	Fe ₂ O ₃	1.68	UO ₂	8.28

2.2. LEACHING RESISTANCE TEST

The method applied consisted in treating a 2 gr sample of ground glass, its granulometry being between 0.297 and 0.595 screen meshes, with 50 cm³ distilled water at 98°C during one hour. The assessment of alcalinity was

performed by means of a potentiometric titration with HCl 0.01 N. Additionally, a quantitative analysis was made of the leachates resulting from tests performed on the parent glasses. Table 3 shows the results obtained in the leaching tests.

Table III

Results of the leaching tests

SAMPLE	PARENT GLASSES		WASTE GLASSES	
	HCl 0.01 N (cm ³ /g)	meq /m ² .h	HCl 0.01 N (cm ³ /g)	meq/m ² .h
A	1.10	0.42	0.92	0.37
B	0.50	0.19	0.42	0.16
C	16.20	6.20	19.30	7.30

Table 4 shows the concentrations of the various parent glass components found in the leachates.

Table IV

Chemical analysis of the leachates
(µg/cm³)

SAMPLE	Na	Ca	Mg	Zn*	Al	Fe*	Si	B
A	7	0.1	0.05	0	1.2	0	14	8.9
B	2	2.2	0.03	0	2.1	0	13	4.1
C	79	0.2	0	0	0.6	0	107	19.5

* Results below the detection limits.

2.3. DIFFERENTIAL THERMAL ANALYSIS

By means of this technique and during the gradual heating of the glasses, the endothermal and exothermal peaks were assessed, corresponding with the transition and maximum crystal growth temperatures (T_g and T_k) (3,4). Each sample weighed 30 mg and a temperature of 900°C was reached at a speed of 10°C/min. The results obtained are shown in Table 5.

Table 5

SAMPLE	T _g (°C)	T _k (°C)
A	560	710
B	590	750
C	530	850

2.4 X-ray diffraction

The diffractometric technique was applied on 400-mesh glass powder, with $K\alpha_{Cu}$ radiation. The studies were performed on parent and waste glasses and the crystallization degree of the various samples was verified.

The parent glasses were annealed, their temperature was rapidly lowered to 500° and then slowly lowered to room temperature, thus sumulating the actual cooling of a container filled with waste glass.

The simulated waste glasses were annealed at 700°C for 120 hours in order to attain their devitrification.

The diffraction results obtained from parent glasses show a virtual amorphous condition, which is an indication of the actual vitreous quality of the analyzed material before simulated waste addition. The tests performed on the annealed waste glasses showed marked devitrification, while it was detected that the magnitude of this phenomenon is directly proportionate to the glass sodium content.

3. EVALUATION OF THE RESULTS AND CONCLUSIONS

As it had already been assumed, the studies on the leaching rate served to verify that there is a direct relation between this parameter and the glass alkali content. The samples that showed the lowest leaching rate are those of the B type, whose Na_2O content is also the lowest. There is also a direct relation between most of the component concentrations in the parent glasses and those in the leachates. The exception is boron, for which an inverse relation was observed.

It was also noticed that the addition of simulated wastes to the parent glasses does not modify substantially their solubility. The X-ray diffraction tests showed that the samples with the lowest crystallization tendency are the ones with the lowest alkali content and, in turn, those less liable to be leached. This is the case of samples of the B type.

An inverse and almost linear relation was verified between the transition temperatures, T_g , and the glass sodium content, as well as between the former and viscosity.

An analysis of the results allows for detecting clear advantages of sample B, as compared with samples A and C and, therefore, future studies will be aimed at the qualification of vitreous compounds similar to the B type.

REFERENCES

- (1) Castro Madero C. "El Plan Nuclear Argentino y su proyección futura". Futurable; vol. 10: p.25-39, (1981).
- (2) Migliori de Beninson, A. and Cancio, D. "Impacto radiológico de la gestión de residuos radioactivos del Plan Nuclear Argention". International Conference on radioactive waste management. Seattle, Wasthington, may 16-20, 1983. Proceedings series. STI/PUB/649. vol.1 : 331-344. REPO-07. CNEA-NT 30/85.
- (3) Malow, G. and Schiewer, E. "Fission products in glasses. Pt.1." Berlin, (Germany, F.R.), Hahn-Meitner-Institut fuer Kernforschung Berlin G.m.b.H., sep.1977. HMI-B-217. 33 p. 13 figs.; 17 tabs.; 21 refs.
- (4) Jones, G.O. "Glass". London, Chapman and Hall Ltd., 1971. 128 p.

