

## Characterisation and Durability of Glass Composite Waste Forms Immobilising Spent Clinoptilolite

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### ABSTRACT

Simulated spent clinoptilolite was immobilised in a monolithic glass composite wasteform (GCM) produced by a pressureless sintering for 2 hours at relative low temperatures 750 °C. The GCM utilises the high durability of alkali borosilicate glass to encapsulate the Cs-impregnated clinoptilolite (Cs-Clino). With this approach mobile radionuclides are retained by a multi-barrier system, comprising the crystalline form of the clinoptilolite and the borosilicate glass. Wastes loading ranging from 1:1 up to 1:10 glass to Cs-clino volume ratios corresponding to 37- 88 mass % were studied. Water durability of GCM was assessed in 7, 14 and 28 days leaching tests in deionised water at 40 °C based on ASTM C1220-98 standard. It was found that the normalised leaching rates of Cs remaining below  $6.35 \cdot 10^{-6} \text{g/cm}^2\text{day}$  in a GCM with 73 mass % waste during a leaching test for 7 days. However, at higher waste loading of  $\geq 80$  mass %, the normalised leaching rate of Cs was as high as  $9.06 \cdot 10^{-4} \text{g/cm}^2\text{day}$ . The normalised leaching rate of Cs decreased within the 28 days of leaching. Microstructure and Energy Dispersive X-ray (EDS) analysis of the GCM with 1:1 glass to Cs-clino vol. ratio shows that there were no changes in phases identified as well as elements present in GCM after 28 days leaching test. The compression strength of the GCM was found to be in a range from 85.5 at waste loading 80 mass % – 394.2 MPa at waste loading 37 mass %.

### INTRODUCTION

Clinoptilolite is a natural zeolite which is used to remove radioactive contaminants such as  $^{134,137}\text{Cs}$  from aqueous nuclear wastes arising from nuclear power plant operation, spent nuclear fuel reprocessing and various nuclear applications. This inorganic ion exchanger has the advantage of a greater selectivity than organic resins for certain radionuclides such as Caesium (Cs) and Strontium (Sr) [1]. In 1985, British Nuclear Fuel plc (BNFL) successfully commissioned the Site Ion Exchange Effluent Plant (SIXEP) which uses clinoptilolite to remove Cs and Sr from fuel cooling pond water [2]. In order to be safely disposed, spent ion exchange material is required to meet specific quality parameters on waste form stability such as enough high chemical and mechanical durability characteristics. Typically, inorganic ion exchangers have been immobilized in cements [2]. However, cement waste form immobilizing low or medium radioactive waste such as  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  has many disadvantages such as high porosity, poor adsorption and relatively poor durability in practical application [3]. Due to this limitation, alternative immobilization routes for spent clinoptilolite are deemed necessary. At present, various works investigate waste forms to immobilizing spent sorbent such as new aluminium-rich alkali slag matrices [3], cement-clay mixtures [4], zeolite-cement blends [5, 6], cement-bentonite clay matrices [7, 8], vitrified product [9], heat-treated zeolite matrices [10], alkaline activated fly ash matrices [11] and glass composite materials [12, 13, 14].

We have previously reported on attempts to immobilize spent clinoptilolite in a glass composite waste form (GCM) produced via low pressure, low temperature sintering route [12, 13, 14]. The

GCM utilizes the high durability of alkali borosilicate glass [15] to encapsulate the Cs-impregnated clinoptilolite (termed here Cs-clino). With this approach, mobile radionuclides are retained by a multi barrier system, comprising the crystalline form of the clinoptilolite and the borosilicate glass. In this paper leaching durability and microstructural characterization are discussed. In addition, the GCM's compression test is also reported for the first time. It should be noted that leaching and mechanical properties are of the paramount features in determining the stability of the waste packages during their transportation, storage and disposal [16].

