

## **DEVELOPMENT OF VITRIFICATION PROCESS AND GLASS FORMULATION FOR NUCLEAR WASTE CONDITIONING**

V. Petitjean  
COGEMA  
2, rue Paul Dautier,  
78141 Vélizy cedex– FRANCE

C. Fillet ; R. Boen  
CEA- VALRHÔ –MARCOULE  
BP 171  
30207 Bagnols sur Seze cedex - France

C. Veyer ; T. Flament;  
SGN  
1 rue des Hérons – Montigny le Bretonneux  
78182 Saint Quentin Yvelines cedex– FRANCE

### **ABSTRACT**

The vitrification of high-level waste is the internationally recognized standard to minimize the impact to the environment resulting from waste disposal as well as to minimize the volume of conditioned waste to be disposed of. COGEMA has been vitrifying high-level waste industrially for over 20 years and is currently operating three commercial vitrification facilities based on a hot metal crucible technology, with outstanding records of safety, reliability and product quality. To further increase the performance of vitrification facilities, CEA and COGEMA have been developing the cold crucible melter technology since the beginning of the 1980s. This type of melter is characterized by a virtually unlimited equipment service life and a great flexibility in dealing with various types of waste and allowing development of high temperature matrices.

In complement of and in parallel with the vitrification process, a glass formulation methodology has been developed by the CEA in order to tailor matrices for the wastes to be conditioned while providing the best adaptation to the processing technology. The development of a glass formulation is a trade-off between material properties and qualities, technical feasibility, and disposal safety criteria. It involves non-radioactive and radioactive laboratories in order to achieve a comprehensive matrix qualification.

Several glasses and glass ceramics have thus been studied by the CEA to be compliant with industrial needs and waste characteristics: glasses or other matrices for a large spectrum of fission products, or for high contents of specific elements such as sodium, phosphate, iron, molybdenum, or actinides. New glasses or glass-ceramics designed to minimize the final wasteform volume for solutions produced during the reprocessing of high burnup fuels or to treat legacy wastes are now under development and take benefit from the latest CEA hot-laboratories and technology development. The paper presents the CEA state-of-the-art in developing matrices or glasses and provides several examples.

### **INTRODUCTION**

Vitrification of high-level liquid waste is the internationally recognized standard to both minimize the impact to the environment resulting from waste disposal and the volume of conditioned waste. Many countries such as the USA, France, the United Kingdom, Germany/Belgium, Japan, Russia, have vitrified high level waste and several more countries are studying application of the technology.

In France, the vitrification of high-level liquid waste produced from nuclear fuel reprocessing has been operating now for more than 20 years with three major objectives: durable containment of the long-lived fission products, minimization of the final waste volume, and operability in an industrial context. As a result, COGEMA, SGN, and CEA, as a team, integrate a unique experience in the field of high-level waste vitrification through:

- The design and operation of facilities with high records of safety, reliability and product quality, in line with efficient reprocessing plants
- The design of various glass formulations including those used in the AVM, R7 and T7 facilities which, together, have produced more than 11,000 glass canisters up to now
- Continuous efforts to improve at the same time the technology (from hot to cold crucible) and the associated matrix formulations, with constant emphasis on quality and volume reduction.

Since the launching of HLW vitrification programs by the CEA in the late 50's, the partners have developed a unique and integrated scientific and technical approach for the implementation of waste vitrification. This approach benefits from a very close relationship between COGEMA, the CEA and SGN, with continuous mutual support and interactions. This working methodology has also been extended to the field of Low and Intermediate Level waste processing.

Several publications have been focused in the recent past on the description and advantages of the CCM for various applications (1). In the present paper, we will focus on the other major, closely connected aspect: matrix design.

## **EFFICIENT MATRIX DESIGN IS RELATED TO THE CAPABILITIES OF THE TECHNOLOGY**

### **Formulation constraints**

The development of matrices for the containment of radionuclides must account for several constraints, the importance of which may vary according to the application:

The matrix must accommodate the given waste composition, and the waste loading must be optimized: the characteristics to be considered are the solubility of the various constituents, phase separation phenomena, and devitrification.

