



IN0301530

BARC/2002/E/031

BARC/2002/E/031

VITRIFICATION OF SPENT MORDENITE MOLECULAR SIEVES

by

N. Sathi Sasidharan, D. S. Deshingkar, Savita Jain

I. J. Singh and P. K. Wattal

Back-End Technology Development Division



भारत सरकार

Government of India

भाभा परमाणु अनुसंधान केंद्र

Bhabha Atomic Research Centre

मुंबई Mumbai - 400 085, भारत India

2002

GOVERNMENT OF INDIA
ATOMIC ENERGY COMMISSION

VITRIFICATION OF SPENT MORDENITE MOLECULAR SIEVES

by

N. Sathi Sasidharan, D. S. Deshingkar, Savita Jain

I. J. Singh and P. K. Wattal

Back-End Technology Development Division

BHABHA ATOMIC RESEARCH CENTRE
MUMBAI, INDIA

2002

BIBLIOGRAPHIC DESCRIPTION SHEET FOR TECHNICAL REPORT
(as per IS : 9400 - 1980)

01	<i>Security classification :</i>	Unclassified
02	<i>Distribution :</i>	External
03	<i>Report status :</i>	New
04	<i>Series :</i>	BARC External
05	<i>Report type :</i>	Technical Report
06	<i>Report No. :</i>	BARC/2002/E/031
07	<i>Part No. or Volume No. :</i>	
08	<i>Contract No. :</i>	
10	<i>Title and subtitle :</i>	Vitrification of spent mordenite molecular sieves
11	<i>Collation :</i>	22 p., 1 fig., 6 tabs.
13	<i>Project No. :</i>	
20	<i>Personal author(s) :</i>	N. Sathi Sasidharan; D.S. Deshingkar; Savita Jain; I.J. Singh; P.K. Wattal
21	<i>Affiliation of author(s) :</i>	Back-End Technology Development Division, Bhabha Atomic Research Centre, Mumbai
22	<i>Corporate author(s) :</i>	Bhabha Atomic Research Centre, Mumbai-400.085
23	<i>Originating unit :</i>	Back-End Technology Development Division, BARC, Mumbai
24	<i>Sponsor(s) Name :</i>	Department of Atomic Energy
	<i>Type :</i>	Government

30	<i>Date of submission :</i>	October 2002
31	<i>Publication/Issue date :</i>	November 2002
40	<i>Publisher/Distributor :</i>	Head, Library and Information Services Division, Bhabha Atomic Research Centre, Mumbai
42	<i>Form of distribution :</i>	Hard copy
50	<i>Language of text :</i>	English
51	<i>Language of summary :</i>	English
52	<i>No. of references :</i>	15 refs.
53	<i>Gives data on :</i>	
60	<i>Abstract :</i>	Vitrification of cesium loaded inorganic ion exchangers (mordenite type molecular sieves/zeolite AR-1) was studied employing borosilicate glass systems. Direct vitrification of aluminosilicates is rather difficult mainly on account of volatility of cesium at processing temperatures of 1100° C-1300° C. In the borosilicate glass system, oxides of lead, sodium and zinc along with boric oxide were employed as major glass formers. Homogeneous glass matrix was obtained incorporating simulated composition of mordenite along with oxides of sodium, lead and boron at the processing temperature of 950° C. The waste oxide loading up to 50% on dry weight basis was incorporated in this glass formulation. Partial replacement of PbO by TeO ₂ , Bi ₂ O ₃ and CaF ₂ resulted in lowering of the processing temperature and also increasing homogeneity of matrix. Based on these results, a glass matrix was prepared with actual cesium AR-1 molecular sieves with processing temperature limited to 925° C. Powdered samples of glass matrix were subjected to leaching as per ASTM-1285 Product Consistency Test in high purity water at 90° C for 28 days. The normalised cesium leach rate of this glass was found to be 3.92x10 ⁻⁶ g/cm ² /day, which is comparable to sodium borosilicate glass matrices currently in use for immobilisation of high level waste. The molecular sieves are also amenable to immobilization in cement matrix. As expected, there is substantial volume reduction by factor 3 in vitrification compared to their immobilization in cementitious matrices. Also the quantity of cesium leached from vitrified product was nearly 10,000 times lower compared to cement based matrix. Vitrification of mordenite molecular sieves would lead to high capacity utilisation of zeolite AR-1 for the treatment of low and intermediate level liquid effluents.
70	<i>Keywords/Descriptors :</i>	CESIUM; VITRIFICATION; MORDENITE; CEMENTS; LEACHING; BOROSILICATE GLASS; HIGH-LEVEL RADIOACTIVE WASTES; INORGANIC ION EXCHANGERS; MOLECULAR SIEVES; RADIOACTIVE WASTE PROCESSING
71	<i>INIS Subject Category :</i>	S12
99	<i>Supplementary elements :</i>	