## EXPERIMENTAL

### Materials

*Cs impregnated Clinoptilolite (Cs-Clino)*. Natural clinoptilolite obtained from the Mojave Desert, California via Nexia Solutions was used to produce the simulant waste. 10 g of Clino was exposed to an ion-exchange reaction with 1M CsCl. After 72 h, the Cs impregnated clinoptilolite was extracted from solution and dried for 24 h at 110 °C. The concentration of Cs in Cs-clino,  $C_{Cs}$  was determined using an Agilent 4500 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) instrument. The detection limit for Cs is 0.002 µg/L. XRD was carried out on Cs-clino powder using a Philips X-ray diffractometer 1130 over a scan range of 20°-80° in 1°/min 2θ step sizes using Cu Kα radiation. Cs-clino particle size was determined using Coulter LS130 laser diffraction particle size analyser and its density was determined using the specific gravimetry method in water. Table I lists the results of Cs-clino characterization.

Table I: Cs-Clino parameters

Analyses	Results
ICP-MS (mass %)	Cs – 21.0
XRD	Potassium Sodium Aluminium Silicate Hydrate $\text{KNa}_2\text{Ca}_2(\text{Si}_{29}\text{Al}_7)\text{O}_{72} \cdot 24\text{H}_2\text{O}$
Mean Particle size (mm)	0.564
Density ( $\text{gcm}^{-3}$ )	2.00±0.23

An assessment of cesium content in Cs-clino ( $C_{cs}$ ) can be found based on clinoptilolite cation exchange capacity using Equation (1).

$$C_{cs} = \text{CEC} \times \text{A.M.U.} \quad (\text{Eq. 1})$$

where CEC is the – cation exchange capacity, meq/g and A.M.U. – is the atomic mass of Cs

It is known that the CEC value of clinoptilolite ranges from 25 to 300meq/100g [17]. Thus the calculated value of  $C_{cs}$  is in a range of 3.32 to 39.87 mass % and the 21 mass % of Cs determined by ICP-MS (Table 1) is in the range of cation exchange capacity of clinoptilolite.

*Glass frit*. The borosilicate glass used was produced from a glass batch melted at 1150 °C for 2 h in an alumina crucible. The cast glass was then annealed at 500 °C for 24 h. Glass was ground using an agate mortar and sieved to obtain glass powder with <75 µm particle size. The nominal glass composition was determined by Inductively Coupled Plasma Atomic Emission

Spectroscopy (ICP-AES) and the glass transition temperature ( $T_g$ ) was determined using Differential Thermal Analysis (DTA) on a Perkin Elmer Pyris ITGA-DTA7 unit. Glass density was determined using the specific gravimetry method in water. Table II lists the properties of glass used as host matrix.

Table II: Properties of borosilicate glass used as matrix

Composition (mass %)	Oxide	Batch*	ICP**
	SiO <sub>2</sub>	50.05	50.43
	Na <sub>2</sub> O	16.72	14.00
	CaO	16.61	16.80
	Al <sub>2</sub> O <sub>3</sub>	2.60	2.74
	TiO <sub>2</sub>	1.56	1.58
	B <sub>2</sub> O <sub>3</sub>	9.34	10.37
	Li <sub>2</sub> O	3.12	2.46
	K <sub>2</sub> O	-	0.75
	Total	100	99.13
$T_g$ (°C)	490±3		
Density (gcm <sup>-3</sup> )	2.60±0.08		

\*calculated from batch composition

\*\*calculated based on elemental composition obtain by ICP-AES

### Sintering

Sintering of GCM has been carried out with both Cs-Clino and borosilicate glass particles <75 µm in diameter with various waste loadings at 750 °C. The glass to Cs-Clino volume ratios investigated were in the range of 1:1 to 1:10 (from 37 to 88 mass % waste loading). Mixtures of appropriate glass and Cs-Clino powders were compacted at room temperature in a 13 mm diameter stainless steel die using 78.3 MPa uniaxial pressure. Each compacted pellet was then sintered for 2 h at 750 °C with heating and cooling rates of 2 °C/min.

The mass fraction of waste in the GCM,  $F_{waste}$  is determined from the relationship:

$$F_{waste} = \frac{m_{waste}}{m_{waste} + m_{glass}}, \quad (\text{Eq. 2})$$

where  $m_{waste}$  is the mass of Cs-clino and  $m_{glass}$  is the mass of glass.

