Design Principles for Optimizing Nuclear Waste Glass Formulation for Industrial Implementation – 14107

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ABSTRACT

With more than 30 years operating HLW vitrification facilities in France on an industrial scale, AREVA has gained a very substantial experience in this field. Over the years, borosilicate glass formulations, defined respectively for the Marcoule AVM and R7/T7 La Hague facilities, have demonstrated their strength for accommodating Fission Product (FP) from reprocessing activities in regard to industrial implementation and the Quality Management System. In the case of R7/T7 glass, this point clearly translated into commercial success with the acceptation and return of more than 3,000 glass canisters to overseas customers.

More recently, adapting to the needs for managing extended range of wastes, the AREVA and CEA integrated team (as part of their Joint Vitrification Laboratory) revisited the methodology and principles to be applied to the design of nuclear wastes glass formulation. The objective was to enhance and optimize these formulations to fit various wastes characteristics while taking into account Long Term Behavior and technological constraints. The industrial experience from the facilities was also included as part of this updated methodology.

Since 2005, AREVA and CEA designed 3 new glass compositions respectively optimized to fit U-Mo waste composition, waste from D&D rinsing operation, and FP solutions. All these have to be processed with Cold Crucible Induction Melter (CCIM) technology at La Hague using this updated methodology.

The aim of this paper is to describe the principles followed by the AREVA and CEA team to design an optimized glass formulation to fit waste characteristics, long term behavior and technological constraints. This methodology also includes the development of appropriate Quality Assurance and Quality Control programs ensuring successful implementation on an industrial scale.

INTRODUCTION

Vitrification of high-level radioactive liquid waste is now an internationally recognized standard. Many countries such as the USA, United Kingdom, Germany, Belgium, Japan, Russia, have already vitrified high level waste and several more countries are studying application of the vitrification technology.

The first work on vitrification of radioactive waste began in France in 1957 at the Saclay nuclear center with the early selection by CEA (French Atomic Energy Commission) of Borosilicate glass as the most suitable containment matrix for waste from spent nuclear fuel. By the mid 60s, borosilicate glasses were selected for the vitrification of HLW solutions as the best compromise in terms of containment (leach resistance, thermal stability, resistance to irradiation), technological feasibility, and cost (via the volume reduction factor). The first high-level radioactive glass blocks, weighing 3 kg each and containing some 111 TBq of activity, were fabricated at the Marcoule industrial site in 1965, in graphite crucibles. Today, borosilicate glasses have become a worldwide standard and have been chosen for nearly all vitrification processes for HLW solutions.

Following these early successes, and for now more than 30 years, French scientists, engineers and nuclear experts have been dealing with vitrification in order to provide a comprehensive solution to HLW management issues by designing optimized glass formulation adapted to waste characteristics, able to meet technological constraints related to manufacturing processes and that result in adequate final products being produced with respect to disposal requirements.

This experience spans from R&D to industrial operation of highly active facilities through engineering design, equipment manufacturing and technological development. The complexity of the field benefits from a fully integrated approach accounting for constraints from waste characteristics, technology requirements and long term behavior with a view toward industrial implementation.

As a result, a methodology has been developed by CEA and AREVA teams to allow for the definition of a Glass Package which includes a reference glass composition together with its acceptable domain allowing for variations (e.g. Chemical variability of the waste, fluctuations met in industrial process, etc.) and is optimized to meet the various requirements.

In addition, the implementation of the process at industrial scale and within a commercial environment necessitates the development and deployment of an appropriate Quality Assurance and Quality Control system.

INDUSTRIAL RECORDS OF LA HAGUE VITRIFICATION FACILITIES [1]

R7/T7 glass package

The glass formulation was adapted for commercial Light Water Reactor fission products solutions, including alkaline liquid waste concentrate, as well as platinoid-rich clarification fines. R7/T7 glass formulation was designed to hold a maximum of 18.5 wt % of radioactive waste oxides (fission products, actinides, noble metals and Zr fines), or equivalently an overall maximum waste-loading ratio of 28 %. This limit was set to avoid excessive heating of the glass during interim storage. The glass product has a high activity (predominantly 137 Cs, 90 Sr) and significant amounts of noble metals (3 wt % max.). The maximum βγ activity at vitrification time is of 28 150 TBq per canister (each canister receiving about 400 kg of glass). Industrial glass samples coming from R7 and T7 facilities have been characterized [2]. Satisfactory quality of the glass has been demonstrated; glasses were homogeneous with no undissolved feed and their characteristics were in full agreement with the expected values. The R7/T7 formulation is known worldwide to have an outstanding durability.