The long-term behavior of the matrix in the future storage and disposal environments must be satisfactory: thermal stability, resistance to irradiation, chemical durability, and mechanical properties. The CEA, driven by the requirements of the French Safety Authorities, in the frame of the French waste management program, has accumulated a unique knowledge for the identification and design of durable matrices.

The matrix must be processed easily in the given technology: the traditional parameters such as melting temperature, viscosity, electrical conductivity, must of course be mastered. In addition, specific care must be applied to the general behavior of the feed in the process, a fact that can be influenced by the formulation of the matrix and of the corresponding additives. In the end, the proposed matrix must be compatible with the materials of the melter.

### **New challenges for vitrification processes**

Of the above constraints, those associated to the technology are often the most limiting.

The achievable melting temperature is one major limit for glass formulation. The possibility to operate routinely at temperatures significantly higher than 1150°C can be a major advantage in terms of waste loading, especially when the feed is rich in insoluble elements, or in elements that increase viscosity (such as alumina). In addition, the possibility to accept higher contents of refractory elements, such as zirconia, alumina or silica, allows considering glass formulations that have an improved long-term chemical durability. In the end, with high temperatures, it is possible to consider other matrices, such as ceramics or glass-ceramics, which may be better adapted than borosilicate glass to some specific types of waste (such as zirconia-rich waste), or designed to provide a superior long-term durability (such as silicotitanate ceramics).

One other limiting factor is the sensitivity of the melter to corrosive elements (sulfate, molybdenum, fluorine, phosphate). In traditional LFCMs or hot crucible melters, it is necessary to limit the corrosiveness of the melt. This

sometimes precludes processing some feeds or some matrices (such as phosphate-based matrices, for instance). A corrosion-resistant melter thus widens the range of matrices and feeds that can be processed.

The last major limiting factor is the ability of the melter to tolerate insoluble materials. For some feeds and some melter types, the waste loading will be limited by the necessity to limit the formation and settling of insoluble sludges that may disturb or even prevent melter operation.

These three limits have been identified quite early and efforts have been under way for a long time now, in many countries (USA, France, Germany, Japan, Russia), to widen the acceptable operational range and thus, the flexibility of the melters with regard to waste composition. This effort, started in France in the beginning of the 80's, ended up with the design and qualification of the presently proposed CCM, which combines features favorable towards all of the three above major limiting factors.

The CCM is a water-cooled induction heated melter in which the glass is melted by direct high frequency induction. The cold wall (a protective, corrosion-resistant glass layer) is formed during start-up of the melter. Since the heat is transferred directly to the melt, high operating temperatures can be reached with no impact on the melter itself. Since the CCM is water-cooled and since there is practically no upper bound on the operating temperature, it can process melts that are either too corrosive, too viscous or too refractory for the standard ceramic type or hot metallic crucible melters. Some silicotitanate melts, for instance, were processed at temperatures of about 1500°C.

The CCM is equipped with a mechanical stirrer directly derived from those used in the presently operating La Hague facilities, which allows providing a good homogeneity of temperature and composition and enables high throughputs.

The CCM is also more tolerant than traditional large size ceramic melters towards the accumulation of insoluble materials such as spinels, chromite or noble metals in the melts, since it combines all of the favorable features identified in recent or less recent publications for that purpose (2, 3):

- High temperatures in the melt,
- Short residence time in the melter,
- Mechanical stirring of the melt,
- Bottom discharge.

In addition to HLW conditioning, a vitrification process based on the CCM can also be used for other types of radioactive (low level, intermediate level, transuranic) or mixed waste with varied chemical and physical waste forms including liquids, slurries, sludges, solids and mixtures of these physicochemical forms.

Indeed, the introduction of this technology has opened new perspectives and enabled the CEA to design a totally new range of matrices for very varied applications.