The mass fraction of glass in the GCM sintered is defined as

$$F_{glass} = 1 - F_{waste} \quad (\text{Eq. 3})$$

The mass fraction of Cs ( $f_{Cs}$ ) in the unleached specimens was determined using equation (4).

$$f_{Cs} = F_{waste} \times C_{Cs} \left( \frac{1}{100mass\%} \right) \quad (\text{Eq. 4})$$

The calculated values are given in Table III.

Table III: Fraction of Cs,  $f_{Cs}$ , in the unleached GCM wasteform

Glass to Cs-Clino Vol. ratio	$F_{glass}$	$F_{waste}$	$f_{Cs}$
1:1	0.63	0.37	0.078
1:2	0.41	0.59	0.123
1:3	0.31	0.69	0.144
1:4	0.27	0.73	0.153
1:5	0.20	0.80	0.169
1:10	0.12	0.88	0.185

### Leaching Test

Leaching tests were done in deionized water based on the ASTM C1220-98 standard at 40 °C for 7, 14 and 28 days duration. The samples were contained in tightly closed teflon containers with specimen support made of teflon in it. The tests were run with a sample surface area to solution volume ( $SA/V$ ) ratio of 10 m<sup>-1</sup> for each test. Here, the volume of leachant used was varied from 30 mL to 51 mL depending on the surface area of each sample used. The concentrations of dissolved Cs ion in the leachates (Table IV) were determined by inductively coupled plasma ICP-MS. The normalized leach rates ( $NR$ ) were calculated using equation (5).

$$NR_{Cs} = \frac{A \cdot V}{(f_{Cs} \cdot SA)t}, \quad (\text{Eq. 5})$$

where  $A$  - concentration of Cs in the leachate (g/L),  $V$ - volume of leachate (L),  $f_{Cs}$ - mass fraction of Cs in the unleached specimen,  $SA$ - specimen surface area, cm<sup>2</sup>,  $t$ - duration of test, day.

Table IV: Concentration of Cs in leachates,  $A$  after 7 days static test.

Glass to Cs-Clino Vol. ratio	$A$ (g/L)		
	7 days	14 days	28 days
1:1	$0.057 \times 10^{-3}$	$0.057 \times 10^{-3}$	$0.037 \times 10^{-3}$
1:2	$0.025 \times 10^{-3}$	$0.030 \times 10^{-3}$	$0.030 \times 10^{-3}$
1:3	$0.555 \times 10^{-3}$	$0.620 \times 10^{-3}$	$1.45 \times 10^{-3}$
1:4	$0.799 \times 10^{-3}$	$1.54 \times 10^{-3}$	$2.00 \times 10^{-3}$
1:5	$106.038 \times 10^{-3}$	$1.52 \times 10^{-3}$	$2.30 \times 10^{-3}$
1:10	$439.995 \times 10^{-3}$	Not carried out	Not carried out

### Characterization

Samples of GCM with 1:1 glass to Cs-clino vol. ratio before and after 28 days leaching test were cross sectioned, ground using SiC grinding wheel and polished using 6, 3 and 1 μm diamond paste. A JEOL JSM 6400 SEM operated at 20 kV and 25 mm working distance, in Backscattered Electron Imaging (BEI) mode coupled with Energy Dispersive X-ray spectroscopy (EDS) analysis was used to determine the microstructure and identify the elements present in the waste form.