TABLE 1: R7/T7 reference glasses (FP: fission products, Act.: Actinides, MP: Metallic particles)

wt %	SiO2	B2O3	Al2O3	Na2O	Fe2O3	NiO	Cr2O3	FP	Act.	MP
R7/T7	45,1	13,9	4,9	10	2,9	0,4	0,5	10,4	2,7	1,6

The R7/T7 glass package specification describing La Hague-produced wasteform has been accepted by the French, German, Belgian, Japanese, Dutch and Swiss customers and their respective Competent Authorities.

Production records and Return to overseas customers

R7 entered active service in June 1989 and began treating 1200 m3 of the backlog HLW solutions that had been accumulated since the start of the first La Hague reprocessing plant, UP2. The challenge for the R7 start-up was to rapidly reach nominal capacity. From this point of view, the start-up was a complete success.

The T7 facility is dedicated to the treatment of the HLW solutions produced by UP3 reprocessing plant. It entered active service in July 1992, 3 years after its twin facility R7. The design of T7 took into account the feedback from R7 operations through:

- Implementation of a new connecting device between the pouring nozzle and the canister, associated with an improved off-gas system;
- Addition of a washable in-cell prefiltering device on the ventilation line of the main hot cells (vitrification, pouring, dismantling) in order to protect HEPA filters from contamination;
- Modification of the cranes to improve the reliability of subcomponents and to reduce maintenance;

- Improvement of the canister decontamination device.

Moreover, T7 operators had the unique opportunity to train on R7 before T7 active start-up. As a consequence, T7 was able to quickly reach its production goals, and the improvements mentioned previously proved to be beneficial in terms of reducted of operating costs, reducted of the volume of waste, reduced doses to personnel, and improved availability. For instance, the use of washable metallic pre-filters led to a reduction, by a factor of about 10, of the number of HEPA filter replacements.

At the beginning of 1994, it was decided to interrupt operations and to upgrade the R7 facility to the same level as the T7 facility, by implementing all of the major improvements that T7 had been built into the T7 design before its start-up in 1992.

All of the goals set at the start of the project were achieved: the doses to the personnel were 10% lower than those estimated, waste volumes generated by the modifications as well as costs were very close to those projected, and R7 resumed operation in March l995, 10 days earlier than planned.

Since the start of operations, the R7 and T7 facilities have demonstrated the industrial maturity of the French two step vitrification process. Nevertheless, AREVA and the CEA have been continuously improving its performance through consistent and long term R&D programs. The plant layout and maintenance concepts, already described previously, have played an important role in meeting these different objectives. The fact that each facility has three lines in parallel has enabled testing most major developments before deployment on all the vitrification lines.

Since start-up, outstanding records of operation have been established by the R7 and T7 facilities. These are given in Table 2 below.

TABLE 2: R7/T7 records of operation (end 2012)

Weight of glass produced since start-up (metric tons)	6 555
Number of canisters produced since start-up	16 885
Total activity immobilized since start-up (10^6 TBq)	280

In addition, the fundamental objectives targeted by the implementation of a strict QA/QC program have been reached: ensuring a reproducible, predictable quality for the wasteform throughout the lifetime of the plant, controlling its composition and activity content by a feed-forward approach, carefully identifying the process parameters that enable good quality and controlling those parameters during production, ensuring traceability and allowing oversight by the customer, the disposal organization and the regulator.

As of today, more than 3 000 canisters have been accepted and returned to AREVA various overseas customers.

New glass package to deal with different wastes characteristics

Recently, adapting to the needs for managing an expanded range of wastes, the AREVA and CEA integrated team (as part of their Joint Vitrification Laboratory) revisited the methodology and principles to be applied to the design of nuclear waste glass formulation while taking into account the extended industrial experience from La Hague facilities described above. The objective of the program was to enhance and optimize the formulations to fit various wastes characteristics while taking into account Long Term Behavior and technological constraints into an integrated approach.

METHODOLOGY FOR DESIGNING OPTIMIZED INDUSTRIAL GLASS FORMULATION FOR NUCLEAR HLW

A review of existing methods or standards related to the various aspects of designing, implementing a qualification process and studying long term behavior of a glass formulation reveal only scattered partial material missing the overall complexity of the field. Put together these methods and standards lack the level of integration required to provide a consistent way to elaborate the wasteform package meeting its final disposal environment from the early knowledge of the radioactive wastes to be dealt with.

