

3rd Summer School on nuclear and industrial glasses for energy transition

Program and abstracts







Sumglass 2023 aims to bring together the research and industrial communities of the glass sector.

This summer school will allow to share the issues and methodologies developed on the vitrification of nuclear wastes and on the manufacture and properties of industrial glasses. New advances in terms of modeling and simulation developed on spatial and temporal scales will be discussed, both to follow glass vitrification process and the behaviour of glass during its life cycle.

International specialists will present reviews or keynotes. A call for abstracts will be proposed for a poster session covering all the topics addressed in the summer school.

Local organizing & scientific committees

Sophie Schuller, Kahina Hamadache, Frédéric Angeli, Stéphane Gin, Jean Marc Delaye, Isabelle Ribet, Paul A. Bingham, Ashutosh Goel, Albert Kruger, John McCloy, Irene Peterson, Richard Pokorny, John Vienna, Léa Brunswic

Email: contact@sumglass.fr

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Table of content

Monday, September 25 th 2023	- 4
vitrification technologies and glass waste form	p.4
Tuesday, September 26 th 2023 Simulation/modeling of vitrification process	p.18
Wednesday, September 27th 2023 Thermodynamic and chemical mechanism modeling of glass and melt	p.36
Thursday, September 28 th 2023 Glass alteration	p.44
Friday, September 29 th 2023 New glasses for energy transition and new advance on high temperature characterization	p.60
Poster session abstracts	
Poster session 1	p.72
Poster session 2	p.88
Poster session 3	p.110
Sumglas 2023 - Participants list	p.126



Monday, September 25th 2023

Vitrification technologies and glass waste form

Chair: Paul A. Bingham (Sheffield Hallam University) & Christophe Girold (CEA DPE)



Program

8:15-9:00	Registration - coffee
9:00-9:15	SummerSchool introduction
	Daniel Meyer (CEA/ISEC - Scientific assistant)
9:15-9:40	SummerSchool introduction
	Gilles Bordier (CEA/DSE - Scientific direction) and Sophie Schuller (CEA/ISEC/DPME)

Waste vitrification technologies

9:40-10:20	French HLW vitrification history and major achievements Régis Didierlaurent (Orano, France)	p.6
10:20-10:50	Coffee break	
10:50-11:30	Waste Vitrification Technologies and Details of the Office of River Protection's Enhanced Waste Glass Program - <i>Albert Kruger (US Dep. of Energy: DOE, US)</i>	p.8
11:30-12:10	Geomelt In Container Vitrification Technology: Latest Developments and Overview of Operational Installations - Cyrille Veronneau (Veolia Nuclear Solutions Europe)	p.9
12:10-14:10	Poster session 1 & buffet	p.72
14:10-14:50	Thermal Plasma Treatment of Dry Waste from Nuclear Power Plants Kai Xu (Wuhan University of Technology, China)	p.11
Glass wa	ste form and issues	
14:50-15:30	Advancement in Waste Glass Formulation Methodology John Vienna (Pacific Northwest National Laboratory, US)	p.12
15:30-16:10	Vitrification of high-level nuclear waste worldwide: Historical perspective, current status and future challenges - Ashutosh Goel (RUTGERS University, US) & Paul A. Bingham (Sheffield Hallam University, UK)	p.13
16:10-16:50	International Perspectives on Glass Waste Form Development for Low and Intermediate Level Radioactive Waste - John McCloy (Washington State University, US) & Paul A. Bingham (Sheffield Hallam University, UK)	p.14
16:50-17:20	Coffee break	
17:20-18:00	Engineering of inorganic waste mixtures for new usable glasses: from glass-ceramics to alkali-activated materials - Enrico Bernardo (Padova university, IT)	p.15
Glass rec	ycling	
18:00-18:40	Glass recycling and decarbonization of glass industry - Exemple of French glass industry roadmap - Xavier Capilla (French Glass federation)	p.16
20:00-21:30	Dinner in Nimes	

2

Waste vitrification technologies

French HLW vitrification history and major achievements

Régis Didierlaurent*¹, Marina Barlet¹, Fabien Pacaud¹, Norma Maria Pereira Machado¹, Victor Piovesan¹, Emilien Sauvage², Alain Ledoux², Patrice Brun², Isabelle Giboire², Elise Regnier², Eleonore Welcomme² 1 Orano Recyclage, Prisme, 125 avenue de Paris, 92320 Châtillon, France 2 CEA, ISEC, DES, DPME, Univ. Montpellier, Marcoule, France

regis.didierlaurent@orano.group

The vitrification of High-Level liquid waste (HLW) produced from nuclear fuel reprocessing has been carried out industrially for over 40 years by Orano with three main objectives: containment of fission products, reduction of the final volume of waste and optimization of plants efficiency in an industrial context. Since the beginning of the French vitrification history in the 50's, continuous efforts have been made to improve processes and technologies and to adapt matrix formulations in accordance with waste features and Waste Acceptance Criteria (WAC).

The vitrification process operated by Orano includes two main steps (Figure 1). First, the nitric acid solution containing the highly radioactive fission products and the noble metals-rich fines suspension are evaporated and calcined into a rotative furnace, the calciner. Then, the resulting calcine is mixed with glass frit and heated in the melter. The gas generated by evaporation and calcination are cleaned by an off-gas treatment system (OGTS). The first stage of the OGTS is a wet dust scrubber which allows most of the dust carry-over to be directly recycled into the process.



Figure 1. R7/T7 two step vitrification process.

Based on the industrial experience gained in the Marcoule Vitrification Facility (namely AVM), the vitrification process was implemented at a larger scale in the late 1980's at the Orano "La Hague" commercial recycling plant in the R7 and T7 vitrification facilities to be operated in line with the UP2-800 and UP3 reprocessing plants. R7 and T7 facilities are both equipped with 3 vitrification lines.

The Induction Heated Metallic Melter (IHMM) has been first developed and successfully operated for over 40 years with continuous improvements of the process through operational feedback and R&D programs [1]. In this technology (Figure 2), the metallic wall of the melter is heated by Joule effect through electromagnetic currents provided by a stack of coils surrounding the melter. The metallic wall of the melter directly heats the glass by thermal conduction. The glass is heated up to a temperature of around 1100°C. The melter is continuously supplied with calcine and glass frit during glass processing, feeds are stopped to pour the glass into the canister. The IHMM has a 25 kg/h glass production capacity and the molten glass surface area is around 0.26 m2.



Figure 2. (a) IHMM design principles. (b) Picture of a IHMM in hot cell

Thanks to CEA (French Alternative Energies and Atomic Energy Commission) and Orano long term R&D experience in vitrification processes, the complete industrial experience acquired by Orano operation teams, the close support from engineering team of Orano Projets and the permanent contact between those entities, this specific organization has managed to support efficiently various improvement programs and contributed to significantly improve the vitrification operation at La Hague plant. The major programs that have contributed to operation improvement have been: an upgrade of the calciner to increase the feed throughput; the optimization of the IHMM technology and operation in order to improve its capacity to operate with high noble metals (NM) incorporation rate and high melting throughput; a major update of operation guidelines for the key equipment in order to consider years of industrial feedback and up to date R&D knowledge; and the improvement of reliability and remote in-cell maintainability.

The Orano continuous improvement policy has also led to the development and implementation of the Cold Crucible Induction Melter (CCIM) technology. The CCIM is characterized by currents directly induced inside the molten glass by a coil (Figure 3). These electromagnetic currents heat the glass inside the melter by the Joule effect. The segmented structure of the crucible enables penetration of electromagnetic field into its volume. Absorption of electromagnetic radiation allows the glass to be heated directly without heating the crucible.



Figure 3. Direct induction melting principle

This technology can be used to vitrify various types of chemical waste. By allowing higher waste loading it also minimizes the total volume of packaged waste. Furthermore, the presence of the cold layer minimizes the impact of the composition of the waste on the lifetime of the crucible.

The CCIM has started hot operation at La Hague plant in April 2010 and has now been in commercial operation for over 12 years. The implementation of the CCIM has been a major breakthrough as it had to be installed in place of an IHMM, in a highly radioactive cell into which human access was prohibited, and without impacting the existing structures and upstream or downstream equipment. The CCIM was first used to vitrify effluents from the La Hague UP2-400 facility D&D operations [2]. This waste stream was vitrified into a borosilicate glass at a temperature of around 1250°C to reach significant waste loading. A dedicated glass frit formulation was developed to avoid foaming phenomena during the treatment as the effluents had a high content of cerium. Around 220 canisters were produced. The CCIM was then used to vitrify around 250 m3 of highlevel liquid waste from reprocessed U-Mo-Sn-Al spent fuel, used in Gas Cooled Reactors (GCR), that were produced during the mid-1960s at La Hague plant. These "UMo" solutions were less radioactive than the current fission products concentrates coming from ongoing reprocessing activities, but were very rich in molybdenum and phosphorus. The high molybdenum and phosphorus contents made the molten glass extremely corrosive and required a special high-temperature glass formulation to obtain sufficiently high waste loading (12 wt% in molybdenum oxide). Since 2020, the CCIM has been operated for the vitrification of the very high-level fission products coming from the ongoing reprocessing activities at La Hague Plant. The "R7T7" UOx glass has an average incorporation rate of 1 Ci/g and can be loaded with up to 3 wt% of NM (RuO2 + Rh + Pd). As a result, Orano, supported by CEA, has developed a unique experience in the field of design, construction, and operation of HLW vitrification facilities with high record of safety, reliability, and product quality in line with reprocessing plant operation objectives. Based on this experience, the consortium of the DEM&MELT project which gathers Orano, CEA, ECM Technologies and ANDRA (French national radioactive waste management agency) has developed a specific In-Can vitrification tool designed to match the requirements and constraints from D&D projects. The DEM&MELT In-Can vitrification process is a robust, simple, and versatile in situ vitrification process. It is designed for high or intermediate level waste and is compact enough to be implemented in an existing facility or close to the waste to be treated. It has been developed to treat both liquid and solid waste, to produce a small amount of secondary waste and to minimize investment and operating costs.

DEM&MELT is an In-Can process for thermal treatment and vitrification of solid and liquid radioactive waste (Figure 4). The canister (or "can") is directly used as a melter — and renewed after each batch — to stabilize and condition the waste, with or without additives, and to form a dense, monolithic, stable, and durable matrix.



Figure 4. (a) Schematic diagram of the DEM & MELT process. (a) DEM&MELT scale 1 pilot unit built and commissioned at CEA Marcoule

The technology was tested at pilot scale with waste of various types [3]: namely alpha liquid waste (full qualification of the process with around 20 pilot tests), solidified fission products, liquid fission products solution, zeolites, silicotitanates, sand, ashes and co-precipitation slurries. The tests carried out confirm the simplicity, robustness and versatility of the process. The technology makes it possible to achieve high rates of waste incorporation into the matrix while guaranteeing good performance of the wasteform — especially with regards to its durability in order to limit the release of radioelements into the biosphere — and ensures very low volatility

of the radioelements during thermal treatment. The main results are presented in the table hereafter.

Waste	WL oxides *	Radionuclides volatility	Wasteform
HL Solid fission products	10 %	0.6 wt% Cs	Glass
HL Liquid fission products	10 %	0.2 wt% Cs	Glass
Alpha-contaminated liquid waste		Confidential	
Ashes	50 %	-	Crystallized glass
Zeolites	50 %	0.08 wt% Cs	Glass
Mix of zeolites, slurries, silicotitanates and sand	80 %	<0.5 wt% Cs; <0.1 wt% Sr	Crystallized glass
Mix of zeolites, silicotitanates and sand	60 %	0.04% wt% Cs; 0.01% wt% Sr	Glass
Coprecipitation slurries	40 %	0.007 % Sr	Glass

Table 1. Pilot tests main results

*
$$WL_{ox}(\%) = \frac{sum \, of \, oxide \, mass es \, composing \, the \, waste \, (kg)}{mass \, of \, waste form \, (kg)} \times 100$$

[1] A. Garcia, L. Gauquelin, M. Gassies, J. Lauzel, Ph. Mahut, E. Boudot, S. Betremieux, S. Ben Lagha, L. Meslin, JF. Hollebecque, "New Operation Records for La Hague R7/T7 Vitrification Facilities: A Success of a continuous Improvement Program", GLOBAL 2015, Paris, France

[2] Régis Didierlaurent, Eric Chauvin, Jacques Lacombe, Christian Mesnil, "Cold crucible deployment in La Hague facility: the feedback from the first four years of operation", WM2015 Conference, March 15 – 19, Phoenix, Arizona, USA

[3] Régis Didierlaurent, Laurent David, Maxime Fournier, Caroline Michel, Jean-François Hollebecque, "DEM&MELT In-Can Melter Solution: from Demonstration Tests to Industrial Design", WM2022 Conference, March 6 – 10, 2022, Phoenix, Arizona, USA



Waste Vitrification Technologies and Details of the Office of River Protection's Enhanced Waste Glass Program

Albert A. Kruger

US Department of Energy, Office of River Protection, PO Box 450, Richland, Washington 99352, USA Albert_A_Kruger@orp.doe.gov

The Hanford site in Washington State houses ~56 million gallons of radioactive wastes historically stored in 177 underground tanks. The waste must be immobilized for a permanent disposition, and the plan since the 1990s has centered on the separation of the tank wastes into low activity waste (LAW) and high-level waste (HLW) streams. The U.S. Department of Energy (DOE) is building a Waste Treatment and Immobilization Plant (WTP) at Hanford site to separately vitrify these two waste streams in borosilicate glass using Joule-heated ceramic melters (JHCM).

The current strategy is separate the LAW fraction of select liquid supernates from the tank waste taking advantage of the Tank Side Cesium Removal (TSCR) facility. This Direct Feed LAW (DFLAW) process is fast approaching sustained operations.

This presentation will address the variety of vitrification technologies considered by the US DOE, as well as elsewhere treatment of reprocessing wastes are known to be undertaken. Attention is turning to the treatment of the HLW solids in the tanks. Hanford HLW exists mostly in the form of sludge and salt cake, rich in sodium and aluminum oxides, nitrates and hydroxides along with the significant concentration of transition metal oxides, for example, Fe2O3, Cr2O3, NiO, Cr2O3, and MnO. Although the process of nuclear waste vitrification seems to be well established, in practicality, it is faced with complex problems starting from the design of glass compositions, to processing in melters and long-term performance of the final vitrified waste forms. The presentation is an overview of our current understanding of critical challenges related to the development and performance of HLW glasses. Though more importantly, this presentation reports on the significant advances delivered by the Office of River Protection Enhanced Waste Glass Program over the waste loading, processing efficiencies and flexibility since the WTP Contract was issued in the 1990s.

Read online: https://www.sumglass.fr/abstract/waste-vitrification-technologies-and-details-of-the-office-of-river-protections-enhanced-waste-glass-program/

Waste vitrification technologies



Geomelt In Container Vitrification Technology: Latest Developments and Overview of Operational Installations

Cyrille Veronneau ¹, Brett Campbell ², Keith Witwer ² ¹ Veolia Nuclear Solutions Europe, 556 Chemin de l'Islon 38670 Chasse sur Rhone , FRANCE ² Veolia Nuclear Solutions Federal Services , 295 Bradley Blvd, Richland, WA, 99352, USA cyrille.veronneau@veolia.com

The GeoMelt® vitrification technology was developed in the early 1980's by the Pacific Northwest National Laboratory (PNNL), for the U.S. Department of Energy (DOE). Today, VNS owns worldwide exclusive rights to this technology. GeoMelt® can be deployed in a number of ways including an in container version called GeoMelt® In Container Vitrification (ICV™). ICV™ is a batch waste treatment process that is performed in a single-use refractory container in which graphite electrodes are inserted. The waste is added with glassformers reagents (if the waste does not contain sufficient glass formers) and melted using Joule heating when an electrical current is applied between the electrodes. The process starts with an initial batch of waste and reagents mixture. Feeding of waste material after the initial batch has melted allows for the container to be filled as the vitrification process continues and volume reduction occurs. Hazardous organics are destroyed by pyrolysis and most inorganic materials are incorporated into the glass matrix. The off-gases are collected and treated in a dedicated unit. Once the container is filled, power is shut off and the molten mixture cools into a homogenous glass monolith. In most applications, the ICV[™] container serves as the disposal container. There is no pouring required nor concerns with refractory corrosion, which allows the process to be highly reliable while accommodating a wide range of waste chemistries and high waste loadings.

The final waste form is an inert, dense, mechanically stable glass. Radionuclides and hazardous metals are included into the glass structure, establishing strong chemical bonds with the glass network components. As a result, they are not preferentially leached even if the glass monolith is broken or size reduced.

Since the introduction of GeoMelt[®], more than 27,000 tons of contaminated soils and waste have been treated successfully in various countries including Japan, Australia, and the United States.

For specific wastes with limited disposition paths, Veolia performs technology advancements to adapt GeoMelt® to the specific needs of these new waste streams. An example of this is for treatment of reactive metal containing waste and other problematic legacy waste or large dimension waste.

This work has been carried out at different scales from laboratory work to industrial plants.

Our presentation shows a description of the Geomelt[®] ICV[™] technology and gives an overview of the different pilot and industrial Geomelt installations available around the world, including the latest developments.

Read online: https://www.sumglass.fr/abstract/geomelt-in-container-vitrification-technology-latest-developments-and-overview-of-operational-installations/

Waste vitrification technologies

Poster session 1

PJ1-1	Molten glass coating for ashes conditionning Hélène NONNET (CEA/DES/ISEC/DPME, France)	p.74
PJ1-2	New Glass Ceramics of CaO-SrO-Al2O3-La2O3-ZrO2 for Encapsulation of MA from Nuclear Wastes - Tetsuji Yano (Tokyo Institute of Technology, Japan)	p.75
PJ1-3	Outline and results of the development of glass matrix for reducing the volume of high-level radioactive waste - Kohei Owaku (Japan Nuclear Fuel Limited)	p.76
PJ1-4	Development of melt contact refractory for glass melter at JNFL Takeshi Tsukada (Japan Nuclear Fuel Limited)	p.77
PJ1-5	In-can incineration and vitrification process: glass formulation and glass melt/liquid metal interactions - <i>Julia AGULLO (CEA/DES/ISEC/DPME, France)</i>	p.78
PJ1-6	In-Can Incineration and Vitrification Processing of Plutonium contaminated mixed organic/metallic waste - Arnaud QUINTAS (CEA/DES/ISEC/DPME, France)	p.79
PJ1-7	Vitrification of waste arising from dismantling operations using Dem&Melt technology Eléonore WELCOMME (CEA/DES/ISEC/DPME, France)	p.80
PJ1-8	In-Can vitrification of spent mineral sorbents using DEM&MELT technology Caroline Michel (CEA/DES/ISEC/DPME, France)	p.81
PJ1- 9	Management of TENORM waste by GeoMelt [®] vitrification – Opportunities in France Pascal Evrard (Waste2Glass, Paris, France)	p.82
PJ1-10	Spherical Briquets as A New Feeding Form of Glass Matrix for Vitrification of High-Level Radioactive Nuclear Waste from Reprocessing of High-Burnup and/or MOX spent fuels Tetsuji Yano (Tokyo Institute of Technology, Tokyo, Japan)	p.83
PJ1-11	Advanced Fuel Cycle Programme (AFCP): Improved Low-Temperature Glass Formulations for Advanced Oxide Fuel - Alex Scrimshire (Materials and Engineering Research Institute, Sheffield,	p.84 UK)
PJ1-12	Recent Progress in Decarbonisation Studies of Raw Materials and Glass Composition of Commercial Glass in the UK - Wei Deng (Materials and Engineering Research Institute, Sheffield,	p.85 , UK)
PJ1-1 3	Higher Activity Waste Thermal Treatment (HAWTT) programme Helen Steele (Sellafield Limited, UK)	p.86
PJ1-14	Progress in development of glass formulas for vitrifying ZrO2- and MoO3-bearing high level liquid waste - Shengheng Tan (Department of Radiochemistry, China Institute of Atomic Energy)	p.87

Thermal Plasma Treatment of Dry Waste from Nuclear Power Plants

Kai Xu and Guang Fang

State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan, China kaixu@whut.edu.cn

In China, 55 commercial nuclear power units are in operation, generating ~420 billion kilowatt hours electricity in 2022, and more than 20 nuclear power units are currently under construction. More than 1,000 m3/y of the dry waste, mainly including the high efficiency particulate air (HEPA) filter, cotton, polyethylene, and absorbent paper will be produced during the operation and maintenance of the nuclear power plants (NPPs). Those dry wastes usually have the low-level radioactivity but the high volume.

To efficiently reduce the volume and safely treat those dry waste, China started to develop thermal plasma technology (TPT) to treat the dry waste since 2009 and has constructed the plant in Gansu Province. The organic matter of the dry waste will be gasified by thermal plasma torch in a gasification furnace, and then the inorganic residual ashes will be melted with glass additives at temperature below 1300°C in a melter, and finally the homogenized melt discharges in the steel canister to form a stable glass waste form.

This talk will provide an overview of the development of TPT to treat the dry waste from NPPs in China. The process of TPT to treat the dry waste will be introduced, and the formulations of the dry waste including the media of HEPA filter, cotton, polyethylene, and absorbent paper for vitrification was investigated. According to the feature of the inorganic residue composition, the glass composition-property model for the high CaO and TiO2 waste was figured out. In addition, the glass fiber as the main component of the HEPA filter used as a glass matrix to immobilize the other residual ashes was studied. Finally, the challenge of TPT for treatment of radioactive waste will be discussed as well.

Read online: https://www.sumglass.fr/abstract/thermal-plasma-treatment-of-dry-waste-from-nuclearpower-plants/

Advancement in Waste Glass Formulation Methodology

John Vienna¹, Xiaonan Lu¹ ¹ Pacific Northwest National Laboratory, Richland, WA 99392, USA john.vienna@pnnl.gov

Historically, nuclear waste glass compositions were developed using laboratory intensive Edisonian approaches. The approach shifted starting in the late 1990's to numerical optimization methods using semi-empirical glass property-composition models based primarily on the component concentrations. Uncertainty quantification, necessary to maintain nuclear waste glass properties within acceptable ranges, were based on Monte-Carlo approximations. Over the last decade, advances in glass structure simulations using molecular dynamics allowed for the development of quantitative glass structure-property relationships (QSPR). The state of the art-in glass formulation optimization shifted to more sophisticated QSPR representations of glass. Starting in the early 2020's new machine learning approaches to design nuclear waste glasses are emerging. These techniques are fueled by larger databases of simulated glass structures and measured glass properties. Methods like Gaussian Process Regression and Random Forrest allow for interpolation of existing data at the same time as new composition region discovery. This talk will summarize the historical development of nuclear waste glass formulation methods and discuss future research directions.

Read online: https://www.sumglass.fr/abstract/advancement-in-waste-glass-formulation-methodology/

Vitrification of high-level nuclear waste worldwide: Historical perspective, current status and future challenges

Ashutosh Goel ¹, Paul A. Bingham ², John McCloy ³, Kai Xu ⁴, Sophie Schuller ⁵ John Vienna ⁶ Albert Kruger ⁷ ¹ Department of Material Science and Engineering, Rutgers, The State University of New Jersey, Piscataway, NJ 08854, United States

² Materials and Engineering Research Institute, Sheffield Hallam University, City Campus, Sheffield, S1 1WB South Yorkshire, UK

³ School of Mechanical and Materials Engineering, Washington State University, Pullman, Washington, USA

⁴ State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, P.R. China

⁵ CEA, DES, ISEC, Université Montpellier, Marcoule, France

⁶ Pacific Northwest National Laboratory, Richland, WA 99354, USA

⁷ U.S. Department of Energy, Office of River Protection, Richland, WA 99354, USA

ag1179@soe.rutgers.edu

The idea of glass being a suitable matrix for the immobilization of nuclear waste was proposed in 1950s. Since then, vitreous waste forms have been the most widely accepted candidates for the immobilization of high-level nuclear waste (HLW) worldwide. While several countries are in the process of vitrifying their HLW, the others are still in the planning phase or starting in the near future. Although the general matrix of HLW glasses remains the same, i.e., borosilicate, the overall design of glass compositions is different worldwide primarily due to the different waste chemistries, thus resulting in different scientific and engineering challenges. The lecture will present a historical perspective of the high-level waste vitrification followed by its current status and future challenges at a global level.

Read online: https://www.sumglass.fr/abstract/vitrification-of-high-level-nuclear-waste-worldwide-historical-perspective-current-status-and-future-challenges/

International Perspectives on Glass Waste Form Development for Low and Intermediate Level Radioactive Waste

John McCloy ^{1,2}, M. Chris Dixon Wilkins ¹, Jonathan Evarts ^{1,2}, John Bussey ¹, Aya Azeddioui ¹, Paul A. Bingham³, Kazuyoshi Uruga ⁴, Damien Perret ⁵, Elise Regnier ⁵, Isabelle Giboire ⁵, Sophie Schuller ⁵

¹ Washington State University, Pullman, WA 99163, USA

² Pacific Northwest National Laboratory, Richland, WA 99352, USA

³ Sheffield Hallam University, Sheffield, UK

⁴ Central Research Institute of Electric Power Industry, Yokosuka, Japan

⁵ CEA/DES/ISEC/DPME, Montpellier University, Marcoule, France

john.mccloy@wsu.edu

The global energy transition to low-carbon energy sources will require a significant contribution of nuclear energy to achieve NetZero goals. Low (LLW) and intermediate (ILW) level wastes are created as a result of various phases in the nuclear fuel cycle for power generation, as well as from nuclear accidents, legacy weapons production, and contaminated site decommissioning. In this review, we will summarize recent developments, state-of-the-art glass formulations, and thermal treatment process development for low and intermediate level radioactive waste vitrification from programs in Europe, Asia, and the USA. Throughout, we will discuss the selection of glass over other possible waste forms and any special processing considerations due to the nature of the waste. The character of the wastes – such as slurries, Advanced Liquid Processing System-Multi Radionuclides Removal from Fukushima, mixed technological waste, waste coming from dismantling of the reprocessing facilities, site decommissioning, etc. – and the technology needed to vitrify it – such as in-can melting, PIVIC-Incineration / In-Can Vitrification Process, GeoMelt and plasma treatment – are summarized. Glass properties and microstructural aspects – such as inclusion of crystals or metallic phases – are compared and contrasted to give an overview of the versatility of packaging matrices, such as homogeneous glasses, composites, and crystalline matrices. Volume and heterogeneity of the waste, as well as radionuclide and low silicate solubility components, factor into the selection of a given waste form, processing route, and technology. Case studies include examples from the US, UK, France, Japan, Korea, and China.

Read online: https://www.sumglass.fr/abstract/international-perspectives-on-glass-waste-form-development-for-low-and-intermediate-level-radioactive-waste/

Engineering of inorganic waste mixtures for new usable glasses: from glass-ceramics to alkaliactivated materials

Enrico Bernardo ¹, Hamada Elsayed ¹, Jozef Kraxner ²

¹ Department of Industrial Engineering, University of Padova, Padova, Italy

² Glass Processing Department, FunGlass, Alexander Dubcek University of Trencin, Trencin, Slovakia enrico.bernardo@unipd.it

Vitrification is one of the safest technologies for the stabilization of inorganic waste. Being capital and energy intensive, its application to industrial waste (such as mining residues, ashes, slags, i.e. beyond radioactive waste) is controversial. A key to sustainability is represented by the definition of useful products, from the reuse of waste-derived glasses, to generate extra revenues. Typical products consist of dense and porous glass-ceramics, from viscous flow sintering of fine glass powders with concurrent crystallization. Dense glass-ceramics, developed from waste-derived feedstock and fired at temperature not exceeding 1000 °C, may offer superior strength and hardness, compared to stoneware ceramics, developed from natural raw materials and fired above 1100 °C. Porous glass-ceramics combine, compared to polymer-based thermal insulators, superior strength and durability: a long service life obviously maximizes the energy saving. In the perspective of valorisation of waste-derived glasses, new opportunities rely on alkali activation, i.e. on the suspension of waste-derived glass powders in aqueous solution of alkali hydroxides, resulting first in surface dissolution and then in progressive hardening, due to condensation reactions occurring to dissolution products (at 40-75 °C). Before complete gelation, suspension may be conveniently foamed, just by intensive mechanical stirring (also with the help of surfactants). Highly porous glass-ceramics are achieved by sinter-crystallization of foamed suspensions, with a clear advantage on conventional methodology, involving gas release by additives operating during sintering: beyond avoiding extra costs from additives (such as SiC), the new method prevents risks of inhomogeneity, resulting from the contrast between gas expansion (requiring low viscosity) and crystallization (increasing the viscosity of softened glass). Alkali activation is not just a processing tool: according to the engineering of the chemical composition (namely Na2O/SiO2, CaO/SiO2, Al2O3/ SiO2 ratios) of waste-derived glass, dissolution and condensation reactions may be tuned in order to provide highly durable (Ca- and Na-) alumino-silicate hydrated gels, defining new construction materials (possibly replacing conventional cements) without any thermal treatment.

Read online: https://www.sumglass.fr/abstract/engineering-of-inorganic-waste-mixtures-for-new-usable-glasses-from-glass-ceramics-to-alkali-activated-materials/

Glass recycling

Glass recycling and decarbonization of glass industry Exemple of French glass industry roadmap

Xavier Capilla¹

¹ Fédération des Industries du Verre, Paris, France xavier.capilla@institutduverre.fr

Glass production requires high temperatures, which are achieved through the use of fossil fuels. This accounts for about 80% of the sector's emissions. The second source of greenhouse gases in glass production is raw materials. Recycling could help to reduce both sources. Recycling glass has several major benefits: saving raw materials and reducing greenhouse gas emissions by reducing the energy required. The French glass industry currently recycles around 2,200 kt of glass, mainly packaging. Our goal, as part of our decarbonisation roadmap, is to collect and recycle at least 600 kt more by 2030.

After a brief presentation of the French glass industry, an overview of initiatives to increase the tonnage collected and recycled in France will be discussed. Finally, the decarbonisation options for the French glass industry will be briefly discussed.

Read online: https://www.sumglass.fr/abstract/glass-recycling-and-decarbonization-of-glass-industry-exemple-of-french-glass-industry-roadmap/





Tuesday, September 26th 2023

Simulation/modeling of vitrification process

Chair:

Richard Pokorny (University of Chemistry and Technology, Prague) & Emilien Sauvage (CEA ISEC)

Program

CFD simulation of vitrification process

8:3 0-9:00	Numerical modeling development of Cold Crucible Induction Melting	p.21
	Emilien Sauvage (CEA ISEC, France)	
9:00-9:30	Donna Guillen (INL, US)	p.22
9:30-10:00	Furnace modelling (CFD) tool for detailed modelling of physical and chemical process in complex shapes (GTM-X) - Ankith John Santosh & Corinne Claireaux (CELCIANS, NL)	p.2 4
10:00-10:30	Numerical modeling of industrial glass furnaces Jiri Brada (Glass Service, CZ)	p.25
10:30-11:00	Coffee break	

Modeling of Physical-chemical properties of glass and melt

11:00-11:30	Modeling of glass properties and their effect on glass production rate	p.26
11:30-12:00	Statistical methods and data-driven models to predict glass melt properties Damien Perret (CEA ISEC, France)	p.27
12:00-12:30	Accelerating glass discovery for nuclear waste applications using AI and machine learning - Anoop Krishnan (Indian Institute of Technology, India)	p.28
12:30-15:00	Poster session 2 & buffet	p.88
15:00-15:30	Conversion degree and heat transfer in the cold cap and their effect on glass production rate in an electric melter - <i>Pavel Ferkl (PNNL, US)</i>	p.30
15:30-16:00	From batch to melt: chemical energy demand and energy balance Corinne Claireaux & Ankith John Santosh (CELCIANS, NL)	p.31
16:00-16:30	Modeling foaming in industrial glasses Franck Pigeonneau (CNRS Nice, FR)	p.32
16:30-17:00	Coffee break	
17:00-17:30	Redox of silicate melts at high temperature Daniel Neuville (IPGP, Paris)	p.33
17:30-18:00	Effect of reducing agents on the redox conditions during melting, Tc/Re retention, and off-gas evolution - Jaroslav Klouzek & Richard Pokorny (University Prague, CZ)	p.34
20:00-21:30	Dinner in Nimes	

SUMGLASS 2023	- Simulation/modeling	of vitrification process
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Numerical modeling developement of Cold Crucible Induction Melting

Emilien Sauvage ¹, Zineb Nabyl ¹, Patrice Brun ¹ ¹ CEA, DES, ISEC, DPME, Univ Montpellier, Marcoule, France emilien.sauvage@cea.fr

A cold crucible induction melter is in operation in La Hague plant, which is operated by ORANO since 2010 for the vitrification of High-Level-Waste (HLW) arising from decommissioning and dismantling operation and old reprocessing of high Molybdenum content fuel. The well-known advantages of the cold crucible compared to the hot metallic inductive melter are (i) a higher elaboration temperature (ii) an extended lifetime and (iii) a better homogeneity obtained by mechanical stirring and gas bubbling. As a result, the global production capacity is expected to be higher as well as the Platinum Group Metal (PGM) particles concentration in the glass.

A part of the development of this technology is made with the help of numerical simulation of the glass flow and heating by direct Joule effect thanks to the high frequency induction power unit. In this talk, the last effort of 3D modelisation of the Platinum-Group-Metals (PGM) particles behavior in the glass and chemical reaction kinetics of the feed are detailed.

During the melting, the glass generally shows a homogeneous liquid phase seeded with non-soluble heavy platinum-group-metal particles mainly made of palladium and ruthenium dioxide. Previous studies [1] reported spatial discrepancies of the local volume fraction of particles in the melt because of particles settling with time. This migration of particles towards less agitated bottom parts of the crucible affects the dynamical, electrical and thermal state of the melt because of concentration-dependent electrical conductivity and viscosity of the suspension. A theoretical one-fluid transport model was developed with the help of small scale experiments carried out with a HLW glass simulant. The model is coupled with existing 3D thermo-hydraulic numerical codes, thus enhancing the precision of heat flux predictions between the melt and the crucible. The feed modelling is also under development. From vitreous precursors (Sodium alumino-borosilicate glass frit) and calcined waste (a mixture of about thirty oxide and nitrate compounds obtained after calcination step), a succession of processes such as impregnation, denitration, crystallization and dissolution occur in order to solubilize the waste into the vitreous network. Mainly focus on thermal and chemical (0D models) approaches the objective aim at coupling the reaction kinetics laws of thermally activated processes (denitration, crystallization, dissolution) to the magneto-thermo-hydraulic model in order to model both physic and chemistry of glass synthesis. The experimental methodology based on the characterization of thermo-activated reaction kinetics by differential and gravimetric thermal analysis (TGA/DTA) and the kinetic parameters identification (such as activation energy, reaction order, pre-exponential factor) [2] [3] will be described. Moreover, an example of simulation integrating the chemical equation solved with CFD tools will be presented and discussed.

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[1] Yoshiyuki Iso, Shinsuke Matsuno, Hiroyuki Uchida, Isamu Oono, Toshiki Fukui, and Takaaki Ooba. Numerical simulation of platinum group metal particles behavior in a Joule-heated glass melter. Journal of Power and Energy Systems, 2:815–825, (2008).