VITRIFICATION OF SPENT MORDENITE MOLECULAR SIEVES

N. Sathi Sasidharan, D.S. Deshingkar, Savita Jain, I.J. Singh & P.K. Watal

Back-End Technology Development Division

1.0 INTRODUCTION

Synthetic zeolites of Indian origin are known to be excellent sorbents¹⁻³ for the removal of radio nuclides from low level radioactive liquid effluent streams generated during nuclear fuel cycle. Studies on evaluation of different indigenously available synthetic zeolites have indicated that, zeolite AR-1, a mordenite, is⁴ most effective in removing radio cesium from different types of waste streams. Being aluminosilicate, these molecular sieves are compatible with both cement and glass matrices. Zeolites themselves have also been suggested as stable matrix by subjecting them to thermal⁵ or hydrothermal treatment⁶, which results in their transformation to new phases, wherein radioactive species get immobilised. However hydrothermal treatment leads to formation of amorphous powder having high surface area. Thermal treatment requires high temperatures in the range of 1100°C-1300°C, which lead to volatilisation of radio cesium.

Our earlier studies have indicated that fixation of molecular sieves into cement matrix is⁴ feasible. However with high cesium content of cement matrix, activity levels of leachants increase significantly, thereby rendering the matrix unacceptable. As an alternative, it is advantageous to immobilise these spent molecular sieves in glass matrix, which is known to be superior. The zeolites being aluminosilicates their vitrification requires addition of boron trioxide and small quantities of oxides of lead, zinc, sodium etc. as glass formers. These glass forming additives have potential to increase the waste loading to as high as 50 %, compared to 25 % reported⁷ for aluminosilicates and high level waste matrices^{8,9}.

The present work discusses the compositional development for cesium loaded molecular sieves AR-1 to obtain a vitreous product having processing temperature below 1000°C and acceptable leach rates.

2.0 EXPERIMENTAL WORK

The mordenite molecular sieves contain Na_2O , Al_2O_3 and SiO_2 in the weight ratio of 1.0 : 1.64 : 9.70. Due to high silica content of the mordenite, it was decided not to add external silica during vitrification. Alumina is known to improve the glass matrix properties in low concentrations but leads to increase of processing temperature at high concentrations. Considering the alumina content of mordenite molecular sieves, any further addition of alumina was ruled out.

Boric oxide is another trivalent glass former which helps in decreasing processing temperature without significantly affecting the leach rates. Additional sodium oxide can lower the processing temperature of glass matrix but can lead to higher leach rates for both sodium and cesium. Lead and zinc oxides have capability to lower the processing temperature of glass without affecting the sodium and cesium leach rates. Considering these aspects, boric oxide and lead oxide were considered as main glass formers along with zinc oxide and sodium oxide.

2.1 Preparation of Glass

Sodium nitrate, cesium nitrate, boric acid, zinc oxide and alumina were dried at 110 °C before use. Moisture content of -100 BSS mesh silica was estimated by heating to 900°C and taken into account while weighing.