## **50 YEARS OF EXPERIENCE IN DEVELOPMENT AND QUALIFICATION OF CONTAINMENT MATRICES**

In parallel to the development of vitrification processes, based on research performed on containment matrices (especially glasses) since the 1950's, the CEA has developed a formulation methodology that has evolved according to the progress in technology and in the knowledge of matrix behavior in disposal conditions.

Among the major glass formulation achievements of the CEA one can list, for instance, the well known R7T7 formulation for raffinates arising from the reprocessing of commercial LWR fuel in the La Hague facilities. This formulation has undergone all the steps of qualification for commercial industrial production (4). The resulting vitrified product has been accepted by the French and Foreign Safety Authorities. Owing to the very close relationship between the matrix and technology developers at all stages of its development and qualification, this matrix has now been successfully processed in the two La Hague vitrification plants, R7 and T7, for more than 10 years with more than 8250 canisters produced. Radioactive samples have been taken and satisfactorily characterized by both CEA and the Japanese client (5). In addition, the R7T7 formulation has become a worldwide reference for matrix durability. Another fully qualified matrix developed by the CEA has also been processed industrially in the AVM facility of Marcoule, for French applications.

## Formulation methodology

Glass formulation must provide an acceptable composition domain to be processed in an industrial plant. The definition of this composition domain accounts for:

- The composition of the feed solution and its possible variations,
- The quality requirements fixed by specification or by regulation.
- Ease of processing. The required characteristics are dependent on the technology.
- Waste loading optimization and limits fixed by the specification.

The methodology used by the CEA for glass formulation involves 4 aspects:

Formulation of a reference composition: at first, in view of the composition of the feed and of its possible variations, a preliminary glass composition domain is defined. Best use is made at that time of the knowledge database accumulated since the beginning of wasteform formulation activities at CEA. In addition, for some specific problems, completely new matrices may also be developed, as it is the case, for instance, for ceramics or glass-ceramics.

Among the characteristics evaluated during this screening phase, one can list fusibility, processability characteristics, crystallization characteristics and leach characteristics (Soxhlet testing to have an indication of the initial dissolution rate of glass and powder leach testing to understand the approach to "saturation" conditions). A reference (or baseline) composition is then selected.

It should be underlined that, from that early stage, the leach behavior of the matrix, estimated by several types of tests, is accounted for in the screening process. Although one cannot predict at that stage what will be the exact long-term behavior of the matrix, it is possible to get helpful indications from this combination of preliminary testing, based on comparisons with a large range of other matrices of known behavior.

Detailed characterization of the reference composition, in order to validate the ease of processing in the given technology and to provide data for the establishment of the vitrified product specification. Physical, chemical and durability characteristics are measured (density, heat conductivity, electrical conductivity, transformation temperature, liquidus temperature, leach rates, volatility, thermal expansion, Young's modulus, temperature of maximal crystallization...). This characterization involves several types of samples: characterization of non-radioactive crucible melts at the laboratory scale, characterization of radioactive crucible melts to demonstrate that the characteristics of the radioactive glass are the same as those of the glasses made with simulants, characterization of non-radioactive glasses produced on large size (full scale) pilots, to demonstrate that the characteristics of the glass produced at large, representative scale are the same as those of the glass produced in the laboratory. In addition, for the R7 and T7 facilities, radioactive samples were taken after the hot start-up of the facilities, and characterized to confirm that the product displayed the expected characteristics.

Sensitivity to composition and operating conditions, to finalize the acceptable glass composition range.