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Numerical modeling of Joule Heated Ceramic Melter

Donna Post Guillen ¹, Alexander W. Abboud ¹, Pavel Ferkl ², Richard Pokorny ^{3,4}, Mark Hall ², Pavel Hrma ⁵, Albert A. Kruger ⁶

¹ Idaho National Laboratory, Idaho Falls, ID 83415, United States of America

² Pacific Northwest National Laboratory, Richland, WA 99354, United States of America

³ Laboratory of Inorganic Materials, University of Chemistry and Technology Prague, Prague 6, 166 28, Czech Republic

⁴ Institute of Rock Structure and Mechanics, Czech Academy of Sciences, Prague 8, 182 09, Czech Republic ⁵ AttainX, Support Services Contractor to the Office of River Protection, U.S. Department of Energy, Richland, WA 99354, United States of America

⁶ U.S. Department of Energy, Office of River Protection, Richland, WA 99354, United States of America Donna.Guillen@inl.gov



Our research team has developed computational fluid dynamics and heat transfer models of waste glass melters in support of the vitrification campaign at the Waste Treatment and Immobilization Plant (WTP) as part of the United States nuclear waste stewardship and environmental protection programs. The WTP melters are being constructed to process legacy nuclear waste into a stable form for disposal. This research strives to ensure that the vitrified waste will be stable, durable, and processed in the safest, most efficient and economical manner possible. Hanford's tank waste is far more complex and varied than the waste treated by other vitrification facilities and both startup and long-term operational challenges are likely to be even greater than prior experience has shown. There are approximately 55,000 different waste compositions that make processing the waste a complex and challenging task. The best capabilities throughout the world have been harnessed and a team of experts has been assembled to apply their knowledge and experience to this legacy cleanup problem. The results of these modeling activities will be used to support startup to hot operations at the WTP. Computational modeling is a powerful complement to experimental testing to provide insights into the complex physicochemical phe-

nomena occurring inside the waste glass melters. The radioactivity, high temperature, opaqueness of the molten glass, and surrounding structure will make it difficult to troubleshoot the melters after they are commissioned and fully operational. Idaho National Laboratory has led the effort to model glass furnaces of various sizes spanning from laboratory crucibles, to pilot-scale melters, to full-scale WTP low-activity waste (LAW) and high-level waste (HLW) melters. Additionally, models have been developed to investigate specific phenomena occurring in the melters, such as pneumatic mixing by melt bubbling to induce forced convection, foaming underneath the cold cap, Joule heating from the electrodes, plenum heat transfer, off-gas generation, refractory corrosion, cold cap motion, and batchto-glass conversion kinetic rates. Validation data were obtained from pilot-scale tests conducted at the Vitreous State Laboratory at the Catholic University of America and laboratory experiments at Pacific Northwest National Laboratory (PNNL), the University of Chemistry and Technology (UCT) Prague, and Savannah River National Laboratory (SRNL).

The commercial computational fluid dynamics (CFD) modeling software STAR-CCM+ is the base platform used to perform simulations. STAR-CCM+ uses the Eulerian multiphase volume of fluid (VOF) approach and the Reynolds Averaged Navier-Stokes equations to model two-phase flow. The solution methodology is based on a finite volume approach with first-order implicit time-stepping and second-order spatial discretization. The segregated flow solver for the Navier-Stokes equations is used, which can handle constant density or mildly compressible flows with a predictor-corrector approach coupling the momentum and continuity equations. A collocated variable arrangement and a Rhie-and-Chow type pressure-velocity coupling are combined with a SIMPLE-type algorithm. Due to the low Reynolds number (~30), the laminar model is used. In most models, bubbling air and foaming gases are represented as single-component gas phases; but some sets of models have been run to distinguish the major gas species for oxygen, nitrogen, water vapor, and carbon dioxide. Mesh convergence on a set of coarse, medium, and fine meshes is assessed using a grid convergence index across all melter sizes.

High-fidelity simulations of forced convection bubbling require the use of a modeling framework capable of fully resolving the free surface at the glass/air interface affected by large, spherical-cap-shaped bubbles produced by orifices located at the base of the melter. STAR-CCM+ uses the VOF method whereby volume fraction equations are solved for different immiscible phases of the system. Simplified models were constructed to reduce the required computational time to a manageable amount. A momentum source term approach has been implemented by necessity in representations that include a more complete description of the melter construction, which includes the refractory and insulation layers, for studying large timescale changes in the temperature for operational step changes or potential failure modes.

The cold cap is modeled using conjugate heat transfer into a rigid solid. Cold cap submodels have been developed based on evolved gas analysis and foam expansion test results conducted at PNNL and UCT Prague for various feed compositions. These submodels are integrated into the overall melter model using fitted polynomial equations of response surfaces. The effect of cold cap motion on heat transfer is being investigated using a dynamic fluid-body interaction submodel that has been validated using experiments in a room temperature, transparent vessel at SRNL. As opposed to a rigid cold cap approximation, the transparent melter experiments are conducted with a 3D printed, flexible material to mimic the cold cap. Machine learning has also been applied to determine the cold cap configuration based on plenum temperatures measured by thermocouples. Air inleakage through the refractory bricks and penetrations has been accounted for using a heat sink term. This information can help operators determine recovery strategies for anomalies or off-normal events.

CFD has been used to understand the effect of cavity movement beneath the cold cap on the batch melting rate both with and without bubbling induced by flowing gas into the melt to promote forced convection. The cavities beneath the cold cap are a result of collapsing primary foam, ascending secondary foam, and bubbling. Simulations for a continuous laboratory scale melter were performed for three gas evolution rates and three cold cap shapes – a solid disk, a disk with a central vent hole, and a disk touching the wall with a central vent hole. Ongoing research is examining the formation and behavior of the cavity layer using in-situ X-Ray computed tomography.

Refractory corrosion has been assessed through thermodynamics modeling and crucible tests exposing the refractory coupons for various durations. Numerical models are being developed to predict corrosion rates and extrapolate melter refractory lifetime to operational melters based on the observed phenomena. This combined experimental-computational approach seeks to overcome the shortcomings of scaled crucible tests in relation to the complex dynamics in operational melters.

The plenum is filled with a large volume of gases generated from the batch reactions. The major gaseous emissions released from the melter are H2O, N2, O2, and CO2 along with various monitored environmental pollutants, such as NO, N2O, NO2, or SO2. In addition, reactions between organics and nitrates in the feed may also form products of incomplete combustion such as carbon monoxide (CO) and acetonitrile (CH3CN). Predictive modeling using both analytical regression-based and machine learning approaches has been applied to determine the gas composition generated by various feeds. This approach can significantly reduce the amount of expensive physical melter testing and assist with the optimization of feed composition with respect to off-gas composition.

Recently, we have been developing a model to use the open source Nek5000 code to provide faster turnaround. This platform uses the spectral element method, which is efficient and scalable. Techniques for Joule heating and two-phase flow are being incorporated. With further development, the NekRS version of the code (which is deployable on GPUs), offers the potential to further increase the turnaround time of numerical simulations to support WTP operations.

The current modeling capability has been developed over the last decade in preparation for melter startup before the end of 2023. The least radioactive of the tank waste (i.e., LAW), which accounts for roughly 90% by volume of the total tank waste, will be treated first. The commissioning process is underway for the two 300-ton LAW melters. The first melter will be heated up, commissioned and verified operational before the second melter is heated and tuned. HLW will be vitrified in a separate facility.

As a result of advances in the understanding of waste processing and underlying glass science for vitrification over the last decade, the Agency is pursuing the concept of direct feed HLW. Without the need for an additional facility at the WTP for the separation of the LAW fraction, there exists the opportunity to realize an economic and schedule opportunity to start treatment of the HLW fraction much sooner.

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Furnace Modelling (CFD) tool for detailed modelling of physical and chemical process in complex shapes

Ankith John Santosh ¹, Andries Habraken ¹ ¹ CelSian, Achtseweg Zuid 241-A 5651 GW Eindhoven, Netherlands ankith.john@celsian.nl

Over the last 25 years, CelSian has been developing a simulation software for glass furnaces. This simulation software, named GTM-X, is similar to the software used in weather forecasting and the automotive and aerospace industries. However, GTM-X is equipped with dedicated models that allow it to accurately describe the phenomena inside a glass furnace.

This presentation aims to showcase modelling as a necessary tool for furnace design and production as it allows us to extract the maximum out of our furnaces and set us up for the future. The various possibilities by carrying out CFD simulations will be demonstrated. These include the ability to analyse critical flow patterns for product quality, gain an in-depth understanding of the melting behaviour with the use of different raw materials, accurately determining refractory contact temperatures and predicting refractory wear.

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CFD simulation of vitrification process

10h00-10h30

Numerical modeling of industrial glass furnaces

Jiří Brada¹, Miroslav Trochta¹, Erik Muijsenberg²

¹ Glass Service, a.s., Software Development Department, Rokytnice 60, Vsetin, 75501, Czechia

² Glass Service, a.s., Vice President, Rokytnice 60, Vsetin, 75501, Czechia

jiri.brada@gsl.cz



In this presentation, we will explore advantages, benefits and usefulness of numerical modeling which has become an indispensable tool for designing, optimizing, and controlling industrial processes. Glass manufacturing is no exception, and numerical modeling of glass furnaces has thus been gaining increasing importance over past few decades.

Glass melting furnaces are a crucial component of the glass manufacturing process and are subject to a variety of complex physical and chemical processes. Associated challenges, such as high temperatures or maintaining precise control over the glass melting process, contribute to a vital need for mathematical models which can help to better understand the process as well as to predict furnace behavior under different conditions. This then leads to improved efficiency, reduced costs, and better product quality. Firstly, ability of numerical modeling to understand complex physical and chemical phenomena that occur inside the furnace will be demonstrated. This understanding enables furnace design optimizations, controlling process variables, and improving quality of produced glass. Furthermore, numerical modeling can help reducing energy consumption and emissions, which is not only economically advantageous, but also environmentally responsible.

Secondly, advantages of numerical modeling's flexibility will be discussed. Numerical models can simulate different scenarios, such as changes in furnace geometry, fuel type, or raw material composition. This flexibility allows furnace operators to predict and mitigate potential problems before they occur, and to optimize the process for various operating conditions.

Finally, challenges associated with developing and implementing mathematical models for glass melting furnaces, including the need to collect accurate data and limitations of current modeling techniques, will be explained.

In conclusion, numerical modeling is a powerful and valuable tool for understanding and optimizing glass melting furnaces, leading to saving energy, improving glass quality, and reducing emissions. With an increasing demand for sustainable manufacturing practices, numerical modeling will continue to play a crucial role in the glass manufacturing industry, both for manufacturers and consumers of glass products.

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Modeling of glass properties and their effect on glass production rate in an electric melter

Pavel Hrma¹, Pavel Ferkl ¹, Richard Pokorny ² ¹ORP US DOE, ¹PNNL, WA, USA, ² UCT, Prague, Czechia ratnottara@aol.com

The lifecycle of nuclear waste disposal by vitrification depends on the waste loading (the fraction of waste in the glass product) and the processing rate (the rate at which the melters are producing the waste glass). While the former has achieved near perfection over decades of glass formulation development, the latter has received attention relatively recently. For a single waste composition, the glass production rate can be maximized empirically, by trial and error, through optimizing the waste treatment, glass-forming and modifying additives, and melter operation parameters. For the Hanford Waste Vitrification and Immobilization Plant (WTP) that will process hundreds, even thousands, compositions of waste, mathematical modeling is the only realistic method for accomplishing such a task. Yet, the conversion of the material charged into the melter to molten glass is enormously complex; its main features have only recently been identified and mathematically formulated. The current state can be characterized as an expensive and cumbersome empirical method on the one hand and a complex, not yet fully developed mathematical modeling on the other. Fortunately, a middle way exists in the form of an engineering approach in which the relationship between the melting rate and the basic parameters is simplified to the utmost possible degree. This approach has been developed within the recent decade and dubbed the melting rate correlation (MRC).

The MRC is based on the boundary layer theory, according to which the heat flux from the melt pool to the cold cap is Q = h(TM - TB)and the shear stress imposed on the cold cap bottom is s = Vdv/dz. Here h is the heat transfer coefficient, TM is the melter operating temperature, TB is the cold cap bottom temperature, V is the glass melt viscosity, v is the glass melt velocity horizontal component, and z is the vertical coordinate. For a melter in which the melt is pneumatically stirred by gas bubbling, log(h) = a + blog(Re), where a and b are adjustable parameters and Re = yu/k, where y is the characteristic melt pool dimension (depth or width), u is the bubbling gas flow rate, and k is the kinematic viscosity.

For the cold cap to which the heat is delivered from below, the glass production rate is j = Q/H, where H is the melter feed-to-glass melt conversion heat. For a glass produced in a melter operated at a constant temperature with melt stirred by bubbling, the unknown parameters are TB, a, and b. We have developed various methods to estimate TB, none of them fully satisfactory, yet enabling us to determine a and b by fitting the MRC relationship to data reported for reduced scale melters. For high-level waste (HLW) glass processing, the values are a = 2,5 and b = $\frac{1}{2}$.

The reacting zone of the melter feed in the cold cap is separated from the melt below by the primary foam layer. Hence, the cold cap bottom temperature, TB, is a temperature at which the primary foam is collapsing: the foam cell walls are breaking and the cavities with gas released are carried away by the melt circulating under the cold cap.

Glass melt foam stability is determined by viscosity. In the primary foam, viscosity is the lowest at the bottom, where the temperature is highest. Thinning of foam cell walls occurs by three mechanisms: first, the surface curvature gradient drives the melt to the Plateau borders; second, gas phase volume in foam bubbles increases through thermal expansion and gas-evolving reactions; third, the external shear stress imposed by the velocity gradient on the melt side imposes strain on the foal cells. Apart from the transient melt viscosity, the critical thickness at which the cell walls break is a function of the fraction and position of the dispersed solid particles. Silica particles are the main solid phase that remains undissolved, yet continues to dissolve, at the cold cap bottom. Since the melt around dissolving silica particles has a high concentration of SiO2, its viscosity is increased and can be up to a hundred times higher than in the bulk melt. In the cell walls, silica particles have destabilizing effect: low viscosity melt outside the silica concentration layer are the weak points. Silica particles promote foam stability in Plateau borders, where the high viscosity opposes the melt flow and hinders cell wall thinning. Similar, though less potent effects, are produced by other solids, such as spinel and zircon.

The purely kinetic effect of silica, in the absence of external forces, on the cold cap bottom temperature was expressed, by Ferkl et al., as TB = T0 - pQ, where the T0 and p values were computed for several melter feeds. This linear formula can be extended to express the effect of the shear stress at the cold cap bottom. Provided that the foam strain is proportional to the bubbling rate, we can write TB = T0 - pQ + ru. Although the primary foam deformability was determined by a recent study of the cold cap rheology, the r value is still waiting to be determined through computational fluid dynamics modeling.

Summarizing, when exposed to a higher heat flux (Q) and an enhanced bubbling (u), the way the primary foam layer can withstand collapse is by allowing the low-viscosity bottom foam cells to break until the transient melt viscosity is high enough to resist the wall thinning forces. As a result, the bottom temperature, TB, decreases. With lower TB, the heat transfer driving force, TMO – TB, increases and thus, the melting rate is faster. Ultimately, the melting rate is maximized when primary foam ceases to exist, i.e., when TB = TF, where TF is the foam onset temperature (the temperature at which the transient melt connects. This option, achievable at elevated melting temperatures, was wasted for LAW glass processing by choosing, needlessly, Inconel electrodes that necessitate processing at a low melting temperature.

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Statistical methods and data-driven models to predict glass melt properties

Damien Perret ¹, Nicolas Bisbrouck ¹, Muriel Neyret ¹, Caroline Chabal ¹ ¹ CEA, DES, ISEC, DPME, Univ Montpellier, Marcoule, France damien.perret@cea.fr

In situations where theoretical models cannot be efficiently applied to calculate glass properties, empirical statistical models are often required. It is typically the case when glass contains a high number of components. Since the end of the 19th century, it is known that under certain conditions, silicate glass properties can be expressed as a simple linear combination of oxide contents. This «Principle of Additivity» was initially introduced to calculate heat capacity of glass, before being extended during the 20th century to a larger number of properties: optical, thermal, mechanical or rheological properties. In the 1990s, American scientists from PNNL developed a statistical methodology to establish robust property-composition models applicable to the formulation of nuclear waste conditioning glass. Since the 2000s, significant increase in the power of computer tools has allowed to use highly efficient algorithms in the predictive methods of data mining. For example, glass transition temperature can be accurately predicted by using neural networks. Glass viscosity prediction is much more challenging because of huge variability of this property on temperature and composition scales. An innovative methodology recently developed by glass formulation scientists at CEA, with the support of Orano and EDF, combines statistical techniques of experimental designs, multilinear regression and neural networks. It uses glass formulation data generated at CEA over the past 30 years as well as large amount of data collected from the literature and from commercial database. Results obtained for glass transition temperature and viscosity predictions are very accurate, compared to other statistical models already published in the literature.

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Accelerating glass discovery for nuclear waste applications using artificial intelligence and machine learning

N M Anoop Krishnan^{1,2}

¹ Department of Civil Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi, India ² Yardi School of Artificial Intelligence, Indian Institute of Technology Delhi, Hauz Khas, New Delhi, India krishnan@iitd.ac.in

Traditional glass discovery relies on trial and error approaches, thereby leading to a design-to-deploy period of 20-30 years. To address this challenge, in this talk, we will discuss the application of artificial intelligence (AI) and machine learning (ML) in accelerating glass modeling and discovery. Specifically, three aspects where AI and ML can be used include: (i) data-driven models for glass property predictions, (ii) natural language processing (NLP) for extracting information from the glass literature, and (iii) reinforcement learning for accelerated aging of glasses. To demonstrate these aspects, three problems will be discussed. The first focuses on developing interpretable ML models for predicting 25 properties of glasses made of a few among 84 elements of the periodic table. This work covers nearly the entire periodic table for glass-forming elements. The second focuses on extracting information on glasses and other materials from literature to answer specific queries. We will also discuss how MatSciBERT, the first materials-aware language model, can be used to extract information regarding composition-property relationships from the glass literature. Finally, we will discuss how reinforcement learning can be used to generate and study ultrastable glasses obtained after significant aging.

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Poster session 2

PJ2-1	Effects of glass composition and High-Level radioactive Waste(HLW) contents on viscosity and electrical conductivity of the borosilicate glass melts Jaehoon Park (Department of Materials, Kyushu University, Japan)	p.9 0
PJ2-2	Effect of melt velocity and temperature on the refractory corrosion during waste glass melting <i>Petra Cincibusova (University of Chemistry and Technology Prague, Czechia)</i>	p.91
PJ2-3	Modeling of liquid nuclear waste vitrification : focus on the chemical processes Zineb Nabyl (CEA, DES, ISEC, DPME, LDPV, Lab. of Vitrification Processes Development, Marcoule	p.92 , France)
PJ2-4	Effect of alumina source and feed reducing agents on the retention of rhenium during vitrification of nuclear waste - <i>Miroslava Vernerova (University of Chemistry and Technology Prag</i>	p.93 gue, CZ)
PJ2-5	Development of PGM detection method by glass melt flow image from HLW vitrification melter Ken Shinohara (IHI Corporation, Japan)	p.94
PJ2-6	Numerical simulation of the temperature and flow field near the bottom of cold crucible Min Qian (Shanghai Institute of Optics and Fine Mechanics (CAS), Shanghai, China)	p.95
PJ2-7	Numerical study of the fracture of vitroceramic materials under self-irradiation Gérald Feugeur (Université Paris-Saclay, CEA, France)	p.96
PJ2-8	Colloidal Forces in Silicate Melts and Glasses Luiz Pereira (Department of Earth and Environmental Sciences, Munich, Germany)	p.97
PJ2-9	Reactions of sodium nitrate in cold cap Kazuyoshi Uruga (Central Research Institute of Electric Power Industry, Japan)	p.98
PJ2-10	Study of the physicochemical properties of glassy oxides as positive electrode active materials of Li-ion batteries - <i>Alexi Cardoso (CEA, DES, ISEC, DPME, Marcoule, France)</i>	p.100
PJ2-11	CALPHAD optimization of SiO2-B2O3-Al2O3-ZnO-CaO-Na2O-Li2O-MoO3 system and their applications to high-level radioactive waste vitrification Toru Sugawara (Akita University, Graduate School of Engineering Science, Japan)	p.101
PJ2-12	The effect of iodine incorporation on the cation in borosilicate glasses Sami Soudani (Université de Nantes, Laboratoire de Planétologie et Géodynamique de Nantes (Ll	p.102 PG))
PJ2-1 3	Structural changes in borosilicate glasses as a function of Fe2O3 content: a multi-spectroscopic approach James D. Eales (Materials and Engineering Research Institute, Sheffiel, UK)	p.103
PJ2-14	Incorporation and structural investigations of dismantling nuclear waste in an alkali-rich borosilicate glass - Sophie Achigar (IRCP, CNRS. CEA, DES, ISEC, DPME, SEME, LFCM, France)	p.104
PJ2-1 5	Composition-structure-property relationship of phosphate glasses: a combination of experiments, simulations, and QSPR analysis Lu Deng (Shanghai Institute of Optics and Fine Mechanics (CAS), Shanghai, China)	p.106
PJ2-16	Oxide Glass Cathode Materials for Sustainable and High-Energy Density Lithium-ion Batteries Taos Guyot (Univ Grenoble Alpes, CEA-Liten, CEA, DES, ISEC, DPME, Univ Montpellier, France)	p.107
PJ2-17	Simulations of multiphase flows with the Lattice Boltzmann method and the phase-field models <i>Capucine Méjanès (CEA Saclay, DES, Gif-sur-Yvette, France)</i>	5 p.108



Conversion degree and heat transfer in the cold cap and their effect on glass production rate in an electric melter

Pavel Ferkl¹, Pavel Hrma², Jaroslav Kloužek³, Albert A. Kruger⁴, Richard Pokorný³

¹ Pacific Northwest National Laboratory, Richland, WA 99354, United States of America

² AttainX, Support Services Contractor to the Office of River Protection, U.S. Department of Energy, Richland, WA 99354, United States of America

³ Laboratory of Inorganic Materials, University of Chemistry and Technology Prague, Prague 6, 166 28, Czech Republic

⁴ U.S. Department of Energy, Office of River Protection, Richland, WA 99354, United States of America pavel.ferkl@pnnl.gov

The legacy nuclear waste stored at the Hanford Site in the U.S. State of Washington will be processed in Joule-heated electric melters into stable borosilicate glass. Because of the high variability in waste composition, each waste batch will be mixed with glass forming and modifying chemicals, yielding a waste glass with unique optimized composition and maximized waste loading while meeting criteria on melt viscosity, electrical conductivity, refractory corrosion, and glass durability.

The glass production rate in an electric melter is a function of (i) melter operating conditions such as the melt pool temperature and the bubbling rate of injected gas to impose forced convection in the melt pool, (ii) glass melt properties such as melt density, viscosity, and thermal conductivity, and (iii) properties of the melter feed (an aqueous slurry) such as its feed-to-glass conversion enthalpy and its propensity to foam at high temperatures.

Using experimental data and the best available estimates for the material properties, we have developed a heat transfer model for several high-level waste (HLW) and low-activity waste (LAW) feeds exemplifying a variety foaming responses. The model considers heat conduction and convection of both gaseous and condensed materials to compute the temperature profile in the cold cap and the thickness of the cold cap reaction zone. Although conversion processes start in the slurry at low temperatures, most batch-melting reactions occur at temperatures above 200 °C. Because the crystalline silica, the major component of nuclear waste feeds, is

distributed throughout the condensed cold cap, we used the dissolved silica fraction as a measure of the feed conversion degree to facilitate the development of a kinetic dissolution model.

The model represents the effects of the material properties of the reacting melter feed, which are functions of temperature and conversion degree, and of the heat flux delivered to the cold cap, on the resulting temperature profile and the cold cap thickness. Cold cap density is virtually constant at low temperatures but substantially increases above the foam onset temperature when the transient melt becomes connected before it abruptly decreases as the transient melt turns into primary foam by trapping evolving gases. Effective heat capacity is highly temperature dependent as it accounts for reaction heat from batch-melting reactions. Because of the effect of radiation, effective thermal conductivity increases with increasing temperature.

The model estimates the effects of feed processing parameters on the glass production rate and the feedback loop between the glass production rate and the primary foam stability that determines the cold cap bottom temperature. Increasing the glass production requires more heat to be transferred through the cold cap. This results in a thinner reaction zone in the cold cap and a higher heating rate experienced by the reacting materials. A higher heating rate affects silica dissolution kinetics and the transient melt a viscosity with a direct impact on primary foam stability.

Read online: https://www.sumglass.fr/abstract/conversion-degree-and-heat-transfer-in-the-cold-cap-and-their-effect-on-glass-production-rate-in-an-electric-melter/

From batch to melt: chemical energy demand and energy balance

Corinne Claireaux ¹, Ankith John Santosh ¹, Mathi Rongen ¹, Luuk Thielen ¹, Johan van der Dennen ¹ ¹ CelSian, Achtseweg Zuid 241-A 5651 GW Eindhoven, Netherlands corinne.claireaux@celsian.nl

Minimizing the energy consumption of glass melters is crucial in the current economic and environmental context. We present a combined approach of experimental analysis, theoretical calculations, and energy balance modeling to help the glass industry make impactful choices toward energy savings and CO2 emission reduction.

The main part of the energy provided by combustion and electric boosting is consumed by the heat demand of the melting process, which is the sum of the energy required to heat the batch, the glass, and the flue gases, and to ensure the conversion of the mineral batch into a melt.

A unique experimental setup was developed with a consortium of glass-related companies to determine the heat demand of the melting process. It is based on the drop calorimetry principle, and it allows the measurement to be performed on a representative quantity (about 200 grams) of batch, with full-size cullet. Experimental results are shown and compared with theoretical calculations for validation based on the work of Conradt. The positive effect of some raw materials such as burned lime, cullet, or dry boron carriers on the heat demand of the melting process is clearly evidenced.

The measured or theoretical data are indispensable inputs to calculate an overall energy balance of a full-scale industrial furnace. The effect of using alternative raw materials on the entire melting process (including emissions, regenerator efficiency, crown hot spot temperatures, overall energy consumption, total CO2, and cost savings) can be evaluated. The potential of the combination of these methods will be demonstrated.

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Modelling foaming in industrial glasses

Franck Pigeonneau¹, Florence Rouyer²

¹ MINES Paris | PSL Research University, CEMEF, CNRS UMR 7635, Sophia Antipolis cedex, France ² Laboratoire Navier CNRS UMR 8205, Gustave Eiffel university, 14/20 Boulevard Newton 77420 Champs sur Marne, France

franck.pigeonneau@minesparis.psl.eu

The melting of raw materials in industrial glass furnace leads to bubble generation. Bubble density and size distribution are initially correlated to the granulometry of raw materials [1]. The carbonate decomposition leads to CO2 release which is a source of large quantity of bubbles due to the low solubility of CO2 [2]. The chemical reaction on silica seeds with precursor liquid leads also to a bubble generation. These phenomena are the origin of the presence of foam above raw materials generally called primary foam. To remove the bubble, glass makers add fining agents. The out-gassing occurring generally at high temperature, T around [1300-1500]°C can lead to a foam creation. A layer of few centimeters of foam can spread over a large part of the glass bath.

From the point of view of the heat transfer, the presence of a foam layer is harmful to the energetic efficiency. According to Fedorov and Viskanta [3], few centimeters of foam reduces dramatically the transmittance. By corollary, the temperature in combustion space increases which is detrimental to the refractory materials.

The creation of a steady-state thickness of foam is a balance of source of bubbles rising from the liquid bath and death of the bubble at the top of the foam. According to Pilon and Viskanta [4], three situations can exist for which the control parameter is the superficial gas velocity jg resulting from a fluid mechanics analysis. Below a threshold jm, the foam is unstable. When jg is equal to jm, a foam appears. Above this threshold, a foam is created. In this lecture, the origin of gas source resulting to fining process will be first presented to determine the main characteristic of the superficial gas velocity. After a review of the onset of foaming, the mechanisms leading to the death of foam will be presented based on film stability as already studied in [5]. A simple model to describe the creation of foam will be also presented.

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Redox of silicate melts at high temperature

Daniel R. Neuville IPGP-CNRS-UP, 1 rue Jussieu, 75005 Paris neuville@ipgp.fr

Glass is a fundamental and necessary material to meet the challenges of the energy transition (manufacture of solar panels, textile fibers for wind turbines, insulation, etc.). Glass is therefore a multifaceted material, necessary for the construction of tomorrow's world, which must be manufactured in a virtuous manner, emitting as little greenhouse gas as possible.

Almost all glasses are manufactured in gas furnaces that produce large quantities of CO2. Gas furnaces have several advantages: they can be used for decades; they offer great operating flexibility, allowing the volume of glass produced each day to vary; they allow the temperature to be adjusted according to the nature of the raw materials, but also to the redox state of the silicate batch. It is indeed relatively easy to intervene on the gas mixture and to regulate the quantity of oxygen available, fO2, at fusion. But the current energy context and the roadmaps of the ecological and sustainable transition demand important modifications of the melting and working processes in the medium term and for all sectors of the glass industry. Glass producers are aware of energy efficiency issues. But drastic changes are needed to develop energy efficient furnaces. Several ways are possible:

- increasing the amount of hydrogen in the gas mixture, but what will be the implications on the redox of the silicate bath,
- · the use of electric furnaces but how to control the redox
- the search for new raw materials by increasing the proportion of cullet and, above all, the abandonment of the use of carbonates and the search for substitutes for their use.

We will review all these scenarii.

Read online: https://www.sumglass.fr/abstract/redox-of-silicate-melts-at-high-temperature/

Effect of reducing agents on the redox conditions during melting, Tc/Re retention, and off-gas evolution

Richard Pokorny¹, Jaroslav Klouzek¹, Miroslava Vernerova¹, Petra Cincibusova¹, Pavel Hrma², Albert A. Kruger³

² AttainX, Support Services Contractor to the Office of River Protection, U.S. Department of Energy, Richland, WA, USA

³ U.S. Department of Energy, Office of River Protection, Richland, WA 99354, U.S.A.

Richard.Pokorny@vscht.cz

The Hanford Waste Treatment and Immobilization Plant (WTP) at the Hanford Site is currently nearing startup to immobilize waste from plutonium production. For the first 10 years the WTP will be fed directly with a low-activity fraction of waste extracted from the 200,000 cubic meters Tank Farm inventory. The WTP is now commissioning and starting up two electric, Joule-heated melters to vitrify low-activity waste (LAW) into a borosilicate glass matrix. In general, LAW melter feed is composed of the Hanford waste tank supernatant liquid, comprising aqueous solutions of sodium, potassium, aluminum, nitrates, nitrites, sulfates, chlorides, fluorides, and organics (such as acetates, formates, or glycolates), together with glass-forming additives, such as silica sand, kyanite, wollastonite, olivine, or zircon. Furthermore, reductants, such as sucrose, formic acid, urea, starch, cellulose, or glycolic acid, are added to LAW melter feeds to prevent excessive foaming by hastening the denitration, i.e., by evolving gases from nitrates and nitrates at temperatures below the primary foaming onset. Besides diminishing primary foaming, the changes in reaction pathways caused by the presence of reducing agents affect also other conversion processes - for example, the retention of radioactive technetium or the composition of gaseous emissions generated during the vitrification process.

In this contribution, we will address the effect of sucrose, a preferred organic reductant due to its solubility in water and high reducing potential, on the melting process during waste vitrification. Using the combination of feed volume expansion test, thermogravimetric analysis, evolved gas analysis, x-ray diffraction, and scanning electron microscopy with energy dispersive x-ray spectrometry, we experimentally analyzed and theoretically described the changes in the feed conversion reactions, showing that as the fraction of sucrose in the feed increases, the extent of foaming decreases. Interestingly, although moderate levels of sucrose addition reduced foaming, they did not significantly affect the glass production rate. This can be attributed to the observation that it is not the foam volume, or the foam porosity, that controls the heat flow from the melt to the cold cap, but the temperature at which foam collapses. Hence, reducing the extent of foaming without affecting the foam collapse temperature does not noticeably affect the rate of melting. Significant foam suppression and decrease of foam collapse temperature were however observed when the carbon-to-nitrogen ratio in the melter feed exceeded one. While such high sucrose levels would increase the rate of melting, they could also lead to the reduction of transition metal oxides to elements.

Moreover, we varied the sucrose fraction in the feeds while measuring the partial pressure of oxygen, iron speciation, and Re (as a surrogate for Tc) retention in two different low-activity waste melter feeds. The results show that almost no Re is lost during the feed conversion reactions below 800°C. The retention of Re at 1150°C then increases with decreasing partial pressure of oxygen, i.e. with increasing sucrose fraction. By reacting with nitrates and nitrites, a higher sucrose content decreases the content of the perrhenate-containing molten salt phase. It is hypothesized that a lower fraction of the salt phase can increase the extent of Re diffusing into the early glass-forming melt, yielding an increased Re retention. We confirmed that a relatively small increase in sucrose level from the current nominal values may significantly improve Tc retention in the melt without forming metallic iron.

Finally, reaction stoichiometry and linear regression were successfully used to estimate the effect of reducing agents on the composition of gaseous emissions, measured by evolved gas analysis. Although linear regression provided satisfactory results, we show that the gas evolution is inherently nonlinear because it depends not only on the content of nitrogen (nitrates, nitrites, nitrides) and organics in the feed, but especially on their ratios, i.e., on the feed redox state. Attempts to estimate the gas evolution based on the feed reaction stoichiometry were satisfactory when a two-step reaction mechanism was considered, consisting of a reaction between organic compounds and nitrates/nitrites producing CO2, NO, and N2, and then the residual decomposition of nitrates and nitrites above ~550 °C, producing NO and O2. The comparison of EGA results with pilot-scale melter data shows that the off-gas emissions trends are qualitatively similar, but the actual values are affected by the differences in melting conditions, atmospheric conditions, or residence time. If these factors are considered, a multiple regression analysis is expected to closely approximate the off-gas compositions for a broad range of melter operating conditions and waste feed chemistries, thus satisfying the need to develop a predictive off-gas emission model and reducing the amount of required physical scaled melter testing.



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¹ University of Chemistry and Technology Prague, Technicka 5/1905, Prague 6, 166 28, Czechia



Wednesday, September 27th 2023

Thermodynamic and chemical mechanism modeling of glass and melt

Chair: John McCloy (Washington State University) & Ekaterina Burov (Saint-Gobain Research Paris)



Program

Modeling thermodynamic of glass and melt

8:30-9:15	Thermodynamic modeling of nuclear glasses and glass forming liquids Pierre Benigni (University Aix Marseille, France)	p.38
9:15-9:45	Thermodynamic models for phase separation and crystallization in nuclear glasses Stéphane Gossé (CEA ISAS, France)	p.39
Modeling	j chemical mechanisms	
9:45-10:15	Modeling chemical diffusion in silicate melts Emmanuelle Gouillart (Saint Gobain, France)	p.40
10:15-10:45	Coffee break	
10:45-11:15	Rheology of partially crystallized simulated nuclear glass melts Elise Regnier (CEA ISEC, France)	p.41
11:15-11:45	Modeling phase separation in the melt Alain Cartalade (CEA ISAS, France)	p.42
Overview	v on glass alteration	
11:45-12:15	Key issues related to the disposal of HL vitrified waste: feedback from Cigeo project	n.43

Key issues related to the disposal of HL vitrified waste: feedback from Cig Stéphan Schumacher (ANDRA, France) Lunch box - Free pic nic, Free time and proposed activities 12:15

Thermodynamic modeling of nuclear glasses and glass forming liquids

Pierre Benigni¹

¹ Aix Marseille Univ, Université de Toulon, CNRS, IM2NP, Marseille, France p.benigni@univ-amu.fr

A nuclear glass is a multicomponent and multiphase material. The methodology for thermodynamic modelling of such materials, namely the CALPHAD approach [1] [2], is well established and widely used. It has been applied for many years with great success, for example on steels or other metal alloys such as Al or Ni based ones. However, nuclear glasses have unique characteristics that present many challenges from the point of view of thermodynamic modelling

The first, most striking and probably most complex feature of nuclear glasses is the massively multi-component nature of the chemical system involved. Taking the French R7T7 glass as a typical example [3][4], about 30 radioelements are present in the reference solution of fission products, to which must be added the constituents of the glass matrix itself. The chemical system resulting from the melting operation hence contains more than 40 chemical components. It is likely to be more multicomponent than any other material of industrial interest.