The glass mixtures were ground in stainless grinder and transferred to alumina crucible. The crucibles were placed in a muffle furnace having temperature not exceeding 200°C. The temperature of furnace was raised to 900 °C in 4 hours and then increased gradually to test the minimum processing temperature of fused glass mass by tilting the crucible inside the muffle furnace itself immediately after opening the door. The glass was soaked to homogenise for at

least 4 hours and poured on to stainless steel tray. While pouring, a thin fibre of glass was drawn and then viewed under microscope to check homogeneity and entrapped gas bubbles.

2.2 Glasses Prepared with Simulated Na-Mordenite Composition

Simulated mordenite composition was prepared by weighing appropriate quantities of sodium nitrate, alumina and silica in proportion to their oxide content in mordenite.

2.2.1 PbO and B₂O₃ as glass formers

Set of glasses were prepared by adding only B₂O₃ as glass former with simulated Na-mordenite loadings varying between 52.6 to 66.7 wt % (B1 to B5). A glass was prepared by adding PbO and B₂O₃ in order to decrease processing temperature, foaming and increase the homogeneity of glass matrix (B6). To further improve homogeneity and reduce the processing temperature, part of lead nitrate was replaced by TeO₂, Bi₂O₃ and CaF₂ (B6A). The glass compositions and observations are indicated in **Table 1**.

2.2.2 PbO, B₂O₃ and ZnO as glass formers

Five glasses were prepared by using ZnO in addition to PbO and B₂O₃ as glass formers along with simulated Na-mordenite (Z1 to Z5). The glass compositions and observations are indicated in **Table 2**.

2.2.3 PbO, B₂O₃ and Na₂O as glass formers

Five glasses were prepared by using Na₂O in addition to PbO and B₂O₃ (N1 to N5). To further improve homogeneity and reduce the processing temperature, two glasses were prepared by replacing part of lead nitrate by TeO₂, Bi₂O₃ and CaF₂ (N4A and N5A). The glass compositions and observations are indicated in **Table 3**.

Table 1**VITRIFICATION OF SIMULATED Na-MORDENITE**

Lead Borosilicate Glass Formulations

Glass Code	Composition in Weight %			Processing Temp. (°C)	Remarks	
	Na-Mordenite AR-1 (Simulated)*	Glass Formers				Additives
		B ₂ O ₃	PbO			
B1	66.7	33.3	0	0	1100	Homogeneous, Very Difficult to Pour at 1000°C, Trapped Gas Bubbles
B2	62.5	37.5	0	0	1100	Homogeneous, Very Difficult to Pour at 1000°C, Slight Foaming
B3	58.8	41.2	0	0	1050	Homogeneous, Difficult to Pour at 1000°C, Slight Foaming
B4	55.5	44.5	0	0	1050	Homogeneous, Difficult to Pour at 1000°C, Significant Foaming
B5	52.6	47.4	0	0	1000	Homogeneous, Difficult to Pour, Highly Foaming
B6	50.0	25.0	25.0	0	1000	Homogeneous, Easy to Pour, Trapped Gas Bubbles
B6A	50.0	25.0	22.0	3 TeO ₂ Bi ₂ O ₃ , CaF ₂	975	Homogeneous, Easy to Pour, Trapped Gas Bubbles

* Weight Ratios of Na₂O, Al₂O₃ & SiO₂ as 1.0 : 1.64 : 9.70

Table 2
VITRIFICATION OF SIMULATED Na-MORDENITE

Zinc Borosilicate Glass Formulations

Glass Code	Composition in Weight %				Processing Temp. (°C)	Remarks
	Na-Mordenite AR-1 (Simulated)*	Glass formers				
		B ₂ O ₃	PbO	ZnO		
Z1	55.56	22.22	11.11	11.11	1000	Nonhomogeneous fused mass, Pourable
Z2	55.56	22.22	5.55	16.67	1050	Nonhomogeneous fused mass, Difficult to Pour at 1000°C
Z3	52.63	23.68	10.53	13.16	1000	Nonhomogeneous fused mass, Pourable,
Z4	52.63	23.68	15.79	7.89	1050	Nonhomogeneous fused mass, Difficult to Pour at 1000°C
Z5	50	25	15	10	1000	Nonhomogeneous fused mass, Pourable

