

BOROSILICATE GLASS BEADS: AN INDIGENOUS TECHNOLOGY FOR IMMOBILIZING HIGH-LEVEL NUCLEAR WASTE

S. MANDAL^{1*}, S. SEN², S. GHORUI¹, S. BARIK¹,
P G PAL CHOWDHURY¹ AND A. ROY CHOWDHURY¹

Energy crisis handling is one of the focused topics of the current 21st century across the globe. Among all the alternative energies, nuclear power is sustainable, economical and scalable to the needs of ever increasing energy demand. Around 10% of the world's electricity is generated by nuclear power reactors across the globe and the construction of new reactors have been increasing consistently. Nevertheless, due to the radioactive nature of the fissile materials like Uranium-235 and Plutonium-239 used in nuclear power reactors, handling of these spent nuclear fuels is highly hazardous and its disposal requires more rigorous technique to avoid any threat to the environment. The philosophy is to reprocess the wastes to recover the useful fissile isotopes so that they can be reused in next generation fast breeder reactors. The reprocessing step involves the extraction of isotopes of uranium and plutonium into the organic phase after fuel dissolution leaving behind the other unwanted radio isotopes in the aqueous phase. The resultant aqueous phase is known as High-level radioactive Liquid Waste (HLW). HLW should thus be converted into a suitable stable solid matrix for its safe disposal. The solidification of HLW turns it into an immobile state; hence the process is also referred to as immobilization. The immobilization of HLW into glass matrix is achieved in furnace at high temperature by allowing HLW constituents to interact with inactive glass frit in proper form; the process termed as vitrification. Frit in the form of glass beads with specific composition are usually fed into a high temperature Joule

Melter along with HLW in a predetermined ratio to make the HLW-Glass composite having desired properties. As the production of nuclear energy increasing consistently, the management of HLW is one of the important issues that need to be addressed.

Slurry based glass additives consisting of glass forming raw chemicals where often used to immobilize the HLW. Commonly, Borosilicate based glass compositions in stead of commotions have been adopted universally owing to its chemical, thermal and radiation stability compared to other glass compositions. However, the exact glass composition and properties are not defined due to strategic constraints as well as the nature of the nuclear waste produced. Since the slurry chemicals are in raw form and glass additive slurry already contains water, it gives extra heat load on the Melter with respect to calcinations of raw chemicals and evaporation of the water content thereby affecting the process throughput. In order to eliminate the process complications, the option of feeding glass beads of the base glass instead of slurry has been adopted in the advanced vitrification plants.

Due to the countries' strategic restrictions, the technology of glass beads was not market friendly and it was an extreme challenge to produce indigenous glass beads of desired properties in view of HLW produced in the contest of nuclear power plants of India. Our group at CSIR-CGCRI has developed a unique technology to produce spherical glass beads of desired characteristics from the glass frit used for the vitrification process along with the conversion of the frit to spherical beads with specific physical and mechanical properties to facilitate feeding into the Joule Melter that allows remote control of the entire operation.

1 Specialty Glass Technology Division, CSIR-Central Glass & Ceramic Research Institute, Kolkata, India

2 Material Characterization and Instrumentation Division, CSIR-Central Glass & Ceramic Research Institute, Kolkata, India

(*Corresponding Author : e-mail: sitendum@cgcric.res.in)

Addressing Technological Challenges

The process technology for making customized glass beads in the five-component borosilicate glass matrix consisting of chemical constituents such as, $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O-Fe}_2\text{O}_3\text{-TiO}_2$ with the impurity level of chloride and sulphate less than 200 ppm, we pursued a major R&D activity that resulted in a limited scale in-house production of glass beads using specified wt% of constituent borosilicate glass compositions. Final glass bead compositions were optimised based on the composition of HLW generated in the nuclear reactors using our technology. Further, CSIR-CGCRI has developed and optimized the process technology of making customized glass frit and beads/nodules in a scale of 150 kg with the Oil-Fired Glass Melting Tank Furnace. Stringent requirements of nuclear establishments were achieved after a series of experiments to encapsulate and immobilize a wide spectrum of spent fission elements within the glass structure resulting in chemically durable high integrity glass products. The base glass composition and their properties were dependent on specific HLW composition generated in the nuclear reactor. Hence, with such variation in HLW composition, the development of appropriate glass bead technology is utmost important for proper immobilization of spent nuclear waste.