The following methodology, based on the experience gained by CEA and AREVA in the various fields required to be part of this complex elaboration process, tries to provide such integrated view which should facilitate the relationships and discussions between the various stakeholders involved in the development of vitrification programs for HLW.

Any new glass must be accepted by the agency responsible for the waste repository and by the nuclear regulatory authorities before production can begin. An application must therefore be filed relying upon the following three aspects:

- Definition of a glass reference composition and optimization of the glass composition range,
- long-term glass behavior,
- process qualification in the frame of an industrial implementation

Optimization of the glass composition range

The work to be implemented as part of the design of an optimized glass composition domain can be decomposed in the following phases:

<u>Definition of the requirements to be accounted for</u>: All the requirements to be met during the formulation work must be collected. In particular, the requirements from the existing or selected process and technology must be reviewed (type of furnace, feeding management, canister geometry, etc.) to help defining operational parameters to be accounted for (e.g. temperature range, physical properties of the glass to be targeted, canister cooling profile). The composition of the waste must also be defined as precisely as possible (incl. a range of variation for the different species). Too large ranges specified due to lack of sampling / analysis can be detrimental to the incorporation performance of the glass to be designed. Radiological characterization of the waste should also be included at this step. Finally the constraints to be

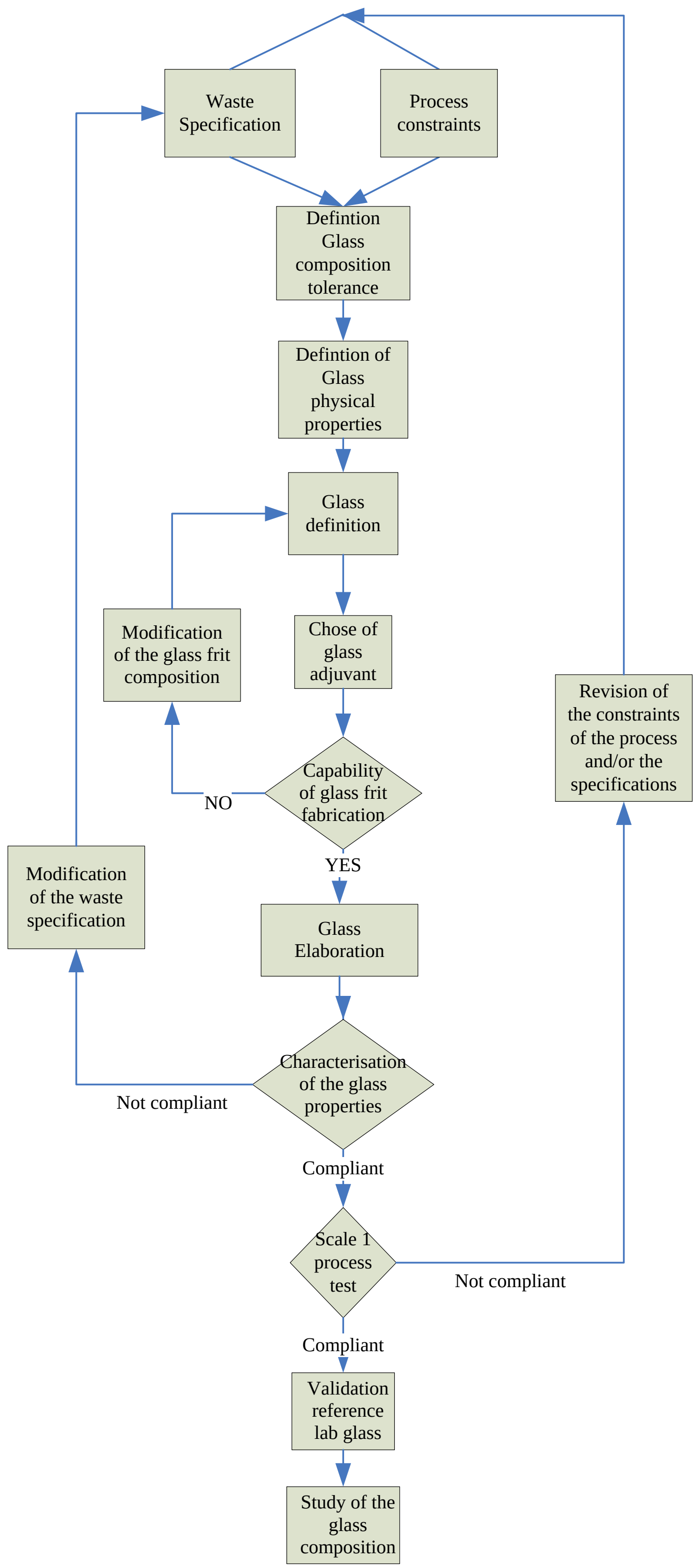
met in terms of Long Term Behavior must also be defined depending on the choices made for final disposal options. Ideally, it should be necessary to determine the requirements for the type of glass matrix sought (homogeneous, partially crystalline, etc.), the geological nature of the disposal environment, the composition of ground water etc.