Secondly, the liquid phase must be accurately described over a wide temperature range, the lower limit of which is the glass transition temperature, i.e. down to a large supercooling. Therefore, the evaluation of thermodynamic functions of the liquid phase must be based on physical models that have reliable extrapolation behavior.

Thirdly, demixing, which is a subtle effect occurring in a solution when the destabilization effect of a positive enthalpy of mixing outweighs the stabilization effect of the entropy of mixing, may take place in both the liquid and glassy phases. In addition, this demixing can sometimes lead to the formation of liquid phases with different types of chemical bonds, e.g. phase separation between a metallic liquid and an oxide liquid [5].

Fourthly, many crystalline phases precipitate because of the limited solubilities of some components in the melt or in the glass [6] [5] and this phenomena is enhanced by prior liquid-liquid demixing [7]. Moreover, experimental thermodynamic data are sometimes missing for these often complex crystalline phases.

Fifthly, structural relaxation is arrested when the glass transition range is crossed during cooling and the configurational state of the metastable liquid oxide is then frozen-in. The glass matrix is a solution phase that is in a non-equilibrium state requiring a specific modeling approach compared to conventional equilibrium phases such as the gas, liquid and crystalline phases.

In this context, the various methodologies which have been adopted in literature for modeling unary and multicomponent glasses and glass forming liquids will be reviewed, with particular emphasis put on the 2nd and 5th items in the above list.

Thermodynamics is the first fundamental brick to build a modeling tool capable of predicting the nature, compositions and quantities of phases in nuclear glasses. A more complete modeling should include additional building blocks to take into account kinetic phenomena such as diffusion, nucleation and growth.

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Thermodynamic models for phase separation and crystallization in nuclear glasses

S. Gossé ¹, P. Fossati ¹, N. Dupin ², A. Deshkar ¹, S. Schuller ³

¹ Université Paris-Saclay, CEA, Service de Recherche en Corrosion et Comportement des Matériaux, 91191, Gif-sur-Yvette, France

² Calcul Thermodynamique, Rue de l'avenir, 63670, Orcet, France

³ CEA, DES, ISEC, DPME, Univ Montpellier, Marcoule, France

stephane.gosse@cea.fr



Radioactive waste vitrification has been carried out industrially in several countries for several decades. In these nuclear waste glasses, fission products and minor actinides are integrated in the vitreous network during high temperature reactions in vitrification furnaces. Meanwhile, research continues to investigates incorporation of new types of nuclear wastes which can lead to aggregates or crystals in glass matrix. During the steps of the process, the solid, liquid and gaseous states of the glass precursor and waste evolve continuously with time and temperature until a high-temperature homogeneous liquid is formed. After cooling, the waste remains integrated at the molecular scale in a homogeneous glass.

This study focuses on the fundamental research conducted to better describe the thermodynamics of these complex systems. Its objective is to better anticipate the behaviour of typical insoluble phases in prototypic nuclear glasses such as platinoid precipitates and complex molybdates that can form beyond their solubility limits. To predict the chemical interactions and the optimal conditions of these processes, a specific database, including the description of a simplified B2O3-Na2O-SiO2 glass melt, has been implemented using the Calphad method. This calculation tool allows to describe the phase equilibria and the phase separation phenomena between either platinoids or molybdates (Fig. 1) – mainly CaMoO4 and Na2MoO4 – and the glass melt. In parallel to a direct comparison between thermodynamic calculations and experimental results, this database is also used for a phase field approach. The objective of this coupling is to provide a consistent formalism between the thermodynamic properties of the chemical system and the local dynamics of the interface between the separate liquid-liquid phases of a heterogeneous glass.

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Modeling chemical mechanisms

Modeling chemical diffusion in silicate melts

Emmanuelle Gouillart¹, Ekaterina Burov², Sophie Schuller³

- ¹ Saint-Gobain Research Paris, Aubervilliers, France
- ² Joint Unit Saint-Gobain / CNRS Surface of Glass and Interfaces, Aubervilliers, France
- ³ CEA Marcoule, France
- emmanuelle.gouillart@saint-gobain.com



Chemical diffusion in silicate melts plays a vital role in a wide range of scientific disciplines, spanning from geology to materials science. Understanding the mechanisms and rates of chemical diffusion in silicate melts is crucial for elucidating geological processes, predicting material behavior, and designing advanced materials, in particular for vitrification technologies. In this talk, I will describe the characteristics of chemical diffusion in silicate melts, and in particular how diffusion is linked to the structure of melts, with the different role of network modifiers and formers. Then I will show how diffusion data can be measured from experiments and simulations, both for diffusion coefficients and multicomponent diffusion matrices. Finally, I will discuss how to build models to predict diffusion rates in various cases.

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Rheology of partially crystallized simulated nuclear glass melts

Jeanini Jiusti ¹, Norma Pereira-Machado ¹, Muriel Neyret ¹, François Faure ², Philippe Marchal ³, Mohamed-Leith Ghazzai ¹, Elise Régnier ¹

¹ CEA Marcoule, ISEC, DPME, Univ. Montpellier, Marcoule, France

² Université de Lorraine, CNRS, CRPG, UMR 7358, 15 rue Notre Dame des Pauvres, F-54501 Vandœuvre-lès-Nancy, France

³ Université de Lorraine, CNRS, LRGP-GEMICO, UMR 7274, 1 rue Grandville, Nancy F-54001, France elise.regnier@cea.fr

In France, high-level wastes (HLW) resulting from the reprocessing of spent Uranium OXide fuel are conditioned in sodium alumino-borosilicate glasses. The formulation of such glass results from a compromise between the waste-loading (waste mass to final glass mass ratio), the technological feasibility of the glass at an industrial scale, and its long-term behavior. To date, the compositions of the alumino-borosilicate glasses are formulated to avoid any crystallization in the melt. However, the tolerance of crystals in the glass melt could allow to reach higher waste loadings, which would decrease the number of glass-containers and therefore the cost of the long-term storage.

Previous studies have shown that the presence of particles alters some properties of the glass melt, particularly its rheology. This is the case of platinoids elements, which are poorly soluble in the glass matrix (solubility limit generally < 100 weight ppm), and which precipitate as RuO2 needles and PdTe beads. Hanotin et al. [1] observed that less than 1 vol% of platinoids particles leads to a very shear thinning behavior. Unlike platinoids particles, for which the volume fraction is constant during glass melting, the fraction of crystals considered in this study depends on temperature and time. Therefore, the study of the effect of crystals on the rheology of the melt has to take into account the time-temperature dependency of the crystal fraction. In addition, crystals morphologies are also likely to change with temperature [2]. Two types of crystals observed in nuclear glasses due to exceeding solubility limits were chosen for this study: 1) cerianite, which generally shows a cubic morphology and slow crystallization kinetics 2) apatite, which generally has an acicular shape and fast crystallization kinetics [2]. The

morphology of crystal is expected to impact the rheology behavior of the melt [3].

In this work, we first evaluate the crystallization properties of both crystal types at high temperatures (around 1100°C) in both static and dynamic conditions (absence / presence of flow). In static conditions, thermal treatments are performed in a tubular furnace. For the experiments in dynamic conditions, a stress-imposed rheometer with a multiblade rotor is used. The stirring is controlled by changing the imposed stress – the viscosity is acquired simultaneously. Post-mortem analyses are carried out for each condition in order to assess the microstructure of the frozen melt. For the studied cerianite fractions (up to \sim 1 vol%), virtually no change in the viscosity is observed. For the apatite case, however, a very shear thinning behavior is observed, similar to that observed for platinoids particles in previous studies. Rheological models are tested to describe the behavior of the glass melt during the vitrification process.

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Modeling chemical mechanisms

Modeling phase separation in the melt

Alain Cartalade ¹, Werner Verdier ¹, Sophie Schuller ², Stéphane Gossé ³, Romain Le Tellier ⁴

¹ CEA ISAS DM2S, 91191 Gif-sur-Yvette cedex, France

² CEA ISEC DPME, 30207 Bagnols-sur-Cèze, France

⁴ CEA IRESNE, 13108 Saint-Paul-lez-Durance, France

alain.cartalade@cea.fr

The glass is a multi-components system which appears as a single liquid phase at high temperature. However, when it is lowered below a critical temperature, several observations show that the melted glass can separate into two liquid phases. Their density ratio is quite low but their viscosity ratio is around 100. Both liquid phases are separated by an interface and their bulk properties are characterized by the equilibrium compositions of each specie. In this talk we present the whole methodology carried out for simulating the phase separation of such systems. It is based on several complementary approaches: 1) a Calphad modeling for thermodynamics of simplified glasses, 2) a mathematical modeling based on the phase-field theory and 3) an efficient computational code (LBM_Saclay) implementing those models for the simulations.

The phase-field theory is a popular approach for modeling phenomena which involve interface dynamics and thermodynamic phase diagrams. A simple free energy functional composed of one double-well term plus one gradient energy term can simulate the phase separation. The well-known Cahn-Hilliard (C-H) equation, which is derived from that functional, mixes the thermodynamics and the interface properties. As an advantage, the interface position as well as the composition can be simultaneously recovered. As a drawback, the fit of the thermodynamics necessarily modifies the interface properties. A first illustration of phase separation is given on a melted glass composed of two components SiO2 -MoO3 (binary mixture). The simulations illustrate the phase separation and the growth of two different initializations.

That simplest free energy functional is next adapted for the ternary phase diagram of SiO2-Na2O-MoO3 and the partial derivative equations are derived. In order to decouple the thermodynamic properties and the interface parameters, the C-H equation is advantageously replaced by an Allen-Cahn equation coupled with two diffusion equations. The first one tracks the interface and involves the surface tension and the mobility. The two other contain the diffusion coefficients of species and their equilibrium compositions in each bulk phase. The simulation of the Oswald ripening is presented as an illustration of that two-phase/three-component model. Finally several simulations will present the fluid flow effect with viscosity contrast when that model is coupled with the Navier-Stokes equations.

Several perspectives of this work are currently in progress. The first one consists to simulate the model expanded with a fourth component (B2O3) and coupled with the temperature equation. Next, comparisons will be done with the experiments performed at CEA/ ISEC.

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³ CEA ISAS, 91191 Gif-sur-Yvette cedex, France

Key issues related to the disposal of HL vitrified waste: feedback from the Cigeo project

Stéphan Schumacher ¹, Christelle Martin ¹, Nicolas Michau ¹, Yannick Linard ¹, ¹ Agence Nationale pour la gestion des déchets radioactifs (ANDRA), Châtenay-Malabry, France stephan.schumacher@andra.fr

On January 16th, Andra submitted the construction license application (DAC) of Cigeo, the French project for the deep geological disposal facility for the most highly radioactive waste. Over an operating period of about 100 years, this repository will receive about 10,000 m3 of vitrified long-lived high-level waste from the reprocessing of spent nuclear fuel, mainly from the "La Hague" plant. This is a crucial step marking both a culmination and a new start for the project. First and foremost, it is the result of 30 years of progressive development under regular evaluation and a process of iteration between knowledge acquisition, design and safety assessment. Over time, the scientific and technological aspects of the project have been refined into well-defined design principles and a robust safety demonstration.

This presentation illustrates some key steps of this iterative process for the high-level vitrified waste disposal cells. It highlights the link between the evolution of environmental conditions in vitrified waste disposal cells (temperature, hydraulics, geochemistry, geomechanics...) and the long-term behavior of the vitrified waste. It specifies the remaining R&D topics to support the design of the disposal cell and to consolidate the robustness of the safety demonstration, drawing on the experience of performance and safety assessments.

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Thursday, September 28th 2023

Glass alteration

Chair: John Vienna (Pacific Northwest National Laboratory) & Daniel Caurant (Institut de recherche de Chimie Paris - IRCP)



8:30-9:00	Alteration of industrial glasses Lég Brunswic (CEA ISEC, France)	p.46
9:00-9:30	Alteration of nuclear glass Stéphane Gin (CEA ISEC, France)	p.47
9:30-10:00	Alteration of UK nuclear waste glasses; evidence from laboratory and field experiments <i>Clare Thorpe (University of Sheffield, UK)</i>	p.48
10:00-10:30	Aqueous dissolution rate of nuclear waste glasses as a function of environmental parameters - Yaohiro Inagaki (Kyushu University, Japan)	p.49
10:30-11:00	Coffee Break	
11:00-11:30	Alteration under atmospheric conditions Aurélie Verney-Carron (University Paris Créteil, France)	p.50
11:30-12:00	Float glass weathering in atmospheric conditions Sophie Papin (Saint Gobain, France)	p.51
12:00-12:30	Glass as a biomaterial - Or: why corrosion can be a good thing Delia Brauer (Otto Schott Institute of Materials Research, DE)	p.52
12:30-15:00	Poster session 3 & buffet	p .110
Modeling	y approaches	
15:00-15:15	Short introduction Jean Marc Delaye (CEA ISEC, France)	
15:15-15:45	Molecular dynamics simulations of nuclear waste glasses and their aqueous corrosion behaviors - Jincheng Du (University of North Texas, US)	p.54
15:45-16:15	Atomistic simulation of glass alteration using the Monte Carlo method Jean Marc Delaye (CEA ISEC, France)	p.55
16:15-16:45	Coffee break	
16:45-17:15	Elucidating glass and alteration gel structure with a combined MD and NMR approach boosted by machine learning - <i>Thibault Charpentier (CEA DRF, France)</i>	p.56
17:15-17:45	Geochemical modeling of glass alteration Pierre Frugier (CEA ISEC, France)	p.58
20:00-23:00	Banquet	



Alteration of industrial glasses

Léa Brunswic ¹, Frédéric Angeli ¹, Stéphane Gin ¹, Thibault Charpentier ², Laurent Gautron ³, Eric van Hullebusch ⁴, Mariona Tarragó ⁴, Daniel Neuville ⁴, Xavier Capilla ⁵, Daniel Coillot ⁶, Ilyes Ben Kacem ⁷, Patrick Ravel ⁸, Johann Brunie ⁹

¹ CEA, DES, ISEC, Université de Montpellier, Marcoule, France

² NIMBE, CEA, CNRS, Université Paris-Saclay CEA Saclay F-91191 Gif-sur-Yvette, France

³ Laboratoire Géomatériaux et Environnement, Université Gustave Eiffel, Marne-la-Vallée Cedex 02, France

⁴ Université Paris Cité, Institut de Physique du Globe de Paris, CNRS, UMR 7154, F-75238, Paris, France

⁵ Fédération du verre et du cristal, 114 rue de la Boétie, 75008 Paris

⁶ Manufacture Baccarat, 54120 Baccarat, France

⁷ Arc France, 104 avenue du Général de Gaulle, 62510 Argues, France

⁸ Pochet du Courval, lieu dit Guimerville, 76340 Hodeng au Bosc, France

⁹ Pyrex, 85 Allée des Maisons Rouges, 36000 Châteauroux, France

lea.brunswic@cea.fr, frederic.angeli@cea.fr,

Changes to European regulations (REACh, materials in contact with foodstuffs, etc.) to meet the requirements of today's society may well have far-reaching consequences for a major part of glass industry. It has become essential to demonstrate the ability of glass to retain potentially hazardous elements. A major comprehensive study of a wide range of commercial glass compositions has been pursued to describe the release mechanisms of various glass elements. Five types of silicate glass have been investigated: lead crystal glass (fine glassware), soda lime glass (containers for food and cosmetic industries), borosilicate glass (cooking dishes), barium glass (tableware) and opal crystallized glass (tableware).

Glass alteration was carried out for three years in acetic acid (4 % vol) at pH 2.4 at 70°C. The confrontation of results allowed establishing a referential for the alteration of commercial glasses in acidic medium and unfolding the links between chemical composition, structure and leaching behavior of various elements. The impact of chromium added as a colorant in lead crystal glass has been investigated, pointing out major changes due to structural modifications. Increasing Cr concentrations demonstrated a dual benefit effect on lead crystal chemical durability by reducing the leaching of Pb and increasing the polymerization of the silicate network.

Different types of surface treatments, from chemical reactions to sputtering deposits, have been evaluated. Five surface treatments were tested, all developed by glass manufacturers to address specific needs of their production such as resistance to mechanical abrasion (SnO2, TiO2), esthetics (TiO2, acid polishing), surface tension modification (SiO2) or Pb leaching reduction (SO2 dealkalization treatment). The unique data collected gives access to quantitative information on glass and coating constituents leached in solution over time. Significant reduction of long-term lead leaching, especially in the case of SO2 dealkalized lead crystal glass, is obtained as well as beneficial effects towards the retention of Ba in Ba-containing glass but shows poor interest for borosilicate glass.

The high resistance to significant alteration conditions can be underlined and their endless recyclability make glass highly suitable candidates for sustainable product consumption and packaging.

Read online: https://www.sumglass.fr/abstract/alteration-of-industrial-glasses/

9h00-9h30

Alteration of Nuclear Glass

Stéphane GIN

CEA, DES, ISEC, DPME, University of Montpellier, Marcoule, F-30207 Bagnols sur Cèze, Montpellier, France stephane.gin@cea.fr

The question of silicate glass chemical durability is at the heart of many industrial and environmental issues, with certain glasses, such as bioglasses, needing to transform rapidly, while others, like nuclear glasses, extremely slowly. Due to the wide diversity of the chemical composition for these types of materials and their metastability – no thermodynamic equilibrium can be reached between glass and solution – the evaluation of chemical durability remains a scientific challenge. In this presentation, we review the current state of knowledge on nuclear glass alteration mechanisms and kinetics.

Thanks to the development of novel techniques and international collaborations, progress has come from both understanding the fundamental processes at molecular level and integrating that knowledge in models. Zooming in at the molecular level reveals extremely complex and dynamic processes. The challenge now is to identify the relevant mechanisms to be implemented in macroscopic models. The overall picture and the applications must always be kept in mind. Experiments in laboratories as well as observations of natural systems have demonstrated that silicate glasses can self-passivate by forming amorphous gels on their surfaces, but the fate of the protected glass strongly depends on the environment. The mechanisms of gel formation are still under debate, although recent results strongly suggest that a continuum exists between the dissolution/reprecipitation model and the leaching/in situ reorganization model.

Mechanistic models have been developed at some specific scales, although holistic models still need further development to link the various scales and perform reliable predictions.



The illustration highlights glass transformation into alteration products. a. Representation of a cross section of an altered piece of glass. The alteration layer is generally made up of a hydrated layer (also called 'interdiffusion' or 'leached' layer), the gel layer (amorphous hydrated polymerized Si-rich material) which can be made of several sub-layers depending on how it forms, and secondary phases (precipitates). b. Scanning Electron Microscopy image of a piece of SON68 glass, a 30 oxide borosilicate glass, altered for 2 months at 150°C in deionized water. The sample was broken and observed from the edge. Secondary phases precipitated on the top of the gel layer consist of poorly crystallized phyllosilicates. c. Transmission Electron Microscopy bright field image of a SON68 glass sample altered for 26 years at 90°C in granitic water. Pores within the gel can be seen in bright.

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9h30-10h00

Alteration of UK nuclear waste glasses; evidence from laboratory and field experiments

Clare Thorpe¹, Garry Manifold ¹, Rachel Crawford ¹, Russell Hand ¹ Claire Corkhill ¹ ¹ Department of Materials Science and Engineering, University of Sheffield. Sir Robert Hadfield Building, Mappin Street, Sheffield, S1 3JD, United Kingdom. clare.thorpe@sheffield.ac.uk

Borosilicate glass is used in the UK, as in many other countries, to immobilise the high activity waste liquors resulting from spent fuel reprocessing. The majority of the 1,500 m3 of vitrified high level radioactive waste (HLW) currently in existence has been produced using an alkali-borosilicate base glass known as Mixture Windscale (MW) with a ~25 % waste loading. However, a transition to a Zn and Ca modified base glass is in progress to improve wasteform durability and prepare for vitrification of post operational clean up wastes from the UK's Highly-Active-Liquor storage tanks. Following government policy, all vitrified HLW is destined for disposal in a geological disposal facility, the siting of which is currently underway using a community consent based process.

This talk will give an overview of the state of knowledge and ongoing research regarding UK HLW glass alteration (MW and Ca/ Zn based compositions) comparing results obtained from shorter term laboratory studies with longer term (> 20 year) field studies. Laboratory experiments have probed the effect of changes in glass chemistry on UK HLW durability in controlled, closed, sterile, systems. Meanwhile, field tests offer insight into glass behaviour in complex open systems with changing geochemistry, influence from near-field mineralogy and geomicrobiology.



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Aqueous dissolution rate of nuclear waste glasses as a function of environmental parameters

Yaohiro Inagaki¹

¹Department of Applied Quantum Physics & Nuclear Engineering, Kyushu University, Japan inagaki.yaohiro.553@m.kyushu-u.ac.jp

Over the last few decades, understanding the kinetics of nuclear waste glass dissolution/alteration in aqueous media has advanced through a large number of the experimental and atomistic simulation studies performed by a large number of researchers in the world, which has contributed successfully to an advance of modeling the glass dissolution/alteration for the geological disposal. For assessing the long-term glass performance in geological disposal with reliability, however, we need a greater understanding of the glass dissolution/alteration kinetics under the actual repository conditions in consideration of the potential long-term evolution of the repository conditions. The greater understanding of the dissolution/alteration kinetics is also required for parameterization of a mechanistic model used to determine the glass dissolution/alteration rate with the radionuclide release rate as a function of key environmental variables such as the solution composition, pH, Eh, temperature, and time.

For the understanding of glass dissolution/alteration kinetics, we need experimental data on the glass dissolution rate measured precisely, consistently and systematically under well-constrained test conditions. Along with the data on the dissolution rate, which is usually determined from solution analysis, we also need the data on the altered glass surface properties, such as morphology of alteration layers, chemical composition, elemental depth profile, crystallinity, stability, density, porosity, permeability of water and glass constituent elements, etc., analyzed for the glass altered under well-constrained test conditions. For the last few decades, a large number of dissolution tests have been performed for the waste glasses, however, there have existed only a few data available for evaluation of the dissolution kinetics, because of difficulties in precise and systematic measurement. With respect to pH dependence of the glass dissolution rate, for example, we have only a few data available for the systematic evaluation, because the test conditions such as the solution composition, pH, and the glass surface area can change easily during the test period against the expectations as a consequence of the nature of the current standard test methods such as MCC-1 and PCT tests. Therefore, we have developed a new test method, "Micro-channel flow-through (MCFT) method", to measure the glass dissolution rate precisely and systematically under various

well-constrained test conditions, and applied it to measurement of the glass dissolution rate as a function of environmental parameters such as the solution composition, pH, temperature.

The MCFT method has been applied first to measurement of the initial dissolution rate, r0, as a function of pH and temperature for an international reference glass ISG and a Japanese reference glass P0798. The r0 has been measured successfully to provide the systematic data of r0 as a function of pH, where ISG showed a "V-shaped" pH dependence with a minimum at pH4, while P0798 glass shows a "U-shaped" pH dependence with a minimum at pH4. While the systematic data of r0 as a function of temperature at each constant pH has provided the apparent activation energy, Eact, for the initial dissolution. The Eact was evaluated to be 60-70 [kJ/mol] at acidic to weakly basic pH for ISG, which suggests a surface-reaction controlled-dissolution mechanism. For P0798, the Eact was evaluated to be 60-70 [kJ/mol] at neutral to weakly basic pH as well as ISG, however, the Eact at acidic pH was evaluated to be 50 [kJ/mol], which suggests a diffusion -controlled dissolution mechanism.

Currently, we have been trying to measure the glass dissolution rate as a function of solution concentration of Si by using the MCFT method and Si-isotopes. The concentration of Si dissolved in solution has been considered to be one of fundamental factors dominating the glass dissolution kinetics, and the rate equation based on the first-order dissolution rate law of pure amorphous silica has been proposed to be applied to modelling the glass dissolution/alteration as follows,

r = r0 (1-[H4SiO4]/K) (eq.1)

where r is the glass dissolution rate, r0 is the initial dissolution rate, [H4SiO4] is the activity of orthosilicic acid at the interface between glass surface and solution, and K is the equilibrium constant (which equals the activity of orthosilicic acid at saturation).

We have been accumulating the data on the glass dissolution rate as a function of solution concentration of Si for ISG and P0798, and some of the interesting results will be introduced in the lecture along with discussions on the glass dissolution/alteration kinetics.

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Alteration under atmospheric conditions

Aurélie Verney-Carron¹ ¹ Univ Paris Est Creteil and Université Paris Cité, CNRS, LISA, F-94010 Créteil, France aurelie.verney@lisa.ipsl.fr

The understanding and modeling of glass alteration in atmospheric medium is a major concern for the conservation of historic glass, as well as for the safety of the nuclear glass geological disposal. For these different cases, the atmospheric conditions are obviously different. Stained glass windows are subjected to rainfall events, wind, solar radiation... and overall changing conditions. Glass in museum collections can be altered by variable relative humidity and temperature and by internal pollution. The expected unsaturated phase in the geological repository of nuclear glass packages is caused by the release of hydrogen during the steel corrosion. The composition of these glass types is also very different as a function of the time period and context. However, the methodology to study atmospheric alteration is similar. Ancient samples of historic glass have been characterized by different techniques to identify the alteration patterns and their formation processes and to measure the apparent

alteration rates. Model historic glass samples have also been exposed in real conditions to investigate the first stages of alteration. And for all types of glass, specific experiments in aqueous medium to simulate rain events and/or at different relative humidity and temperature values, sometimes with additional gases, to simulate the vapor phase, have been performed to determine mechanisms and kinetics. Results show that the alteration mechanisms involved during the atmospheric alteration are quite similar (hydration, interdiffusion, hydrolysis, secondary phase precipitation) but their relative contribution differ in the different situations and by comparison to aqueous medium. We will therefore provide an overview of these mechanisms, of the associated kinetics as a function of specific environmental parameters and of the options to model the alteration of historic and nuclear glasses under atmospheric conditions.

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Float glass weathering in atmospheric conditions

Sophie PAPIN ¹, Amandine SERVE ¹², Hervé MONTIGAUD ², Odile MAJERUS ³ & Daniel CAURANT ³ ¹ Saint-Gobain Research Paris

² joint CNRS/Saint-Gobain Research Paris lab Surface du Verre & Interfaces

³ Institut de Recherche de Chimie de Paris

sophie.papin@saint-gobain.com

The compositions of industrial soda lime glasses were optimized according to customer needs and technical specifications. For standard applications, weathering or corrosion problems are rather rare and always connected to wet conditions during storage and/ or transport where the stuffy atmosphere favours a high rate of humidity.

The involved mechanisms are different from those of the most studied alteration, which is in immersion conditions. Indeed, the alkali and alkaline-earth cations released from the alteration reactions cannot diffuse away. They stay on the surface or in the alteration layer of the glass. They can lead to the formation of alteration salts on the surface by reacting with atmospheric gases. These salts are the classic outward sign of weathering: microscopic crystals of sodium and calcium carbonates.

Glass weathering issues are crucial for coated products. The influence of the glass composition is not so obvious to study as the manufacturing process spontaneously generates at the subsurface a specific gradient of composition depending on the process conditions (as well illustrated for the bath / atmosphere sides in the float process). We will present the results of weathering studies of lab model glasses (PhD thesis of Amandine Serve), which allow us study the influence of the different oxides on glass weathering behaviour for standardised melting and preparation conditions

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12h00-12h30

Glass as a Biomaterial - Or: Why Corrosion Can Be a Good Thing

Delia S. Brauer ¹

¹ Otto Schott Institute of Materials Research, Friedrich Schiller University Jena, Fraunhoferstr. 6, 07743 Jena, Germany delia.brauer@uni-jena.de

While we usually think of inorganic glasses as inert materials, they do usually react with water, albeit slowly only. In most cases, this corrosion is an undesired process and significantly deteriorates the glass surface and reduces glass quality. There are, however, special inorganic glasses which are successfully used as biomaterials in the clinic to help heal bone defects, and for these glasses the reaction with water is not only beneficial but even a key step in the bone regeneration process. These glasses are therefore designed to undergo fast reactions with aqueous solutions such as body fluids, release ions into solution and even form surface layers helping bone cells to adhere and form bone. Their fast reaction with water makes this type of silicate glasses interesting for several reasons. On the one hand, it is fascinating to see how a material with a composition not unlike to that of window glass can help healing bones to improve the lives of patients. But on the other hand, these glasses allow us to get insight into many steps of glass corrosion in relatively short time periods.

This presentation therefore introduces silicate glasses used as biomaterials and gives examples of what we can learn from them about the corrosion reaction between silicate glasses and water.

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Poster session 3

PJ4-1	Self-healing of nuclear glass alteration gels under irradiation - Pierre de LAHARPE (Institut de Chimie Séparative de Marcoule (UMR 5257), Nanomaterials for Energy and Recycling), France	p.112
PJ4-2	Characterization of glass alteration layers to study the evolution of its morphology Sathya Narayanasamy (CEA, DES, ISEC, DPME, University of Montpellier, Marcoule, France)	p.113
PJ4-3	Effect of complex irradiation scenarios on the structure and properties of ISG and SON68 glass <i>M. Taron (CEA, DES/ISEC/DPME, ICSM, CEA, CNRS, ENSCM, Univ Montpellier, France)</i>	p.114
PJ4-4	Glass characterization with XPS and ToF-SIMS techniques Laurent DUPUY (SERMA TECHNOLOGIES, ECULLY, FRANCE)	p.115
PJ4-5	Impact of different irradiation scenarios on the long-term behavior of ISG glass Hélène Aréna (CEA, DES, ISEC, DE2D, Université de Montpellier, Marcoule, France)	p.116
PJ4-6	New insights into Monte Carlo simulation of borosilicate glass aqueous alteration <i>S. Tiwari (CEA Marcoule, France)</i>	p.117
PJ4-7	MoO3 solubility and chemical durability of simulated radioactive waste glass containing V2O5 Minako Nagata (Akita University, Akita, Japan)	p.118
PJ4-8	Predicting alteration layers volume for the glasses with various glass composition Ryuki Kayano (Faculty of Engineering, Dep. of Applied Chemistry and Biotechnology, Chiba, Japan	p.119 n)
PJ4-9	Monitoring of alpha-decay radiation damage in a 241Am-doped glass-ceramic material S. Miro (CEA, DES, ISEC, DE2D, Université de Montpellier, Marcoule 30207, France)	p .120
PJ4-10	Structure and Dynamics of Hydrous Silicate Gels by Molecular Dynamics Calculations Takuma Hatori (Graduate School of Engineering, Chiba University, Japan)	p.121
PJ4-11	Application of glass structural gene modeling in the simulation of chemical durability and liquidus temperature in HLW glass - Liyan Zhang (Shanghai Institute of Optics and Fine Mechanic Chinese Academy of Sciences, Shanghai 201815, China)	p.122 cs,
PJ4-12	Influence of glass composition and morphology on its solubility in simulated physiological fluids (SPF) - Sarah Gandon (Saint Gobain Recherche Paris, CEA Marcoule, France)	p.123
PJ4-1 3	Effect of Gadolinium Oxide on Structure and Chemical Stability of Borosilicate Glass with Simulated Nuclear Power Plants HLLW Hua Zhang (Radioactive Chemistry Department, China Institute of Atomic Energy)	p.124
PJ4-14	Chemical durability of commercial silicate glasses and the impact of surface treatments Léa Brunswic (CEA, DES, ISEC, DPME, Université de Montpellier, Marcoule, France)	p.125

Modeling approaches

Molecular dynamics simulations of nuclear waste glasses and their aqueous corrosion behaviors

Jincheng Du¹ ¹ Department of Materials Science and Engineering, University of North Texas, U.S.A. jincheng.du@unt.edu

Understanding corrosion of nuclear waste glasses in aqueous environments is critical to the assessment of effeteness of these materials as a medial to immobilize medium and high level nuclear wastes. Despite advances of analytical techniques that provide a wealth of information of water-glass interactions, there remain many unanswered questions in fundamental steps and mechanisms. In this talk, I will introduce applications of atomistic simulation methods in understanding of the glass-water interaction and corrosion behaviors of silicate and borosilicate nuclear waste glasses. Starting from generation of accurate structural models of multicomponent borosilicate nuclear waste glasses using molecular dynamics simulations, particularly recent development of interatomic potentials that enable these simulations, glass surface-water interactions from simulations using reactive potentials will be then presented. Quantitative Structure-Property Relationship analysis based on structural features from these simulations and its usage to correlate with measured dissolution rates will be discussed. Dissolution gel layer formation as a result of glass corrosion and related structural and transport behaviors from atomistic simulations will also be discussed.

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Atomistic simulation of glass alteration using the Monte Carlo method

Jean-Marc Delaye¹, Sumit Tiwari¹, Stéphane Gin¹, Paul Fossati², Andrey Kalinichev³

¹ CEA, DES, ISEC, DE2D, University of Montpellier, Marcoule, Bagnols sur Cèze, Montpellier F-30207, France

² Université Paris-Saclay, CEA, Service de la Corrosion et du Comportement des Matériaux dans leur

Environnement, 91191, Gif-sur-Yvette, France

³ Laboratoire SUBATECH UMR6457- Institut Mines-Télécom Atlantique, CNRS/IN2P3, Université de Nantes, Nantes, France

jean-marc.delaye@cea.fr

As glass used to confine the long-lived radionuclides arising from spent nuclear fuel are intended to be stored definitively in a deep geological repository, it is important to predict the glass dissolution rate when being in contact with underground water. Indeed, this material alteration rate is directly linked to the release of the radioelements into the environment, thus the safety of the disposal. For the development of a predictive model, the first step is to determine the preponderant elementary mechanisms originating the glass alteration.

More and more sophisticated stochastic approaches based on Monte Carlo algorithms have been developed in previous years to try to capture these elementary mechanisms and determine the rate limiting once depending on the glass composition and the alteration conditions.

This presentation starts with a history of these developments from the very first model proposed by M. Aertsens around 1995 until the one currently under development.

The first attempt to simulate nuclear glass alteration using a Monte Carlo approach is due by M. Aertsens from Mol in Belgium. An ordered SiO2-Na2O network in contact with water was built to simulate the glass alteration and a set of probabilities were introduced to represent the release of Si into the solution and the Na+-H+ exchange mechanisms. Unfortunately, this method was limited because of a too-long computational time.

Then a refined algorithm was developed at CEA Marcoule [1,2]. The glass compositions considered were more complex (up to five oxides SiO2-B2O3-Na2O-CaO-ZrO2) and the glass structure was still represented by an ordered network in contact with water. A larger set of probabilities was used to simulate the hydrolysis of glass formers (Si, Al). One Si or one Al ion in contact with water was released into the solution with a probability depending on the local degree of polymerization of its site. The B ions were immediately released in the solution when in contact with water. Using this more sophisticated algorithm, it has been possible to reproduce with good agreement some experimental results, such as the behavior of B, a glass dissolution tracer, for a series of SiO2-B2O3-Na2O glasses altered at different S/V ratios, or the strengthening effect of ZrO2. Later, S. Kerisit at PNNL [3] continued to improve the Monte Carlo method first by adding Al2O3 to the glass composition, then by considering the boroxols rings effect. He developed his own code, before a new collaboration with CEA started. He observed a non-linear impact of Al2O3 on the glass alteration and an acceleration of the glass alteration with the number of boroxol rings.