In parallel with the characterization of the reference composition, sensitivity testing is carried out, at first at the laboratory scale. Two methods can be used. In some instances parametric studies, which test some specific ranges of variations, are enough. These can include systematic variation of single or several components, or of the waste loading. More recently, a method involving empirical modeling of glass properties vs. composition using computer-aided statistical treatments has been developed. Based on previous knowledge, a first or second-order model taking into account the major interactions liable to exist between some constituents is postulated. Specifically selected glass compositions are melted and characterized to obtain the coefficients for these relationships. The minimum number of compositions is selected using the NEMROD software tool (6). The coefficients of the "property versus composition" model are obtained by applying linear regression on experimental responses. The model is then validated on test points not used to determine the model coefficients and located into the composition range. If the model is found too imprecise, higher order models can be postulated and calculated using additional compositions. This approach considerably optimizes experimental efficiency and minimizes the number of melts required when the composition domain to be investigated is large. This approach has been used, for instance, to qualify the AVM formulation range.

In addition, and because the scale and conditions of these laboratory tests are very different from what happens in a real process, sensitivity testing is also performed on the large size pilots, to further define the acceptable composition range and account for variations in the chemical composition of the solutions and in the process parameters.

The result of these sensitivity studies is the definition of an allowable domain within which the glass displays all the required qualities while being easily processable in the given technology.

A fourth part of the glass characterization, required for its acceptance, is the evaluation of its long-term performance. This stage includes irradiation stability, thermal stability, and long-term leach testing. This stage is necessary to provide information to the organization in charge of disposal (ANDRA in France), for incorporation into the Safety Analysis of the future disposal site.

For the R7T7 glass, for instance, a first performance assessment has been performed by ANDRA using, as a bounding hypothesis, a constant dissolution rate equal to the initial rate of glass alteration. It was found that the regulatory constraints were achievable, even with this very conservative assumption. Efforts are under way, now, to quantify and model more precisely the long-term rate of glass alteration in order to be able to take advantage of the attenuation that is effectively observed in the long term for this glass and, thus, optimize the design of the disposal facility.(7)

Irradiation stability is evaluated mainly by studying glasses doped with alpha and/or gamma emitters, and assisted by numerical methods to understand the mechanisms.

Thermal stability is studied by subjecting the glasses to various types of heat treatment to identify the critical temperatures (liquidus, maximum crystallization temperature) and the maximum amount and nature of the crystals formed.

### **The tools**

In order to carry out these studies, the CEA has been equipped with various tools, most of which are situated on the same site of Marcoule, a fact which allows easy interaction among the various workers:

- Non-radioactive laboratories are able to melt samples of various sizes, up to several kg. These laboratories are equipped to carry out the full characterization of these matrices.
- Non-radioactive laboratories specialize in the assessment of the long-term behavior of matrices, with standard water-based tests, but also with capabilities to operate tests simulating closely the environmental conditions of the disposal site.
- A radioactive facility, the DHA (8), recently started in the ATALANTE plant, where fully radioactive glasses can be fabricated using either a small mock-up of the La Hague process or a conventional crucible able to reach temperatures as high as 1500°C. In the DHA, equipment is also provided to characterize these radioactive samples: sample preparation, physical measurements (mechanical properties, gamma scanning, density, thermal conductivity, macroscopic examination), heat treatment, calorimetric measurements, leach behavior (short- and long-term, static or dynamic), microstructure characterization and microprobe analysis ...
- A test hall is equipped with pilots of various sizes and with various set-ups, that range from stand-alone CCMs with simplified off-gas treatment, for process and matrix evaluations to full size pilots with complete feeding and off-gas systems (with or without calciner), for full scale process demonstrations and wasteform qualification.

### **SOME APPLICATIONS**

During the 50 years of matrix development, many types of wastes have been studied, with a very wide range of compositions. The older programs have been focused on the hot crucible technology implemented in the AVM facility at Marcoule and the R7 and T7 facilities at La Hague. Those facilities feature induction-heated metallic hot crucibles operated at 1150°C coupled to continuous rotating calciners. Since the 80's, new developments have been performed in relation with the CCM, both with calcine or liquid feeding.

### **Matrices that can be produced in the hot-crucible technology**

The hot crucible technology is well adapted to the production of borosilicate glasses at typical temperatures of 1150°C.