* Weight Ratios of Na₂O, Al₂O₃ And SiO₂ as 1.0 : 1.64 : 9.70

Table 3
VITRIFICATION OF SIMULATED Na-MORDENITE

Sodium Borosilicate Glass Formulations

Glass Code	Composition in Weight %				Processing Temp. (°C)	Remarks	
	Na-Mordenite AR-1 (Simulated)	Glass Formers					Additives
		B ₂ O ₃	PbO	Na ₂ O			
N1	52.63	23.68	18.42	5.26	0	975	Homogeneous, Slight Foaming, Pourable
N2	52.63	23.68	13.16	10.53	0	975	Non-homogeneous, Slight Foaming. Slight Phase Separation., Pourable.
N3	50	25	20	5	0	1025	Non-homogeneous, Slight Foaming. Slight Phase Separation., Difficult to Pour at 1000°C
N4	50	25	15	10	0	975	Homogeneous, Pourable
N4A	50	25	12	10	3 TeO ₂ , Bi ₂ O ₃ , CaF ₂	950	Homogeneous, Pourable
N5	40	30	18	12	0	950	Homogeneous, Pourable
N5A	40	30	15	12	3 TeO ₂ , Bi ₂ O ₃ , CaF ₂	950	Homogeneous, Pourable

* Weight ratios of Na₂O, Al₂O₃ And SiO₂ as 1.0 : 1.64 : 9.70

2.3 Glasses Prepared with Simulated Cs--Mordenite Composition

Simulated Cs-mordenite composition was prepared by replacing half of Na_2O by equivalent Cs_2O . Two glasses were prepared by adding B_2O_3 , PbO and Na_2O to the simulated Cs-mordenite(N4A-Cs and N5-Cs). The glass compositions and observations are given in **Table-4**. Based on these results, one was selected for vitrification of Cs-AR1 Molecular sieves.

2.4 Vitrification of Cs- AR-1 Molecular Sieves using Selected Composition

2.4.1 Preparation of glass

24 gms of mordenite type AR-1 molecular sieves (supplied by Indian Pertochemical Corporation Limited, Mumbai) were equilibrated with 0.45 M cesium nitrate solution for three days, with intermittent shaking. The phases were separated by filtration, washed, and dried at 200°C . 20 gms of Cs-loaded AR-1 molecular sieves so obtained were mixed with 20 gms of selected glass formers and heated in furnace to get sample N4A-Cs-AR-1. Details of glass composition are included in **Table-4**.

2.4.2 Sodium and cesium content of glass

Sodium and cesium content of N4A-Cs-AR-1 glass was determined by dissolving 0.1 gm in $\text{HF}+\text{H}_2\text{SO}_4$ and analysed¹⁰ by ion chromatography using Dionex-600 ion chromatograph fitted with 10 μL capacity Rhyodyne injection valve, CG12 guard column, CS12 analytical column, CSRS ultra membrane suppresser and CD25 conductivity detector. 0.022 N H_2SO_4 in high purity water was used as eluent at flow rate of 1 ml /min.

2.5 Procedure For Leaching Experiments

Glass samples short listed for vitrification of Cs-AR1 molecular sieves were crushed to -100 , $+200$ BSS mesh. The powdered glass was washed with acetone to remove fines, dried in an

Table 4**VITRIFICATION OF SIMULATED Cs-MORDENITE AND Cs- LOADED AR-1 MOLECULAR SIEVES**

Sodium Borosilicate Glass Formulations- N4 A and N5

Glass Sample	Composition in Weight Percent				Process-ing Temp. ($^{\circ}$ C)	Remarks	
	Cs-Mordenite	Glass Formers					Additives
		B ₂ O ₃	PbO	Na ₂ O			
N4A-Cs	50*	25	12	10	3 TeO ₂ Bi ₂ O ₃ , CaF ₂	950 Homogeneous,Pourable	
N5-Cs	40*	30	18	12	Nil	950 Homogeneous, Easily Pourable	
N4A-Cs-AR1	50**	25	12	10	3 TeO ₂ Bi ₂ O ₃ , CaF ₂	925 Homogeneous, Easily Pourable	