### Compression Test

Compressive strength testing was performed on GCM samples using a Hounsfield screwdriven Universal testing machine. The machine was operated in compression to extension mode, using a 100 kN load cell, at a crosshead speed of 0.5 mm/min with none preload applied. The samples

were cylinder in shape, with a diameter to height ratio of a range 1.3-1.5. In order to yield plane and parallel surface, the ends of all samples were ground using SiC grinding wheel and polished using 6, 3 and 1  $\mu\text{m}$  diamond paste. A thin ductile aluminium foil was inserted between the contact samples and the platen of the machine to eliminate microscopic unevenness [18]. For each waste loading GCMs, at least 7 samples were used. During the test, specimens were axially pressed between two parallel plates with continuously increasing pressure until destruction of the specimen ensued. Compressive strength was then calculated using equation (6).

$$C = \frac{P}{A}, \quad (\text{Eq. 6})$$

Where  $C$ - compressive strength of the sample (MPa),  $P$  –total load on the sample at failure (N) and  $A$ - calculated area of the bearing surface of the specimen ( $\text{mm}^2$ ).

## RESULTS

### Leaching test

Leach testing for 7 days results (Fig. 1) showed that normalised Cs leach rates increased gradually as the waste loading increased up to the 1 to 4 glass to Cs-clino volume ratio (73 mass % waste loading). However, it was also noticeable that the leaching rate at 1 to 2 glass to Cs-clino volume ratio was lower than that at lower (e.g. 1 to 1) glass to Cs-clino volume ratio. The normalized Cs leaching rates remain below  $6.35 \cdot 10^{-6} \text{ g/cm}^2\text{day}$  up to the waste loading of 73 mass %. A drastic increase by more than 2 orders of magnitude of Cs leaching rate was observed for GCM at 1 to 5 glass to Cs-clino volume ratio (80 mass % waste loading).

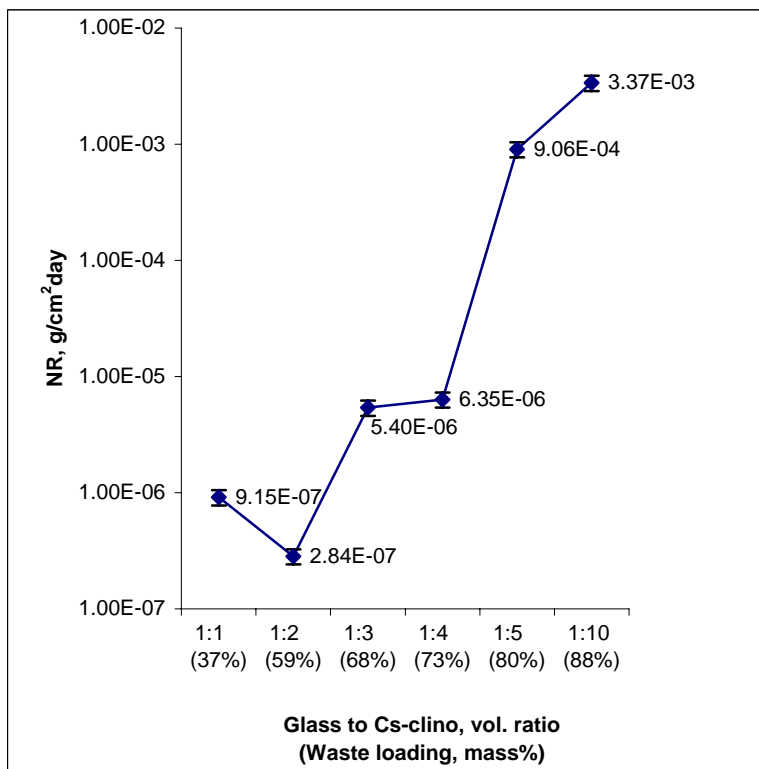


Fig. 1: Cesium normalized leaching rates of glass composite waste form with the increase in waste loading.

Fig 2 shows the normalised Cs leaching rate of GCM for 7, 14 and 28 days of leaching test. It shows that the  $NR_{Cs}$  of each GCM decreased with time. The highest  $NR_{Cs}$  were found after 7 days of leaching.