#### Development of the R7T7 glass

The work to immobilize HLW has been started in 1957. The CEA has first investigated several types of matrices among which crystalline materials, phosphate glasses and borosilicate glasses. It was found rapidly that borosilicate glasses were the best adapted to the immobilization of fission product solutions resulting from the reprocessing of LWR fuel using a PUREX-type process.

The studies, which lasted for several years, were based on several hypotheses regarding the composition of the feed and evolving sets of criteria. As a result, a large number of compositions were tested in the silica-boron-soda system, including glasses with very high waste loadings. The influence of several constituents has been investigated (iron, gadolinium, lithium, zinc, aluminum, calcium, molybdenum, phosphate, magnesium, titanium, zirconium, tin...). These studies, which involved the fabrication of hundreds of non-radioactive and radioactive melts, enabled the accumulation of a very large knowledge database.

The final formulation, which is produced in the presently operating R7 and T7 facilities at La Hague, is the well known "R7T7" or "SON 68" (the contraction of SON 68 18 17 L1C2A2Z1) glass. The maximum oxide waste loading for this glass is 28 %, which corresponds to a maximum of 18,5 % of radioactive waste oxides (fission products, actinides, noble metals and Zr). The waste loading in this case is limited by the heat output to avoid devitrification during storage and to comply with the allowable heat rating at the time of transport (2 kW for a 400 kg glass canister). The quality criteria used during this formulation work were focused on glass homogeneity, leach behavior, thermal stability and physical properties.

#### Future evolutions to account for higher burnup fuels

The present reference fuel reprocessed in the La Hague plants has a burn-up of 33.000 MWd.t<sup>-1</sup>. The waste loading in the glass is such that between 0.54 and 0.7 glass canister is produced for each ton of fuel. In the future, fuels with higher burn-ups will be reprocessed: 45.000 or even 60.000 MWd.t<sup>-1</sup>. These fuels will contain higher amounts of fission products and actinides, a fact that may lead to the production of a larger number of glass canisters per ton of fuel reprocessed. COGEMA, complying with its policy of waste volume minimization, is now considering the possibility of increasing the waste loading for these solutions.

The first step of the study consists in trying to optimize the present formulation in order to accommodate the modified waste composition. For intermediate burn-ups, it may be possible to limit the volume increase to a reasonable figure while remaining in the presently defined domain.

To confirm this hypothesis, a program has been started to study the effect of increased irradiation levels on the long-term stability of the matrix. Glasses with the R7T7 composition doped with Cm-244 oxides at levels of 0.043wt%, 0.43wt%, and 1.5wt% are now being fabricated and characterized. These glasses will be periodically characterized to determine the effect of the dose rate and of the cumulated dose on their evolution.

For higher burn-ups, in order to limit the volume increase, it might be necessary to change the formulation, and to increase the melting temperature (see below).

#### The AVM glass

The AVM facility at Marcoule, the first industrial vitrification facility ever operated in the world, based on the same process as the R7 and T7 facilities of La Hague, has vitrified solutions arising from the reprocessing of various types of fuels in the UP1 facility. The borosilicate glass compositions produced could contain up to 1.8wt% fluorine, 7.5wt% magnesium oxide, 1.7wt% phosphate or 12.5wt% alumina. For this wide operating range, property-composition models have been established.

### **Matrices that can be produced in a CCM**

As described above, the availability of the corrosion-resistant, solids- tolerant and high temperature CCM allows a considerable extension of the composition domain available for vitrification. This technology provides a unique tool to stabilize difficult wastes with optimized waste loadings.

#### *New matrices requiring high temperatures for the incorporation of fission product solutions from high burn-up fuels*

As described above, for the higher burn-up fuels to be reprocessed at La Hague, a new formulation will have to be designed. Apart from the heat rating, the major limiting elements are cerium and molybdenum, which are difficult to digest at low temperature. As a result, an increase in melting temperature will be required to dissolve higher amounts of this waste composition in a glass. This matrix must also be able to resist a higher heat load, since this parameter may also become limiting. Studies have now started to formulate a new matrix that can be melted in a CCM in a temperature range of around 1300°C. An additional, very favorable, feature of the CCM in that case is the presence of the mechanical stirrer, which, by providing a very good thermal homogeneity, prevents the separation of a molybdate phase on cold spots.