* Simulated Cs-Mordenite Composition Having 50 % Na Replaced By Equivalent Cs and Na₂O, Cs₂O, Al₂O₃ And SiO₂

In The Weight Ratio Of 1.0 : 4.55 : 3.29 : 19.40

** Cs-loaded AR-1 Molecular Sieves (12.9 Wt% Cesium)

oven at 110°C and finally exposed to ambient air before use. A portion of each glass was used for estimation of density.

For comparison of chemical durability of different glasses, the most widely accepted method for determining chemical durability of nuclear waste glasses: Product Consistency Test (PCT) procedure (ASTM standards C 1285-94¹¹) was applied.

For leaching experiments, Teflon lined stainless steel containers were fabricated as indicated in **Fig.1**. After leak testing, the containers were leached in concentrated NaOH and then in high purity water at 120 °C for a week to check for amount of fluoride and silica leached. The containers showing negligible leaching of silica and fluoride were used for leach tests.

One gm. of each glass of -100, +200 BSS mesh size was taken in 25 ml high purity water in the containers which were sealed, weighed and kept in oven at 90°C. A set of two glasses along with a blank was removed at time interval of 4, 7, 14, 21 and 28 days. Leachates were cooled, weighed, filtered through 0.45 micron syringe filters. Their pH was estimated immediately. The sample flasks with 3 % weight loss were considered for the estimation of amount of sodium and cesium leached, whereas the samples with more than 3 % weight loss were discarded.

The sodium and cesium content of leachates were estimated as indicated in 2.4 above by ion chromatography after appropriate dilution in 0.022 N H₂SO₄. Boron and silica were analysed spectrophotometrically using curcumine¹² and ammonium molybdate¹³ respectively.

2.6 Estimation of Normalised Leach Rates (NLR)

The chemical durability of glass matrix is a measure of its resistance to corrosion. The chemical durability is estimated from the rate of weight loss of glass matrix. The glass matrix may dissolve congruently or incongruently. Incongruent dissolution of glass matrix leads to selective leaching of some of the glass components. As a result, the concentration of other components increases on the glass surface leading to formation of leached layer, which can retard leach rates as the time proceeds. The weight loss measurements provide fast reliable data for the congruent leaching of glass matrix only. For incongruent leaching of glass matrix it is