CEA and PNNL codes were later compared successfully during A. Jan's thesis [3]. One of the main objectives of this thesis was to use these Monte Carlo codes to try to reproduce the increase of glass alteration after irradiation of the material by heavy ions. But it has not been possible to trigger the Monte Carlo probabilities to reproduce the experimentally observed radiation effects. From this work, it has been concluded that other important elementary mechanisms were still missing.

For this reason, a new Monte Carlo algorithm is currently in development. The main difference with the previous CEA and PNNL codes is the possibility for water to diffuse inside the glass (this has never been considered so far) and the possibility to represent the alteration layer ripening. Thanks to these new options, it should be possible to represent more precisely both the radiation effects on glass alteration, along with the so called residual rate. The first results obtained with this refined Monte Carlo method will be presented for a series of SiO2-B2O3-Al2O3-Na2O glasses.

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Elucidating Glass and Alteration Gel structure with a combined MD and NMR approach boosted by Machine Learning

Thibault Charpentier¹, Federica Lodesani¹, Jean-Marc Delaye², Frédéric Angéli²

¹ Université Paris-Saclay, CEA, CNRS, NIMBE, 91191 Gif-sur-Yvette France

² CEA, DES, ISEC, DPME, University of Montpellier, Marcoule, F-30207 Bagnols sur Cèze, France thibault.charpentier@cea.fr



Because of the lack of long-range order, the structure of amorphous materials such as glasses remains difficult to study. Among the spectroscopic approaches that can be used, magic-angle sample spinning nuclear magnetic resonance (MAS NMR) has firmly established itself as one of the most powerful technique to determine the local environment of atoms allowing the building block of the glass network to be determined and quantified, such as SiO4, AlO4, BO4 and BO3 in aluminoborosilicate glasses (which is the base composition of nuclear waste glasses) with 29Si, 27Al and 11B NMR, respectively. With the help of isotopic enrichment, 170 MAS NMR can reveal essential information such the mixing between the network formers (Al, B, Si) and the organization and role of the network modifiers (Na,Ca). With the increase of computation resources, NMR can now be combined efficiently with Molecular Dynamics Simulations (MD) with the help of DFT calculations (the GIPAW method [1,2]). From MD structural models, NMR properties of each atom can be computed and NMR spectra can be simulated for a direct comparison with the experiments. On the one hand, this approach offers an effective way of assessing quality of MD simulations, on the other hand, NMR fingerprints of specific environments can be identified and this can greatly improve the interpretation of the NMR data. Several recent applications of the so-called MD-GIPAW to glass structure elucidation can be found in Refs. [3-6]

In the context of chemical durability of nuclear waste glasses, methodologies based on selective oxygen-17 enrichment of the alteration layer that form on the glass surface under aqueous or atmospheric alteration has been developed.[7] Such an approach is complementary to the use of proton NMR (1H) to selectively probe the alteration layer, which structural evolution is not completely understood. The latter can be seen as a hydrated nano-porous aluminosilicate materials that can retain residual amount of boron and sodium (those elements are generally used as tracer of the alteration kinetics as being leachable). However, in order to help the interpretation of the NMR spectra, the application of the MD-GIPAW methodology is still limited because of the difficulty to generate structural models of hydrated nano-porous gels by molecular Dynamics. Several recent approaches have been recently proposed. Generally, one builds initial materials with a controlled porosity,[8] insert water molecules and then relax the obtained structures. Because of the proton, sophisticated potentials such as reactive

potentials (ReaxFF),[9, 10] or diffusive charge description of the proton (DCRP) are necessary.[11, 12]

In this work, we have generated several models of hydrous sodium and calcium aluminosilicate gels using the charge scaling procedure,[8, 13] where the Coulombic interactions are used to control the pore morphologies. Three potentials (two reactive ReaxFF, DCRP and a rigid ionic potential PMMCS, [14, 15]) were then used in a melt-quench approach to produce the final structural models of gels. The MD-GIPAW could then be applied to model the NMR spectra and compared with recent experiments on simplified nuclear glasses, using oxygen-17 NMR experiments (among others). Interpretation of 1H is also greatly improved with the help of such models, as will be discussed.

Nevertheless, MD-GIPAW calculations are severely limited in system size by the high-computational cost of the DFT computations. Typically systems up to 800 atoms can be considered with current HPC resources. A similar dilemma arises the choice of force-fields in MD simulations. Classical MD based on empirical models of interatomic interactions enable fast and scalable computations but at the expense of the accuracy permitted by ab initio (DFT) methods that are however computationally expensive. To solve this dilemma of accuracy versus efficiency, machine learning (ML) approaches have recently emerged as a powerful method for accelerating MD simulations and computing materials properties with an accuracy close to that of DFT methods.

This approach was pioneered by Behler and Parrinello [16, 17] (for recent reviews, see for example Refs [18, 19]) which made use of a deep neural network (NN) to represent the potential energy. The key of their approach was the introduction of so-called atomic descriptors that map the Cartesian coordinates of the atoms in the surroundings of a central atom into symmetry adapted functions used as inputs of the NN. As an alternative, Kernel Ridge Regression (or Gaussian Processes) can be used and lead to the Gaussian Approximation Potential (GAP) approach that is also very popular and found several applications to glasses. Those methods will be illustrated with application to the prediction of NMR properties [20] with the appealing perspectives of scaling up the MD-GIPAW methodology to models of several thousands of atoms or to include at affordable cost the impact of the finite temperature (mobility) in computed NMR spectra.

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Modeling approaches

Geochemical modeling of glass alteration

Pierre Frugier ¹,Maxime Delcroix ¹, Marie Coste ¹, Yves Minet ¹, Nicole Godon ¹ ¹ CEA, DES, ISEC, DPME, Univ Montpellier, Marcoule, F-30207 Bagnols sur Cèze, France pierre.frugier@cea.fr



Modeling the alteration of radioactive waste confinement glasses presents three main challenges:

i) Chemical complexity: The numerous major chemical elements in the glass, fluid, and environmental minerals interact with each other through fluid and gas.

ii) Temporal constraints: The goal is to predict confinement efficiency over several hundreds of thousands of years using data acquired over only a few months or years in the laboratory.

iii) Spatial constraints: This is demonstrated through key material transfers that occur both at the centimeter scale through diffusion/ convection within the porous medium consisting of the fractured glass block and at the nanometer scale within the passivating gel on the surface of each glass piece.

To address the chemical complexity issue (i), thermodynamic databases like Thermochimie (Giffaut et al. (2014) that describe chemical reactions between elements can be used. Reactive transport codes can be applied to both laboratory experiments and waste packages in geological disposal, demonstrating the ability to use the same calculation tool for long-term predictions validated on laboratory experiments (ii). To address the spatial issue (iii), the GRAAL model can be used (Frugier et al. 2018), which allows for the implicit implementation of the passivation phenomenon in a reactive transport code that already contains the differential equations of diffusive-convective transport (Steefel et al. 2015). The GRAAL model can be run using the HYTEC reactive transport code (Van der Lee et al. 2003), as well as other similar codes: CRUNCH and PHREEQC.

Geochemical modeling occupies a central position in the multi-scale modeling of glass alteration. Probabilistic atomistic models allow the exploration of mechanisms at small scales, such as those related to the formation of passivating gel (Jan et al. 2019), while models further simplify mechanisms to facilitate scale changes, highlight predominant mechanisms, or improve communication and decision-making (Frugier et al. 2023).

Research directions of the ISEC/DPME related to the geochemical modeling of glass alteration include: (i) enriching the GRAAL model with a generalized passivation law and a more detailed chemical model to describe gel solubility to improve the model's ability to take into account the chemical elements of the environment, resulting in the GRAAL2 model; (ii) conducting experiments on simple and complex glasses to parameterize and qualify the predictive capabilities of the GRAAL2 model; (iii) continuing experiments on the interaction between glass and environmental minerals to validate the model; and (iv) progressing with predictive simulations on complex systems at the glass block (Repina 2019) and studying scale change strategies.

The hypotheses and equations of the GRAAL2 model are presented before providing examples of its application to experimental data (Figure 1).

Although geochemical modeling still relies on experimental measurements that provide essential thermodynamic and kinetic constants, it also uses technological innovations such as those implemented in geochemical codes (e.g. modeling of biphasic media by HYTEC), statistical calculation tools (e.g. URANIE uncertainty and sensitivity platform (Gaudier 2010)), and modern programming environments to manipulate large amounts of data and compare them with experimental data. Therefore, inferring the uncertainties in modeling parameters from experimental data and evaluating how these uncertainties impact the model's predictions will aid in assessing the level of precision required to use geochemical models effectively.

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Friday, September 29th 2023

New glasses for energy transition and new advance on high temperature characterization

Chair: Ashutosh Goel (RUTGERS University) & Elise Regnier (CEA ISEC)



Program

New advance on glass development for energy transition

8:30-9:00	Sealing glasses for high temperature electrolysis	p.62
9:00-9:30	Self-healing glass sealant for SOFC/SOEC technology Francois Méar (Université Lille, France)	p.63
9:30h-10:00	Zirconia Crystallization - A View from Different Tools Irene Peterson (Corning US, US)	p.64
10:00-10:30	Coffee Break	
10:30-11:00	In-situ visual observations of glass melting processes José Marcial (PNNL, US)	p.6 5
11:00-11:30	Observation of glass synthesis by in-situ high temperature ESEM Renaud Podor (CEA ISEC, France)	p.66
11:30-12:00	Closing summer school (CEA/ISEC/DPME)	
12:00-13:00	Lunch box & End of the summer school	

Sealing glasses for high temperature electrolysis

Annabelle LAPLACE ¹, Rémi MOLES ¹, Jean-Gabriel BEGOS ¹, Charlène VALLAT ¹, Elise REGNIER ¹, Lilou SCHINTU ¹, Alexandre SIERK ¹, Karl VULLIEZ ²

¹ CEA, DES, ISEC, DPME, Univ. Montpellier, Laboratoire de Formulation et Caractérisation des Matériaux Minéraux, Marcoule, France

² Univ. Grenoble Alpes – CEA/LITEN, 38054, Grenoble, France

annabelle.laplace@cea.fr

In the context of renewable energies and the energy mix, dihydrogen production is particularly important. The production of dihydrogen by steam electrolysis at high temperature (700-900°C) using Solid Oxide Cell technology (SOC), has the advantage of producing dihydrogen with a better efficiency as compared to low temperature water electrolysis. In addition, this technology is able to operate in reversible mode, which can ensure electricity production in reverse mode.

The SOC high temperature electrolysis technology is based on a successive stack of single repeat units (SRU) made of cells and metallic interconnects ensuring both the collection of oxygen and hydrogen and the electronic conduction between the different SRUs. In such complex systems, ensuring the sealing of this ceramic/ metallic multilayer assembly fed with different gases is technically very challenging. The specifications that seals must meet are particularly demanding. In addition to sealing, the material must have mechanical, thermomechanical and chemical properties, as well as sufficient electrical resistivity (Figure 1) [1].

The high temperature characteristics of glass oxides and glass-ceramic seals make this type of material one of the few candidates for use as sealants. Furthermore, the geometries are complex and the lengths to be sealed are important. These numerous constraints lead to the use of glass powder suspended in organic solvents. This process allows for the installation of the seal by simply depositing the suspension on the areas to be sealed. A heat treatment is then applied to shape the material and ensure the sealing of the system. The use of a composition that tends to crystallize allows, a priori, improving the thermal and mechanical properties [2].

The usual thermal treatment consists in a first temperature rise followed by a crystallization stage. As the temperature rises, the organic solvents evaporate producing CO2 and gas present in the furnace atmosphere may be trapped during sintering, which causes porosity to appear. Early surface crystallization can also compete with the sintering phenomenon and prevent the maximum densification of the glass ceramic by freezing the structure. Crystallization stage will then occur.

The general objective of the study is to control the material microstructure (crystallization, porosity) in order optimize sealing properties. A detailed knowledge of the material microstructure is necessary in order to optimize the thermal treatment of the glass-ceramic formation and anticipate the possible microstructural evolution of the glass-ceramic seal operating in the stack. Two studies were conducted in parallel on a specific sealant.

The first one focuses on the evolution of the porosity (percentage, pores mean diameter and density) as a function of time and temperature. Swelling, coalescence and rising of the pores are observed at high temperature.

The second study focuses on the material crystallization: phases identification, evolution of crystals morphology as a function of temperature and crystalline surface fraction analysis as a function of time and temperature. These data allow to obtain the equilibrium crystalline fraction as a function of temperature for further modelling.

This paper will first recall the specifications that seals must meet in Solid Oxide Cells stacks. It will then present an overview of our methodology and preliminary results of our studies on the material microstructure.

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Self-healing glass sealant for SOFC/SOEC technology

François MEAR¹, Renaud PODOR ², Lionel MONTAGNE ¹ ¹ Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000, Lille, France. ² ICSM, Univ Montpellier, CNRS, ENSCM, CEA, Marcoule, France. francois.mear@univ-lille.ffr Glass and glass-ceramics have shown potential as sealants materiafter destructive actions of external environment or under influence

als for solid oxide fuel cell (SOFC) and solid oxide electrolysis oxide (SOEC). SOFCs are subjected to different thermal cycles, which required that the sealant materials have long term thermal stability and are able to repair the damages due to long term operation. It is reported these damages can be repaired by the flow of glass in the micro-cracks. However, sufficient flow of glass takes place at elevated temperature, which can deteriorate the other components of the SOFCs. Therefore, it is desired to repair the damages at lower temperature.

The self-healing in materials science is defined as the ability to recover the mechanical integrity and initial properties of a material after destructive actions of external environment or under influence of internal stresses. Self-healing has been claimed to enable an increase of the operating duration of glass seals for SOFC/SOEC. The self-repairing effect is obtained simply by heating the sealing glass above its softening temperature. This effect was shown to operate also in glass-ceramic sealants, provided that the amount of residual glass is enough to enable softening and healing.

In this lecture is presented our work both on non-autonomous and autonomous self-healing processing in glassy materials. It will be illustrating with some examples of self-healing involving glasses in the high-temperature sealing of SOFC/SOEC.

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Zirconia Crystallization - A View from Different Tools

Irene Peterson¹, Ying Shi¹, Yan Chen², Ke An², Joe Wright¹, Alex Priven³, Susan Halstead¹, Bryan Wheaton¹, Galan Moore ¹, J. Bussey ⁴, Minghui Zhang ⁵ ¹ Corning Research and Development Corporation, Corning, New York, USA

²Neutron Scattering Division, Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA

³ Corning International, Corning Korea, Seoul, Korea

⁴ Washington State University, Pullman, Washington, USA

⁵ GlobalFoundries, Albany, New York, USA

petersonim@corning.com

A wide variety of measurement techniques are available to study crystallization behavior, from a thermal, chemical and structural standpoint. In this study, crystallization of zirconia from a sodium magnesium aluminosilicate glass was evaluated using a variety of different techniques, including x-ray diffraction, neutron diffraction, scanning electron microscopy, differential scanning calorimetry, Raman spectroscopy and x-ray nano-computed tomography.

This talk will discuss the different kinds of insight on solubility, nucleation and growth, and microstructure provided from these measurements.

Neutron diffraction data were gathered using VULCAN, the Engineering Diffractometer at the Spallation Neutron Source at Oak Ridge National Laboratory.

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In-situ visual observations of glass melting processes

Jose Marcial¹, Miroslava Peterson ¹, Richard Pokorny ², Jaroslav Klouzek ², Steven Luksic ¹, Pavel Hrma³, Albert A Kruger⁴ ¹ Pacific Northwest National Laboratory, Richland, WA, 99352, USA ² University of Chemistry and Technology Prague, Technicka 5/1905, 166 28, Prague 6, Czech Republic ³ AttainX, Support Services Contractor to the Office of River Protection, U.S. Department of Energy, Richland, WA, USA ⁴ U.S. Department of Energy, Office of River Protection, Richland, WA, 99352, USA

Jose.Marcial@pnnl.gov

High-temperature visual observation of glass melting has been used for decades to understand processes that occur during glass production and to improve the overall process efficiency. Because of its simplicity, visual observations are broadly used to investigate bubble nucleation, fining, or refractory corrosion. For both commercial glassmaking and nuclear waste vitrification, visual observations provide a cost-effective method to study the influence of composition and makeup of commercial glass batches and waste glass melter feeds on the conversion process and the phenomena that influence the rate of glass production. We present an overview of experimental configurations used to elucidate aspects of



batch-to-glass conversion with specific focus on foaming. This includes the feed expansion test (FET), a method that provide insight into the modes of foam growth and collapse in heated glass batch samples, X-ray computed tomography (XCT), and evolved gas analysis (EGA). However, understanding dynamics of the foam layer at the bottom of the batch blanket requires other experimental methods to be employed. We are in the process of developing an observation setup in which foam at the interface between the batch and molten glass is directly viewed and monitored. Overview of results obtained thus far on commercial batches and nuclear waste melter feeds will be presented.

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Observation of glass synthesis by in-situ high temperature ESEM

Renaud PODOR¹, Joseph LAUTRU¹, Zineb NABYL², Richard POKORNY³, Sophie SCHULLER²

¹ ICSM, Univ Montpellier, CNRS, CEA, ENSCM, Marcoule, France

² CEA, DES, ISEC, Univ Montpellier, Marcoule, France

³ University of Chemistry and Technology Prague, Prague, Czechia

renaud.podor@cea.fr

The elaboration of glass from primary components is a complex process, the complete description of which requires the use of various characterization techniques. The use of global analysis techniques such as differential thermal analysis and/or thermogravimetric analysis (DTA-TGA) provides thermal information, but does not describe the chemical processes involved. A technique often used is to heat treat samples at different temperatures, soak them at room temperature and then identify the phases formed by XRD, SEM, etc. This technique is time consuming and tedious. It can lead to biases that are linked to the sample quenching (crystallization of molten phases at high temperature, amorphous phases that are not identified by XRD, for example) or to the choice of the quenching temperatures (some rapid transformations or those taking place in a narrow temperature range may not be identified). To overcome these limitations, it may be necessary to implement in-situ characterization techniques, where the analysis is carried out during the heat treatment. In-situ high temperature Environmental Scanning Electron Microscopy, ESEM, possibly coupled with EDS analysis, is a technique that is particularly interesting for identifying the chemical reactions and various transformations taking place between the primary components and then between the different phases formed1. Two studies using this technique have recently been carried out to investigate high temperature chemical reactivity during glass elaboration. They will be used as examples to illustrate the contribution of this technique in this particular field of study.



The direct observation of the elaboration of a glass melt from simple compounds was conducted from room temperature to 1000°C2 (Fig. 1). This first step allows the determination of the main morphological transformations and the temperatures at which elemental distribution maps should be recorded. Coupling this information allows us to determine that the sequence of chemical reactions is as

follows: 1) dehydration and decarbonation of the RT compounds up to 500°C, 2) From 500°C to 550°C, beginning of the reaction of Nabearing compounds with silica (in particular), and increase of this reaction up to 567°C. Some compounds, such as sulfates or alumina, are not incorporated into the glass at this stage. 3) At 630°C, the compounds MgO, CaO, and partly Al2O3, are dissolved in the glass melt. The solid sulfates float to the surface of the glass bath. 4) At 647°C, the composition of the glass melt is homogeneous and the sulfates form lakes on the surface of the silicate melt. These steps clearly illustrate the phase separation processes described in the literature (arrow in Fig. 1). 5) When the heating is prolonged to 1000°C, the volatilization of sulfates is observed, as well as the (unexpected) precipitation of phases that float on the surface of the glass bath ((Ca, Mg)2SiO4, ZrO2, iron and zinc oxides).

A second series of experiments was carried out to study a new way of vitrifying nuclear wastes which consists of introducing the waste-containing liquid directly into the molten glass, called liquid feeding3. The aim of the study is to identify the reactivity of a glass with chosen compounds (NaNO3, Ba(NO3)2, Mo compounds, REE compounds, etc) and to determine the ability of the glass to incorporate these elements during a heat treatment. The same approach as described above was applied. It was possible to qualify the chemical reactions between the compounds alone, and then their reaction with the glass and the molten glass (Fig. 2). When the different compounds are observed separately from the glass, they do not react chemically together and only physical processes (decomposition and / or melting) are clearly identified. When they are mixed with small pieces of glass (glass frit) prior to the experiment, the global behavior is more complex. Indeed, below the softening temperature of the glass, the compounds react as if there is no glass. At higher temperature, the formation of Na2O yields to the fast reaction with glass. The melting of glass is observed is at temperature lower than 500°C. When temperature reaches 1000°C, crystals containing REE elements and molybdates remain present at the glass melt surface. REE silicates and CaMoO4 crystals are formed during the heat treatment and then not dissolve due to the lower temperature than the nominal glass synthesis (1100°C, 1200°C)

In order to complement the data obtained during in-situ ESEM experiments as described above, complementary experiments can be performed. For example, it is often interesting to stop experiments at a given temperature. Then the analysis of the metallographic preparation of the sample makes it possible to qualify the equilibria between phases and to quantify the compositions of the compounds in equilibrium.

These two examples of in-situ HT-ESEM studies of glass elaboration clearly illustrate that this technique is well adapted to the identification of phase transformations and to the characterization of chemical reactions in complex systems. It allows the identification of reaction pathways and the monitoring of the behavior of particular elements during the heat treatment. The experimental strategy should be adapted precisely to the system to be studied according to the physicochemical properties of the precursors and glasses (liquidus temperature, viscosity). Thus in-situ HT-ESEM can be coupled with other characterization techniques to complete the description of chemical and/or physical reactivity in the system to be studied.

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Poster sessions abstracts



Monday, September 25th 2023

Poster session 1

List of the presented abstracts

PJ1-1	Innovative molten glass coating for the immobilization of radioactive waste ashes p Hélène NONNET (CEA/DES/ISEC/DPME, France)		
PJ1-2	New Glass Ceramics of CaO-SrO-Al2O3-La2O3-ZrO2 for Encapsulation of MA from Nuclear Wastes - Tetsuji Yano (Tokyo Institute of Technology, Japan)	p.75	
PJ1-3	Outline and results of the development of glass matrix for reducing the volume of high-level radioactive waste - <i>Kohei Owaku (Japan Nuclear Fuel Limited)</i>		
PJ1-4	Development of melt contact refractory for glass melter at JNFL Takeshi Tsukada (Japan Nuclear Fuel Limited)	p.77	
PJ1-5	In-can incineration and vitrification process: glass formulation and glass melt/liquid metal interactions - <i>Julia AGULLO (CEA/DES/ISEC/DPME, France)</i>	p.78	
PJ1-6	In-Can Incineration and Vitrification Processing of Plutonium contaminated mixed organic/metallic waste - Arnaud QUINTAS (CEA/DES/ISEC/DPME, France)	p.79	
PJ1-7	Vitrification of waste arising from dismantling operations using Dem&Melt technology Eléonore WELCOMME (CEA/DES/ISEC/DPME, France)	р.80	
PJ1-8	In-Can vitrification of spent mineral sorbents using DEM&MELT technology Caroline Michel (CEA/DES/ISEC/DPME, France)	p.81	
PJ1-9	Management of TENORM waste by GeoMelt® vitrification – Opportunities in France Pascal Evrard (Waste2Glass, Paris, France)	p.82	
PJ1-10	Spherical Briquets as A New Feeding Form of Glass Matrix for Vitrification of High-Level Radioactive Nuclear Waste from Reprocessing of High-Burnup and/or MOX spent fuels Tetsuji Yano (Tokyo Institute of Technology, Tokyo, Japan)	p.83	
PJ1-11	Advanced Fuel Cycle Programme (AFCP): Improved Low-Temperature Glass Formulations for Advanced Oxide Fuel - Alex Scrimshire (Materials and Engineering Research Institute, Sheffield,	p.84 UK)	
PJ1-12	Recent Progress in Decarbonisation Studies of Raw Materials and Glass Composition of Commercial Glass in the UK - Wei Deng (Materials and Engineering Research Institute, Sheffield,	p.85 UK)	
PJ1-13	Higher Activity Waste Thermal Treatment (HAWTT) programme Helen Steele (Sellafield Limited, UK)	p.86	
PJ1-14	Progress in development of glass formulas for vitrifying ZrO2- and MoO3-bearing high level liquid waste - Shengheng Tan (Department of Radiochemistry, China Institute of Atomic Energy)	p.87	



Innovative molten glass coating for the immobilization of radioactive waste ashes

Hélène NONNET¹, Virginie ANSAULT ¹ ¹ French Alternative Energies and Atomic Energy Commission (CEA), DES, ISEC, DPME, Univ. Montpellier, Marcoule - France helene.nonnet@cea.fr

The utilisation of molten glass coating for the safe, efficient densification of loose simulant radioactive ashes has been investigated. As part of a multinational project looking at pre-disposal thermal treatment of organic material (PREDIS), we have investigated several glass formulations to maximize the waste load incorporation inside the glassy matrix. Short term lixiviation tests have been performed to assess the performances of such matrix.

The ashes arise from processing organic materials surrogates (simulating materials contaminated by α -emitting actinides) within the IRIS process (Installation for Research on Incineration of Solids) in CEA Marcoule France. It is a multi-step process able to treat high chloride containing wastes via a combined pyrolysis and calcination process. Simulant inactive ashes arising from the IRIS process are comprised of a calcium-zinc aluminosilicate rich material, with a very

low level of residual carbon – making these ashes ideal candidates for HIP processing for example but also for glass incorporation. Molten glass coating trials were undertaken by mixing IRIS ashes into glass powder at low melting temperature, resulting in a 30 to 40 % waste loading. Post-processing characterisation revealed the formation of a polycrystalline material. These trials have demonstrated the suitability of molten glass process towards the processing of such ash materials, resulting in a solidified product. Though forming a solid product, substantial porosity remains within the final product, creating potential for wasteform improvements. Further wasteform optimisation is ongoing to investigate the impact of the glass composition, along with studies into the long-term aqueous durability of these materials.

PJ1-1

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New Glass Ceramics of CaO-SrO-Al2O3-La2O3-ZrO2 for Encapsulation of MA from Nuclear Wastes

Tetsuji Yano ¹, Yushin Kinoshita ¹, Kenta Kuroda ¹, Tetsuo Kishi¹, Daiki Atarashi ² ¹ Tokyo Institute of Technology, Tokyo, Japan ² Shimane University, Shimane, Japan tetsuji@ceram.titech.ac.jp

Minor actinoids from the reprocessing of MOX spent fuels are expected to be greatly increased compared with the amount from the present spent fuels of UO2. Their high-decay heat prevents high loading to the glass waste form and so they should be separated from other waste elements and encapsulated for immobilization and disposal, because glass matrices for this application have a limit against the temperature increase due to decay heat by "glass transition temperature" at maximum. On the other hand, glass ceramics do not have this kind of limitation if the constituent crystalline phases have a high melting point and thermal stability. For future reprocessing and disposal after MOX fuel utilization, we need to prepare suitable materials which have high capability and ability to encapsulate MA for geological periods of time. Separation of this kind of nuclear wastes and encapsulation would promise the reduction of space for geological disposal.

Recently, our group has developed a new glass forming system, RO-Al2O3-La2O3-ZrO2, by an In-Flight Melting technique, and also found that this system has good potential to form glass ceramics suitable for the encapsulation of MA; consisting of crystalline phases with very high melting point, very small residual glass phase, very low porosity, high mechanical properties etc.

In-Flight Melting experiment using oxy-hydrogen combustion flame was performed for calcined oxide mixtures of RO-Al2O3-La2O3-ZrO2, (R=Ca and Sr) as starting materials. Introduced oxide powders were heated in the combustion flame and melted to form liquid droplets in flight. After departing from the combustion flame, the droplets were cooled rapidly in air and collected. Figure 1 shows a photograph of the prepared glass particles from the CaO-SrO-Al2O3-La2O3-ZrO2 system. High transparency and spherical shape indicate the formation of a melt and quenching in air. From thermal analyses, the obtained glasses were found to have glass transition temperatures in the range 750-800 oC; these are "glasses".

Crucible melting has also been conducted using a Radio-Frequency (RF) Induction heating system and metal crucible on the same calcined oxide mixture as in the In-Flight melting experiment. Availability of crucible melting is very important to confirm the potential of practical development at large scale. At present, small scale melting of about 4.5 g glass has been conducted. However, even after 10 min melting, formation of a melt in the crucible, and no corrosion of the metal crucible were confirmed, and pore-free glass ceramics were formed, as shown in Figure 2. Powder X-ray diffraction measurements showed the main crystalline phases of perovskite LaAlO3 (melting point=2100 oC) and alkaline earth oxide containing ZrO2-based crystals (melting point >2325 oC) without glass/amorphous phase. MA would be incorporated in LaAlO3 by replacing La. The microstructure is shown in Figure 3. Micrometersize crystal growth with fine "vein-of-leaf" structure was found in all samples. Vicker's indentation test revealed Hv=9-10 GPa and KIC>3 MP/m1/2, corresponding to Cordierite (Mg2Al3(AlSi5O18)) or alumina (Al2O3). These high mechanical properties were due to the components and microstructure after crystallization from the melt. Thermal and mechanical stabilities and resistance of these glass ceramics are the factors to be given to the matrix for MA encapsulation. In the presentation, more details of functionalities and nature of these glass ceramics are shown.

This work was carried out using the grant of research program of Chubu Electric Power Inc., Japan, 2021-2022.



Figure 1. Photograph of the In-Flight melted glass particles of CaO-SrO-Al₂O₃-La₂O₃-ZrO₂ system.



Figure 2. Photograph of the glass ceramics taken from the metal crucible. Melting was conducted using RF induction heating system. Surface curvature showed the formation of melt on heating.



Figure 3. SEM image of the polished cross section of prepared glass ceramics. White vein-of-leaf structure is consisting from perovskite LaAlO₃ crystal, and other are consisting of ZrO₂ based crystalline phases.

Read online: https://www.sumglass.fr/abstract/ new-glass-ceramics-of-cao-sro-al2o3-la2o3-zro2-for-encapsulation-of-ma-from-nuclear-wastes/

Outline and results of the development of glass matrix for reducing the volume of high-level radioactive waste

Kohei Owaku¹, Ryo Souma¹, Yoshiyuki Miura¹, Takeshi Tsukada¹, Norio Kanehira¹, Toru Sugawara ², Sohei Sukenaga³, Hiroyuki Shibata ³, Tetsuji Yano⁴, Noritaka Saito⁵, Kunihiko Nakashima⁵

¹ Japan Nuclear Fuel Limited

² Akita University

³ Tohoku University

⁴ Tokyo Institute of Technology

⁵ Kyushu University

kouhei.oowaku@jnfl.co.jp

In Japan, the burnup of nuclear fuel is being promoted to improve the operating rate of nuclear power plants and reduce fuel costs. In addition, the use of MOX fuel is expected to increase due to the promotion of the nuclear fuel cycle. Therefore, it is expected that reprocessing of high burnup fuel and MOX fuel will be carried out in the future. When reprocessing fuels with properties different from those of current nuclear fuels, the composition of High-level radioactive Liquid Waste (HLW) generated in the reprocessing process changes, and further technological development including treatment and disposal methods is required. Therefore, from 2019, in the project commissioned by Ministry of Economy, Trade and Industry «vitrification technology for waste volume reduction», we are developing vitrification technology that can stably vitrify HLW generated by reprocessing of high burnup fuel and MOX fuel. In this project, we are studying scenarios related to nuclear power generation, developing glass materials, and operating control methods for glass melters. In this presentation, we will report on the progress of research on the development of glass materials by 2022.

In the vitrification of radioactive waste in Japan, the generation of a low-viscosity fluid mainly composed of molybdenum called the yellow phase (YP) is an issue. In HLW generated by reprocessing of high burnup fuel and MOX fuel, a glass material for processing high burnup fuel and MOX fuel without generating YP is required.

In this project, we aim to process high burnup fuel and MOX fuel without generating YP by two methods of changing the composition and shape of the glass material. Borosilicate glass is used in vitrification in Japan. In changing the composition of the glass material, glass with a different ratio of network-former (NWF) and network-modifier (NWM) is produced, and YP inhibitory properties and chemical durability are evaluated. We are also investigating a method of adding rare earth element oxides and the like to borosilicate glass to improve YP inhibitory properties.

Glass beads are used in vitrification in Japan and are mixed with HLW in a melter. In order to improve the reactivity with waste liquid when changing the shape of glass materials, we are studying materials such as glass fiber cartridges and briquettes, which are formed from fibers and powdered glass.

Until 2022, we mainly examined glass materials for vitrifying HLW generated by reprocessing of high burnup fuel. As a result of the

examination, a candidate composition that can achieve the target waste-loading without generating YP by changing the composition of the glass material was obtained. The properties such as chemical durability, viscosity, electrical conductivity were evaluated. Also, the effects of changing the glass shape(glass fiber cartridge and/or briquette) on generating YP by vertical gradient furnace tests. This work was carried out as a part of the basic research programs of vitrification technology for waste volume reduction[JPJ010599] supported by the Ministry of Economy, Trade and Industry, Japan.

Table.1 Evaluated items for glass matrix

Category	Items			
	Waste loadings			
	Homogeneity			
	Melting temperature			
	Density			
Manufacturing	Glass transition temperature			
	Viscosity			
	Electrical conductivity			
	Electrode corrosion			
	Refractory corrosion			
	Short term chemical durability			
Disposal	Long term chemical durability			
	Thermal stability			

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Development of melt contact refractory for glass melter at JNFL

Yuki Ota¹, Katsuyuki Higashino¹, Akira Sasahara¹, Kiyoshi Anzai¹, Takeshi Tsukada¹, Yoshin Morigaki ², Yasufumi Usui ², Ryosuke Ito ², Masatoshi Murata ² ¹JAPAN NUCLEAR FUEL LIMITED, 4-108, Okitsuke, Obuchi, Rokkasho-mura, Kamikita-gun, Aomori-ken 039-3212, Japan

²IHI Corporation, 1, Shin-nakahara-cho, Isogo-ku, Yokohama 235-8501, Japan takeshi.tsukada@jnfl.co.jp

Waste solutions generated from reprocessing of nuclear spent fuel are nitric acid solutions containing high-level radioactive waste. The waste solution is melted together with glass in the melter. After cooling, consolidated radioactive waste with glass will then be disposed in deep geological layers.

Since the glass melt containing waste components is highly corrosive to the melter, inner refractories in contact with the glass melt require high corrosion resistance. The melt contacted refractory must also have high electric resistivity so that current does not leak when the glass is heated by Joule heating.

Our current melter adopts a ready-made refractory as the melt contact refractory with high corrosion resistance and high electrical resistivity. The glass melter will be renewed regularly because of deterioration or damage of the melt contact refractory. Because it is necessary to procure melt contact refractories stably for a long time, the development of new melt contact refractories are being promoted. A Cr2O3 type sintered refractory is studied to make it a product that can be manufactured in Japan.

In the glass melter of the reprocessing plant, the nitric acid solution containing high level active waste is mixed with the glass melt. Therefore, replacement or repair of the melt contact refractories are virtually impossible after the operation of the melter. The melt contact refractory for the glass melter requires more variable functions and higher performance compared with the refractory used in general industry. It is difficult economically and time-wise to evaluate the required function and performance repeatedly by mock-up tests using same size refractory of an actual melter. In addition, qualitative and quantitative viewpoints for adopting new glass melt contact refractories have not been defined. In our development, the same performance of the refractory adopted in existing melters is used as benchmark criteria for the new refractory.

