ANALYSIS OF DIFFERENT VITREOUS MATRICES OF THE BOROSILICATE TYPE

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

Comisión Nacional de Energía Atómica, Argentina

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 GW_e. 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.

EXPERIMENTAL WORK PERFORMED

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 fritting. 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 ellaborated in a muffle furnace at 1100°C for 8 hours inside ceramic crucibles.

Table 1

Composition of the parent glasses
(in weight percentages)

Type	SiO_2	B_2O_3	Al_2O_3	CaO	Na_2O	TiO_2	Fe_2O_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 2

Composition of the simulated waste oxides
(in weight percentages)

RuO_2	6.89	La_2O_3	22.68	SrO	2.45	Cr_2O_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_2O_5	6.46
Cs_2O	6.39	Rb_2O	0.99	Fe_2O_3	1.68	UO_2	8.28

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 meshs, with 50 cm^3 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 3

Results of the leaching tests

Sample	Parent glasses		Waste glasses	
	HCl 0.01 N (cm^3/g)	$meq/m^2 \cdot h$	HCl 0.01 N (cm^3/g)	$meq/m^2 \cdot h$
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 4

Chemical analysis of the leachates
($\mu g/cm^3$)

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.

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 (Tg and Tk)(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	Tg (°C)	Tk (°C)
A	560	710
B	590	750
C	530	850

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 crystalization 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 simulating 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 vitual 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.

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, Tg, 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.

BIBLIOGRAPHY

1. Castro Madero, C. "El Plan Nuclear Argentino y su proyección futura". Futurable (Buenos Aires) v.10: 25-39, 1981.

2. Migliori de Beninson, A. and Cancio, D. 1983 IAEA-CN-43/118

3. Mallow, G. and Schiewer, E. 1977 HMI-B217, Part I.

4. Jones, G.O. "Glass". 2. ed. London, Chapman & Hall, 1971. 128 p.