#### *Matrix for the vitrification of corrosive, difficult to dissolve molybdenum-rich effluents*

At La Hague, some legacy solutions derived from the reprocessing of spent Mo-Sn-Al fuels in the former UP2-400 plant are still being stored. COGEMA is committed to stabilize these wastes, which are much less radioactive than the current fission product concentrates, but are very rich in molybdenum

Such high amounts of molybdenum cannot be accommodated in the present R7T7 glass formulation, or would lead to unacceptable volumes of low activity glass. It has thus been decided to design a new glass formulation. This calcium and zirconium-enriched aluminoboro-silicate matrix, able to incorporate 12wt. % of molybdenum oxide, is corrosive due to its phosphate and molybdenum contents and must be melted at temperatures close to 1300°C, which cannot be reached with the present hot crucible melters.

To prepare the replacement of one of the hot melters of the R7 facility by a cold-crucible melter able to process this new matrix (still coupled to the calciner), a full-scale pilot has been implemented in the test hall of Marcoule and is now being used to perform the tests necessary for wasteform optimization and qualification.

#### *The ENEA program for MTR wastes*

The Italian organization ENEA has selected the CCM technology to vitrify a backlog of legacy waste resulting from the reprocessing of MTR fuel. The objective of the program is to design, build and commission a vitrification facility in an existing hot cell in the EUREX plant. Limited space has led to the selection of a liquid-fed CCM due to its very compact size and the possibility of avoiding a pre-treatment step. The liquid feed is in the form of a nitric solution with significant levels of sulfur and uranium.

The proposed wasteform is a borosilicate glass in the composition domain of the AVM matrix, with an average SO<sub>3</sub> content of 0.5wt% and uranium levels of about 7wt%. The glass qualification program is under way, with a full-scale demonstration already performed with the baseline composition on the full-scale pilot and laboratory work in progress to qualify the whole expected operational range. The melting temperature is around 1280°C.

#### *Vitrification of LLW and ILW with high contents of sulfur*

When considering the application of vitrification to new types of wastes the amount of sulfur can be a recurrent limiting factor. Sulfate has a limited solubility in glass and tends to form a separate molten salt phase at the surface of the melt. This molten salt phase is not desirable, since it is soluble in water and tends to concentrate some fission products. It may also have an impact on the throughput of the melter.

Two methods are considered to avoid this phenomenon:

- The volatilization of sulfur-bearing species can be promoted by introducing reductants in the feed or by increasing the melting temperature. The introduction of reductant in the feed, however, needs to be controlled very carefully to avoid over-reducing the melt and the associated operational difficulties, especially in electrode-heated melters. With the CCM, a significant amount of sulfur volatilization can be achieved more simply by raising the melt temperature. In both cases however, the off-gas system must be designed to separate this sulfur stream from the rest of the entrained elements to limit sulfur recycling into the melter.
- Sulfur can be incorporated into the glass. Conventional borosilicate glasses can only accommodate a limited amount of this element. New types of formulation must be considered.

For several years now, the CEA has launched a specific program to incorporate sulfur in the glass. This program resulted in a glass able to incorporate more than 1.5 wt% SO<sub>3</sub> during a full-scale pilot test using a liquid-fed CCM operated at 1200°C.

#### Studies for US applications that require optimized waste loadings

Since the mid-90's, in the frame of the various US programs, studies have been performed on a wide number of waste compositions, among which Hanford and Idaho-type compositions.