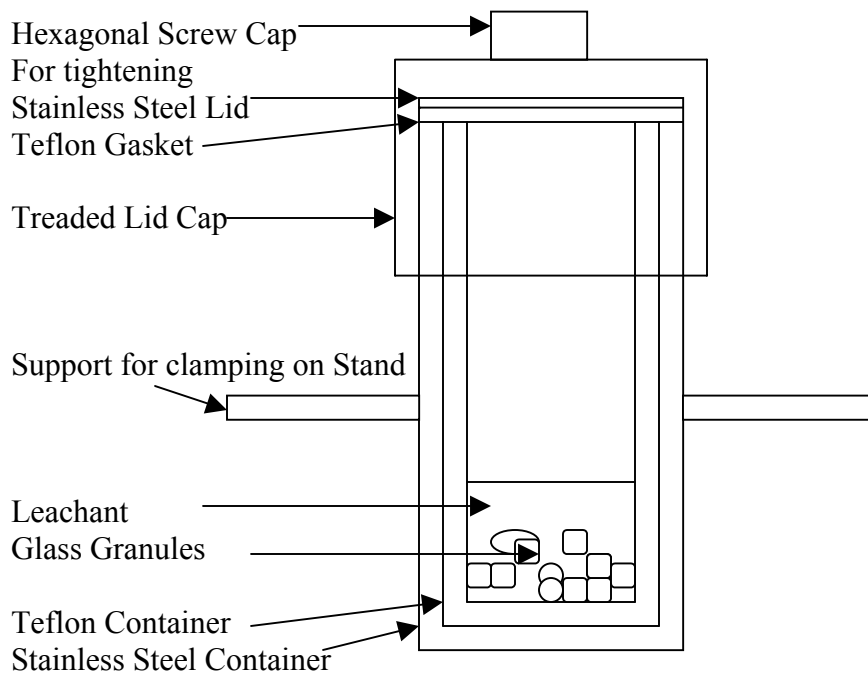


Fig.1 TEFLON LINED STAINLESS STEEL CONTAINER USED FOR PRODUCT CONSISTENCY TEST OF GLASS MATRIX

more appropriate to find leach rates of glass matrix by analysis of leachates at the end of predetermined leach period.

The normalised elemental mass loss (NL_i) were calculated⁹ from the concentrations of individual ions obtained by the analysis of leachate and leachant volume.

$$NL_i = C_i V / S f_i$$

Where C_i = Analysed concentration of the component (gms/ml)

V = Volume of leachant (ml)

S = Surface area of sample (cm^2)

f_i = Weight fraction of the i^{th} component in the sample.

The normalised leach rate is calculated based on the normalised elemental mass loss during the time of leaching (days)-

$$NLR_i = NL_i / t = C_i V / S f_i t \quad \text{The } NLR_i \text{ is expressed in terms of } \text{gm}/\text{cm}^2/\text{day}.$$

The NLR-Sodium, NLR-Cesium, NLR-Boron and NLR-Silica for N4, N4A, N5, N4A-Cs, N5-Cs and N4A-Cs-AR-1 glasses are summarised in **Table 5**.

2.7 Comparison of Glass and Cement Matrices

Using the data generated in this study and our earlier work on cement matrix⁴ computations were done for 1 kg AR-1 molecular sieves. The results are indicated in **Table 6**.

3.0 RESULTS AND DISCUSSIONS

3.1 Optimisation of Glass Formers

Simulation of Na-mordenite composition was used in the initial trials to optimise the glass composition. Results in **Table-1** shows the change in processing temperature and homogeneity of glass samples using B_2O_3 and / or PbO as glass formers. Use of B_2O_3 alone as glass former required quantities nearly equal to that of simulated Na-mordenite. Even though the homogeneous glass matrix could be prepared at processing temperature of 1000 to 1100°C, there was considerable foaming. Thus addition of B_2O_3 alone as glass former could not be considered. Use of PbO and B_2O_3 as glass formers gave homogeneous matrix having processing

Table 5**SUMMARY OF NORMALISED LEACH RATES FOR BORON, SILICA, SODIUM AND CESIUM**

Glass Sample	Normalised Leach Rate (gm/cm ² /d)			
	Boron	Silica	Sodium	Cesium
N4-Na	3.908×10^{-6}	8.245×10^{-7}	3.085×10^{-5}	Not Present
N5-Na	3.149×10^{-8}	1.0476×10^{-6}	3.4623×10^{-5}	Not Present
N4A-Na	6.382×10^{-8}	2.766×10^{-6}	3.0886×10^{-6}	Not Present
N4A-Cs	1.271×10^{-7}	1.973×10^{-6}	1.223×10^{-6}	3.6128×10^{-6}
N5-Cs	1.015×10^{-7}	2.245×10^{-6}	9.3912×10^{-7}	6.6156×10^{-6}
N4A-Cs-AR-1	3.05×10^{-7}	2.502×10^{-6}	4.3425×10^{-5}	3.915×10^{-6}

Table.6**COMPARISON OF CEMENT VS GLASS MATRIX**

Basis- 1 kg AR-1 Molecular Sieves having 25 % Moisture Content

Waste Loading - 60 wt. %

Description	Cement Matrix ⁴	Glass Matrix
Block Specific Gravity	2.3	2.66
Volume Reduction Factor	0.55	1.67
Volume of matrix	1818.5 ml	600.6 ml
Surface Area (cm ²)	981	469
Cesium Loading (gms)	0.0568	206.4
Estimated Quantity of Cesium Leached in 28 days	5 mg at Ambient Temperature	3 mg at 90°C

temperature of 1000°C with simulated Na-mordenite loading of 50 %. Addition of TeO₂, Bi₂O₃ and CaF₂ as additives replacing 3 % PbO results in bringing down the processing temperature to 975 °C.