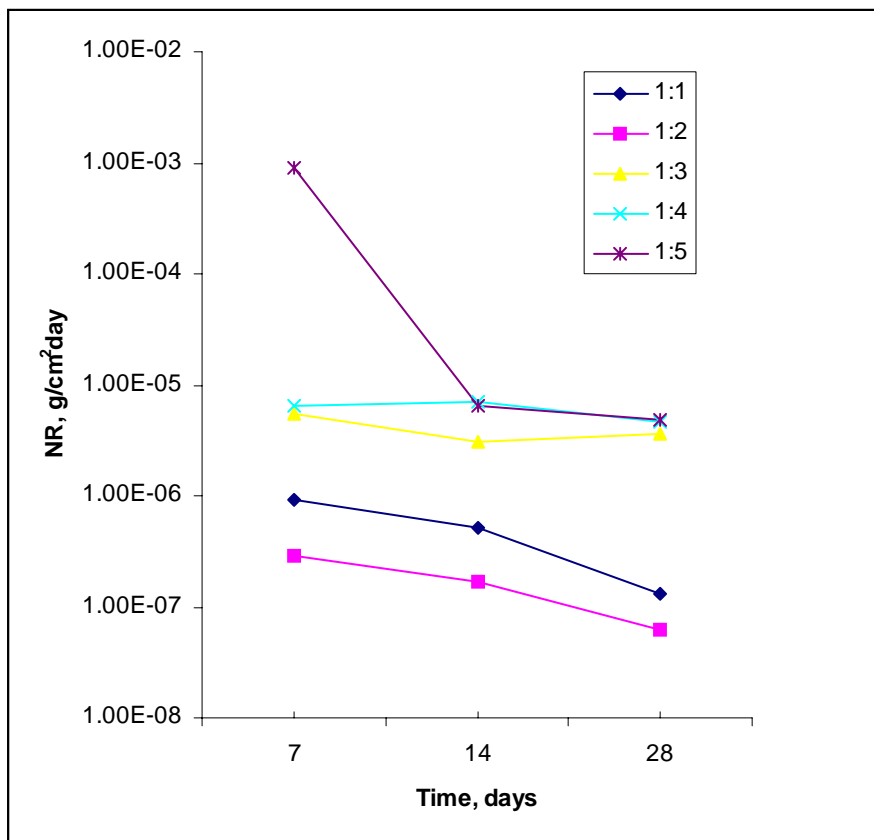


Fig. 2: Cesium normalized leaching rates of glass composite waste form with time.

### Microstructure Characterisation

Microstructures of GCM before and after leaching test in deionised water for 28 days (Fig. 3) demonstrated that GCMs consist of three major phases that are the glass matrix, clinoptilolite and wollastonite. This is in agreement with XRD analysis carried out earlier. In addition to this phase, peaks identified as sodalite, pollucite and CsCl is also traceable in the GCM XRD pattern. However, these phases do not present with distinguished microstructure features. Types of elements present in each phase observed during the microstructure analysis are shown in the EDS spectra. It can be seen that the same elements were identified in each phase before and after the leaching.