- REPO-01 Beninson, D.; Migliori de Beninson, A.
"Radiological impact of radioactive waste management"
- REPO-02 Lucero Michaut, H.
"Aplicación de la geoestadística a la resolución de problemas estructurales en macizos rocosos homogéneos"
- REPO-03 Ventura, M.; Ferreri, J.C.
"Evolución temporal de un macizo granítico bajo cargas térmicas generadas por productos de fisión"
- REPO-04 Ventura, M.; Ferreri, J.C.
"Evolución temporal de un macizo granítico bajo cargas térmicas generadas por productos de fisión (estudio paramétrico)"
- REPO-05 Beninson, D.
"Radioactive emissions and radiation exposures resulting from nuclear power production"
- REPO-06 Beninson, D.; Lindell, B.
"Application of ICRP recommendations to radioactive waste isolation"
- REPO-07 Migliori de Beninson, A.; Cancio, D.
"Impacto radiológico de la gestión de residuos radiactivos del Programa Nuclear Argentino"
- REPO-08 Migliori de Beninson, A.; Palacios, E.
"Política en materia de gestión de desechos y su aplicación en Argentina"
- REPO-09 Palacios, E.; et al.
"Bases conceptuales para la construcción de un repositorio en la Argentina".
- REPO-10 Palacios, E.; et al.
"Estudios para la selección del emplazamiento de un repositorio en Argentina"
- REPO-11 Matar, J.A.; Girardi, J.P.; Matar de Sarquís, M.
"Aplicación de técnicas geoestadísticas al estudio de una formación granítica destinada a la construcción de un repositorio"
- REPO-12 Ferreri, J.C.; VENTURA, M.
"Numerical aspects of the study of the regional thermal impact of a radioactive waste repository"
- REPO-13 Ferreri, J.C.; Caballero, C.H.
"Difusión de calor a partir de una fuente plana rectangular finita"
- REPO-14 Beninson, D.; González, A.J.
"Radiological protection criteria for radioactive waste repositories"
- REPO-15 Palacios, E.; Ferreri, J.C.
"Marco conceptual para el desarrollo de los modelos de predicción de los efectos locales de un repositorio de residuos radiactivos de alta actividad"

- REPO-16 Ferreri, J.C.; Ventura, M.
"Aspectos numéricos del modelado de los efectos locales de un repositorio de residuos radiactivos de alta actividad"
- REPO-17 Beninson, D.
"Criterios de radioprotección en el caso de eventos disruptivos probabilísticos"
- REPO-18 Ferreri, J.C.; Grandi, G.
"Models for the study of the local effects produced by a high-level radioactive waste repository"
- REPO-19 Beninson, D.J.; et al.
"The argentine radioactive waste repository: basic criteria, preliminary siting and design conceptual basis"
- REPO-20 De Micheli, S.M. de; et al.
"Uso del plomo en contenedores de residuos radiactivos de alta actividad: estudio de resistencia a la corrosión"
- REPO-21 Peruca, J.C.; et al.
"Investigaciones geológicas e hidrológicas con procesamiento geoestadístico en la preselección del emplazamiento de un repositorio subterráneo para los residuos radiactivos de alta actividad del Programa Nuclear Argentino"
- REPO-22 Varani, J.L.; et al.
"Analysis of different vitreous matrices of the borosilicatype"
- REPO-23 Varani, J.L.; Petraitis, E.J.; Vazquez, A.
"Vitrificación de residuos radiactivos líquidos de alta actividad"
- REPO-24 Varani, J.L.; Petraitis, E.J.; Pasquali, R.C.
"Evaluación de matrices vitreas para inclusión de residuos radiactivos"
- REPO-25 Russo, D.; Messi de Bernasconi, N.; Audero, M.
"Fijación de residuos de alta actividad en matriz vítrea sinterizada"
- REPO-26 Wetten, C.; Grassi, J.I.
"Hydrogeological features of a rocky massif to be used as a nuclear repository"
- REPO-27 Girardi, J.P.; Matar de Sarquís, M.
"Selection of a minimum fracturation area by means of geostatistic for emplacement of subsurface civil works of a nuclear repository in crystalline rock"
- REPO-28 Matar, J.A.; et al.
"Geostatistical investigations of rock masses. The Sierra del Medio case (Argentina)"
- REPO-29 Perucca, J.C.; et al.
"Geological and geophysical investigations at Sierra del Medio Massif - Argentina"

- REPO-30 Russo, D.O.; Messi de Bernasconi, N.; Audero, M.A.
"Inmovilización de residuos de alta actividad en vidrios sinterizados: 1) Proceso de prensado en caliente"
- REPO-31 Bevilacqua, A.M.; et al.
"Inmovilización de residuos de alta actividad en vidrios sinterizados: II) Proceso de prensado a temperatura ambiente"
- REPO-32 Ventura, M.
"Predicción de la migración de radionucleidos en un medio rocoso. Parte I"
- REPO-33 Ventura, M.
"Predicción en la migración de radionucleidos en un medio rocoso. Parte II-Caso bidimensional"
- REPO-34 Palacios, E.
"Política argentina para la eliminación de residuos radiactivos"
- REPO-35 Pahisa, M.; et al.
"Primeros ensayos vinculados a la vitrificación de residuos líquidos de alta actividad".

COMISION NACIONAL DE ENERGIA ATOMICA
Gerencia Protección Radiológica y Seguridad

	Domicilio Postal Postal Address	Télex	Facsimil	Telefono
Sede Central (Main Headquarters)	Av. Libertador 8250 1429 - Euenos Aires Argentina	21388 PREAT AR	701 - 2431 (int. 248) (ext. 248)	701 - 2431
Centro Atómico Ezeiza Ezeiza Atomic Center	Casilla de Correo 40 1802 - Aeropuerto Ezeiza Argentina	23462 CAE PRS AR	620 - 0480	620 - 0160