In the development, manufacturing conditions of refractory (raw material, forming and baking conditions) are researched systematically and exhaustively at lab scale at first. Next, the manufacturing conditions were determined from the viewpoint of the corrosion resistance and the electrical resistivity, which are the required functions. Corrosion is the phenomena of chemical and physical reactions at the interface between the refractory and glass melt and the electrical resistivity is a macroscopic physical property unique to the composition and construction of the refractory. Therefore, it can be considered that the dependence of corrosion resistance and electrical resistivity on the test scale is small. In the next step, the size of the candidate refractory manufactured under the selected manufacturing conditions is increased. The larger refractory is placed in the test melter and actual scale evaluation proceeds in the environment of the actual glass melter. The required performances unique to melt contact refractory (such as spalling and corrosion resistance under the electrical current in the glass melt) are estimated continuously by lab scale tests. We then determine the test items conducted by the lab scale by comparing the results obtained at lab scale and the actual scale samples.

Based on the results obtained from the lab-scale tests that can acquire detailed and multifaceted analytical information, we will develop reasonable and accountable glass melt contacted refractories. We will proceed with cross-scale studies on a lab-scale and an actual scale and these studies should advance to application development in the future

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In-Can Incineration and Vitrification Process: glass formulation and glass melt/liquid metal interactions

Julia Agullo¹, Annabelle Laplace¹, Damien Perret¹, Isabelle Giboire ¹ Arnaud Quintas ¹, Patrice Charvin ¹, Stéphane Lemonnier ¹ ¹ CEA, DES, ISEC, DPME, Univ Montpellier, Marcoule, France

julia.agullo@cea.fr

The PIVIC project was dedicated for the management of solid technological waste, mainly made up of metals, organic matter (plastics), and silica-based fibber bags. The project aims at developing a sequential single process that thermally treat this technological waste and then condition in metallic containers the resulting Intermediate-Level Long-Lived radioactive waste.

During the high temperature conditioning step ($\approx 1400^{\circ}$ C), the liquid metal phase strongly interacts with the molten glass: redox reactions, crystallization and dissolution mechanisms occur which has an impact on both glass melt viscosity, glass composition and final microstructure. The process environment is highly reducing. Furthermore, due to the coexistence of both metal and glass liquid phases, aluminum from the metal phase can be oxidized, leading to an increase of glass alumina content. Lastly, in the configuration where the waste is introduced in silica-based fibber bags, the silica content of the glass phase will increase, which has to be taken into

account when evaluating candidates for glass formulation. It is important to remember that silica, alumina and alkaline contents play a key role on the glass melt viscosity.

In order to reach good process reliability and to master the final conditioning material, such reactions have to be controlled along with a good knowledge of both phases behavior and glass melt viscosity. Furthermore actinides surrogates localization is also required.

This R&D collaborative project was conducted with Orano, CEA and Andra, and supported by the French government program "Programme d'Investissements d'Avenir".

This poster presents the impact of metal-glass composition, temperature and actinides surrogates on the viscosity of glass melt and on final conditioning matrix.

Read online: https://www.sumglass.fr/abstract/in-can-incineration-and-vitrification-process-glass-formulation-and-glass-melt-liquid-metal-interactions/

In-Can Incineration and Vitrification Processing of Plutonium contaminated mixed organic/metallic waste.

Arnaud QUINTAS¹, Patrice CHARVIN¹, Stephane LEMONNIER¹, Magaly TRIBET¹, Hélène PABLO², Sylvain PELLETIER², Benjamin FRASCA³

¹ French Alternative Energies and Atomic Energy Commission (CEA), DES, ISEC, DPME, Univ. Montpellier, Marcoule - France

² Orano Cycle, Le Prisme, 125 Avenue de Paris, 92320 Châtillon, France

³ Andra, 1-7 rue Jean-Monnet, 92298 Chatenay-Malabry Cedex, France

arnaud.quintas@cea.fr

Nuclear fuel cycle industry generates a wide variety of wastes some of which are composed of variable mixtures of organic, metallic and mineral materials. These wastes, contaminated with transuranic elements, mainly plutonium and americium, need a specific conditioning solution for deep geological disposal.

A thermal treatment process has extensively been studied these last years through the PIVIC project (Process for Incineration and Vitrification In Can). In this process, the waste first undergoes an incineration step to achieve destruction of the organic fraction, followed by the melt of the mineral residues as well as the metallic materials. The two steps PIVIC core process is performed in an integrated reactor taking advantage of combination of advanced technological components such as oxygen plasma torch and in can low frequency direct induction to achieve the highest level of process compactness. The PCM (plutonium contaminated material) waste is transferred from its original drum to an appropriate feeding basket without any preprocessing (grinding for instance) nor sorting operation. The process output is composed of a dense multiphasic glass/ metal package which allows volume reduction and immobilization of the radionuclides in an inert matrix.

Following the commissioning of an inactive prototype of the PIVIC process in 2018 at the CEA R&D vitrification facility in Marcoule site, an R&D program has been carried out to provide proof of concept. This R&D collaborative project, conducted with Orano, CEA and Andra, was supported by the French government program "Programme d'Investissements d'Avenir".

This poster intends to describe the features of the PIVIC process, and to present the scientific and technical issues as well as the main results and achievements obtained after 4 year of tests and developments.

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Vitrification of waste arising from dismantling operations using DEM&MELT technology

Aliénor VERNAY¹, Eléonore WELCOMME¹, Caroline MICHEL¹, Jean-François HOLLEBECQUE¹, Hélène NONNET¹, Isabelle BARDEZ-GIBOIRE¹, Maxime FOURNIER¹, Yann PAPIN¹, Damien PERRET¹, Nicolas BISBROUCK¹, Milène DELAUNAY¹, Claire GOBAUT², Régis DIDIERLAURENT² ¹ CEA, DES, ISEC, DPME, Univ. Montpellier, Marcoule, France ² Orano Recyclage, 125 avenue de Paris, 92320 Châtillon, France eleonore.welcomme@cea.fr

Dismantling operations of end-of-life nuclear facilities produces, or will produce, various new waste, mostly of lower activity than fission products, among which significant volumes of ILW-LL – long lived intermediate level activity waste, which will need to be managed. The nature of the waste is very wide-ranged, compared to the waste usually vitrified, in terms of chemical composition and physical form (solid deposits, sludge or liquid solution), depending on their origin and according to the mode of recovery or storage of this waste during dismantling and decommissioning operations.

Among them, sludges/slurries represent a significant part of the produced waste. Their chemical composition and their humidity level, which can be variable, make their conditioning a challenge. One way to manage this waste is the vitrification process. This process has the advantage of stabilizing the waste in an inert mineral matrix, and of reducing the volume of waste to be stored, thanks to the high waste incorporation capacity of glass. In order to significantly increase the waste loading, a crystallized matrix or a composite matrix can be considered.

The In-Can vitrification tool DEM&MELT, developed by the consortium CEA (The Alternative Energies and Atomic Energy Commission), Orano and ECM Technologies is flexible enough to accommodate a varied waste stream and particularly adapted to sludges/slurries from dismantling operations. For this purpose, it is important to develop a vitrification adjuvant with optimized composition, in a suitable form in accordance with feeding system options. Examples on inactive surrogates slurries from Fukushima Effluent Treatment* and on a sulphate-rich-sludge will be described in this poster. If the first example has been investigated from the Laboratory to Pilot scale; for the second one, the temperature should be lower than usual ones used for glass elaboration, due to the composition of the waste, involving the use of low-viscosity frits. In this case, only lab scale route has been explored up to date.

Thanks to a panel of characterization methods such as differential thermal analysis (DTA), thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), chemical analysis and viscosity measurements, precursors and wasteforms have been analysed, in terms of microstructure, durability, wastefrit reactivity and some adjuvants have been selected as promising precursors. Thanks to these results, the formulation of the different adjuvants will be optimized and tested on different sludges. The pilot scale extrapolation and the sustainability of the wasteform over time will then be explored.

This work was carried out as part of the PROVIDENCE project, this project has been funded by the French government in the framework of "France 2030".

DEM&MELT is a partnership between Orano, CEA, ECM technologies. It has been supported by the French government program "Programme d'Investissements d'Avenir".

*Fukushima Effluent Treatment Waste refers to the secondary wastes generated from the decontamination systems for contaminated water in Fukushima Daiichi Nuclear Power Station.

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In-Can vitrification of spent mineral sorbents using DEM&MELT technology

Caroline Michel¹, Jean-François Hollebecque ¹, Yann Papin ¹, Aliénor Vernay ¹, Regis Didierlaurent ² ¹ CEA, ISEC, DES, DPME, Univ. Montpellier, Marcoule, France ² Orano Recyclage, Prisme, 125 avenue de Paris, 92320 Châtillon, France caroline.michel@cea.fr

The numerous constraints associated with the management of highly active nuclear waste lead to the consideration of thermal treatment solutions given that these offer multiple advantages. Thermal treatments such as vitrification processes enable significant volume reduction, chemical waste stabilization and efficient radioelements containment in a glassy or glass-ceramic matrix. Moreover, vitrification processes have proven their adaptability to intermediate and high-level waste and can be flexible enough to accommodate a varied waste stream composition. In this context, Orano, CEA and ECM Technology, with the support of Andra through the French governmental program "Programme d'Investissement d'Avenir" have developed a new full scale In-Can vitrification tool, called DEM&MELT. The DEM&MELT process is an innovative and compact process that can be deployed in the existing premises or nearby. This process benefits from wide experience, coming from more than 40 years of operation at Marcoule first and then at La Hague plant with 6 high level waste vitrification lines currently operating. It has been designed to match the requirements and constraints of waste streams arising from remediation or decommissioning and dismantling operations; it is an easy-to-run process, equipped with a multiple resistive zone furnace and an off gas system designed to obtain high decontamination factors, which is

crucial when it comes to the last step of a plant life. It benefits from a modular design, adaptable to nuclear operator needs and its operation takes into account the compositional uncertainties linked to such types of waste. The process allows a significant volume reduction in addition to safe radionuclide containment with moderate investment and operating costs. It can deal with a wide range of nuclear waste, ranging from intermediate to high-level waste, with different compositions and forms such as sludge, liquid or solid, including for the latter, one of the most common dismantling wastes: mineral sorbents, used for the radiological decontamination of effluents, such as zeolites or silicotitanates. This waste must be conditioned in a safe and durable manner and its powdery nature eliminated. This paper presents, through an up-scaling methodology, going from laboratory-scale tests up to full-scale pilot tests, the most significant results obtained, performed for mineral sorbent conditioning. The results are presented, with an emphasis on the process parameters such as temperature, waste loading and glass throughput. A first viscosity domain in which the DEM&MELT process can be applied, is approached. The wasteform properties and the radionuclide volatility are also presented. Perspectives on the evolution of the prototype are discussed.

Read online: https://www.sumglass.fr/abstract/in-can-vitrification-of-spent-mineral-sorbents-using-demmelt-technology/

Management of TENORM waste by GeoMelt® vitrification – Opportunities in France

Pascal Evrard ¹, François Dumortier ¹ ¹ Waste2Glass, Paris, France pascal.evrard@Waste2Glass.com

Waste2Glass is a company created and owned by Cyclife EDF and Veolia Nuclear Solutions. It is dedicated to the development of the GeoMelt[®] vitrification technology in Europe.

Technologically Enhanced Naturally Occuring Radioactive Material waste issues from several human industrial activities based on mining including, for example, Zircon and Rare Earth production. Due to the industrial process, the NORM present in the ore are commonly concentrated and more dispersible, resulting in hazard potential for humans and the environment. In addition, these wastes usually contain high concentrations of chemicals such as chlorides or nitrates. Therefore, TENORM are classified as nuclear hazardous waste.

TENORM contain very long lasting radionuclides Thorium and Uranium. During decay, these nuclides produce Radium that itself generates Radon Gas. The radium proportion in the radionuclides varies significantly regarding the origin of the waste and has a great influence on the nuclear hazard. Waiting for the radioactive decay is not an option for TENORM.

TENORM are common in large volumes in countries where the nuclear industry is developed, including France and the USA. In France, two main categories of TENORM waste are distinguished; the one with the higher content ratio of Radium is denominated "Radifère'. The volume of that category in France is estimated to be 50 000 cubic meters (65 000 cubic yards) by 2040, most of it already produced by 2022.

TENORM requires long-term storage management in drastically simpler and cheaper conditions compared to other long-lived waste, such as fuels. There is today no solution in France for the long-term storage of these wastes. The ANDRA, French disposal operator, plans to store it in a near surface disposal utility currently under development (FA-VL). This disposal is scheduled in a clay layer at 'Vendeuvre-Soulaines' location. The repository, dedicated to 'low activity-long life' waste would accept not only TENORM but also other wastes such as graphite and bitumen based mixes. Nevertheless, these categories are heterogeneous with radionuclides, activity and physico-chemical parameters different from one family to the other. In addition, the overall volume of the repository would not be large enough for the full amount of targeted waste. So, in the National Plan for management of radioactive waste 2022-2026, the French state asked the ANDRA to optimize the global strategy for the 'low activity-long life' wastes, identify as far as necessary new options for some wastes and study the filling of the 'Vendeuvre-soulaines' future repository.

Waste2Glass considers that the GeoMelt $^{\circ}$ vitrification process applied to TENORM is a good opportunity to contribute to this optimization because:

- It commonly results in a reduction of the volume of the waste. TENORM are stored in drums or stacks. Using the GeoMelt $^{\circ}$ 'In

Container 'Vitrification' option, allows an increase of the overall density even if vitrification agent has to be added. In addition, the resulting material is easier to handle.

• The associated radiological hazards are greatly reduced. The vitrification process transforms a dispersible and leachable waste into a dense and monolithic block. Thus, the radiation levels and contamination risks are reduced and controlled in normal and accidental conditions. The release of Radon gas is reduced because of the retention of the gas in the solid during it's lifetime.

• The chemical hazard is usually reduced. The thermal treatment can destroy or convert several toxic species and reduce the potential mobility of the nuclides in the clay layer.

• The physico-chemical retention properties of the glass-like structure are very long lasting and well adapted to the Radium activity (half-life 1602 years).

As a consequence the GeoMelt[®] vitrification process applied to TENORM can dramatically reduce the constraints applied to the repository design for these wastes and thus allow easier, safer, larger and cheaper long term storage of the TENORM waste. It could also improve the confidence of the public for the development of the repository. It could also divert some of the TENORM to other sites than 'Vendeuvre-Soulaines', typically landfill accepting Very Low Level Nuclear Wastes.

In 2021, Waste2Glass designed a project named 'Rad2Glass' to make a demonstration of this opportunity. The project started in March 2022 and will be completed at the end of 2023. It includes theoretical and experimental proofs of concept at bench-scale and engineering scales. The project is managed together with French TENORM owning companies interested in the results. The project is supported by the French state via the 'Banque Publique d'Investissement'.

The results obtained up to now with that project for the waste in simulated conditions are encouraging:

-A mass integration rate of waste in the glass material has been obtained at more than 50% and up to 80% for a priority waste.

-The accelerated ageing of the glass confirms a containment efficiency in accordance with the expected requests of the safety case of the repository, at least in the absence of concrete.

The work is today in progress in several other aspects:

-Radon Gas retention in the vitrified product measurement, -Design of the engineering pilot tests with waste simulants (500 kg

vitrified material), -Environmental and Economical performance assessments,

-Extension of the studies to other wastes streams,

Regarding the results, industrial facilities could start in the following years the vitrification of TENORM in France, in association with the waste owners.

Read online: https://www.sumglass.fr/abstract/management-of-tenorm-waste-by-geomelt-vitrificationopportunities-in-france/

Spherical Briquets as A New Feeding Form of Glass Matrix for Vitrification of High-Level Radioactive Nuclear Waste from Reprocessing of High-Burnup and/or MOX spent fuels

Tetsuji Yano¹, Mizuto Saito¹, Hiroyuki Kadono¹, Tetsuo Kishi¹, Ryo Souma², Kohei Owaku², Norio Kanehira²

¹ Tokyo Institute of Technology, Tokyo, Japan

² Japan Nuclear Fuel Limited, Aomori, Japan

tetsuji@ceram.titech.ac.jp

Strategic management of electric power supply has been one of the most important issues all over the world. The operation of nuclear power plant has been changed according to the demands from the society. In the advanced operations of nuclear power plants, the degree of burnup of UO2 based fuels has been and will be increased up to ~60GWd/t for the efficient usage and energy extraction of UO2 fuel. MOX fuel is also planned to be used to promote the plutonium thermal use (Pluthermal). New types of spent fuels will be produced and should be reprocessed in near future. For the encapsulation of high-level radioactive nuclear wastes (HLW) from these spent fuels, vitrification process should also be advanced, because these HLWs are estimated to contain the chemical elements like Mo, minor actinoids, noble metals etc, in higher concentration than those from the previously produced spent fuels. In this research, a new feeding form of glass matrix, Spherical Briquet (BQT), has been developed for the vitrification of HLW from spent fuels of high-burnup UO2 and/or MOX.

BQT feeding form consisting of borosilicate glass powder has been fabricated intending to have following functionalities; high strength to ensure stable transportation for feeding operation, and high reactivity with HLW solution to form slurry immediately (homogeneous mixture of glass powder and wastes). In this research, the preparation condition of BQTs and their chemical reactions examination with simulated HLW solution from high-burnup and MOX spent fuels including the melting test in small scale melter have been carried out to satisfy the required functionalities,

Glass powder was prepared from present borosilicate glass beads (Li2O-Na2O-CaO-ZnO-Al2O3-B2O3-SiO2), which will be conventionally used, by pulverizing followed by ball milling process. After dried once, appropriate amount of water and the selected inorganic binder were added and mixed well to form paste. A pair of hemispherical molds were used to mold paste into spherical shape. After drying at 85 oC in maximum, spherical BQTs were obtained as shown in Figure 1.

Mechanical strength was evaluated using uniaxial pressing (crushing test) by autograph, and crushing strength was determined from yield stress as a function of concentration of binder. Chemical reaction of BQT with simulated HLW solution has been done using dipping test at room temperature. Behaviors of soaking of HLW into BQT and collapsing of BQT were monitored and evaluated.

Figure 2 shows the strain-stress curve of BQT using 2.5% Borax (sodium tetraborate decahydrate) as an inorganic binder, and high crushing strength was obtained. Increasing with the concentration of binder, crushing strength of BQT increased as shown in Figure 3.

The appearance of BQT soaked in simulated HLW was shown in Figure 4. Collapse of BQT in a few minutes was clearly observed in case of Borax while no collapsing was observed in case of waster glass as binder although HLW solution soaked inside well.

Chemical reaction was checked by confocal Raman spectroscopy. Binder components were found to be concentrated around the BQT surface due to the transportation from inside with water during drying. Fortunately, condensing of binder component near surface is effective to increase crushing strength with the minimum addition. In case of Borax BQT, Raman signals assigned to BO4 tetrahedral units disappeared after the immersion of HNO3 solution. Extraction of Na2O from Borax by strong acid is considered to decrease strong binding function among glass powder in BQT. Borax binder satisfies the required functionalities, and BQT form is one of the alternative feeding forms to the present glass beads and increases effective contact of glass surface with HLW, which is expected to incorporate MoO3 component into glass melt earlier and faster to prevent formation of Yellow Phase.

In the presentation, the results of feeding experiments of BQT with simulated HLW solution (high-burnup and/or MOX) will be shown using the compact glass melter with the capacity of 0.3-0.5L.



This work was carried out as a part of the basic research programs of vitrification technology for waste volume reduction[JPJ010599] supported by the Ministry of Economy, Trade and Industry, Japan.

Read online: https://www.sumglass.fr/abstract/spherical-briquets-as-a-new-feeding-form-of-glass-matrix-for-vitrification-of-high-level-radioactive-nuclear-waste-from-reprocessing-of-high-burnup-and-or-mox-spent-fuels/

Advanced Fuel Cycle Programme (AFCP): Improved Low-Temperature Glass Formulations for Advanced Oxide Fuels

Alex Scrimshire ¹, Jessica C. Rigby ¹, James D. Eales ¹, Katrina L-H. Skerratt-Love ¹, Prince Rautiyal ¹, Joshua T. Radford ², Julian T. Spencer ³, Michael T. Harrison ³, Lisa Hollands ², Claire L. Corkhill ², Neil C. Hyatt ², Russell J. Hand ², and Paul A. Bingham ¹

¹ Materials and Engineering Research Institute, Sheffield Hallam University City Campus, Howard Street, Sheffield, S1 1WB, United Kingdom

² Department of Materials Science and Engineering, University of Sheffield, Sir Robert Hadfield Building, Mappin Street, Sheffield, S1 3JD, United Kingdom

³ National Nuclear Laboratory, Central Laboratory, Sellafield, Seascale, Cumbria, CA20 1PG, United Kingdom a.scrimshire@shu.ac.uk

With the UK nuclear sector transitioning towards advanced fuels and advanced fuel cycles, current glass compositions used for waste immobilisation will need revising to accommodate the new waste chemistries expected. The revised glass composition will probably require an increased glass transition temperature (Tg) due to the higher heat loading from the expected future wastes. Several glass matrices from established nuclear sectors across the globe were selected for suitability testing in this initial study. These included 2 UK glasses (MW and CaZn); a modified US glass (C-104-M), a US-Brazil glass (BaBAl), a Japanese glass (P0798), and a number of modified Indian glasses (NaBSi, SB-44, SB-44-M, WTR-62 and WTR-62-M). Preliminary analysis showed that 5 candidate glasses could feasibly incorporate 25 wt% non-active surrogate waste loading and still form a stable waste form using the current UK HLW vitrification technology in use at the Sellafield site. Wider glass properties, including Tg, chemical durability (PCT-B), and melter corrosivity, were all tested. All 5 candidate glasses, down-selected from those tested, showed promising initial results, with compositional adjustments recommended for each prior to further R&D.

The WTR-62-M composition, adapted from an Indian glass formulation, for immobilisation of AFCP wastes in the current melter technology, would require compositional modification to counter its few, but potentially important, limitations. Optimisation of the composition to increase Tg would likely counter some of its more desirable features such as fluidity and low processing temperature, and while it shows good chemical durability the precipitation of metals is a cause for concern when considering the species not included in this simplified waste stream. The modified Indian SB-44-M and WTR-62-M glass formulations highlighted a range of compositional options available in these families, and whilst some barriers must be overcome (such as melting behaviour), these families warrant further investigation.

Although not conclusive from this initial study, water-soluble phases present in the waste glass samples are detrimental to long term durability. Based on this criterion alone sample SB-44-M would be suitable for long term storage. However, 7-day PCT-B durability testing results have shown that the other glasses have superior chemical durabilities, and Mo release was higher from the SB-44-M glass than some other glasses. Given that the other glasses have higher chemical durability by 7-day PCT-B, perhaps including Ca or Ba in those base compositions to form insoluble crystal phases would provide value. The better-performing glasses overall contained divalent cations such as Ca, Zn, Ba and Pb, which appear to help prevent formation of water-soluble alkali molybdate phases. For this reason, further development of divalent cation-richer glass compositions, whilst also delivering an acceptable balance of melting behaviour, thermal properties, and chemical durability, is warranted. Many of the desired properties interfere, either constructively or destructively, for example suppressing water soluble phases and improving chemical durability are constructive, whilst increasing Tg while keeping a low melting temperature is challenging. For this reason, iterations of selected glass compositions would be necessary to optimise glass properties for the AFCP wastes and processing technology. Overall, with further development, glass formulations that maximise waste loading whilst meeting the criteria for preparing acceptable AFCP glass wasteforms using the current WVP/VTR AVM process used at Sellafield and NNL, may indeed be achievable, with CaZn, P0798, C-104-M, WTR-62-M and SB-44-M glasses all showing initial promise.

Read online: https://www.sumglass.fr/abstract/advanced-fuel-cycle-programme-afcp-improved-low-temperature-glass-formulations-for-advanced-oxide-fuels/

Recent Progress in Decarbonisation Studies of Raw Materials and Glass Composition of Commercial Glass in the UK

Wei Deng¹, Daniel J. Backhouse¹, Elliott Wakelin¹, Erhan Kilinc¹, Feroz Kabir Kazi¹, Ronak Janani¹, Chris Holcroft², Marlin Magallanes², Martyn Marshall², Caroline M. Jackson³ and Paul A. Bingham¹ ¹. Materials and Engineering Research Institute, Sheffield Hallam University, Sheffield S1 1WB, UK.

². Glass Technology Services Ltd, 9 Churchill Way, Chapeltown, Sheffield, S35 2PY, UK.

³. Department of Archaeology, University of Sheffield, Minalloy House, 10-16 Regent Street, Sheffield, S10 2TN, UK.

wei.deng@shu.ac.uk

Based on current UK decarbonization policies, a general outlook on potential routes for the glass industry to achieve net zero is discussed and the differentiation during decarbonization is specified. Alternative glass batch raw materials and glass composition reformulation are highlighted here as important enablers for the glass industry to reduce its energy consumption and CO2 emissions.

Biomass ash is considered a potential alternative raw material for low-carbon glass manufacture as it is rich in certain advantageous components, chiefly network modifiers without carbonate. A biomass ash that was generated within the UK was successfully introduced into container glass in lab-based research and underwent pilot-scale trials. Simple sieving processes were shown to effectively separate impurities according to particle size distribution. UV-Vis-near IR absorption spectra of representative green container glasses produced using this biomass ash confirmed that ~5 wt.% ash in representative glass batches had little impact on the colour and redox state of glasses.

Related ongoing research aims to investigate the compositions of commercial glasses currently present in the UK market. This study has involved sampling and analysing the compositions of over 30 commercial container and float glass samples from the UK market. These analyses reveal that commercial glasses of the same colour and function, from different manufacturing companies or sites exhibit different properties, with a difference in Log 2 viscosity (melting temperature) of over 20 oC in some cases. This study has identified significant energy-saving potential for some commercial glasses and provides further insight into the underlying reasons for differences in properties.

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Higher Activity Waste Thermal Treatment (HAWTT) programme

Helen Steele¹ ¹ Sellafield Limited, United Kingdom helen.steele@sellafielsites.com

Sellafield Limited (SL) are currently undertaking a programme of work centred on the Thermal Treatment of Higher Activity Waste (HAW). This programme of work is split into three principal workstreams, these being:

- Tranche 1: Plutonium Contaminated Material (PCM)
- Tranche 2: Pumpable Intermediate Level Waste (ILW)
- Tranche 3: Mixed Beta Gamma Waste (MBGW)

Tranche 1 is investigating Twin Electrode Plasma Furnace, to the existing technology. Tranche 1 uses a lost crucible methodology where the crucible becomes the product.

PJ1-13

Tranche 2 is investigating the potential application of continuously operated Joule Heated Ceramic Melter (JHCM). Tranche 2 feedstocks have different physical and chemical characteristics to the anticipated feedstocks for the existing technology.

The HAWTT research programmes are in their infancy. Initial findings and future research ambitions will be presented

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Progress in development of glass formulas for vitrifying ZrO2- and MoO3-bearing high level liquid waste

Shengheng Tan¹, Jiong Chang ¹, Jiateng Wang ¹, Cheng, He ¹, Hua Zhang ¹ ¹ Department of Radiochemistry, China Institute of Atomic Energy, 1 Sanqiang Road, Xinzhen, Fangshan, Beijing, China. tanshengheng@ciae.ac.cn

On the development of cold crucible induction melter (CCIM) technology for high level liquid waste (HLLW) vitrification in China, a full scale research prototype of CCIM has recently been established by China Institute of Atomic Energy. The major systems, including an induction melter, a rotary kiln and a simplified off-gas treatment system, have been successfully tested for a 240-hour continuous operation in September 2022. About 6 t glass wasteforms at a targeted HLLW loading of 20 wt% were produced at a production rate of 25 kg/h, equivalent to a ~90 L/h of HLLW treatment capacity. The processing arts of melter starting-up, HLLW calcining, calcine feeding, glass melting, melt stirring, periodic pouring and system restart have been validated during the test and the properties of the glass products are proven to have met the requirements for geological disposal. The glasses have shown excellent chemical durability and thermal stability; especially, the abundant elements in HLLW, such as Mo, Zr and Ln, are not prone to crystallize from glass melts during the heat treatment. Following the success of the test, a full scale engineering prototype of CCIM is under establishment and is scheduled for a longer-term (2000 h) continuous operation in 2023.

Read online: https://www.sumglass.fr/abstract/progress-in-development-of-glass-formulas-for-vitrifying-zro2-and-moo3-bearing-high-level-liquid-waste/



Tuesday, September 26th 2023

Poster session 2

List of the presented abstracts

PJ2-1	Effects of glass composition and High-Level radioactive Waste(HLW) contents on viscosity and electrical conductivity of the borosilicate glass melts Jaehoon Park (Department of Materials, Kyushu University, Japan)	p.90
PJ2-2	Effect of melt velocity and temperature on the refractory corrosion during waste glass melting <i>Petra Cincibusova (University of Chemistry and Technology Prague, Czechia)</i>	p.91
PJ2- 3	Modeling of liquid nuclear waste vitrification : focus on the chemical processes Zineb Nabyl (CEA, DES, ISEC, DPME, LDPV, Lab. of Vitrification Processes Development, Marcoule	p.92 , France)
PJ2-4	Effect of alumina source and feed reducing agents on the retention of rhenium during vitrification of nuclear waste - <i>Miroslava Vernerova (University of Chemistry and Technology Prag</i>	p.93 jue, CZ)
PJ2-5	Development of PGM detection method by glass melt flow image from HLW vitrification melter <i>Ken Shinohara (IHI Corporation, Japan)</i>	p.94
PJ2-6	Numerical simulation of the temperature and flow field near the bottom of cold crucible Min Qian (Shanghai Institute of Optics and Fine Mechanics (CAS), Shanghai, China)	p.95
PJ2-7	Numerical study of the fracture of vitroceramic materials under self-irradiation Gérald Feugueur (Université Paris-Saclay, CEA, France)	p.96
PJ2-8	Colloidal Forces in Silicate Melts and Glasses Luiz Pereira (Department of Earth and Environmental Sciences, Munich, Germany)	p.97
PJ2-9	Reactions of sodium nitrate in cold cap Kazuyoshi Uruga (Central Research Institute of Electric Power Industry, Japan)	p.98
PJ2-10	Study of the physicochemical properties of glassy oxides as positive electrode active materials of Li-ion batteries - <i>Alexi Cardoso (CEA, DES, ISEC, DPME, Marcoule, France)</i>	p.100
PJ2-11	CALPHAD optimization of SiO2-B2O3-Al2O3-ZnO-CaO-Na2O-Li2O-MoO3 system and their applications to high-level radioactive waste vitrification Toru Sugawara (Akita University, Graduate School of Engineering Science, Japan)	p.101
PJ2-12	The effect of iodine incorporation on the cation in borosilicate glasses Sami Soudani (Université de Nantes, Laboratoire de Planétologie et Géodynamique de Nantes (Ll	p.102 PG))
PJ2-1 3	Structural changes in borosilicate glasses as a function of Fe2O3 content: a multi-spectroscopic approach James D. Eales (Materials and Engineering Research Institute, Sheffiel, UK)	p.103
PJ2-14	Incorporation and structural investigations of dismantling nuclear waste in an alkali-rich borosilicate glass - Sophie Achigar (IRCP, CNRS. CEA, DES, ISEC, DPME, SEME, LFCM, France)	p .104
PJ2-1 5	Composition-structure-property relationship of phosphate glasses: a combination of experiments, simulations, and QSPR analysis Lu Deng (Shanghai Institute of Optics and Fine Mechanics (CAS), Shanghai, China)	p. 10 6
PJ2-16	Oxide Glass Cathode Materials for Sustainable and High-Energy Density Lithium-ion Batteries Taos Guyot (Univ Grenoble Alpes, CEA-Liten, CEA, DES, ISEC, DPME, Univ Montpellier, France)	p.107
PJ2-17	Simulations of multiphase flows with the Lattice Boltzmann method and the phase-field models	p.108

232-17 Simulations of multiphase flows with the Lattice Boltzmann method and the phase-field models**p.108** Capucine Méjanès (CEA Saclay, DES, Gif-sur-Yvette, France)

Effects of glass composition and High-Level radioactive Waste(HLW) contents on viscosity and electrical conductivity of the borosilicate glass melts

Jaehoon Park¹, Noritaka Saito¹, Kunihiko Nakashima¹, Ryo Souma², Kohei Owaku², Takeshi Tsukada², Norio Kanehira²

¹ Department of Materials, Kyushu University, 744, Motooka, Nishi-ku, Fukuoka, 819-0395 Japan.

² Japan Nuclear Fuel Limited., 4-91, Okizuke, Obuchi, Rokkasho village, Aomori, 039-3212, Japan. park.jaehoon.942@s.kyushu-u.ac.jp

In vitrification process of HLW in Japan, Joule heating method is adopted. In this method, the electrical conductivity of glass melts affects melting temperature and other properties such as viscosity. In addition, the high-temperature viscosity affects the convection in the furnace and the flow rate into the stainless canister. Therefore, it is important to obtain basic data on the high-temperature properties of melts for the advancement and optimization of the vitrification process. In this study, we investigated the effects of the glass composition and the HLW contents on the viscosity and electrical conductivity of SiO2-B2O3-Al2O3-Na2O-Li2O-CaO-ZnO.

The glass composition was classified by composition parameters K [SiO2/B2O3], K' [SiO2/(B2O3+Al2O3)], R'' [(Na2O+Li2O+CaO)/ (B2O3+Al2O3)]. The viscosity of glass melts was measured by rotating crucible viscometer from 1223K to 1673K. And the electrical conductivity of glass melts was measured by adapting four-probe method from 1273K to 1673K. Both measurements were performed at intervals of 50K at a cooling rate of 5K/min from the maximum temperature.

Fig.1 shows the temperature dependences of the logarithm of viscosity (logn) and electrical conductivity (log κ) of the SiO2-B2O3-Al2O3-Na2O-Li2O-CaO-ZnO glasses. In all samples, both of lognand log κ were found to show linear relationships with reciprocal temperature (1/T) and to follow the Arrhenius equation. Then, the viscosity of glass melts is increased with increasing K and K'. On the other hand, the viscosity of glass melts is decreased with increasing R''.



The electrical conductivity of glass melts is decreased with increasing K and K' and increased with decreasing with R". The results are explained in terms of cation-oxygen interactions of component oxides.

This work was carried out as a part of the basic research programs of vitrification technology for waste volume reduction[JPJ010599] supported by the Ministry of Economy, Trade and Industry, Japan.