Results in **Table-2** presents the nature of glass samples prepared using ZnO along with PbO and B₂O₃ as glass formers. The addition of ZnO lead to non-homogeneous fused masses at 1000-1050°C. In view of higher processing temperature, these glass compositions were not considered further.

Use of Na₂O in place of ZnO gave lower processing temperature for all glass samples as indicated in **Table-3**. Glass compositions of N4 and N5 were modified by addition of 1% each TeO₂, Bi₂O₃, and CaF₂ replacing 3 % PbO. This improved homogeneity and reduced the processing temperature of N4A glass. Similar effect was not observed for N5A glass. Out of above glasses only N4, N4A, N5 and N5A had reasonable processing temperature (950°C to 975°C) and could be prepared without foaming. The glasses N4A and N5 had the least processing temperature among all base glasses studied. These 2 compositions were selected to prepare glass with simulated cesium mordenite as indicated in **Table 4**.

Compositions N4, N4A and N5 were short listed for chemical durability test. As seen in **Table-5**, NLR-Boron of N4A and N5 were about two order of magnitude lower than that for N4. NLR-Sodium was lowest for N4A glass. As NLR-Boron, NLR-Cesium and NLR-Sodium are most important. NLR-Boron represents true matrix dissolution rate. NLR-Cesium and NLR-Sodium have diffusion controlled ion exchange mechanism of leaching. As seen in **Table 5**, NLR-Boron of N4A-Cs and N5-Cs glasses were comparable at about 1×10^{-7} gm/cm²/d. NLR-Cesium of N4A-Cs glass was 3.6×10^{-6} gm/cm²/d compared to 6.6×10^{-6} gm/cm²/d for N5-Cs glass. N4A-Cs glass had 50 wt % waste loading compared to 40 % of N5-Cs glass. In view of higher waste loading and comparable boron and cesium leach rates, glass having composition N4A was selected for testing with cesium loaded AR-1 molecular sieves.

The glass (N4A-Cs-AR1) was prepared from AR-1 molecular sieves containing 12.9 wt. % cesium. Processing temperature of the N4A-Cs-AR-1 molecular sieve glass was 925°C,

which was lower by 25°C compared to N4A-Cs glass. This decrease in temperature may be due to use of phosphate binder in the molecular sieves.

NLR-Cesium of N4A-Cs-AR1 glass was 3.915×10^{-6} gm/cm²/d. NLR-Boron, NLR-Silica and NLR-Sodium of this glass were comparable to those reported^{14,15} for high level waste glasses.

3.2 Comparison of Cement vs Glass Matrices

To understand the advantages of vitrification over cementation, comparison was made for one kg Cs-AR1 molecular sieves.

Table 6 gives comparisons of two matrices with respect to volume reduction factor achieved and quantity of cesium leached in relation to cesium loading. The glass matrix volume is 3 times lower as compared to cement matrix. As seen in **Table 6**, quantity of cesium loaded in glass matrix was 3630 times more than cement matrix. The quantity of cesium leached from N4A-Cs-AR-1 glass matrix in 28 days at 90°C would be 3 mg as against 5 mg from cement matrix at ambient temperature in the same period. The quantity of cesium leached from glass matrix is likely to decrease substantially at lower temperatures. Thus vitrification of AR-1 molecular sieves has an advantage over cementation in terms of volume reduction, loading of cesium and its leach rates.

4.0 CONCLUSIONS

Mordenite type molecular sieves can be vitrified using lead oxide, sodium oxide and boric oxide as major glass formers at the processing temperature of nearly 925°C. The mordenite loading of 50 % on dry weight basis was achieved. The normalized cesium leach rate was 3.92×10^{-6} gm/cm²/day being comparable to glass matrices currently being used for immobilization of high level waste. Estimated leaching of cesium from glass matrix is about 10000 times lower compared to cement matrix at equal loading. Volume reduction factor achieved for glass matrix is 3 times higher than that for cement matrix. The low cesium leach rates enhance the feasibility

of fully using high capacity of mordenite type molecular sieves for cesium removal from low and intermediate type liquid radioactive wastes. The vitrified AR-1 molecular sieves is a highly superior matrix in comparison with cement.