Evaluation of the constraints critical for the glass formulation: The need to use specific process additives (e.g. reducing species, calcination enablers, etc.) must be considered early enough as these may generate constraints on formulation choices. An early evaluation of specific hard to manage species (e.g. Cl, S, etc.) in the waste composition must also be performed as this may significantly constrain the available options to design glass formula. Obviously major species in the waste must also be considered when planning for the glass formulation.

Definition of the formulation for the reference glass: This step includes (1) the production of a series of glasses on which minimal characterization is performed. Only the most promising glass formulation in terms of incorporation performances will be fully characterized (2) the characterization of physical and chemical properties of the selected glass known as the reference composition. The selection considers a central composition in relation to expected waste variations and optimal Long Term Behavior properties. This is performed as an iterative process implemented at lab scale; (3) the necessity or not to use a glass frit of given composition. In this case, availability and feasibility of the adequate glass frit must be checked with the supply chain; (4) the feasibility of manufacturing the glass at industrial scale with the same characteristic as the one produced at lab scale (including thermal stability, mechanical properties, physical properties, thermal properties, Long term behavior characteristics).

Feasibility testing on pilots: Further tests at pilot scale must then be performed to define the nominal operating parameters to be applied to manufacture the glass and check the stability of this operation at this scale.

Definition of the acceptable composition domain: Based on the anticipated variability of the waste composition, the glass frit and analytical uncertainties and on the expected variation during the manufacturing process at industrial scale, an acceptable composition domain will be defined within which the composition of the glass produced will be deemed acceptable regarding its mains properties (homogeneity, density, liquidus temperature, viscosity, etc.). The qualification of this domain is managed through appropriate and structured experimental plan to cover the required range.



Block diagram 1 : Glass Formulation Method

Long Term Behavior [3, 4]

High level waste (HLW) management requires being able to demonstrate the safety over geological timescales, typically several hundred thousand years. This can be made possible by using a rigorous, complex and iterative scientific approach called Long-term Behavior Science. The methodology relies on experiments and modeling. A large multi-scale approach is required and involves a mechanistic understanding of the key phenomena controlling the source term (i.e. the flux of radionuclides released from the waste as a function of time), as well as parametric studies, integrated and in situ tests. As a result, it is eventually possible to develop an operational model based on clever simplifications of a very complex reality, ensuring that predictions will always remain conservative despite conceptual and numerical uncertainties. Finally, predictive models must be validated based on the study of natural or archaeological analogues.

Long-term Behavior Science has been developed as a tentative answer to the intricate issue concerning the long-term (up to one million years) and wide-range extrapolation of elementary processes occurring at a local scale and leading to the release of radio-nuclides from waste forms. The aim is to establish a relationship between the evolution of the system and the various individual elementary mechanisms and to simultaneously rank these mechanisms in order to identify the governing mechanisms. Theoretical and experimental work must be performed until the development of a robust and reliable model that can finally be used for predictive purposes.

A consensus on results obtained from the field of Long-term Behavior Science could help make decisions on future disposal and provide standard support to glass formulation programs. The international scientific community decided recently to reinforce collaboration in this field.

Process Qualification in the frame of an industrial implementation [4]

The qualification of a glass in the frame of an industrial implementation follows the formulation studies as described above. The process qualification program includes five types of tests to specify the conditions necessary to obtain a material compliant with the requirements. In this section we will give examples relating to the glass matrix designed for immobilizing decommissioning effluents in the cold crucible melter at La Hague.

<u>Tests to determine the nominal operating parameters</u> guaranteeing the quality of the material fabricated at industrial pilot scale by final characterization of its physical and chemical properties compared with the same material synthesized in the laboratory.

<u>Two types of sensitivity tests:</u>

- A chemical composition sensitivity test similar to laboratory studies intended to synthesize the potentially most difficult glass composition to fabricate at full scale, considering the technological performance possible from the selected vitrification process.
- Tests of sensitivity to the operating conditions to specify possible parameter variation ranges acceptable for the material and for the process. For CCIM glass, the parameters are the temperature, the stirring speed and the bubbler air flow rate.