Meeting the Enhanced Needs through Private Public Partnership

With the continued expansion of nuclear activities in the country, the demand of the glass bead is expected to increase in the coming years. A pertinent question that arose under such changing scenario was whether CSIR-CGCRI should expand its activity on special glass beads (nodules) production and move into a bigger program. Being essentially a R&D institute, this approach seemed to be incongruous with the institutional mandate. Further, in consonance with CSIR business policies, it was important to disseminate the process technology through licensing to an industrial partner towards commercialization of the technology. The institute therefore took up the



Speciality Borosilicate glass frit and bead indigenously developed by CSIR-CGCRI



Commercial production of glass frit and bead at M/s Prism Johnson Limited facility

initiative to transfer the technology to an industry that would enable scale up in the production process to the tune of 40-50 MT output.

A major industrial partner (M/s Prism Johnson Limited, Mumbai) is currently assigned the task of this scale up of institutional knowledge base. The bench-scale demonstration has been provided to the industrial partner at their facility to produce glass bead in a scale of 150 kg, followed by trial production to the tune of 3.5 MT. The material is now being commercially produced by M/s Prism Johnson Limited, Mumbai.

The technology developed by CSIR-CGCRI marked a significant step forward towards country's self-reliance in this important strategic sector. Till date 83.25MT of glass bead of varying compositions have been supplied to vitrification plants in Trombay, Tarapur and Kalpakkam.

The below table summarizes the compositional variations to immobilize the specific HLW produced from the nuclear power plants without contamination of the Joule Melter.

Socio Economic Impact and Recognitions

The technology for borosilicate glass beads for immobilisation of nuclear waste represents a key milestone in acquiring indigenous production capabilities that would

Compositions	Purpose
Five Component Regular Glass Bead	Immobilisation of normal HLW
Five Component Low Sodium Content Glass Bead	Immobilisation of normal HLW with high Na content
Five Component Low Melting High Sodium Content Glass Bead	Decontamination of Joule Melter
Seven Component Low Melting Glass Bead	Test run of immobilisation of normal HLW with improved performance and to address the variations and fluctuations in composition of HLW with respect to the sodium content and iron content.

have not been possible through external dependency. It occupies a unique niche in the country with no competing elements. Apart from knowledge consolidation, the technology has the potential of creating employment. Its potential to produce materials applicable to fixation of nuclear waste at any source irrespective of their geographical location makes it amenable to technology transfer. It is estimated that the value of the technology/products stands at Rs. 4 crore / annum while the R & D input costs is of the order of only Rs. 0.33 crore, thereby reflecting a significant revenue potential for the country.

The technology has received wide acceptability. Over the years it has been recognised with major awards such as NRDC Meritorious Innovation Award (2013), Institutional Best Technology Award (2013, 2014 & 2015), Skotch Order

of Merit Award (2017), “Certificate of Merit” under CSIR Technology Award for Innovation (2017) and CSIR Technology Award for Innovation (2018). □

Further Reading

1. “Process for the stabilization of radioactive wastes”: US Patent no. 4464294 dated 29th July 1982
2. C.M. Jantzen E.I. du Pont de Nemours & Co, “Systems approach to nuclear waste glass development” in 2 July 1986, Pages 215–225 Section IV. General aspects of nuclear waste vitrification, Savannah River Laboratory, Aiken, SC 29808, USA
3. I. W. Donald, B. L. Metcalfe, R. N. J. Taylor, “The immobilization of highlevel radioactive wastes using ceramics and glasses”, Journal of Materials Science 32, 1997 5851–5887, Atomic Weapons Establishment, Aldermaston, UK
4. J. Mukerji “Development of Borosilicate Matrix for Vitrification of HLW – Details of work done at CGCRI, Calcutta, Indian Nuclear Society News Vol. 5, No. 4, p 12, Oct. – Dec. 2008
5. M. S. Sonavane “Development for vitreous matrix for Immobilization of High-level Radioactive Liquid Waste Generated from Reprocessing of Power Reactor Fuel” Indian Nuclear Society News Vol. 5, No. 4, p 5, Oct. – Dec. 2008.
6. Nasir H Hamodi, Yaseen Iqbal, ‘Glass Melting Techniques used in Radioactive Waste Immobilization’, J Pak Mater Soc 2009 3 (2), Material Research Laboratory, Institute of Electronics & Physics, University of Peshawar, Khyber-Pukhtunkhwa, Pakistan.
7. J. Mukerji “Borosilicate & Phosphate Glasses as a Medium for Containment of High Level Nuclear Waste and for its Ultimate Disposal (Part I & II), KANCH, Vol. 5 No.1, October – December 2011
8. T.P.Valsala, P. K. Mishra, D. A. Thakur, D. E. Ghongane, R.V. Jayan, U. Dani, M.S.Sonavane & Y Kulkarni “ Formulation of Specialty Glass Frit and Its Use for Decontamination of Joule Melter employed for Vitrification of High Level Radioactive Liquide Waste” Transaction Indian Ceramic Society, Vol. 72, no 1 pp 43-46 (Jan. – March, 2013)