Read online: https://www.sumglass.fr/abstract/effects-of-glass-composition-and-high-level-radioactivewastehlw-contents-on-viscosity-and-electrical-conductivity-of-the-borosilicate-glass-melts/

Effect of melt velocity and temperature on the refractory corrosion during waste glass melting

Petra Cincibusova¹, Miroslava Vernerova¹, Richard Pokorny¹, Jaroslav Klouzek¹, Tongan Jin², Alexander W. Abboud³, Donna P. Guillen³, Jake Amoroso⁴, Albert A. Kruger⁵

¹ University of Chemistry and Technology Prague, Technicka 5/1905, Prague 6, 166 28, Czechia

² Pacific Northwest National Laboratory, Richland, WA, 99354, USA

³ Idaho National Laboratory, 995 University Blvd., Idaho Falls, ID 83401, United States of America

⁴ Savannah River National Laboratory, Aiken, South Carolina, USA

⁵ U.S. Department of Energy, Office of River Protection, Richland, WA, 99354, U.S.A. cincibup@vscht.cz



The Hanford Site, situated in Washington State, houses 56 million gallons of radioactive waste historically stored in 177 underground tanks. To mitigate the risk posed by this hazardous material, the United States Department of Energy is finishing the construction of the Hanford Waste Treatment and Immobilization Plant (WTP). The WTP will utilize Joule-heated ceramic melters to vitrify the low-activity waste (LAW) and high-level waste (HLW) into borosilicate glass at a temperature of 1150°C. Ensuring the integrity of the melting vessel is a critical technical issue – its failure during vitrification can result in severe safety and financial consequences. Thus, such melting vessels require specific refractory liners to withstand high temperatures and corrosive environments for an extended period. The Monofrax K-3 refractory has been identified as the optimal refractory material to be used in the melters at the Hanford site. K-3 refractory is a ceramic material that consists of a combination of (Mg, Fe)O·(Al, Cr)2O3-based spinels, corundum-based solid solutions, such as (Al, Cr)2O3, and a small quantity of SiO2. Its corrosion resistance is attributed to the elevated Cr2O3 content (about 27 wt. %) that exhibits low solubility in borosilicate-based glass melts. The high-temperature and corrosive environments of the vitrification process impose both chemical and physical wear on the refractories. The dissolution of the refractory material and the destruction of intergranular bonding due to chemical interactions between the K-3 refractory and the melt lead to the material's degradation.

Additionally, erosion causes removal of the dispersed refractory grains.

In the past, a number of studies evaluated the K-3 corrosion as a function of glass composition, developing empirical property-composition models to predict the compositional dependence of K-3 refractory corrosion (neck loss) during the vitrification of LAW glasses. However, much less attention has been paid to the effects of melt velocity. Thus, in this contribution, we will report initial results obtained from the dynamic corrosion testing. During dynamic corrosion tests, the refractory samples are eccentrically fixed in the platinum crucible (height 10 cm, width 10 cm) filled with molten glass. The velocity of the melt flow around the refractory material sample is regulated by the speed of rotation of the crucible with the glass melt. A range of flow velocities was tested based on the velocities obtained by the CFD simulations of the whole waste glass melter. After completion of each test, the refractory plates (coupons) were removed from the glass, cooled, embedded in epoxy resin, and sectioned. The corrosion rate in the suspended part and in the flux line region (neck loss) was measured by an image analyzer. The measured corrosion rate was evaluated as a function of melt flow velocity and temperature, and will be used to provide data for the development of the corrosion model to be implemented in the CFD model of the whole waste glass melter.

Read online: https://www.sumglass.fr/abstract/effect-of-melt-velocity-and-temperature-on-the-refractorycorrosion-during-waste-glass-melting/

Modeling of liquid nuclear waste vitrification : focus on the chemical processes

Zineb Nabyl¹, Sophie Schuller², Renaud Podor³, Joseph Lautru³, Guilhem Quintard³, Carine Castano¹,

Alain Artico¹, Virginie Benavent¹, Milene Delaunay¹, Emilien Sauvage¹

¹ CEA/DES/ISEC/DPME/LDPV (Laboratory of Vitrification Processes Development) , Université de Montpellier, Marcoule, France.

² CEA/DES/ISEC/DPME, Université de Montpellier, Marcoule, France.

³ ICSM (Marcoule Institute in Separation Chemistry), UMR 5257 - CEA/CNRS/UM2/ENSCM, Bagnols-sur-Cèze, France.

zineb.nabyl@cea.fr

Vitrification process is a technology commonly used for the treatment and the immobilisation of high-level radioactive waste resulting from spent fuels. In France, the waste are conditioned in glass matrix which provide a stable and sustainable confinement. A nitric solution of the waste is first calcined and the residual calcine is then added to glass melt in a cold crucible by induction processes (solid feeding). Another way of waste vitrification could be to introduce the waste solution directly at the glass melt surface (liquid feeding) in order to avoid the calcination step. Simulation studies 1-3 have enabled to propose a 3D model of nuclear waste vitrification in cold crucible by solid feeding, taking into account the fluid mechanics, the induction heating, the thermal and the chemical aspects. However, no modeling of vitrification by liquid feeding has been proposed yet. Such modeling could bring new information on the evolution of the chemical processes and help to predict and optimise the waste vitrification by liquid feeding.

In this context, this study aims to bring new constrain to the 3D modeling on the thermal and chemical reactions occuring during vitrification process by liquid feeding. In situ experiments in temperature have been performed (ESEM and XRD) in order to study the microstructure and to characterise the phases. This first experimental approach has allowed to identify the steps of phase transformation in the liquid in interaction with glass frit (nitrate melting, nitrate decomposition, glass softening, melting and phase dissolution), from the ambiant temperature to 1200°C. Ex situ experiments in furnace have also been performed to characterise the evolution of glass composition. Element concentrations have been analysed for different temperature (from 800 to 1200°C) at different dwell time (2, 5, 30, 120 and 480 minutes). The evolution of concentrations allow to determine the liquid dissolution kinetics occuring during vitrification by liquid feeding. The results will pave the way to a global 3D model of liquid radioactive waste vitrification.

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Effect of alumina source and feed reducing agents on the retention of rhenium during vitrification of nuclear waste

Miroslava Vernerova^{* 1}, Petra Cincibusova ¹, Richard Pokorny ¹, Jaroslav Klouzek ¹, Pavel Hrma ², Albert Kruger ³ ¹ University of Chemistry and Technology Prague, Technicka 5/1905, 166 28 Prague 6, Czechia

² AttainX, Support Services Contractor to the Office of River Protection, U.S. Department of Energy, Richland, WA, USA

³ U.S. Department of Energy, Office of River Protection, Richland, WA 99354, U.S.A. arkosiom@vscht.cz

At the Hanford Site in Washington State, U.S., nearly 210,000 m3 of nuclear waste generated during 45 years of plutonium production is slated to be vitrified in the Hanford Tank Waste Treatment and Immobilization Plant (WTP). The current strategy is to separate the low-activity waste (LAW) fraction from the tank waste, mix it with glass-forming and -modifying additives, and charge it into electric melters at the WTP. A similar process will be followed for the high-level waste (HLW). Molten glass will be poured from the melters, which are operated at ~1150 °C, into stainless-steel canisters or containers where it will cool and solidify, immobilizing both the HLW and LAW fractions in the form of borosilicate glass, a stable waste form suitable for long-term disposal.

Technetium-99 (99Tc) is a long-lived (half-life = 211,100 years) fission product, abundant in Hanford waste, that is highly mobile in subsurface soils, creating challenges for the safe, long-term disposal of Hanford nuclear waste. In addition to these environmental challenges, the volatility of Tc creates a significant challenge during the waste vitrification itself. The volatilized Tc compounds have to be captured from the off-gases and be either recycled into the melter or stabilized in alternative waste forms, increasing the processing costs and the amount of waste created. As a result, a significant of Tc and its nonradioactive surrogate, rhenium (Re), whose volatility generally exhibits behavior analogous to that of Tc, regardless of the differences in their speciation.

The retention of Tc/Re during the melting of LAW feeds is strongly affected by their composition. Addition of reducing agents, such as sucrose, increase Tc/Re retention. Sulfate has an opposite effect: perrhenate/pertechnetate dissolves in the sparsely soluble sulfate phase that inhibits Re incorporation in the glass-forming melt and promotes its Re volatilization when segregated on the glass melt surface. However, effects of other feed components on the Tc/Re retention are still poorly understood.

Recently, we observed that the chemical form of alumina might affect Tc/Re retention – the Re retention in AP-107 LAW glass was lower than in a compositionally similar AN-105 LAW glass, the difference being that AP-107 LAW melter feed contained kyanite (Al2SiO5) whereas AN-105 LAW feed contained mostly gibbsite (Al(OH)3) with a low fraction of kyanite. To investigate this effect, we measured the Re retention in a series of AP-105 and AN-102 LAW melter feeds with different alumina sources – nominal feeds with kyanite, feeds in which 50 % of kyanite substituted with gibbsite, and feeds with kyanite fully replaced with gibbsite. All feeds were spiked with Re2O7 solution corresponding to 300 ppm Re in glass. Approximately 50 g of dry powder feed was heated in glazed porcelain crucibles at 10 K min–1 under air atmosphere from room temperature to 1150 °C. After quenching, the samples were ground and crushed to below 100 um grain size.

In both AP-105 and AN-102 feeds, the Re retention increased significantly when gibbsite replaced kyanite. On heating, Al(OH)3 produces amorphous alumina with a high specific surface area. We reason that adsorption of sulfate-perrhenate melt on amorphous alumina increased its contact area with the glass-forming phase and the high contact area then enhanced the rate of sulfate-per-rhenate dissolution in the glass-forming melt, reducing the rate of sulfate-perrhenate segregation and volatilization.

Because the differences in the chemical and/or mineralogical alumina sources also affect the feed-to-glass conversion process, we used the feed expansion test to visually observe the effect of the Al-source on high-temperature foaming. We observed that Al(OH)3 promotes foaming. This is because gibbsite is an early dissolving Al-sources, which increases the glass-forming melt viscosity at a lower temperature than kyanite, a late dissolving Al-source. This keeps the glass-forming melt viscosity low up to a high temperature. A high viscosity leads to extended foaming, a low viscosity leads to a faster foam collapse.



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Development of PGM detection method by glass melt flow image from HLW vitrification melter

Ken Shinohara ¹, Hiroshi Ikai ¹, Tatsuya Yamashita ¹, Yoshiki Hamamoto ¹, Iku Miyasaka ¹ Ryoya Koyama ², Shunji Honma ²

¹ IHI Corporation, 1, Shin-Nakahara-cho, Isogo-ku, Yokohama-shi, Kanagawa 235-8501, Japan.

² Saitama University, Shimo-Okubo 255, Sakura-ku, Saitama-shi, Saitama 338-8570, Japan.

miyasaka3772@ihi-g.com

High level waste is stabilized with Joule-heated vitrification melter in Japan. Platinum group metals (PGMs), which are Ru, Rh and Pd included in high level waste, form micrometer-sized dense particles in molten glass and increase viscosity and electric conductivity of glass. Distribution of PGM particles is one of the key factors in the operation of the vitrification melter, however, it is hard to measure PGM particle concentration directly because of radioactive environment. In this study, we present a conceptual system for PGM concentration estimation by non-contact monitoring of glass flow from outlet nozzle.



This system consists of two parts, which are glass viscosity estimation by glass flow profile and temperature measurement of glass flow by non-contact devices (Fig. 1 a). Measured temperature and estimated viscosity of glass are associated with PGM concentration by temperature-viscosity curves of molten glass (Fig. 1 b).

For this purpose, we carried out two examinations. One is numerical experiences of glass flow from outlet nozzle of melter to correlate flow glass profiles with boundary conditions and glass properties. The other is application of radiation thermometer to glass flow to construct a non-contact measurement device. The results showed the feasibility of the proposed estimation method after integration of numerical experiences and accuracy improvement of radiation thermometer.

This work was carried out as a part of the basic research programs of vitrification technology for waste volume reduction[JPJ010599] supported by the Ministry of Economy, Trade and Industry, Japan.

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Figure 1. Conceptual sketch of PGM concentration estimation by glass flow image monitoring

Numerical simulation of the temperature and flow field near the bottom of cold crucible

Min Qian¹, Sijun Fan¹, Guangqing Pei¹

¹ Shanghai Institute of Optics and Fine Mechanics (CAS), Shanghai, China qianmin@siom.ac.cn

The cold crucible vitrification technique is one of the most promising techniques to vitrify the nuclear waste. However, the low temperature near the bottom of the crucible will increase the viscosity and thus decrease the fluidity of the glass melt, leading to a thick layer of cold glass and possibly blocking the discharge port. Optimizations of the crucible bottom structure and melting process are therefore essential. Numerical simulation has been widely used to provide the oretical guidance for cold crucible structure design and melting process research. In this work, we applied the electromagnetic induction models to investigate the heating efficiency of different bottom structures of cold crucibles. In addition, a magneto-thermo-fluid model was applied to study the temperature field and heat convection of glass melt under induction heating. Moreover, the flow field with and without agitation were also compared, using Frozen rotor

approach to accelerate the flow field calculation. The results show that increasing the slit width can enhance the magnetic field inside the crucible, reduce the electromagnetic, and increase the heating efficiency of the glass melt by about 6%. In addition, increasing the slit length can increase the magnetic induction intensity and heating efficiency of the glass near the discharge port. The maximum temperature near the bottom of the crucible is only 330°C due to the combination of the weak magnetic field and water cooling. The flow velocity of the glass melt near the bottom is low because of the low temperature. The velocity of fluid near the bottom increases by one order of magnitude to 0.1 m/s under mechanical agitation. Based on the numerical simulation results, the optimized structure design of the cold crucible bottom and agitator improve the temperature and flow velocity near the discharge port and the discharge efficiency.

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Numerical study of the fracture of vitroceramic materials under self-irradiation

Gérald FEUGUEUR¹, Lionel GÉLÉBART¹, Corrado MAURINI², Sandrine MIRO³

¹ Université Paris-Saclay, CEA, Service de Recherche en Matériaux et procédés Avancés, 91191, Gif/Yvette, France

² CNRS, Institut Jean Le Rond d'Alembert, Sorbonne Université, UMR 7190, 75005, Paris, France ³ CEA, DES, ISEC, DPME, Université de Montpellier, Marcoule, France

gerald.feugueur@cea.fr



The nuclear glasses currently used for the containment of fission products and minor actinides can include a mass loading rate of up to 18.5%. The glass-ceramic materials envisaged for this application would be an interesting alternative that would allow the volume of the package to be reduced by increasing this loading rate. However, during storage, the crystalline phase inclusions, rich in fission products, are subject to self-irradiation α causing swelling which may lead to cracking of the glass matrix. The objective of this thesis is to set up a powerful numerical simulation tool in order to evaluate the effect of the microstructure on the cracking of the material by relating to quantities of interest such as the time to first crack or the cracked surface.

FFT methods are particularly well suited to simulating the mechanical behaviour of heterogeneous materials. Indeed, compared to the use of «standard» Element-Finite codes, FFT codes are often much more efficient and very well adapted to a parallel implementation in distributed memory. Initially proposed for local, linear or non-linear behavioural models, the use of these methods is now being extended to the framework of non-local models, such as gradient damage [2]. In addition, for simulating cracking, phase field models [3], [4] are of increasing interest in the mechanics community. Thus, the implementation of the phase field model proposed by Bourdin et al [4] has recently been implemented in FFT codes [2] and in particular in the massively parallel code AMITEX_FFTP. Particular attention will be paid here to the use of composite voxels [5] in order to improve the quality of the numerical simulations. The analyses were first performed on small cells and then on larger cells with a random distribution of inclusions using generic tools developed at the CEA to generate the microstructures, voxelise them and identify the composite voxels.

Finally, a part will be devoted to the first FFT simulations of the cracking of heterogeneous materials with swelling inclusions. A semi-analytical approach based on a homogeneous damage field per phase has recently been implemented in AMITEX_FFTP in order to estimate the critical swelling and will be compared with the numerical and analytical approaches. The analyses presented will be performed on geometries of increasing complexity ranging from a single inclusion to several randomly distributed inclusions.

If the objectives of the thesis are met, it will give access to the simulation of the failure of glass-ceramic matrix with swelling inclusions. The approaches developed will be used to estimate quantities of interest such as the critical swelling or the cracked surface as a function of microstructural parameters.

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Colloidal Forces in Silicate Melts and Glasses

Luiz Pereira¹, Rodrigo L. Oréfice¹, Donald B. Dingwell¹

¹ Department of Earth and Environmental Sciences, Ludwig-Maximilians-University Munich, Munich, Germany ² Department of Metallurgical and Materials Engineering, Federal University of Minas Gerais, Belo Horizonte,

luiz.pereira@min.uni-muenchen.de

Colloid, from the Greek $\kappa \delta \lambda \alpha$ (glue), refers to a dispersed phase of a two-component system in which the elements of the dispersed phase are small enough (i.e.: < 10 μ m) to be affected by thermal forces. In colloidal science, the so-called DLVO theory (named after their establishers: Derjaguin, Landau, Verwey, Overbeek) is the most employed theory to explain particle union. It consists in a balance of attractive van der Waals (vdW) and repulsive electrostatic double layer (EDL) forces. These colloidal forces are present in a variety of domains, ranging from cheese production and blood coagulation to industrial paint manufacturing. Colloidal forces are of paramount importance in dictating how these mentioned processes take place.

Molten silicates containing suspended crystals are of extremely importance in natural and industrial scenarios. In the former, these complex silicates are one of the most important geomaterials in volcanology. In the latter one, silicates containing suspended crystals are extremely relevant in nuclear waste vitrification. In silicate glasses and melts, there has been observed evidences of colloidal forces through several properties and features. Here, we bring a variety of evidence, ranging from structural modifications to abnormal viscosity behaviour of specific family of crystals (platinum-group element) suspended in silicate melts. It is observed that for these specific silicate melts, viscosity could increase of up to ~5 orders of magnitude just due to crystal aggregation, process which in turn is controlled by colloidal forces.

In both volcanology and in glass science, the understanding of the existence of these colloidal forces, together with the effects, particularly on viscosity, will certainly allow us to better understand magma dynamics as well as to enhance our understanding on glass melting processes, such as nuclear waste vitrification processes.

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Brazil

Reactions of sodium nitrate in cold cap

Kazuyoshi Uruga¹, Yuma Sekiguchi¹, Tsuyoshi Usami¹ ¹ Central Research Institute of Electric Power Industry k-uruga@criepi.denken.or.jp



Fig.1. Reached fraction of Mo and Na at respective temperatures.



Fig.3. Thermogravimetry to measure the denitration completion temperature.

Fig.2. Time evolution of reached fraction of Mo



Fig.4. Denitration completion temperatures for various combinations of simulant



Fig.5. NO release from specimens heated at respective temperatures.

Fig.6. Comparison between NO release and total amounts of NO₃ detected by XRD.

Sodium nitrate (NaNO3) which is contained in high-level liquid waste (HLLW) is one of the key components for vitrification of the waste since it may react with Mo in cold cap to form water soluble secondary phase, so called, yellow phase (YP). The major component of YP is Na2MoO4. In this reason, understanding and control of the reactions of NaNO3 is important for production of qualified waste glass. Using a glass frit that have high specific surface area such as powder is a promising method to prevent the formation of yellow phase [1]. The reason of the effect of this prevention might be because the NaNO3 more preferably reacts with the frit than Mo, and the formation of Na2MoO4 is precluded. However, detail reactions among NaNO3-frit-Mo in the cold cap is not fully elucidated. In this study, reactions of NaNO3 in the cold cap were examined in terms of formation of water-soluble Mo at respective temperatures, denitration temperature of NaNO3 and reactions in NaNO3-frit binary system.

1. Formation of water-soluble Mo compounds in a temperature range of 400-650 $^\circ \text{C}$

Crucible scale batch experiments were performed to examine the fraction of Mo to become water-soluble compounds (=YP) in a temperature range of 400-650 °C. Two frits of powder (<64 μ m) and bead (mean diameter: 2 mm) were used to compare the fraction. Simulant of HLLW containing 25 elements including NaNO3 was dried out at 250 °C and mixed with the frit. The mixture was then heated at respective temperatures for 3 hours. The heated specimen was contacted with pure water to leach water-soluble Mo and Na.

When the powder frit was used, the fraction of Mo leached in water increased with increase in the temperature below 550° C and then decreased at the above. The fraction was only 4% at 650° C (Fig.1). On the other hand, the fraction continuously increased and reached to 86% at 650° C when the bead frit was used. This result clearly showed the advantage of using frit with high specific surface area. Leached fraction of Na decreased monotonically with increase

in temperature. This decrease indicates that NaNO3 reacted and dissolved into the frit to become insoluble state. Since the molar ratio of Na in the effluent was 10.4 times higher than that of Mo, Na that reacted with Mo was estimated to be 10% in maximum when the powder frit was used. The remaining approximately 90% of Na successfully reacted with frit. In the case of the bead frit that have smaller surface area, the relative proportion of NaNO3 reacting with Mo became increased.

Time evolution of the leached fraction of Mo was examined at 500 and 650 °C (Fig.2). Even for 650 °C, nearly half of the Mo once converted to water-soluble compound and then reconverted to insoluble one. Heating at higher temperature showed faster conversion and reconversion kinetics and smaller final fractions of water-soluble Mo. X-ray diffraction analysis (XRD) of the heated specimens revealed that the water-soluble compounds was Na2MoO4·2H2O in most cases.

Through these experiments, it is considered that NaNO3 reacts with glass or Mo depending on the contact probability during denitration. Mo which reacted with Na forms a water-soluble transient compound. However, at a later stage, Na in this Mo compound would dissolve in the frit while Mo would combine with Ca in the frit or rare earths in the simulant to reconvert into more stable insoluble compounds.

2. Denitration temperature of NaNO3 in multicomponent system In the cold cap, most of the components once form nitrates when the liquid waste is dried out, and then denitration of these nitrates proceeds with increasing temperature. Since NaNO3 is assumed to denitrate when reacting with frit or Mo, the reaction temperature could be estimated from the denitration temperature. NaNO3 is one of the components that is denitrated at the highest temperatures. Thus, we have examined the denitration completion temperature of frit powder-HLLW simulant mixture by thermogravimetry with varying waste components in the simulant. When the simulant included only Na and Mo, denitration was completed around 650 °C (Fig.3). On the other hand, in case of the simulant composed of 25 elements including Na, the denitration temperature decreased down to 561°C. Addition of elements individually to the simulant revealed that transition elements, especially Mn (tried as a surrogate of Tc), contributed the most for this decrease of the denitration

temperature (Fig.4). This result indicated that Mn had a catalytic function to facilitate the denitration of NaNO3. However, this acceleration of the denitration did not provide positive effect on YP suppression. The amount of water-soluble Mo rather increased at 500°C due to accelerated denitration and reaction between Mo and NaNO3. While at 600°C, there was no difference in the amount of water-soluble Mo because the denitration of NaNO3 promoted regardless of the addition of Mn.

3. Reactions in NaNO3-glass frit binary system

Detail reactions between NaNO3 and frit were examined under simplified NaNO3-frit binary system. Mixture of NaNO3 and frit powder was heated at 400, 500, 550 and 600°C for 3 hours, and then quenched and rinsed with water to remove unreacted NaNO3. From XRD, sodalite including NO3 in its lattice, Li2SiO3 and NaNO3 were detected in the specimens heated at 550°C or higher. The detected NaNO3 might have been encapsulated in the fused frit and remained in the specimen even after the rinsing.

Analysis of the released gases during heating of these specimens up to 1000°C revealed that NO was continuously released at temperatures below 660°C, and then spike-like release of NO was observed with foaming of the glass at temperatures above 660°C (Fig.5). The higher the fabrication temperature of the specimens, the more NO was released. The amount of NO released from the specimen was larger than the amounts of total nitrates detected by the XRD (Fig.6). These results might indicate that some NaNO3 once dissolved in the glass to become amorphous, and then denitrated and released NO with glass foaming at temperatures above 660°C.

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Study of the physicochemical properties of glassy oxides as positive electrode active materials of Li-ion batteries

Alexi Cardoso¹, Julia Agullo¹, Damien Perret¹, Sébastien Martinet², Loïc Simonin², Taos Guyot^{1,2} ¹ CEA, DES, ISEC, DPME, Univ Montpellier, Marcoule, France

² Université Grenoble Alpes, CEA-Liten, Grenoble, France alexi.cardoso@cea.fr

The world's high demand for electrical energy calls for the development of advanced storage technologies. Li-ion batteries are currently the best performers in terms of specific energy and power density. The principle of this technology is to exchange lithium ions between a negative and a positive electrode by means of a separator impregnated of electrolyte that ensures electronic insulation between the electrodes but allows ionic diffusion of the lithium ions from one electrode to the other (figure 1).



Schematic illustration of how a Li-ion battery works, With permission from Ref. [2]

Much attention has been paid to the chemical composition and atomic arrangement of the positive electrode to improve Li-Ion cell performances. Currently the active materials making up the positive electrode are mostly crystalline, and generally contain chemical elements that are critical from an environmental point of view, as well as in terms of abundance and cost (e.g. cobalt, lithium). The work presented here is part of ESTELLA project aimed at developing positive electrodes for Li-ion batteries based on breakthrough materials such as glassy oxides [1], while guaranteeing energy densities exceeding 300 Wh/kg at the Li-Ion cell level.

The aim is to identify the most relevant physicochemical properties of glass that lead to improved electrochemical performance (energy density, cycling).

To better understand involved processes, the glasses studied are composed of three oxide families : a network-forming element (Si, B, P), a transition metal (Mn, Fe, ...) and an alkali (Li, Na).

Our work shows that materials produced by the melt-quenching method are amorphous (XRD) and have specific microstructures (Raman Spectroscopy) depending on their chemical composition (SEM/EDX). Some parameters (eg. Tg, ...) which can provide information on the mechanical behavior of the glasses' atomic structure, was also determined (DTA). The comparison of these different glass properties with electrochemical characterizations of systems representative of Li-ion batteries will help guide our future development of positive electrode materials with the desired energy densities.

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CALPHAD optimization of SiO2-B2O3-Al2O3-ZnO-CaO-Na2O-Li2O-MoO3 system and their applications to high-level radioactive waste vitrification

Toru Sugawara¹, Toshiaki Ohira¹, Ryo Souma², Kohei Owaku², Norio Kanehira², Takeshi Tsukada² ¹ Akita University, Graduate School of Engineering Science, Japan

² Japan Nuclear Fuel Limited, Japan

toru@gipc.akita-u.ac.jp



Figure 1, Plot of MoO_3 solubility in the $SiO_2-B_2O_3-Al_2O_3-ZnO-CaO-Na_2O-Li_2O$ glass against log viscosity at 1200°C. The melt viscosity is calculated by the method of Brosh et al. (2012).

In vitrification of high-level radioactive waste, molybdenum (Mo) contained as a fission product tends to separate into a low-viscosity fluid called the yellow phase when the waste loading is high. The occurrence of yellow phase is attributed to phase separation of the Mo phase in the borosilicate melt. The yellow phase can incorporate various radioactive elements and is highly water-soluble. It is necessary to understand the behavior of molybdenum in borosilicate melts in order to develop glass matrix with sufficient chemical durability and high waste loading.

We carried out the phase equilibrium experiments for molybdenum-bearing borosilicate systems. The thermodynamic database for calculating phase separation between silicate liquid and molybdate liquid were developed by means of the CALculation of PHAse Diagram (CALPHAD) technique.

Phase equilibrium experiments were performed with 94 different chemical compositions in the system SiO2-B2O3-Al2O3-ZnO-CaO-Na2O-Li2O-MoO3. An excess amount (13-15mol%) of MoO3 was added to ensure phase separation. The reagent mixture was placed in a platinum crucible and held at 1200°C or 1000°C for 24 hours and then rapidly cooled with water. All experimental samples were phase-separated, yielding a silicate glass and an underlying molyb-denum-rich layer. Both phases were analyzed by EPMA, XRF and ICP-AES.

Figure 1 shows MoO3 solubility as a function of melt viscosity. We found that the MoO3 solubility increases with decreasing viscosity and Na2O activity at constant temperature. The experimental results of phase separation were analyzed by combining literature data on the phase equilibria of binary and ternary systems including MoO3 and a thermochemical data of oxides. The enthalpy of mixing was approximated by the Redlish-Kister polynomial. The database

 Table 1, Comparison between experimental and calculated

 compositions of phase-separaed two liquids at 1200°C (H1).

	Initial composition / mass %	Silicate	e liquid	Molybda	te liquid
		Exp.	Calc.	Exp.	Calc.
SiO ₂	39.82	39.07	38.87	0.75	0.94
B ₂ O ₃	9.46	9.22	8.90	0.23	0.56
Al ₂ O ₃	4.22	4.21	4.04	0.01	0.18
ZnO	2.60	2.46	2.30	0.14	0.30
CaO	4.45	3.59	2.80	0.86	1.65
Na ₂ O	13.71	9.49	10.24	4.22	3.47
Li ₂ O	3.08	2.35	1.95	0.73	1.13
MoO ₃	22.67	7.48	5.88	15.19	16.79
Total	100.00	77.87	74.98	22.13	25.02

in the system SiO2-B2O3-Al2O3-ZnO-CaO-Na2O-Li2O developed by GTT Technologies Inc. (GTOX) was used as the basic oxide database. Then, Na2MoO4, CaMoO4, Li2MoO4 and ZnMoO4 were set as associate species. In the CALPHAD analysis, the newly measured enthalpy and heat capacity for Na2MoO4 and the recently modified phase equilibria for SiO2-Na2O-MoO3 system were considered. The calculation was performed with thermochemical software, FactSage 8.2.

Table 1 indicates an example of comparison between the calculated and the experimental results of phase separation. The multicomponent phase separation between borosilicate and molybdate melts was well reproduced by calculation, including not only the major elements but also trace components such as SiO2 and B2O3 in the molybdate melt. The standard deviation between the experimental and calculated values of MoO3 content in the silicate melt is $\pm 2.3\%$ in the range of 3–22 wt%.

As an example application of thermodynamic database developed in this work, we will demonstrate the following:

(1) Calculation of compositional dependence of MoO3 solubility in borosilicate glass and search for glass matrix with high waste loading.

(2) Consideration of glass compositions that combines high MoO3 solubility and durability.

(3) Calculation of phase separation and crystallization of molybdenum phase in various temperature ranges in a glass melter.

This work was carried out as a part of the basic research programs of vitrification technology for waste volume reduction[JPJ010599] supported by the Ministry of Economy, Trade and Industry, Japan.

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The effect of iodine incorporation on the cation in borosilicate glasses

Sami Soudani ^{1,2}, Yann Morizet ¹, Michael Paris ²

 ¹ Université de Nantes, Nantes Atlantique Universités, Laboratoire de Planétologie et Géodynamique de Nantes (LPG), UMR CNRS 6112, 2 rue de la Houssinière, 44322 Nantes Cedex, France
 ² Université de Nantes, CNRS, Institut des Matériaux Jean Rouxel (IMN), 44000 Nantes, France sami.soudani@etu.univ-nantes.fr

We have recently developed an approach using high-pressure synthesis conditions able to incorporate large quantities of iodine in aluminoborosilicate glass with the aim to propose a durable solution for the immobilisation of iodine radioisotopes such as 129I. For aluminoborosilicate glasses, it has been demonstrated that the incorporation of iodine is strongly dependent on the presence of alkali or alkaline-earth cations to form iodide (I-) or iodate (IO3-) molecular groups that are charge compensated by surrounding Na+ or Ca2+ for the most important. It is well-accepted that alkali or alkaline-earth cations in glasses act as a network modification role or as a compensation role to network species. The first case occurs in glasses enriched with respect to alkaline (or earth-alkaline) cations whereas the second case applies when additional positives charges are required for negative charge compensation of network units. In the particular case of the aluminoborosilicate glasses, two species require charge compensation to fulfil their charge neutrality: BO4 and AlO4 tetrahedrons. It has already been observed that the compensation of the AlO4 units prevails on the BO4 units compensation. This latter one is able to convert into BO3 that does not require charge compensation. However, even at low alkali content (i.e. peraluminous compositions), the amount of BO4 present in the glass is non-zero, indicating that depending on the composition, the aluminium priority for charge compensation is somehow limited. In the present work, the effect of the applied pressure on the structure of the quenched glasses is fairly apprehended; conversely, the effect induced by the incorporation of iodine on the glass structure is poorly known. This latter aspect is crucial in order to formulate a specific matrix composition able to immobilize iodine radioisotopes. We have conducted a series of high-pressure experiments (1.0 GPa) on several aluminoborosilicate glasses in the SiO2-Al2O3-B2O3-Na2O system with 5 and 20 mol.% B2O3, 20 mol.% Na2O, 5 mol.%

Al2O3 and 55 and 75 mol.% SiO2. The starting glass was equilibrated at high-pressure with an iodine fluid phase using either I2 or I2O5 as a starting source. Those investigated compositions were also enriched with 170 isotope in order to study the distribution of oxygen species (Bridging, Non-Bridging and Free Oxygen) within the glass. The iodine content in the recovered glass reaches up to 2 mol.% and appears to be more soluble under oxidized conditions (i.e. I2O5) in agreement with previous works. The I-bearing glasses were characterized by 11B, 17O, 23Na and 27Al Solid-State NMR. For the investigated compositions, Al is mainly present as AlO4 units in agreement with previous works for Na-bearing glasses. Whereas the pressure conditions produce a noticeable effect on the glass structure by increasing the N4 value (BO4/BO4+BO3); the effect of iodine remains weak. In detail, the incorporation of iodine as I- slightly decreases the N4 from 0.66 to 0.63; whereas the incorporation of iodine as IO3- (I5+) does not seem to affect the N4 value.

The preliminary results obtained from 170 NMR do not reveal the presence of additional resonance that could be assigned or related to the dissolution of iodine. The most important change is observed on the 23Na diso of charge-compensating Na that appears to be affected by the iodine incorporation.

Our preliminary results show that the iodine dissolution into aluminoborosilicate glasses under high-pressure conditions does not dramatically influence the glass structure and the degree of polymerization appears to be roughly constant. Owing to the small change observed, the choice of a specific glass matrix for the immobilisation of iodine nuclear waste that is chemically durable seems not to be dictated by the iodine dissolution itself; at least for the strongly polymerized investigated glass compositions. Nevertheless additional work is required for investigating the iodine impact on more depolymerized glasses.

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Structural changes in borosilicate glasses as a function of Fe2O3 content: a multi-spectroscopic approach

James D. Eales ¹, Anthony M. T. Bell ¹, Derek A. Cutforth ², Albert A. Kruger ³, Paul A. Bingham ¹ ¹ Materials and Engineering Research Institute, Sheffield Hallam University, Sheffield, S1 1WB, United Kingdom

² Pacific Northwest National Laboratory, Richland, WA 99352, USA

³ Office of River Protection, Hanford Site, Richland, WA 99354, USA

To support the vitrification of high-Fe radioactive wastes stored at the Hanford Site, USA, this study has considered the structural impacts of iron oxide on the borosilicate glass network. Three series of borosilicate glass were designed and prepared, from simple sodium borosilicate glasses (SCFe series), to more complex borosilicate glasses (CCFe Series), to full Hanford analogue glasses (HAFe series). These three glass series were analysed using XRF and ICP-OES, with XRD to study any crystalline phases. The SCFe and CCFe samples were X-ray amorphous, while the two highest-iron HAFe samples showed an iron-rich spinel phase present in the glass. 57Fe Mössbauer and Fe K-edge XANES spectroscopies showed that the iron exists exclusively as Fe3+ in predominantly distorted tetrahedral structures ([4]Fe3+), with evidence for lower abundances of higher-coordinated [5 or 6]Fe3+. Raman, B K-edge, and B 1s, Si 2p XPS spectroscopies qualitatively demonstrated that Fe3+ preferentially integrates into the borosilicate network through the silicate sub-network in the simplest glasses, the SCFe series, whereas in more complex borosilicate glasses it preferentially integrates through the borate sub-network. The [4]B3+ fraction for the SCFe and CCFe glasses was shown to be ~0.45 and ~0.35 respectively, with minimal changes as a function of Fe content. This suggests that while the Fe ions may bond into the borate sub-network, the concentration of Fe ions has no effect on the born coordination and is therefore unlikely to be competing with the [4]B3+ groups for charge compensation, qualitatively supporting the presence of complex competition between multiple FeO4- / BO4- / AlO4- tetrahedral avoidance hierarchies.