Transient mode tests to determine melter control parameters and ensure adequate product quality in any situation: the feed shutdown or calciner standby periods and the melter startup conditions were studied for Decommissioning Glass to be produced in the CCIM at La Hague.

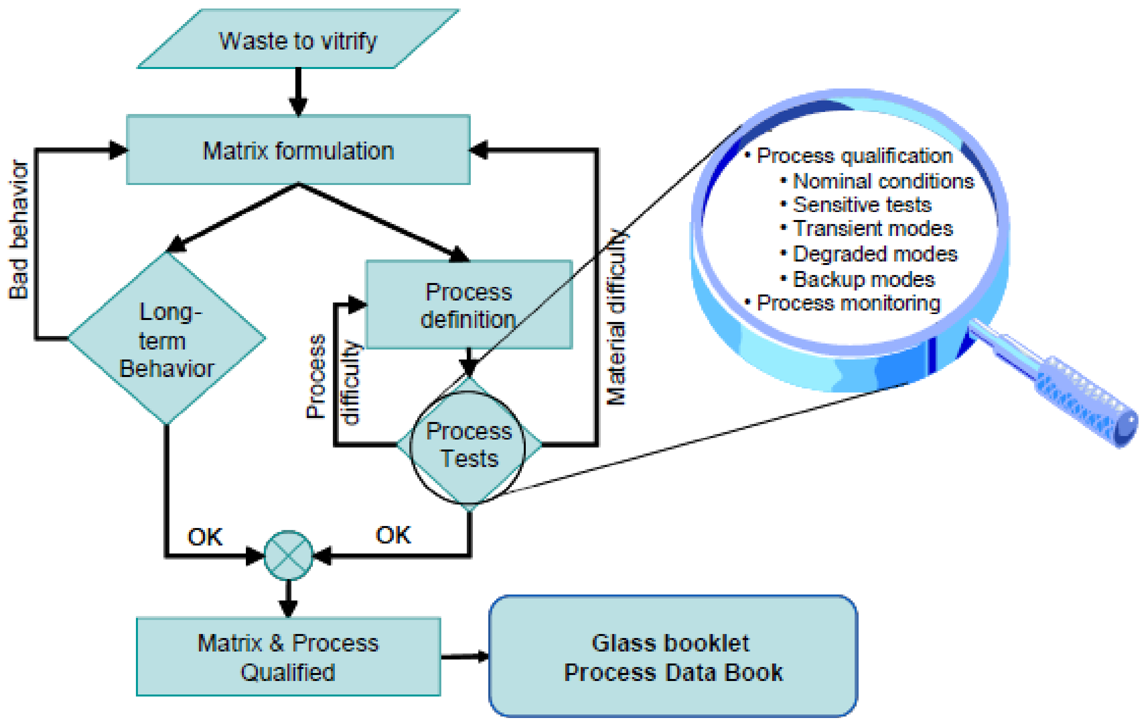
Degraded mode tests to identify procedures for offsetting or mitigating the impact of incidents on the material. Examples of degraded modes that can be investigated are:

- the impact on the material of an interruption in the glass frit feed;
- the consequences on the material of restarting a full melter following an unexpected stop

Extended long-term testing with the main objective of demonstrating that process operation is not subject to variation, that the operating conditions specified for nominal operation as well as during transient phases are applicable, and that the material properties remain constant over time.

The implementation of such program must focus on the critical properties and phenomena to be investigated according to the knowledge gained on the material during design and optimization phase of the composition range, the results of long term behavior studies and the specificities of the process to be implemented (e.g. rheological, electrical and thermal properties, risk of crystallization or phase separation, and presence of volatile compounds). These tests have to be carried out on an industrial scale or full scale pilot.

Fig. 1 Process and matrix qualification methodology



INDUSTRIAL QUALITY ASSURANCE AND QUALITY CONTROL PROGRAMS [5, 6]

The results and knowledge gained as part of the implementation of the previous programs will be critical to develop an adequate Quality Control and Quality Assurance program for the industrial facility to ensure:

- reproducible and predictable product quality and performance,
- reliable declared characteristics,
- traceability

Product quality is defined with reference to: matrix quality, canister and canister closure, removable contamination, cooling and storage conditions

Quality Control

Matrix quality. In view of the level of radioactivity of the material, routine analysis and testing of the glass product would be virtually impossible: it would be a time-consuming operation, which would subject the personnel to unnecessary radiological exposure. Moreover, rework of the product, if non-compliant, would not be practical. As a result, it has been decided to rely on “before the fact” process control, similar to the approach used in other facilities (such as Savannah River for instance), in order to avoid conditions leading to an eventual non-conforming product. This approach is supported by the extensive qualification work prior to facility commissioning described above, and the implementation of a rigorous quality control scheme.