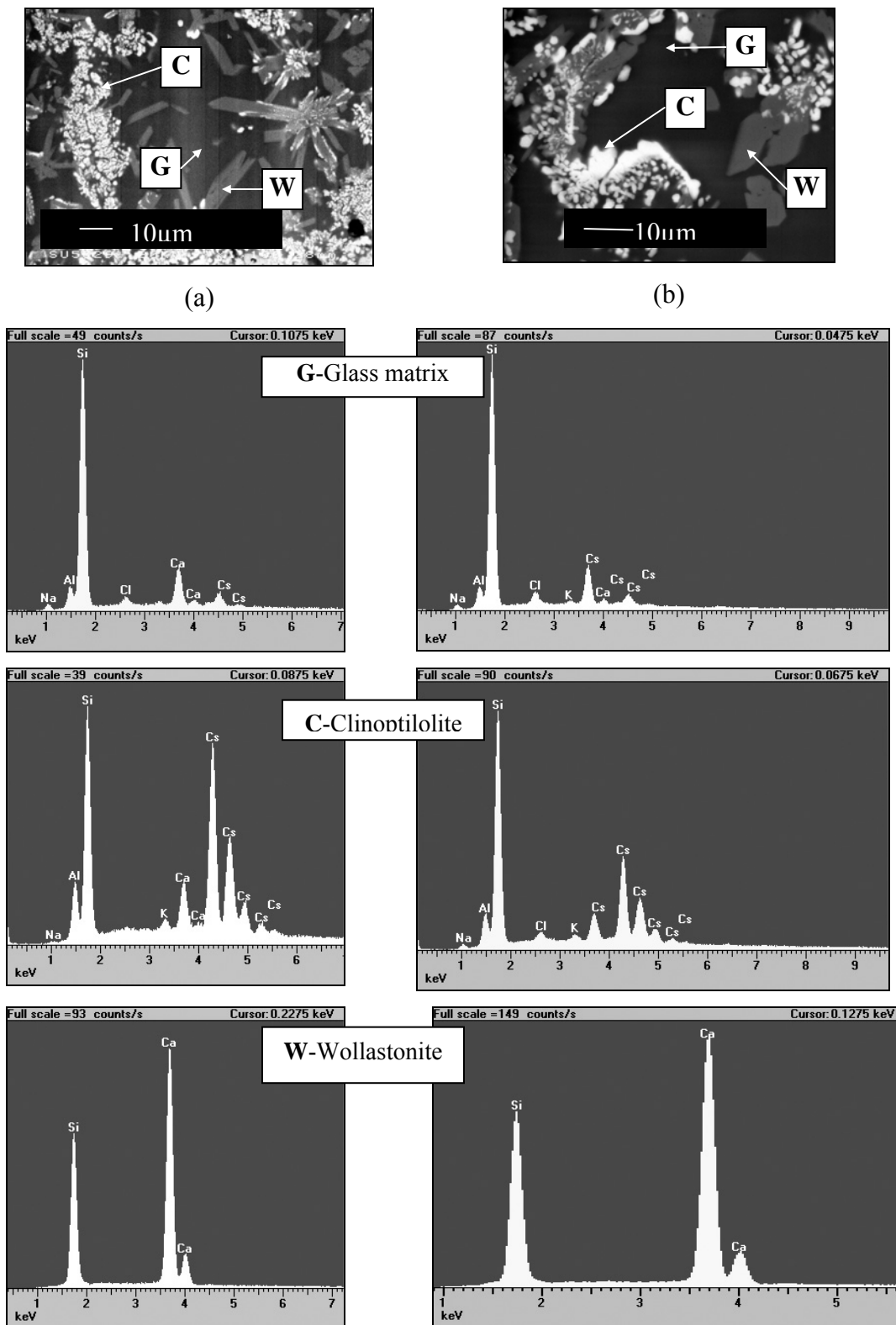


Figure 3: BEI micrograph and EDS spectra of three basic phases of GCM waste form with 1 to 1 glass to Cs-clino vol. ratio a) before leaching b) after 28 days leaching

## Compression Strength

As can be seen from Fig. 4, the compression strength of the GCM decreased with the increase in the waste loading. In contrast to dramatic changes in water durability, the mechanical properties of GCM demonstrate a smooth change with waste loading.