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b8033567@hallam.shu.ac.uk

Incorporation and structural investigations of dismantling nuclear waste in an alkali-rich borosilicate glass

Sophie Achigar ^{1,2}, Daniel Caurant ¹, Elise Régnier ², Odile Majérus ¹, Thibault Charpentier ³ ¹ IRCP, Chimie ParisTech CNRS, Paris, Ile de France, France. ² CEA, DES, ISEC, DPME, SEME, LFCM, Univ Montpellier, Marcoule, France. ³ CEA CNRS Université Paris-Saclay, CEA, Gif-sur-Yvette, France. daniel.caurant@chimieparistech.psl.eu

Dismantling nuclear facilities leads to radioactive waste which may have highly variable compositions. In this study, we focused on waste coming from the dismantling operation of the spent fuel reprocessing facility UP1 stopped since 1997 (Marcoule, France), that mainly contains Zr, Si, P, Mo, Fe, Na and Al, and whose activity is essentially due to radioactive 137Cs (Cs2O representing about 1 wt% of the waste, but increased to 10 wt% in this study to facilitate Cs detection) [1]. For this waste, vitrification is studied using an incan vitrification furnace (heated metallic container) designed to be installed directly on the dismantling site [2].

In this work, we firstly studied the ability of an alkali-rich glass matrix belonging to the SiO2-B2O3-Al2O3-Fe2O3-Na2O-Li2O-CaO complex system (Na2O + Li2O ≈ 33 mol% (28.5 wt%)) to solubilize P205, MoO3, ZrO2 and Cs2O that are present in the waste, by melting a mixture of inactive raw materials at 1100°C. Due to their high field strength, P5+, Mo6+ and Zr4+ ions may exhibit a high tendency to separate from the silicate network in glass structure [1,3,4]. To determine the capacity of this matrix to accept a wide range of waste composition, several glass series were prepared by increasing the total amount of oxides representing the waste (10-30 wt% waste loading) and by varying the relative proportions of P2O5, MoO3 and ZrO2 within the waste from 0 to 50 wt% in order to take into account the potential variability of the waste composition (the case of P2O5 is shown in Fig. 1). Their incorporation in the melt was studied by analyzing the microstructure of quenched glasses by XRD and SEM-EDS, whereas the phase separation and crystallization tendencies during melt cooling in the metallic container were studied by analyzing the microstructure of samples cooled to room temperature at 1°C.min 1 (Fig. 1). It appeared that the investigated glass can accept a wide range of waste compositions without exhibiting heterogeneities. For all the compositions studied, the melt remained homogeneous with 10 wt% waste loading. Nevertheless, during slow cooling, P2O5 and MoO3 may lead to phase separation and crystallization of Na2MoO4, CsLiMoO4, NaCaPO4, NaLi2PO4, and Li3PO4 (Fig. 1). The increasing order of oxides solubility in the glass was found to be the following: MoO3 < P2O5 < ZrO2. A 10 wt% waste loading appears acceptable as almost all the glass compositions resulting from this loading value were homogeneous after slow cooling (only the one with 50 wt% MoO3 leads to molybdate phase separation followed by crystallization of Na2MoO4 and CsLiMoO4) [1]. During these studies, it appeared that ZrO2 never leads to phase separation or crystallization, possibly because of the existence of strong connections between Zr and Si through Zr-O-Si bonds [5]. To complete this work on the complex glass, XRD, Raman and multinuclear (31P, 29Si, 23Na, 27Al, 11B) MAS NMR studies have been performed on a simplified quenched or slowly cooled glass belonging to the SiO2-B2O3-Al2O3-Na2O-CaO system derived from the

complex composition by removing among other things iron oxide and by adding increasing P2O5 content (0 - 10 mol%), to investigate the crystallization of phosphate phases and the evolution of the structural environment of phosphorus. It appeared that above 2 mol% P2O5 phase separation followed by crystallization of F-Na3PO4 occurs, then followed by NaCaPO4 and even Na4P2O7 for the highest P2O5 contents. Moreover, according to 31P MAS NMR and Raman spectroscopies, it appeared that phosphorus is mainly present in glass structure as PO₄³- (orthophosphate) entities and probably also as $P_2O_7^4$ - (pyrophosphate) mobile entities non-connected to the silicate network and located in depolymerized regions of the glass structure (Fig. 3). The possible existence of P-O-Si, P-O-Al and P-O-B connections will be discussed. Due to the mobilization of Na+ and Ca2+ as charge compensators of phosphate entities in the glassy (Fig. 3) and crystalline phases, an increase of the polymerization of the glassy network as shown by 29Si MAS NMR associated with an increase of the glass transformation temperature from 454°C (0% P2O5) to 553°C (8% P2O5) were also put in evidence.

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Figure 1. Increase of the proportion of P_2O_5 in the waste (0, 21.6 and 50 wt%) considering 20 wt% waste loading in the glass, leading to 0, 4.33 and 10 wt% (0, 2.02 and 4.79 mol%) P_2O_5 in the glass. The microstructure (SEM images) and crystallization (XRD patterns) of phosphorus-rich crystalline phases in the melt (quenched sample) and in the glass (slowly cooled sample) with 50 wt% P_2O_5 in the waste



Figure 2. Evolution of the ${}^{31}P$ MAS NMR spectrum (11.72 T) of a simplified quenched glass containing increasing P₂O₅ amounts (SiO₂-B₂O₃-Na₂O-CaO-Al₂O₃ + x P₂O₅) derived from the complex nuclear glass.

Figure 3. Proposition of structural scheme showing the location of orthophosphate isolated (PO4³⁻) entities in the non-bridging oxygens (NBOs)and (Na+,Ca2+)-rich depolymerized regions of the glass structure (dimeric pyrophosphate (P2O74-) entities are probably also these depolymerized present in regions).

Composition-structure-property relationship of phosphate glasses: a combination of experiments, simulations, and QSPR analysis

Lu Deng ¹, Minzhi Ruan ², Jingping Yan ¹, Yajiao Zhang ¹, Feimei Wang ¹, Zhongdi Li ²

¹ Shanghai Institute of Optics and Fine Mechanics (CAS), Shanghai, China

² China Nuclear Power Engineering Co. Ltd., Beijing, China

denglu@siom.ac.cn



From left to right column, the structural descriptor E_{net} is correlated to the experimental density, hardness, glass transition temperature, and thermal expansion coefficient, respectively.

Phosphate glasses have various applications in fields including biomedical materials, optical components, and sealing materials. In addition, its ability, containing more rare-earth elements than the borosilicate glass, makes it become a potential candidate of the high-level nuclear waste virtification for those with high rare-earth content. Therefore, it is important to understand the composition-structure-property relationship of the phosphate glasses. In this paper, an architype of multi-component phosphate glasses, sodium aluminophosphate (SAP) glasses, has been investigated by using molecular dynamics (MD) simulations. In addition, experiments of Raman and synchrotron X-ray total scattering have been performed to characterize the glass structures and validate the simulation results. Moreover, the Quantitative Structure-Property Relationship (QSPR) analysis was performed to correlate the simulated glass structures with the experimentally measured properties, such as the density, Tg, CTE, and hardness. Results show that additional aluminum content will lead to a gradual replacement of the P-O-P linkages by the P-O-Al linkages, and it will also modify the long chains of the SAP glass into three-dimensional ring structures. The QSPR models show linear relationships between the structural descriptors from simulations and the measured properties; in addition, its ability to predict certain glass properties based on the simulated glass structures has also been validated.

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Oxide Glass Cathode Materials for Sustainable and High-Energy Density Lithium-ion Batteries

Taos Guyot^{1,2}, Julia Agullo², Damien Perret², Loïc Simonin¹, Sébastien Martinet¹ ¹ Université Grenoble Alpes, CEA-Liten, Grenoble, France ² CEA, DES, ISEC, DPME, Univ Montpellier, Marcoule, France denglu@siom.ac.cn

As energy concerns grow and the society needs more sustainable and renewable energy sources, the ability to effectively store and retrieve energy is paramount. Currently, rechargeable lithium-ion batteries (LIB) seem to be one of the best alternatives to reduce our dependency on fossil fuels. LIB are made of cathodes materials based on polycrystalline oxides or polyanion compounds[1]. However, some of them have their performance limited by their crystalline structure where other compounds suffer from irreversible phase changes against cycling[2]. To overcome these key shortcomings, implement glasses or glass-ceramics as cathode materials seems to be an interesting approach. Glasses have a structure composed of more free volume, which can accept a large amount of lithium[3] and easily accommodate structural changes upon lithium ions extraction/insertion[4]. Furthermore, glass production is scalable and commercially easier to implement than most of synthesis processes of conventional cathodes materials.

In this study, various types of oxide glasses have been investigated as promising cathode materials for sustainable and high energy density lithium batteries. The influence of the nature of the transition metal (Fe, Mn, ...) and the polyanion (PO4, BO3, SiO4) on the microstructural and electrical properties of the as-prepared glasses were examined. Electronic and ionic conductivities were measured by Electrochemical Impedance Spectroscopy (EIS). The electrochemical properties in terms of specific capacity, redox potentials vs Li+/Li, first cycle capacity loss, coulombic and energy efficiencies of these materials were investigated in coin-cell by Galvanostatic Cycling (GC). Finally, to elucidate the reaction mechanisms of the electrochemical processes involved in these materials, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) at room temperature were coupled and performed on the as-prepared glasses and on ex-situ (after cycling) materials at different electrochemical states of charge. This new study will bring significant elements to optimize both the glass composition and its elaboration conditions to obtain high performance cathode materials without critical materials.

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Simulations of multiphase flows with the Lattice Boltzmann method and the phase-field models

Capucine Méjanès ¹, Teo Boutin ¹, Pierre Kestener ², Alain Cartalade ¹ ¹ CEA Saclay, DES, Gif-sur-Yvette, France ² CEA Saclay, DRF, Gif-sur-Yvette, France denglu@siom.ac.cn

The Lattice Boltzmann Method is a powerful numerical tool for simulating fluid flows with or without phase change. This poster provides an introduction to the phase-field method and the Lattice Boltzmann Method, demonstrating how the partial differential equations of a coupled hydrodynamics and thermodynamics model can effectively be solved. A phase-field model, derived from a thermodynamic functional based on the grand-potential, is used to simulate the evolution of the phase interface. One of the key advantages of the grand-potential approach is the ability to reformulate the problem in terms of chemical potentials, which are equal in each phase at the thermodynamic equilibrium. Based on that theoretical framework, a showcase of the capabilities of the LBM_Saclay code is presented, ranging from classical 2D two-phase phenomena to more complex 3D three-phase simulations. The code is currently applied for simulating the phase separation of binary or ternary nuclear glasses and the maturation of gels (solid/liquid phase change), involving significant density or viscosity ratio. The simulations were performed on several supercomputers (Jean-Zay and Topaze) equiped with the most recents GPUs.

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Thursday, September 28th 2023

Poster session 3

List of the presented abstracts

PJ4-1	Self-healing of nuclear glass alteration gels under irradiation - Pierre de LAHARPE (Institut de Chimie Séparative de Marcoule (UMR 5257), Nanomaterials for Energy and Recycling), France	p .112
PJ4-2	Characterization of glass alteration layers to study the evolution of its morphology Sathya Narayanasamy (CEA, DES, ISEC, DPME, University of Montpellier, Marcoule, France)	p.113
PJ4-3	Effect of complex irradiation scenarios on the structure and properties of ISG and SON68 glass <i>M. Taron (CEA, DES/ISEC/DPME, ICSM, CEA, CNRS, ENSCM, Univ Montpellier, France)</i>	p.114
PJ4-4	Glass characterization with XPS and ToF-SIMS techniques Laurent DUPUY (SERMA TECHNOLOGIES, ECULLY, FRANCE)	p.115
PJ4-5	Impact of different irradiation scenarios on the long-term behavior of ISG glass Hélène Aréna (CEA, DES, ISEC, DE2D, Université de Montpellier, Marcoule, France)	p.116
PJ4-6	New insights into Monte Carlo simulation of borosilicate glass aqueous alteration <i>S. Tiwari (CEA Marcoule, France)</i>	p.117
PJ4-7	MoO3 solubility and chemical durability of simulated radioactive waste glass containing V2O5 Minako Nagata (Akita University, Akita, Japan)	p.118
PJ4-8	Predicting alteration layers volume for the glasses with various glass composition Ryuki Kayano (Faculty of Engineering, Dep. of Applied Chemistry and Biotechnology, Chiba, Japan	p.119 n)
PJ4-9	Monitoring of alpha-decay radiation damage in a 241Am-doped glass-ceramic material S. Miro (CEA, DES, ISEC, DE2D, Université de Montpellier, Marcoule 30207, France)	р .120
PJ4-10	Structure and Dynamics of Hydrous Silicate Gels by Molecular Dynamics Calculations Takuma Hatori (Graduate School of Engineering, Chiba University, Japan)	p.121
PJ4-11	Application of glass structural gene modeling in the simulation of chemical durability and liquidus temperature in HLW glass - Liyan Zhang (Shanghai Institute of Optics and Fine Mechani Chinese Academy of Sciences, Shanghai 201815, China)	p.122 cs,
PJ4-12	Influence of glass composition and morphology on its solubility in simulated physiological fluids (SPF) - Sarah Gandon (Saint Gobain Recherche Paris, CEA Marcoule, France)	p.123
PJ4-1 3	Effect of Gadolinium Oxide on Structure and Chemical Stability of Borosilicate Glass with Simulated Nuclear Power Plants HLLW Hua Zhang (Radioactive Chemistry Department, China Institute of Atomic Energy)	p.124
PJ4-14	Chemical durability of commercial silicate glasses and the impact of surface treatments Léa Brunswic (CEA, DES, ISEC, DPME, Université de Montpellier, Marcoule, France)	p.125

Self-healing of nuclear glass alteration gels under irradiation

Pierre de LAHARPE¹, Xavier DESCHANELS¹, Sylvain PEUGET², Hélène ARENA², Mélanie TARON^{2,3}, Jun LIN¹, Bertrand SIBOULET⁴, Jean-Marc DELAYE⁵

¹ Institut de Chimie Séparative de Marcoule (UMR 5257), Nanomaterials for Energy and Recycling *

² CEA, DES, ISEC, DPME, Univ Montpellier, Marcoule, Active Materials and Processes *

³ Institut de Chimie Séparative de Marcoule (UMR 5257), Study of Matter in Environmental Conditions *

⁴ Institut de Chimie Séparative de Marcoule (UMR 5257), Mesoscopic Modelling and Theoretical Chemistry *

⁵ CEA Marcoule – Study of Materials in Complex Environment *

(*) site de Marcoule, 30207 Bagnols sur Cèze Cedex, FRANCE

pierre.delaharpe@cea.fr

Disposal in deep geological layers is the main course of action envisaged in France for the management of high-level nuclear waste, the chemical immobilization of radionuclides being ensured by the use of borosilicate glass. Over time and as groundwater permeates through the waste package's protective barriers, the glass matrix is expected to undergo chemical alteration. Simplified borosilicate glass alteration in the presence of water and self-irradiation (α , β , γ) from radionuclides has been an object of research for several decades, and it was established that energy deposition via self-irradiation increases the alteration rate and formation of an altered layer [1], [2]. The observed morphology of the altered glass layer features a structure of pores up to a few nms in diameter [2], [3], the long-term role of which is still unclear [4]. The closure of such pores under certain conditions was observed as well [5], suggesting that competing processes may be at work. Concomitantly, electron and ion irradiation of mesoporous silica such as SBA-15 and MCM-41 was recently investigated, and the collapse of the pore structure was monitored using Small-Angle X-Ray Scattering (SAXS) [6], [7]. Here we propose a novel approach to the study of borosilicate glass alteration layers via the sol-gel synthesis of an appropriate mesoporous substitute, suitable for SAXS monitoring. Since the presence or absence of water is suspected to be a determining factor [5], an experimental setup is devised to provide a wet environment while irradiating the material.

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Characterization of glass alteration layers to study the evolution of its morphology

Sathya Narayanasamy ¹, Thibault Charpentier ², Sumit Tiwari ¹, Stéphane Gin ¹ ¹ CEA, DES, ISEC, DPME, University of Montpellier, Marcoule, F-30207 Bagnols sur Cèze, France ² Université Paris-Saclay, CEA, CNRS, NIMBE, 91191, Gif-sur-Yvette Cedex, France sathya.narayanasamy@cea.fr

In the context of chemical durability studies of nuclear waste glasses, glass alteration rates in water are usually described as initial glass alteration rate (r_{ρ}) and residual glass alteration rate (r_{ρ}) . The r_r is lower than r_o by up to several orders of magnitude depending on the glass composition and environmental conditions. The consensus is that the primary mechanisms responsible for this rate drop are a reduction in chemical affinity for Si dissolution due to solution saturation limits, and a passivation mechanism imposed by the formation of an alteration layer (gel). Open questions remain about the domination of one effect over the other, the exact mechanisms of gel passivation and their evolution over time. These unknowns make the development of mechanistic models and prediction of r_{r} over long term challenging. Therefore, in this study we aim to develop a deeper understanding of the process of maturation of the gel layer by studying the evolution of the structure of the gel layer, porosities, pore-size distributions, and diffusion of water and aqueous glass species. To do so, we study the glass powders altered for over 30 years with >80% gel layer using ¹⁷O isotope impregnation

followed by NMR and water sorption isotherms. We compare these results to those acquired on glass powders altered for only a few days or weeks. This gives information about the rigidity and the reorganization capacity of the gel layer network. Additionally, we also use short-term and long-term static glass-alteration experiments at pH_{90°C} 9 and 90°C on glass powders and monoliths of 5 different glass compositions. We characterize the altered monoliths using ¹⁰B ¹⁸O tracing experiments and ToF-SIMS to get information about the retention of boron in the gel layer and its diffusion coefficient, and Spectroscopic Ellipsometry to study the potential gradients of porosity. We characterize the altered glass powders using TGA and NMR to estimate the porosity and study the evolution of the gel layer structure respectively. Furthermore, TEM studies on the gel layer could give information about the pore-size distributions. Data analysis, interpretation and confrontation of these results with existing mechanistic models for the prediction of r_{r} should then enable us to fill the remaining gaps regarding the accountability for the evolution of the passivation effect of the gel layer.

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Effect of complex irradiation scenarios on the structure and properties of ISG and SON68 glass

M. Taron ^{1, 2}, H. Aréna ¹, C. Gillet ¹, F. Perrudin ¹, R. Podor², M. Tribet ¹, S. Miro ¹, S. Peuget ¹ ¹ CEA, DES, ISEC, DPME, Université de Montpellier, 30207 Marcoule, Bagnols-sur-Cèze, France ² Institut de Chimie Séparative de Marcoule, ICSM, CEA, CNRS, ENSCM, Univ Montpellier, Marcoule, France melanie.taron@cea.fr

The management option of fission products and minor actinides originating from fuel reprocessing from the French nuclear industry is vitrification of this high-level long-lived radioactive waste. The planned outlet is deep geological disposal of these radioactive glass packages with the objective of long-term radionuclides confinement, reducing and controlling their radiological impact on the environment. After several thousand years, and the corrosion of the steel overpack, the Callovo-Oxfordian groundwater will encounter the glass, causing it to deteriorate. It is therefore necessary to understand the alteration behavior of the glass and evaluate its alteration rate to assess the release and transport of radionuclides contained within it. The impact of self-irradiation of nuclear glass on its structure and properties must be determined to estimate its long-term chemical and physical durability. In the short term, the energy deposited in the glass, also called dose, is mainly due to beta decays and gamma transitions of fission products but in the long term, alpha decays become the main source of radiation from minor actinides. These different types of decay, however, continue to occur simultaneously, leading to a complex irradiation scenario. Given the difficulty associated with studies on radioactive materials, ion and electron irradiations are used to simulate the effect of irradiation damage caused by two types of interactions, nuclear or electronic, depending on the decay involved. In this work, the structural changes for different irradiation scenarios of a complex SON68 type glass as well as its equivalent simple glass ISG are studied. The effect of different couplings between nuclear and electronic interactions for different electronic stopping power are simulated by Au and He ions and electron irradiations. 2 MeV electron irradiations simulate the damage of beta and gamma radiations at saturation of effects. 7 MeV Au irradiations and 2 MeV He simulate the damage of the recoil nuclei of alpha decays and alpha particles respectively. Au irradiations induce mainly nuclear interactions with matter while the electron and He irradiations lead to electronic interactions, except at the end of the path for He, but correspond to different stopping powers (higher for He than for electrons). Sequential irradiations are performed to reproduce the coupling effect of these different interactions on the structure and properties of the glass. These modifications are determined by Raman, FTIR, NMR, optical interferometry, contact angle measurement and TEM observation.

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Glass characterization with XPS and ToF-SIMS techniques

Laurent DUPUY, Julien AMALRIC, Céline BRUNON SERMA TECHNOLOGIES, 64 chemin des Mouilles 69130 ECULLY, FRANCE l.dupuy@serma.com

At SERMA TECHNOLOGIES we provide analysis service for academics and industrial companies. Through examples we will demonstrate the interest of XPS and ToF-SIMS techniques to study glass alteration, glass treatments and glass defects.

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Impact of different irradiation scenarios on the longterm behavior of ISG glass

Célia Gillet ¹, Hélène Aréna ¹, Magaly Tribet ¹, Stéphanie Szenknect ², Sandrine Miro ¹, Sylvain Peuget ¹ ¹ CEA, DES, ISEC, DE2D, Université de Montpellier, Marcoule, France ² Institut de Chimie Séparative de Marcoule, ICSM, CEA, CNRS, ENSCM, Univ Montpellier, Marcoule, France helene.arena@cea.fr

In France, borosilicate glass, known as R7T7, is used to contain the long-lived high-level radioactive waste remaining after reprocessing of spent nuclear fuel. The objective of the R&D studies is to predict their long-term behavior to ensure the safety of the disposal solution: the physical and chemical stability of the glass on a geological time scale must therefore be demonstrated, which requires studying the response of the glass to the radiation emitted by the nuclear waste as well as its behavior when subjected to alteration by water. This work focuses on the leaching behavior of a chemically simplified borosilicate glass, chosen by the international community, called ISG (International Simple Glass). Pristine glass pellets were subjected to several external irradiation scenarios (electrons, Au ions, electrons followed by Au ions) in order to simulate the different irradiation sources of a real radioactive glass, inducing electronic and/or nuclear interactions. The irradiation dose values were chosen to induce significant changes in the structure and properties of the glass and they also correspond to the dose level expected in storage conditions when water will come in contact with the glass.

The effects of the irradiations on the structure and properties of the glass were studied by various techniques.

Pristine and irradiated glass pellets were then altered for several months in pure water at 90 °C and high surface-to-volume ratio (SA/V = 200 cm-1) to rapidly reach the residual alteration rate regime expected in long-term storage conditions. The thickness of the gel layer was measured by ToF-SIMS to calculate the glass alteration rate and TEM characterizations with cryogenic sample holder were performed to describe the nanostructure of the gel layer.

The results show that electron irradiation induces only small changes in the structure and properties of the glass, including its alteration behavior. However, irradiation with Au ions induces changes in the structure and properties of ISG glass, as well as an increase in the glass alteration rate. The results obtained for the sequentially irradiated glass (electrons followed by Au ions) are close to those obtained on the glass irradiated with Au ions only. This suggests that long-term glass leaching is sensitive to structural changes induced by nuclear damage, simulated here by external irradiation with Au ions.

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New insights into Monte Carlo simulation of borosilicate glass aqueous alteration

Sumit Tiwari¹, Jean-Marc Delaye¹, Stephane Gin¹, Paul Fossati², Andrey Kalinichev³

¹ CEA, DES, ISEC, DPME, SEME, LEMC, Univ Montpellier, Marcoule, France

² CEA Saclay, 91191 Gif-sur-Yvette, France

³ Laboratoire SUBATECH UMR6457- Institut Mines-Télécom Atlantique, CNRS/IN2P3, Université de Nantes, Nantes, France

sumit.tiwari@cea.fr

To elucidate the residual rate in the realm of glass alteration, the underlying mechanisms remain a subject of ongoing debate, as they potentially encompass multiple channels that collectively result in a decrease by several orders of magnitude of the initial alteration rate [1].

The Monte-Carlo (MC) method is an effective method for studying complex scientific problems. For studying the glass dissolution by the Monte-Carlo method, early attempts were made in the late 20th century by Aerstens and Van Iseghem followed by Devreux [2] and in the near past by Sebastian Kerisit and his coworkers [3]. The major limitations of the models developed was that it had no way to explain the residual rate and the evolution of gel maturation.

In my thesis, we investigate glass alteration using a new Monte-Carlo code described below to explore the role of the different elements. In parallel, classical force fields for molecular dynamics (MD) simulation are developed to simulate boron diffusion in water within a model alteration gel. Additionally, experiments are performed with glasses containing different Al2O3 quantities. The MD simulations and the experiments will help to determine the Monte Carlo parameters. At the end, we plan to obtain a better description of the role of the different elements on glass alteration in the so called residual rate regime.

This poster is dedicated to the Monte Carlo method. The algorithm has been developed by J.-M. Delaye and coworkers. It differs from the previous algorithm in the fact that the diffusion of water inside the solid is taken into account, using two intricated networks to represent the glass on one side, and the solution on the other side. The MC code is able to reproduce the formation of an alteration layer in glasses containing Si, B, Na and Al. Even if the current version of the code is quite slow, which imposes limitations on the number of calculations that can be executed, we have simulated the alteration of three distinct glass compositions each characterized by varying quantities of Al2O3. The Monte Carlo parameters have been fitted to reproduce at the best the experiments, in particular the quantity of Si and B released in solution. Our findings will demonstrate that two different types of passivating layers can form depending on the way Si is released in solution. When a large quantity of Si atoms is rapidly released in solution, it can lead to the formation of an external layer characterized by a notable enrichment of Si. Conversely, when the release of Si into the solution occurs in a more continuous manner, no layer enriched in Si is observed but the external part of the gel undergoes a progressive reticulation process. These two distinct mechanisms offers a plausible explanation for the alteration behavior change observed with an increase in Al2O3 content [4].

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MoO3 solubility and chemical durability of simulated radioactive waste glass containing V2O5.

Minako Nagata¹, Toru Sugawara¹, Toshiaki Ohira¹ ¹Akita University, Akita, Japan m8022936@s.akita-u.ac.jp

Table 1. Composition of glass for MoO ₃ solubility experiment (mol%).										
Sample	SiO ₂	B_2O_3	Al_2O_3	ZnO	CaO	Na_2O	Li ₂ O	V_2O_5	MoO_3	
19A2	39.8	15.4	2.4	1.8	5.3	16.0	6.2	0.0	13.0	
21E	38.2	14.8	2.3	1.7	5.3	16.0	6.2	2.4	13.0	
21E2	34.6	18.4	2.3	1.7	5.3	16.0	6.2	2.4	13.0	
Table 2. Rest	ults of gl	lass ana	lysis af	ter Mo	D3 solu	bility e	xperim	ent (mo	1%).	
Sample	τ	SiO ₂	B ₂ O ₃	Al_2O_3	ZnO	CaO	Na ₂ O	Li ₂ O	V ₂ O ₅	MoO ₃
19A2		53.5	11.8	3.2	2.3	5.3	13.7	5.9		4.3
21E	1200	50.3	9.8	3.1	2.2	4.9	13.4	8.7	2.1	5.6
21E2		45.7	12.3	3.1	2.2	5.3	14.5	6.1	2.3	8.6
19A2	1000	53.9	14.3	3.2	2.6	4.7	13.1	5.6		2.6
21E2	1000	48.5	15.7	3.2	2.3	4.4	13.7	5.6	2.1	4.5
Table 3. Composition of glass for chemical durability test (mol%).										
Sample	SiO ₂	B_2O_3	Al_2O_3	ZnO	CaO	Na ₂ O	Li ₂ O	V_2O_5	MoO ₃	Others
19A2	54.7	12.1	3.3	2.4	5.4	14.0	6.1	0.0	2.0	
21E	52.2	10.2	3.2	2.3	5.1	13.9	9.0	2.1	2.0	
21E2	49.0	13.2	3.3	2.3	5.7	15.5	6.5	2.5	2.0	
Bead	51.3	14.4	3.2	2.3	3.8	10.6	8.2	0.0	2.0	4.3

High-level radioactive waste generated in the reprocessing of spent fuel is melted together with glass beads and disposed of as vitrified product. The molybdenum (Mo) in the waste has a low solubility in borosilicate melt, so separation of Mo phase and borosilicate melt occurs during the melting. This Mo phase is called yellow phase. Because the yellow phase incorporates radioactive elements and is water soluble, it can significantly reduce the chemical durability of waste form. Various glass compositions have been studied to increase chemical durability and MoO3 solubility in glass. In this study, we investigated effect of V2O5 on the MoO3 solubility and chemical durability of the glass in the system SiO2-B2O3-Al2O3-ZnO-CaO-Na2O-Li2O.

For this work, three glasses (Table 1) were synthesized by melt quenching method. To ensure phase separation, an excess amount of MoO3 (13 mol%) was added to all samples. The 19A2 is made so that the composition of silicate glass after phase separation is close to that currently assumed to be used in Japan. The 21E and 21E2 are the composition of which V2O5 and V2O5+B2O3 are added to the 19A2, respectively. The mixed reagent was placed in a platinum crucible, held at 1200°C or 1000°C for 24 hours and then quenched by water. The collected samples were observed and analyzed by using EPMA, ICP-AES and XRF.

In all samples, borosilicate glass and MoO3-rich white precipitate formed by phase separation were observed. Table 2 shows the analytical results of the borosilicate glasses. At 1200°C, MoO3 solubility of 19A2 was 4.3 mol%, while 21E2 (adding V2O5 and B2O3) was



8.6% and 21E (adding V2O5) glass was 5.6%. MoO3 solubility was also increased in the V2O5 containing glass at 1000°C.

Chemical durability of glasses with the same composition as Table 2 and simulated waste glass with simulated waste components (Bead glass) were examined by MCC3 method. Then, 2mol% of MoO3 were added in all glasses (Table 3). To the leachate, 1 L of ultrapure water was adjusted to pH 9 (at room temperature) using KOH, and 0.235 g of glass powder with a particle size of 40-75 μ m was added. Surface area (SA) of the sample was determined using BET nitrogen adsorption. The SA/V ratio was 118 m-1. The experimental temperature was 90°C. Leachate was collected after 2, 4, 6, 8, 24, 30, and 48 hours. Leachate concentrations were measured by ICP-AES, and normalized leaching rates were determined.

Figure 1 shows results of normalized leaching rate of boron as a function of time. The leaching rate of V2O5 containing glasses (21E and 21E2) were higher than 19A2 and bead. The bead glass had the slowest leaching rate in the early stage, but there was a reversal after one day, the result after two days test showing the highest leaching rate.

In this study, we have shown that the V2O5 can effectively improve the MoO3 solubility, but decrease the chemical durability of borosilicate glass. The chemical durability is considered to have decreased due to the change in the ratio of network forming components. Leaching behavior of the bead glass is clearly different from other glasses, suggesting that the waste components have a significant impact on glass corrosion and formation of gel layer.

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Predicting alteration layers volume for the glasses with various glass composition

Ryuki Kayano¹, Takahiro Ohkubo², Ryuta Mastubara³, and Keisuke Ishida³

¹ Faculty of Engineering, Department of Applied Chemistry and Biotechnology,

- Chiba University, 1-33 Yayoi-cho Inage-ku, Chiba 263-8522, Japan
- ² Graduate school of Engineering, Chiba University, 1-33 Yayoi-cho Inage-ku, Chiba 263-8522, Japan
- ³ Nuclear Waste Management Organization of Japan (NUMO), Mita NN Building, 2nd Floor, 1-23 Shiba 4-chome, Minato-ku, Tokyo 108-0014, Japan 20t1479y@student.gs.chiba-u.jp

Glass dissolution resulting from a dissolution of soluble elements from the glass surface forms the alteration layer. It is known that the chemical structure and volume of the alteration layer vary with different dissolution conditions, such as solution, glass compositions and time. In this study, we study a model to estimate the alteration layers volume via experimental and modeling approaches aided by a machine-learning.

The glass dissolution tests were performed for the 20 glasses with various compositions. The pristine glasses has the composition based on ISG1 shown in Image 1 and are prepared by the customary melt quenching method. The dissolution was conducted under static conditions at 140°C for seven days according to the standard for glass melting tests. The normalized mass loss (NL) of each element in the pristine glass was calculated from the elemental analysis of the leaching solution. The coordination structures of Si and B for pristine and altered glasses were determined from solid state 11B and 29Si NMR spectroscopy.

The alteration layer volume was calculated from the leaching amount of B. The data showed the nonlinear behavior for Na content in glass compositions, meaning that the simple ion exchange model between H3O+ and Na could not explain the formation volume of the alteration layer.

The correlation matrix for all compositions and leaching elements was computed. The highest correlation in NLs was found for Na-Si, and Na-B. Solid-state 29Si NMR spectra showed several peaks with broadened line shapes, which were assigned to the Qn structure involving neighbor AlO4. Due to the broad line shape, it is not easy to quantify these chemical species by deconvolution. The deconvolution was roughly performed using two Gaussian functions assuming Q3 and Q4 or Q4(1Al, 2Al) structures.

Solid-state 11B NMR spectra were also deconvoluted by considering second-order quadrupolar interaction. Four peaks corresponding

to ring and non-ring 3-coordinate B and two 4-coordinate B species were assumed. A series of the experimental dataset for atomic species derived from solid-state NMR were used to calculate correlation the correlation matrix. The correlation matrix showed that the Q4 population has a negative correlation with Al NL (correlation coefficient: -0.66). Finally, a prediction model of B NL from compositions, the population of atomic species, and pristine glass density were built using linear regression.

	SiO2	AI2O3	B2O3	Na2O	CaO
ISG1	61.15	3.91	16.25	12.87	5.83
ISG1-S45	45.00	5.53	23.00	18.22	8.25
ISG1-S50	50.00	5.03	20.91	16.56	7.50
ISG1-S55	55.00	4.52	18.82	14.91	6.75
ISG1-S60	60.00	4.02	16.73	13.25	6.00
ISG1-S75	75.00	2.51	10.45	8.28	3.75
ISG1-A0	63.63	0.00	16.91	13.39	6.07
ISG1-A2	62.36	2.00	16.57	13.13	5.95
ISG1-A4	61.09	4.00	16.23	12.86	5.82
ISG1-A6	59.81	6.00	15.89	12.59	5.70
ISG1-A8	58.54	8.00	15.56	12.32	5.58
ISG1-B0	73.01	4.66	0.00	15.37	6.96
ISG1-B8	67.17	4.29	8.00	14.14	6.40
ISG1-B16	61.33	3.92	16.00	12.91	5.85
ISG1-B24	55.49	3.55	24.00	11.68	5.29
ISG1-B32	49.65	3.17	32.00	10.45	4.73
ISG1-N8	64.56	4.13	17.16	8.00	6.16
ISG1-N12	61.76	3.95	16.41	12.00	5.89
ISG1-N16	58.95	3.77	15.66	16.00	5.62
ISG1-N20	56.14	3.59	14.92	20.00	5.35
ISG1-N24	53.33	3.41	14.17	24.00	5.09

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Monitoring of alpha-decay radiation damage in a 241Am-doped glass-ceramic material

S. Miro¹, N. Sellami¹, P. Chevreux¹, G. Jouan¹, M. Tribet¹, C. Jégou¹, I. Bardez-Giboire¹, S. Peuget¹ ¹ CEA, DES, ISEC, DE2D, Université de Montpellier, Marcoule 30207, France sandrine.miro@cea.fr

In the French nuclear waste management strategy, after reprocessing of nuclear spent fuel, Fission Products (FP) and Minor Actinides (MA) are confined in R7T7 borosilicate glass, which can incorporate up to 18.5 wt.% of FP and MA oxides [1]. Glass-ceramic matrices (GCM) could be an alternative way to immobilize higher amounts of high level waste than current borosilicate nuclear glasses and could offer a higher flexibility in the management of various waste streams to be vitrified. GCM have chemical and structural heterogeneities originating from the mixing of glassy and ceramic phases [2]. Their design can be adjusted by varying the material chemical composition, but one of the main potential ceramic phases that can be formed is silicate apatite that can crystallize from the glass melt if the lanthanide and actinide loading factor is high [3]. The development of these new class of conditioning materials requires the study of their long-term behavior, especially their self-irradiation response.