Glass composition is controlled by controlling several process parameters, e.g.:

- HLW solution composition: the adjusted solution in the feed makeup tank is sampled and analyzed and calculations are performed to determine the target waste loading and heat release. The batch is cleared for transfer to the feed tank only if the adjusted batch allows producing an acceptable glass.
- Feed homogeneity: the feed tank is continuously stirred at a specified rotation speed in order to keep a homogeneous composition throughout the processing of the batch.
- HLW feed rate: the HLW solution is continuously fed by a measuring wheel. Direct parameters as well as double-check parameters are monitored to ensure an adequate feed rate. In a case of a two step process, the calciner parameters are also monitored (i.e. in La Hague process), to ensure adequate calcine quality.
- If fed separatly, the frit feed rate is also controlled and monitored in conjunction with the HLW solution feed rate, and verified by regular weighing of the feeding hopper. The frit is subjected to a strict procurement and acceptance process.

Canister cooling in the storage vaults must be performed so that the glass centreline temperature never exceeds 510°C in the French context. The canisters are stored in cooled wells. The air outlet temperature of the storage facility is monitored continuously and extra cooling systems can be activated if required.

Canister tracking: the uniquely identified canisters are tracked through the process using a video monitoring system and the operating control system.

Quality Assurance

A Product Specification document describing the expected characteristics of the product has been established. In addition to a description of the product, the specification provides some "guaranteed parameters" related to the above process functions which must be complied with in order to certify each canister as compliant. These guaranteed parameters include the chemical composition of the glass, the per canister radioactive concentrations (e.g. for Cs-137, Sr-90, for actinides) and some characteristics of the canister (dimensions, materials of construction, removable surface contamination, and heat release at the time of dispatching).

For R7/T7 glass, the Glass Residue Specification has been approved in July 1986 by the French Nuclear regulatory Authority and by ANDRA, the organization in charge of HLW disposal in France. The specification has been subsequently approved by the customers in Belgium, Germany, Japan, the Netherlands and Switzerland. A full Quality Control/ Quality Assurance program, complying with ISO-9002 requirements, has been implemented to ensure compliance and traceability for all important aspects relating to product quality. This program covers all aspects:

- ☐procurements (glass frit, materials for the canisters, fabrication of the canisters, swab pads for smear test machine, welding torches);
- procedures (operations, maintenance analytical laboratory...);
- ☐documentation: each canister is accompanied by complete QA documentation containing all the pertinent data relating to its production, including analytical results on the adjusted feed solution, the glass composition calculation sheet, and a description of processing operations for the corresponding glass batches. This documentation is thoroughly reviewed by AREVA before granting a certification for shipment and disposal.

The QA/QC program related to R7/T7 has been reviewed by ANDRA (the French National Agency for Radioactive Waste Management), acting on behalf of the Safety Authorities, during the Licensing Process for the facilities. An independent QA auditing company (Bureau Veritas), acting on behalf of AREVA's customers, regularly verifies the quality of the final product through inspections and audits. The foreign customer also performs inspections at the time of dispatching.

CONCLUSIONS

AREVA and CEA benefit from a long experience in developing vitrification solution to manage HLW covering a broad field of competencies from R&D to plant operation through engineering, technical development, glass formulation and long term behavior.

Based on this experience, an integrated approach is proposed for designing optimized glass formulation with respect to a given waste and for qualifying the glass product in the frame of industrial implementation. This approach is covering every important aspect needed to reach satisfactory wasteform performance and ensure ability to manufacture such waste form at industrial scale on the long term.

This work is leading the way for a close collaboration with the BNEN, the part of the French national standardization body AFNOR working on the development of standards in the nuclear domain

Several guides are expected: The first one will cover the procedure for designing a formulation that is the best compromise between ability to accommodate waste composition and variability, ease of manufacturing in the proposed industrial vitrification technology, and optimal long term durability. Later, two other guides describing (1) the process for qualifying a process and glass product for industrial production and (2) the implementation of long term behavior studies will be drafted.

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