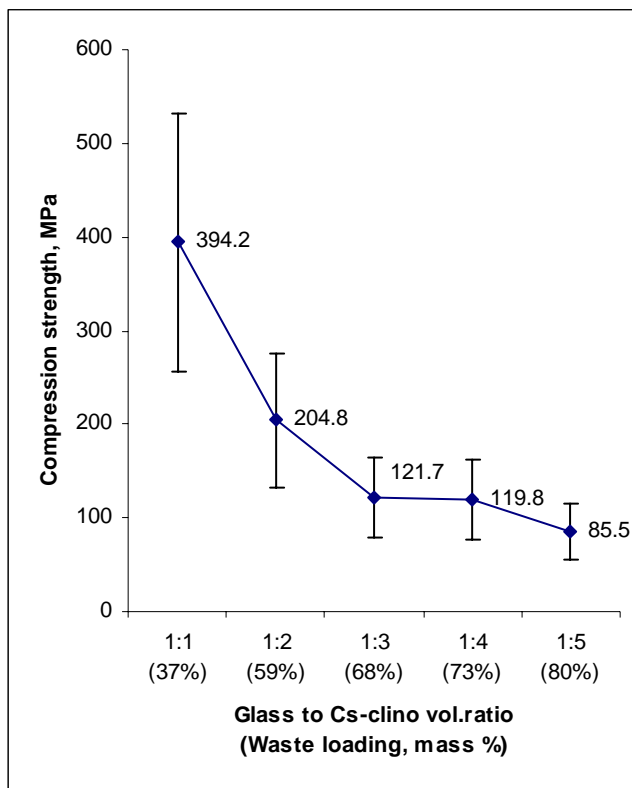


Fig. 4: Compression strength of glass composite waste form with the increase in waste loading.

## DISCUSSION

In our work, the normalized leaching rates of Cs remain below  $6.35 \cdot 10^{-6} \text{ g/cm}^2\text{day}$  with up to 73 mass % waste loading. The longer duration of the leaching the lower  $NR_{cs}$  observed. Determined  $NR_{cs}$  were significantly lower compared to Portland and alumina cement with 12-19 mass % spent ion exchange resin content [7] and cement-bentonite clay wasteforms with a waste load of  $290\text{-}350 \text{ kg/m}^3$  [19] which has a leaching rate of Cs in a range of  $\sim 10^{-3}\text{-}10^{-4} \text{ g/cm}^2\text{day}$ . Low leaching rate of Cs is due to the complete encapsulation of the clinoptilolite particles by the glass matrix in the GCM microstructure with up to waste loading 73 mass %. The typical microstructure of this type of GCM is as such as shown in Fig. 3. The Cs normalized leaching rate becomes  $>9.06 \cdot 10^{-4} \text{ g/cm}^2\text{day}$  for GCMs containing  $\geq 80$  mass % of spent clinoptilolite. This drastic increase can be explained by formation of percolating clusters made of inter-connected clino particles. At such high waste loading, the clinoptilolite particles are no longer being encapsulated by the matrix, hence Cs can easily being leach out from the GCM.



The microstructure of GCM is generally not much affected by the leaching. It can be seen that the same three major phases (glass matrix, clinoptilolite and wollastonite) were identified in each GCM microstructure before and after leaching. In addition, sodalite, pollucite and CsCl peaks are also traceable in the GCM XRD pattern. However, these phases do not appear with distinguish microstructure features. In each phase observed in the GCM microstructure, the same elements were identified during the EDS analysis. Thus it indicates there is no significant migration of elements and phase transformation during leaching. It should be noted that Cs was found in clinoptilolite particles as well as in the glass matrix. This shows that some Cs migrate from clinoptilolite particles during high temperature sintering but then safely captured by the glass matrix. Therefore, it can be deduced that it is essential to ensure that the clinoptilolite particles be encapsulate by the glass matrix as to prevent Cs migration to the surrounding.

In general, GCM has a comparable high compression strength in a range from 85.5 at waste loading of 80 mass % – 394.2 MPa at waste loading of 37 mass %. It can be seen that the compression strength decreased with the increased waste loading. This had also been found in cement system where its' compressive strength is remarkably reduced by increasing the amount of natural sorbents [8]. However, the generally high compression strength of the GCM is considered to be satisfying the requirement of the waste form mechanical stability [20].

## CONCLUSION

GCM are durable waste forms to immobilize spent clinoptilolite from aqueous radioactive waste treatment facilities. The normalized leaching rate of Cs from GCMs remains below  $6.35 \cdot 10^{-6}$  g/cm<sup>2</sup> day with up to 73 mass % waste loading but becomes as high as  $9.06 \cdot 10^{-4}$  g/cm<sup>2</sup> day for GCM containing  $\geq 80$  mass % of spent clinoptilolite. There is no change in phases as well as the elements present in GCM subjected to leaching. The compressive strength of GCM was generally high being in a range of 85.5 (waste loading of 80 mass %) – 394.2 MPa (waste loading of 37 mass %).