In this context, we followed the evolution under alpha decay self-irradiation of a 241Am doped glass-ceramic containing apatite crystals. For this purpose, a synthesis of an aluminoborosilicate SiO2-B2O3-Na2O-Al2O3-CaO-La2O3-Am2O3 glass-ceramic was carried out in hot cells. The chosen cumulative concentrations of La2O3 and AmO2 (21.83 wt%) above the incorporation limit allowed the crystallization of the apatite phase. Indeed, initial observations show that about 10% of the surface is occupied by the crystals. These crystals exhibit a hexagonal-shaped morphology, with crystals elongated along the c-axis of the hexagonal structure, characteristic of apatite crystals. Their chemical composition and cell parameter were found to be close to those expected for an apatite phase of stoichiometric composition Ca2La4Am4(SiO4)6O2. Within the glassy matrix, a depletion of lanthanum and americium is observed near the apatite crystals, which is more marked for americium, showing a preferential incorporation of this alpha-emitter in the apatite phases.

Structural and microstructural evolutions under alpha-decay self-irradiation were followed for 8 years by regularly analyzing the crystals and the residual glassy matrix. The combination of XRD and Raman spectroscopy data suggest a drastic transformation of the apatite structure with the alpha-decay dose. In a first dose range, the transformation results in the loose of the long range order, characterized by the disappearance of the XRD peaks, which corresponds to a progressive radiation-induced amorphization of the crystals. This amorphization appears to directly occur within the collision cascade of the 241Am recoil nucleus, by elastic-collision process, according to a direct impact model. The fully amorphous state is reached at around $3x10^{18} \alpha/g$ of apatite. In a second dose range, between 2.8 and 4.23x10^{18} α/g of apatite, a very rapid or sharp transformation was observed by Raman spectroscopy. This last transformation, never observed before in silicate minerals, is associated to a modification of the medium range order of the metamict state with further

accumulation of alpha-decay dose and is characterized by the increase of the connectivity in SiO4 tetrahedra.

The crystalline-to-amorphous transformation is accompanied by an increase in macroscopic volume (swelling). Raman imaging highlighted an emergence of amorphized crystals from the glassy matrix. This out-of-plane expansion is of around 3 μ m. Differential swelling between the apatite crystals and the glassy matrix is a possible reason of this out-of-plane expansion. This macroscopic dimensional changes is also associated to a decohesion of the crystals from the glassy matrix. Indeed, SEM observations reveal the appearance of holes caused by the loosening of some crystals. This decohesion underlines a significant mechanical degradation of the amorphized crystals. However, optical and SEM images of the surface of the glass-ceramic did not reveal any significant cracks in the residual glass induced by self-irradiation.

This study shows that the microcracking of GCM due to differential swelling under self-irradiation ageing can be avoided and is certainly strongly depending on the material microstructure. Some future works are needed to improve our understanding of the conditions that control the microcracking of GCM under irradiation and therefore to develop some mechanical resistant glass-ceramics with respect to their radiation ageing.



X-ray diffraction pattern of glass-ceramic containing $Ca_{2,02}La_{3,06}Am_{4,07}(SiO_4)_6O_{1,99}$ apatite crystals at 6 different cumulative doses

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Structure and Dynamics of Hydrous Silicate Gels by Molecular Dynamics Calculations

Takuma Hatori¹, Takahiro Ohkubo ¹, Ryuta Matsubara ², and Keisuke Ishida ²

¹ Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho Inage-ku, Chiba 263-8522, Japan ² Nuclear Waste Management Organization of Japan (NUMO), Mita NN Building, 2nd Floor, 1-23 Shiba 4-chome, Minato-ku, Tokyo 108-0014, Japan

4-Chome, Minato-ku, Tokyo 108-0014,

710takuma@gmail.com

The alteration layer that forms on the surface of the nuclear waste glass plays a crucial role in controlling the long-term dissolution behavior. To accurately predict this behavior, it is essential to understand the chemical structure and mass transfer characteristics within the alteration layer. Unfortunately, obtaining comprehensive information about the alteration layer from experimental approaches is limited due to the difficulties in analyzing nanometer-scale surfaces. In this study, molecular dynamics (MD) calculations, which can model realistic atomic structures, were conducted to evaluate the alteration layer's structural properties and the water molecules' kinetic properties.

The structure within an alteration layer may change significantly depending on environmental conditions such as water content. Therefore, we created several alteration layer models with water content as a parameter and systematically investigated whether the characteristics of the alteration layer changed. The water content was set in 10 wt% increments from 10 to 100 wt%, and the ratio of SiO2 and H2O was adjusted at each water content so that the total number of atoms was 9,000 atoms. MD calculations were performed for each model by annealing at 6000 K under constant volume until the structure reached full equilibrium, then cooling at a rate of 20 K/ps to obtain the equilibrium structure at 300 K. The atomic structure was sampled and used in the analysis to evaluate the silicate backbone structure and water mobility. The reactive force field (ReaxFF) optimized to simulate the glass-water interface was used to build the alteration layer model.

Structural analysis of the silicate framework revealed that with increasing water content, the Si bridging structure was changed

depending on water content. The Q4 and Q3 structures, which have four or three cross-linked oxygen atoms, were dominant in the model with low water content. In contrast, the high water content structure showed that the bridging structure of the silicate framework was almost broken, and Si species about 80% is in the Q0 structure without bridging oxygen. Pore size distribution and the volume fraction filled with water were examined to characterize the porous structure. The pore was defined as the excluded volume with all water molecules in the cell.

All pore size distributions with different water contents were found to be Gaussian line shapes, and the mean pore size was increased with increasing water content. The mean pore radius for the model with the lowest water content (10wt%) was 1.8%, which is expected to be constrained water dynamics in such a small pore. Water cluster analysis on the basis of hydrogen bonds between water molecules was performed to investigate the aggregated state of water.

The results revealed that most of the water was isolated within the pores with lower water content, and the translational movement of water was significantly limited. To evaluate the translational motion of water, the self-diffusion coefficient was calculated from the mean square displacement (MSD) of water. The diffusion coefficients dramatically increase with increasing water content. To organize the relationship between diffusion coefficients and porous structure, the diffusion data were fitted with linear function against mean porosity. The fitting successfully explained the diffusion data, meaning that the geometric parameters of the porous structure for alteration layers can model the mass transfer.

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Application of glass structural gene modeling in the simulation of chemical durability and liquidus temperature in HLW glass

Liyan Zhang¹, Zhongdi Li²

¹ Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201815, China. ² China Nuclear Power Engineering Co., Ltd., Beijing 100840, China

zhangliyan@siom.ac.cn

Composition-structure-property (C-S-P) modeling, named as "glass structural gene modeling (GSgM), is a method that threads composition-structure (C-S) and structure-property (S-P) modeling together to carry out accurate simulation. High accuracy of GSgM comes from the transformation of the nonlinear relationship of C-P to two linear relationships of C-S and S-P. The combination of C-S and S-P models produced the modeling platform to carry out the bi-directional C↔S↔P modeling. It is known that both chemical durability and liquidus temperature (TL) are difficult to achieve accurate simulation with limited data by C-P modeling in HLW glass, and C-S-P method is proved to be a valuable alternative to solve this problem. Integral area of Gaussian peaks derived from FTIR or Raman peak fitting was used as the structural data to build S-P models of leaching rate and TL. Fig.1 is the S-P models of Na+, Li+, B3+ leaching rate and TL established by 11 HLW borosilicate glasses. Same as C-P method, S-P modeling alone can be used independently to simulate glass property. Results show that GSgM is highly suitable for the initial glass composition screening and property prediction purpose with limited data and future database development.



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Influence of glass composition and morphology on its solubility in simulated physiological fluids (SPF)

Sarah Gandon ^{1, 2}, Stéphane Gin ², Quentin Hérault ¹, Maxime Jacquemin ¹, Frédéric Angeli ², Agathe Houzet ² ¹ Saint Gobain Recherche Paris, 39 Quai Lucien Lefranc, 93300 Aubervilliers, France ² CEA, DES, ISEC, DPME, Univ Montpellier, Marcoule, France sarah.gandon@saint-gobain.com



Depending on the field of application, glass durability can be a key property to control (nuclear waste vitrification, pharmaceutic and food containers, insulation fibers, ...). The testing conditions depend on the application: for instance, for food and pharmaceutical containers, the alteration takes place in aqueous conditions and the release of elements is monitored (release of lead from lead crystal material in the beverage for example). On the other hand, for insulation fibers, the focus is on the bio-solubility of fibers. Indeed, to be commercialized, those fibers must pass an in-vivo lung dissolution test on rats. To study this dissolution, simulated lung fluids are used. These fluids are neutral (pH 7,5) or slightly acid (pH 4,5) aqueous solutions.

This project is a CEA/Saint-Gobain collaboration and aims to understand the impact of several oxides, including aluminum oxide on the solubility of glass fibers in simulated lung fluids. In a first step, the impact of the morphology of glass samples was studied. Indeed, fibers can be tricky to produce at a lab scale. Consequently, "easy-to-produce" morphologies were evaluated. The dissolution behavior of fibers was compared to that of bulk glass, powders from crushed bulk glass, and powders from crushed fibers.

For this preliminary study, two types of glasses with high and low aluminum oxide content were studied. These samples were altered, and both the alteration solutions and the glasses were analyzed using ICP-AES and SEM, respectively. These analyses help to understand the congruent/incongruent behavior of the dissolution.

Notably, the dissolution of high aluminum content glass was proven to be congruent and follow a shrinking-core model for all studied morphologies as shown in figure 1 for the fiber samples.

This preliminary study will allow to consider the influence of the composition without taking into consideration the morphology anymore.

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Effect of Gadolinium Oxide on Structure and Chemical Stability of Borosilicate Glass with Simulated Nuclear Power Plants HLLW

Hua Zhang ¹, Cheng He ¹, Shengheng Tan ¹, Jiong Chang ¹, Zheng Li-Zhang Keqian ¹ ¹Radioactive Chemistry Department, China Institute of Atomic Energy - P.O.Box 275-93, Beijing,102413 zhanghua_ciae@163.com

Due to the high radioactivity, high corrosiveness, high toxicity, and high heat release rate, safe and proper treatment of high-level radioactive waste is always the important point in waste management. In order to properly handle the high-level liquid waste generated from the post-treatment of spent fuel in power reactors, this article focuses on the molar ratio of $SiO_2:B_2O_3: Na_2O=1:0.23:0.54$ type borosilicate basic glass, studied on its performance on the structure and chemical durability with containing 20 wt.% the simulated 33GW·d/tU spent fuel HLW and the addition of gadolinium oxide (with amounts of 0, 2, 4, 6, 8, and 10 wt.%). XRD analysis shows that the glass samples exhibit stable amorphous glass states.

Raman analysis results show that as the increase of Gadolinium(III) oxide addition, the Q3 structures of Si-O in the glass structure tend to move to the low frequency region. At same time, the nuclear magnetic resonance analysis results show that the proportion of Q3 (B) structure shows a trend of first decreasing and then gradually increasing, while the proportion of Q4 (B) structure shows first increases and then gradually decreases. As regard the chemical stability, the PCT results show that as the addition of Gadolinium(III) oxide, the leaching amount of Si, B, Na and other elements in the glass solidified sample decreases significantly, the chemical stability of those glass samples is significantly improved.



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Chemical durability of commercial silicate glasses and the impact of surface treatments

Léa Brunswic¹, Frédéric Angeli¹, Thibault Charpentier², Stéphane Gin¹, Laurent Gautron³,

Eric van Hullebusch ⁴, Mariona Tarragó ⁴, Daniel Neuville ⁴, Xavier Capilla ⁵, Daniel Coillot ⁶, Ilyes Ben Kacem ⁷, Justine Fenech ⁸, Johann Brunie ⁹

¹ CEA, DES, ISEC, DPME, Université de Montpellier, Marcoule, France

² NIMBE, CEA, CNRS, Université Paris-Saclay CEA Saclay F-91191 Gif-sur-Yvette, France

³ Laboratoire Géomatériaux et Environnement, Université Gustave Eiffel, Marne-la-Vallée Cedex 02, France

⁴ Université Paris Cité, Institut de Physique du Globe de Paris, CNRS, F-75005, Paris, France

⁵ Fédération du verre et du cristal, 114 rue de la Boétie, 75008 Paris

⁶ Manufacture Baccarat, 54120 Baccarat, France

⁷ Arc France, 104 avenue du Général de Gaulle, 62510 Arques, France

⁸ Pochet du Courval, lieu dit Guimerville, 76340 Hodeng au Bosc, France

lea.brunswic@cea.fr

Given the present regulatory framework (REACH, Food Contact Materials EU Directives), understanding the mechanisms of glass alteration is increasingly required to guarantee the safe use of daily glassware over their lifetime. A major comprehensive study of a wide range of commercial glass compositions has been pursued on five types of silicate glasses from four major French glass manufacturers. The investigated glasses, lead crystal glass (fine glassware), soda lime glass (containers for the food and cosmetic industries), borosilicate glass (cooking dishes), barium glass (tableware) and opal crystallized glass (tableware) are all bestseller products. A single alteration procedure was used in this work to offer a wide comparison of these glass articles.

Glass alteration experiments were carried out for 3 years in acetic acid (4 % vol.), the reference medium for food contact alteration, imposing a pH of 2.4, at a temperature of 70 °C. It was demonstrated that although the polymerization degree of the glassy network varied between the different glasses, the rate of hydrolysis, determined from the leaching of Si remained similar for all. However, it appears that the structure of the silicate network is strongly correlated with the leaching of Na, considered as a tracing element of alteration. The altered depths of Na ranged between a few tens of nanometres for borosilicate, the most polymerized glass, to a few microns for lead crystal, less polymerized. The retention of lead was effective after 56 days of alteration and lasted until the end of the experiment, explained by the local recondensation of the glassy network. The alteration mechanisms of opal glass (including NaF, BaF2 and CaF2 crystals) were different between powder and slab samples highlighting the heterogeneity of the distribution of crystals depthwise in glass plates, although the hydrolysis rate of the powder was similar to the one measured in fully vitreous glasses.

Another part of this work focused on the impact of surface treatments of industrial interest on glass durability on commercial treated glass slabs. Five surface treatments were selected, three chemical deposits of oxide layers: SNO_2 , TiO_2 , and SiO_2 as well as two acidic attacks: SO_2 dealkalization and acid polishing, which were applied on each of the five investigated glass compositions. Glass surface characterizations pointed out some changes with different impacts on the alteration behaviour observed for 1.3 years. The unique data collected shows significant reduction of long-term lead leaching, especially in the case of SO_2 dealkalized lead crystal glass. Beneficial effect towards the retention of Ba in Ba-containing glasses was also determined but these surface treatments showed poor interest for borosilicate, as their mechanism relies on the reduction of the interdiffusion rate, while borosilicate's alteration is controlled by hydrolysis.

Finally, the impact of chromium, added as a colorant in lead crystal, has been investigated because of the high toxicity of hexavalent chromium for human health. Major changes on the leaching of lead crystal glass induced by the presence of Cr were uncovered, even at very low concentrations (Cr < 0.03 mol%). Increasing Cr concentrations demonstrated a dual beneficial effect on lead crystal chemical durability by reducing the leaching of Pb and increasing the polymerization of the silicate network. Both observations were rationalized by the specific insertion of Cr in certain glass domains. Additionally, chromium was never found under its hexavalent form in the pristine nor altered glasses under experimental uncertainties, nor available in solution.

The confrontation of results from local and global scales allowed establishing a referential for the alteration of commercial glasses in acid medium, unfolding the links between structure and alteration for these compositions and highlighting the effects of surface treatments.

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Sumglass 2023 - Participants

Organisators

Angeli Frédéric | CEA - ISEC Marcoule - BP17171, Bagnols-sur-Cèze, France | frederic.angeli@cea.fr Bingham Paul | Sheffield Hallam University City Campus, Howard Street, Sheffield, UK | p.a.bingham@shu.ac.uk Brunswic Léa | CEA - ISEC Marcoule - BP17171, Bagnols-sur-Cèze, France Gin Stéphane | CEA - ISEC Marcoule - BP17171, Bagnols-sur-Cèze, France Goel Ashutosh | RUTGERS University 607 Taylor Road, Piscataway, USA | ag1179@soe.rutgers.edu Delaye Jean-Marc | CEA - ISEC Marcoule - BP17171, Bagnols-sur-Cèze, France | jean-marc.delaye@cea.fr Kruger Albert | United States Department of Energy (DOE) PO Box 450, Richland, USA | Albert_A_Kruger@orp.doe.gov McCloy John | Washington State University 405 Spokane Street, Pullman, USA | john.mccloy@wsu.edu Peterson Irene | Corning Research and Development Corporation US 21 Lynn Morse Drive, Painted Post, USA | petersonim@corning.com Pokorny Richard | University of Chemistry and Technology Prague Technicka 5, Prague 6, Czechia | Richard.Pokorny@vscht.cz Ribet Isabelle | CEA Marcoule - BP17171, Bagnols-sur-Cèze, France Schuller Sophie | CEA - ISEC Marcoule - BP17171, Bagnols-sur-Cèze, France Schuller Sophie | CEA - ISEC Marcoule - BP17171, Bagnols-sur-Cèze, France

Chairmans

Bingham Paul | Sheffield Hallam University City Campus, Howard Street, Sheffield, UK | p.a.bingham@shu.ac.uk
Burov Ekaterina | Joint Laboratory CNRS/Saint-Gobain Research Paris, Aubervilliers, France | ekaterina.burov@saint-gobain.com
Caurant Daniel | IRCP Chimie ParisTech / CNRS UMR 8247 11, rue Pierre et Marie Curie, Paris, France
Girold Christophe | CEA - DES - DPE Marcoule BP 17171, Bagnols-sur-Cèze, France | christophe.girold@cea.fr
Goel Ashutosh | RUTGERS University 607 Taylor Road, Piscataway, USA | ag1179@soe.rutgers.edu
McCloy John | Washington State University 405 Spokane Street, Pullman, USA | john.mccloy@wsu.edu
Pokorny Richard | University of Chemistry and Technology Prague Technicka 5, Prague 6, Czechia | richard.pokorny@vscht.cz
Regnier Elise | CEA - ISEC Marcoule - BP17171, Bagnols-sur-Cèze, France | elise.regnier@cea.fr
Sauvage Emilien | CEA - ISEC Marcoule - BP17171, Bagnols-sur-Cèze, France | emilien.sauvage@cea.fr
Vienna John | Pacific Northwest National Laboratory Battelle Blvd, Richland, USA | john.vienna@pnnl.gov

Speakers

Angeli Frédéric | CEA - ISEC Marcoule - BP17171, Bagnols-sur-Cèze, France | frederic.angeli@cea.fr Ankith John Santosh | CelSian Achtseweg Zuid 241-A, Eindhoven, Netherlands | ankith.john@celsian.nl Benigni Pierre | Institut Matériaux Microélectronique Nanosciences de Provence - UMR CNRS 7334, Marseille, France Bernardo Enrico | Department of Industrial Engineering, University of Padova Via Marzolo, 9, Padova, Italy | enrico.bernardo@unipd.it Bingham Paul | Sheffield Hallam University City Campus, Howard Street, Sheffield, UK | p.a.bingham@shu.ac.uk Bordier Gilles | CEA - DES Marcoule BP 17171, Bagnols-sur-Cèze, France | gilles.bordier@cea.fr Brada Jiří | Glass Service, a.s. Rokytnice 60, Vsetín, Czechia | jiri.brada@gsl.cz Brauer Delia | Friedrich Schiller University Jena - Otto Schott Institute of Materials Research Fraunhoferstr. 6, Jena, Germany Brunswic Léa | CEA Marcoule - BP17171, Bagnols-sur-Cèze, France Burov Ekaterina | Joint Laboratory CNRS/Saint-Gobain Research Paris, Aubervilliers, France | ekaterina.burov@saint-gobain.com Capilla Xavier | Institut du verre 112-114 rue de la Boétie, Paris, France | xavier.capilla@institutduverre.fr Cartalade Alain | CEA - ISAS, Gif-sur-Yvette, France Charpentier Thibault | CEA Paris-Saclay DRF/IRAMIS/NIMBE Bat 125, Gif-sur-Yvette, France | thibault.charpentier@cea.fr Claireaux Corinne | CelSian, Eindhoven, Netherlands Delaye Jean-Marc | CEA - ISEC Marcoule - BP17171, Bagnols-sur-Cèze, France | jean-marc.delaye@cea.fr Didierlaurent Régis | ORANO 125 Av. de Paris, Châtillon, France Ferkl Pavel | PNNL 902 Battelle Boulevard, Richland, USA | pavel.ferkl@pnnl.gov Frugier Pierre | CEA, DES, ISEC, DPME, Univ Montpellier Marcoule, F-30207, Bagnols-sur-Ceze, France Gin Stéphane | CEA - ISEC Marcoule - BP17171, Bagnols-sur-Cèze, France Goel Ashutosh | RUTGERS University 607 Taylor Road, Piscataway, USA | ag1179@soe.rutgers.edu Gossé Stéphane | CEA - ISAS Bâtiment 450 N, Gif-sur-Yvette, France | stephane.gosse@cea.fr Gouillart Emmanuelle | Saint-Gobain Research Paris, Aubervilliers, France | emmanuelle.gouillart@saint-gobain.com Guillen Donna | Idaho National Laboratory 955 MK SImpson Blvd, Idaho Falls, USA | donna.guillen@inl.gov Hrma Pavel | US DOE, Richland, USA | ratnottara@aol.com Inagaki Yaohiro | Kyushu University (Japan) Moto-oka 744, Fukuoka 819-0395, Fukuoka, Japan | inagaki.yaohiro.553@m.kyushu-u.ac.jp Krishnan N M Anoop | Indian Institute of Technology Delhi Hauz Khas, New Delhi, India | krishnan@iitd.ac.in Kruger Albert | United States Department of Energy (DOE) PO Box 450, Richland, USA | albert_a_kruger@orp.doe.gov Laplace Annabelle | CEA - ISEC Marcoule - BP17171, Bagnols-sur-Cèze, France | annabelle.laplace@cea.fr Marcial Jose | Pacific Northwest National Laboratory, Richland, USA McCloy John | Washington State University 405 Spokane Street, Pullman, USA | john.mccloy@wsu.edu Mear Francois | Lille University - UCCS Cite scientifique, Villeneuve d'Ascq, France Neuville Daniel | IPGP-CNRS-UP 1 rue Jussieu, Paris, France

Papin Sophie | Saint-Gobain Research Paris 39, Quai Lefranc B.P. 135, Aubervilliers Cédex, France
Perret Damien | CEA - ISEC Marcoule - BP17171, Bagnols-sur-Cèze, France | damien.perret@cea.fr
Peterson Irene | Corning Research and Development Corporation US 21 Lynn Morse Drive, Painted Post, USA | petersonim@corning.com
Pigeonneau Franck | MINES Paris - PSL 1 Claude Daunesse CS 10207, Sophia Antipolis, France | franck.pigeonneau@minesparis.psl.eu
Podor Renaud | ICSM Site de Marcoule, Bâtiment 426 BP 17171, Bagnol/Ceze, France | renaud.podor@cea.fr
Pokorny Richard | University of Chemistry and Technology Prague Technicka 5, Prague 6, Czechia | richard.pokorny@vscht.cz
Regnier Elise | CEA - ISEC Marcoule - BP17171, Bagnols-sur-Cèze, France | elise.regnier@cea.fr
Sauvage Emilien | CEA - ISEC Marcoule - BP17171, Bagnols-sur-Cèze, France | emilien.sauvage@cea.fr
Schuller Sophie | CEA - ISEC Marcoule - BP17171, Bagnols-sur-Cèze, France | sophie.schuller@cea.fr
Schuller Sophie | CEA - ISEC Marcoule - BP17171, Bagnols-sur-Cèze, France | sophie.schuller@cea.fr
Schumacher Stéphan | Andra 1-7 rue Jean Monnet, Châtenay-Malabry, France | stephan.schumacher@andra.fr
Thorpe Clare | University of Sheffield University of Sheffield, Sheffield, UK | clare.thorpe@sheffield.ac.uk
Verney-Carron Aurélie | Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), Créteil, France
Veronneau Cyrille | Veolia Nuclear Solutions Europe 556 Chemin de l'islon, Chasse sur Rhone, France | cyrille.veronneau@veolia.com
Vienna John | Pacific Northwest National Laboratory Battelle Blvd, Richland, USA | john.vienna@pnnl.gov
Xu Kai | Wuhan University of Technology Luoshi Road 122, Wuhan University of Technology, Wuhan, China | kaixu@whut.edu.cn

Poster presentators

Agullo Julia | CEA Marcoule - BP17171, Bagnols-sur-Cèze, France | julia.agullo@cea.fr Arena Hélène | CEA Marcoule - BP17171, Bagnols-sur-Cèze, France | helene.arena@cea.fr Brunswic Léa | CEA Marcoule - BP17171, Bagnols-sur-Cèze, France Cardoso Alexi | CEA Marcoule D765, 30200 Chusclan, Chusclan, France | alexi.cardoso@cea.fr Caurant Daniel | IRCP Chimie ParisTech / CNRS UMR 8247 11, rue Pierre et Marie Curie, Paris, France Cincibusova Petra | University of Chemistry and Technology Prague, Prague 6, Czechia | cincibup@vscht.cz De Laharpe Pierre | CEA Centre de MARCOULE Bât. FORMATION Nº 403 - BP 17171, Bagnols-sur-Cèze, France Deng Lu | Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences 390 Qinghe Road, Jiading, China Deng Wei | Sheffield Hallam University Howard St, Sheffield, UK | wei.deng@shu.ac.uk Du Jincheng | University of North Texas 1155 Union Circle # 305310, Denton, USA | jincheng.du@unt.edu Dupuy Laurent | SERMA Technologies 64 chemin des Mouilles, ECULLY, France | I.dupuy@serma.com Eales James | Sheffield Hallam University, Sheffield, UK | b8033567@hallam.shu.ac.uk Evrard Pascal | Waste2Glass Av Dreyfous Ducas, Limay, France | pascal.evrard@Waste2Glass.com Feugeur Gérald | Université Paris-Saclay, CEA, Service de Recherche en Matériaux et procédés Avancés, France | gerald.feugueur@cea.fr Gandon Sarah | Saint Gobain Recherche Paris 39 Quai Lucien Lefranc, Aubervillier, France Guyot Taos | CEA 4 rue Aristid Berges, Grenoble, France | taos.guyot@cea.fr Hatori Takuma | Chiba University 1-33 Yayoi-cho Inage-ku, Chiba 263-8522, Chiba city, Japan Higashino Katsuyuki | Japan Nuclear Fuel Limited, Rokkasho-mura, Kamikita-gun, Japan | katsuyuki.higashino@jnfl.co.jp Kayano Ryuki | Chiba University 1-33 Yayoi-cho Inage-ku, Chiba, Chiba city, Japan | 20t1479y@student.gs.chiba-u.jp Méjanès Capucine | CEA Saclay, Gif sur Yvette, France | capucine.mejanes@cea.fr Michel Caroline | CEA Marcoule - BP17171, Bagnols-sur-Cèze, France Miro Sandrine | CEA Marcoule - BP17171, Bagnols-sur-Cèze, France | sandrine.miro@cea.fr Nabyl Zineb | CEA Marcoule - BP17171, Bagnols-sur-Cèze, France | zineb.nabyl@cea.fr Nagata Minako | Akita University 1-1, Tegata Gakuenmachi, Akita, Japan | m8022936@s.akita-u.ac.jp Narayanasamy Sathya | CEA Marcoule, Bagnols-sur-Cèze, France Nonnet Hélène | CEA Marcoule, Bagnols-sur-Cèze, France Owaku Kohei | Japan Nuclear Fuel Limited 4-108, Okitsuke, Obuchi, Rokkasho, Japan Park Jaehoon | Kyushu University 744 Motooka, Nishi Ward, Fukuoka-shi, Japan | park.jaehoon.942@s.kyushu-u.ac.jp Pereira Luiz | University of Munich LMU Theresienstrasse 41, Munich, Germany | luiz.pereira@min.uni-muenchen.de Pokorny Richard | University of Chemistry and Technology Prague Technicka 5, Prague 6, Czechia | Richard.Pokorny@vscht.cz Qian Min | Shanghai Institute of Optics and Fine Mechanics (CAS) 390 Qinghe Road, Shanghai, China Quintas Arnaud | CEA Marcoule DES/ISEC/DPME/SEIP/LNPA, Bagnols-sur-Cèze, France | arnaud.quintas@cea.fr Scrimshire Alex | Sheffield Hallam University Harmer 2219, City Campus, Howard Street, Sheffield, UK | a.scrimshire@shu.ac.uk Soudani Sami | Laboratoire de Planétologie et Géosciences 2 rue de la Houssinière, Nantes, France | sami.soudani@etu.univ-nantes.fr Steele Helen | Sellafield Ltd, Seascale, UK | helen.steele@sellafieldsites.com Sugawara Toru | Akita University Tegatagakuenmach 1-1, Akita, Japan Tan Shengheng | China Institute of Atomic Energy, Beijing, China | tanshengheng@ciae.ac.cn Taron Mélanie | CEA Marcoule - BP17171, Bagnols-sur-Cèze, France Tiwari Sumit | CEA Marcoule - BP17171, Bagnols-sur-Cèze Cedex, France | sumit.tiwari@cea.fr Uruga Kazuyoshi | Central Research Institute of Electric Power Industry 2-6-1 Nagasaka, Yokosuka, Japan Vernerova Miroslava | University of Chemistry and Technology, Prague 6, Czechia | arkosiom@vscht.cz Welcomme Eléonore | CEA Marcoule - BP17171, Bagnols-sur-Cèze, France Yano Tetsuji | Tokyo Institute of Technology Ookayama, 2-12-1, Meguro-ku, Tokyo, Japan Zhang Hua | china institute of atomic energy, beijing, China | zhanghua@ciae.ac.cn Zhang Liyan | Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai, China | zhangliyan@siom.ac.cn

Other participants

Ayling Jenny | The University of Sheffield Western Bank, Sheffield, UK | jmsayling1@sheffield.ac.uk Bart Florence | CEA ISEC DPME Marcoule - BP17171, Bagnols-sur-Cèze, France | florence.bart@cea.fr Brun Patrice | CEA Marcoule - BP17171, Bagnols-sur-Cèze, France Calas Georges | Sorbonne Université 4 PlaceJussieu, Paris, France | georges.calas@sorbonne-universite.fr Chabilan Cathy | Orano 23 place de Wicklow, Montigny-le-Bretonneux, France | cathy.chabilan@orano.group Charton Frederic | CEA ISEC Marcoule - BP17171, Bagnols-sur-Cèze, France | frederic.charton@cea.fr Clifford Callum | Sellafield Limited Sellafield, Seascale, UK Crawford Rachel | The University of Sheffield Western Bank, Sheffield, UK | rcrawford1@sheffield.ac.uk Delaunay Milene | CEA Marcoule - BP17171, Bagnols-sur-Cèze, France | milene.delaunay@cea.fr Deschanels Xavier | CEA/ICSM Marcoule - BP 17171, Bagnols-sur-Cèze, France | xavier.deschanels@cea.fr Fan Sijun | Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences 390 Qinghe Road, Jiading, China Firon Muriel | CEA Marcoule - BP17171, Bagnols-sur-Cèze, France | muriel.firon@cea.fr Fossati Paul | CEA Centre de Saclay, Gif-sur-Yvette, France | paul.fossati@cea.fr Fournier Maxime | CEA DES/ISEC/DPME/SEME/LEMC - Bat. 208, Bagnols-sur-Cèze, France | maxime.fournier@cea.fr Galoisy Laurence | SU/IMPMC 4 place jussieu - case 115, Paris, France | laurence.galoisy@sorbonne-universite.fr Ghazzai Mohamed-Leith | CEA Marcoule - BP17171, Bagnols-sur-Cèze, France | mohamed-leith.ghazzai@cea.fr Klouzek Jaroslav | University of Chemistry and Technology Prague Technicka 5, Prague, Czechia | klouzekj@vscht.cz Lacombe Jacques | CEA Marcoule - BP17171, Bagnols-sur-Cèze, France | jacques.lacombe@cea.fr Lemonier Stéphane | CEA Marcoule - BP17171, Bagnols-sur-Cèze, France Li Zhongdi | China Nuclear Power Engineering Co., Ltd. China, Beijing, China | lctcj@sina.com Manifold Garry | University of Sheffield Department of Material Science and Engineering, Sheffield, UK | gmanifold1@sheffield.ac.uk Matsubara Ryuta | NUMO Mita NN Bldg. 2F, 4-1-23 Shiba, Minato-ku, Japan | rmatsubara@numo.or.jp Nakano Masanori | AGC Inc. 1-1 Suehiro-cho Tsurumi-ku, Yokohama, Japan | masanori.nakano@agc.com Ohkubo Takahiro | Chiba univeirsity 1-33 Yayoi-cho Inage-ku, Chiba, Chiba, Japan | ohkubo.takahiro@faculty.chiba-u.jp Pereira Machado Norma Maria | Orano Recyclage, Châtillon, France | norma-maria.pereira-machado@orano.group Perrin Stéphane | CEA Marcoule - BP17171, Bagnols-sur-Cèze, France | steph.perrin@cea.fr Peuget Sylvain | CEA DES/ISEC/DPME/SEME/LMPA, Bat 166, Atalante, Bagnols-sur-Cèze, France | sylvain.peuget@cea.fr Roussel Céline | Orano 23 place Wicklow, Saint Quentin en Yvelines, France | celine.roussel@orano.group Sessegolo Loryelle | CEA Marcoule - BP17171, Chusclan, France | loryelle.sessegolo@cea.fr Shaw Robert | Veolia Nuclear Solutions 18 Nuffield Way, Abingdon, UK | robin.herrick@veolia.com Sumita Takehiro | Kyushu University 744 Motooka, Nishi-ku, Japan | sumita.takehiro.799@m.kyushu-u.ac.jp Tribet Magaly | CEA Marcoule - BP17171, Bagnols-sur-Cèze, France | magaly.tribet@cea.fr Vernay Aliénor | CEA D765, Marcoule, Chusclan, France Virginie Ansault | CEA Marcoule - BP17171, Bagnols-sur-Cèze, France | virginie.ansault@cea.fr Yoshizawa Fatima Tiemi | IRAP / SVI / Saint-Gobain Recherche, Toulouse, France | fatimatiemi.y@gmail.com

Zhang Ke Qian | China institute of atomic energy Fangshan District, Beijing, China | 17316086034@163.com

SUMO Contractor September 25-29th 2023