5.0 ACKNOWLEDEMENT

The authors thank Mr. B. N. Bansal, Head, BETD Division for his valuable suggestions and guidance during the course of this work.

5.0 REFERENCES

1. Savita jain, M. Ramaswamy and T.K. Theyyuni “ Removal of Cesium and Strontium from Low Active Waste Solutions” BARC Report BARC/1994//E/042 (1994).
2. I. J. Singh, S. Sathi and T. K. Theyyuni “ Use of Molecular Sieves Zeolite-4A for Removal of Cesium and Strontium from Low Level Waste Effluents of BWR origin” BARC Report BARC/1995/E/003(1995).
3. C. Janardanan, Savita Jain and P.V. Achuthan “ Removal of Cesium from High Level Waste Originating from Purex Process using Synthetic zeolite” ” BARC Report BARC/2000//E/30(2000).
4. I. J. Singh, Savita Jain, N. Sathi Sasidharan and D.S. Deshingkar Treatment option of low level liquid Radioactive wastes of ETP origin by synthetic zeolites BATRC Report BARC/2001/E/O14
5. H. Mimura, M. Shibata and K. Akiba “ Hydrothermal reactions of Zeolites Loaded with Cesium and Strontium” J. Nucl. Sc. & Tech. 27(2) 167-173 (1990)
6. T.Kanno and H.Mimura “ Ion Exchange Properties of Zeolites and Their Applications to Processing of High Level Liquid Waste “ IAEA-TECDOC-337 , pp 237-247 (1985).
- 7.D.M. McPherso, B. W. Bowan and L.D. Pye “The Dissolution of Zeolitic Compounds in Borosilicate Glass Melts” Collected papers of XIV Internatiuonal Congress on glass held at CGCRI. Calcutta (1986).

8. Kim, S. S., Lee, J. G., Choi, I. K., Lee, G.H. and Chun, K. S. "Effects of metals, metal oxides and metal hydroxides on the leaching of simulated Nuclear Waste glass.", *Radiochimica Acta* 79, 199-205 (1997).
9. Kim, S. S., Kim, J. G., Kim, J. S. and Chun, K. S. "The effects of pH and buffer materials on the leaching of simulated waste glass." *Journal of Korean Nuclear Society* Vol. 30, No.1 pp.1-7, February (1998).
10. Vrunda S. Yalmali, D. S. Deshingkar and P. K. Watal "Chemical durability of lead borosilicate glass matrix under simulated geological conditions" Report No. BARC/2002-E/005.
11. Standard test Method for determining Chemical Durability of Nuclear waste Glasses: The Product Consistency Test (PCT) ASTM Standards C 1285-94 American Society of Testing and Materials Philadelphia (1995).
12. Silverman, L. and Trego, K. "colorimetric Micro determination of Boron by Curcumine Acetone Solution Method." *Analytical Chem.* 25 (8) 1264-67(1953).
13. Jeffery, G. H., Bassett J, Mendham J. and Denney, R.C. "Vogel's Textbook of Quantitative Chemical Analysis." Fifth Edition Chapter 17, 703-704 English Language Book Society, London (1989).
14. D.L.Moir and Chatt, A., "Studies on Leaching Behaviour of Sodium Borosilicate glasses by Neutron Activation: Effect of Ground water composition, pH Surface Area to Volume and temperature." *J. Radioanalytical & Nuclear Chemistry Articles* Vol.161 No.2 503-526(1992).
15. Hong Li, and Tomozawa, Minoru "Effects of water in simulated borosilicate based nuclear waste glasses on their properties." *J. Non Crystalline Solids* 195 188-198 (1996)