## REFERENCES

1. A. Dyer, D. Keir, "Nuclear waste treatment by zeolites", *Zeolites*, **4** [July] 215 (1985).
2. Application of ion exchange processes for the treatment of radioactive waste and management of spent ion exchangers, in Technical Reports Series No. **408**, International Atomic Energy Agency, 2002: Vienna.
3. G. Qian, D. D. Sun, J.H. Tay, "New aluminium-rich alkali slag matrix with clay minerals for immobilizing simulated radioactive Sr and Cs waste", *J. Nuc. Mater.*, **299**, 199-204 (2001).
4. A. E. Osmanlioglu, "Immobilization of radioactive waste by cementation with purified kaolin clay", *Waste Management*, **22**, 481-483 (2002).
5. A. M. El-Kamash, M.R. El-Naggar, M. I. El-Dessouky, "Immobilization of cesium and strontium radionuclides in zeolite-cement blend", *J. Haz. Mater.*, 2006, In press.
6. S. Bagoši, L. J. Csetenyi, "Immobilization of caesium loaded ion exchange resins in zeolite-cements blends", *Cement and Concrete Research*, **29**, 479-485(1999).
7. I. Plecas, R. Pavlovic, S. Pavlovic, "Leaching behavior of <sup>60</sup>Co and <sup>137</sup>Cs from spent ion exchange resins in cement-bentonite clay matrix", *J. Nucl. Mater.*, **327**, 171-174(2004).
8. I. Plecas, S. Dimovic, I. Smiciklas, "Utilization of bentonite and zeolite in cementation of dry radioactive evaporator concentrate", *Progress in Nuclear Energy*, **48**, 495-503(2006).

9. M. I. Ojovan, A. A. Sobolev, S.A. Dimitriev, F. A. Livanov, A. P. Kobolev, S. V. Stefanovsky, "Vitrification processes for low, intermediate radioactive and mixed wastes", *Glass Technol.*, 46 (1), 28-35 (2005).
10. P. Bosch, D. Caputo, B. Liguori, C. Colella, "Self Trapping of Cs in heat-treated zeolite matrices", *J. Nucl. Mater.*, 324, 183-188 (2004).
11. A. Fernandez-Jiminez, D. E. Macphee, E.E. Lachowski, A. Palomo, "Immobilization of cesium in alkaline activated fly ash matrix", *J. Nucl. Mater.*, 346, 185-193 (2005).
12. J.M. Juoi, M.I Ojovan and W.E. Lee, "Development of glass composite materials for radioactive waste immobilisation", *Proc. ICEM'05*, September 4-8, Glasgow, Scotland, ICEM05-1069, ASME (2005).
13. W.E. Lee, M. I. Ojovan, M.C. Stennett and N. C. Hyatt, "Immobilisation of Radioactive Waste in Glasses", *Glass Composite Materials and Ceramics, Advances in Applied Ceramics*, 105 [1], 3-12 (2006).
14. W.E. Lee, J.Juoi, M.I. Ojovan and O.K. Karlina, "Processing ceramic for radioactive waste immobilisation", *Advances in Science and Technology*, 45, 1986-1995 (2006).
15. M. I. Ojovan, W.E.Lee, *An introduction to nuclear waste immobilisation*. 2005. Elsevier, Amsterdam.
16. Requirements and methods for low and intermediate level waste package acceptability, in IAEA-TECDOC-864, International Atomic Energy Agency, 1996, Vienna.
17. A. E. Osmanlioglu, "Treatment of radioactive liquid waste by sorption on natural zeolite in Turkey", *J. Haz. Mater.*137 [1], 332-335 (2006).
18. J. Menčík, *Strength and fracture of glass and ceramic*, *Glass Science and Technology*, 12, Elsevier, Amsterdam, 1992.
19. V. N. Epimakhov, M. S. Oleinik, "Inclusion of radioactive ion-exchange resins in inorganic binders", *At. Energ.*, 99, 607-611 (2005).
20. J.Y.Kim, C.L.Kim, C.U. Chung, "Leaching characteristics of paraffin waste forms generated from Korean nuclear power plants", *J. Waste Manage.* 21, 325-333 (2001).