During the Hanford TWRS-P phase IA program, for instance, in collaboration with PNNL, two very good quality borosilicate glasses had been designed for melting at temperatures around 1200°C with waste loadings of 32 and 44 wt%, as required by the contract. (9) Two pilot-scale demonstrations were performed using a CCM coupled to a calciner. Since then, direct liquid feed has been successfully tested for both effluents and the same glasses with very good capacities (10). Some modeling and laboratory studies have indicated that higher waste loadings could be achieved (more than 40% and more than 50 % respectively, with melting temperatures that can reach 1300°C).

Some preliminary studies have also been performed with Idaho-calcine formulations. These studies have demonstrated that waste loadings of 40wt% and 30wt% could be achieved for the Zr-rich and Al-rich calcines respectively. The CCM, with its corrosion resistant shell and its ability to reach high temperatures is particularly well adapted for waste loading optimization with this type of waste. The next step for waste loading increase with Idaho-waste could also be to formulate glass-ceramics that would allow waste loadings of the order of 60% for some calcines.

#### Development and characterization of matrices tailored for specific radionuclides

In the framework of the French program for the management of nuclear waste, one option considered is the separation of minor actinides and other long-lived elements and their immobilization in dedicated matrices. The availability of the CCM able to operate at very high temperatures allows considering a new, easy, processing route for ceramics and glass-ceramics: the melt/controlled-cooling route. Several matrices are now under study in collaboration, notably, with the ANSTO, with specific emphasis on microstructure and leach behavior characterization:

- Synroc-type ceramics that can be melted at temperatures as high as 1600°C (11).
- Zirconolite ceramic produced by rapid cooling of a melt produced at 1600°C from an oxide mixture with the stoichiometry of zirconolite. This matrix is considered for the immobilization of actinides.
- Zirconolite-based glass ceramic produced by heat treatment of a parent aluminosilicate glass containing titanium, zirconium and neodymium oxides molten at 1450°C from a mixture of oxides (12-15). This matrix is considered for the immobilization of actinides.
- Various other types of glass ceramics, that can be melted at temperatures ranging from 1300 to 1500°C.



## CONCLUSIONS AND PERSPECTIVES

Through 50 years of experience, the CEA has accumulated a unique knowledge for the formulation of immobilization matrices. The major objectives of the methodology implemented at the CEA, in partnership with COGEMA and SGN, include optimization of the waste loading, ease of processing in an industrial plant and long-term stability of the matrix. The close relationship that exists between the various partners of the vitrification team (matrix design, process design, plant design and operation) allows an efficient integration of all available knowledge for all the aspects of the programs, including of course matrix formulation.

The introduction of the CCM technology has opened completely new perspectives in terms of matrices for waste immobilization, while it allows keeping a simple and easily operable melting process very similar to those operated successfully for more than 20 years now. Since the limits of temperature, corrosiveness and tolerance to solids are pushed backwards, it becomes possible to consider new wastes that could not be processed in a classical melter, significant improvements of waste loadings for classical wastes, and wasteforms with improved durability for very long-term containment of specific radionuclides, such as ceramics or glass-ceramics.

## REFERENCES

1. R. BERA, R. DO QUANG, A. JENSEN, J. LACOMBE, G. MEHLMAN – “*The cold-crucible Induction Melter: an innovative vitrification technology*” – SPECTRUM 2000
2. J.M. PEREZ, D.F. BICKFORD, D.E. DAY, D.S. KIM, S.L. LAMBERT, S.L. MARRA, D.K. PEELER, D.M. STRACHAN, M.B. TRIPLETT, J.D. VIENNA – R.S. WITTMAN – “*High-Level waste melter study report*” – PNNL-13582 – July 2001
3. D.KIM, P. HRMA – “*PNL vitrification technology development project – high waste loaded high-level waste glasses for high temperature melter: letter report.*” – PNNL-10984 – February 1996.
4. J.L. DEVAUX, D. JEAN, L. BAILLIF – “*Industrial HLW immobilization in glass in France: vitrified waste characterization and quality control program.*” – IAEA-SM-326/42 – Antwerp, Belgium – 1992.
5. P. CHERON, P. CHEVALIER, R. DO QUANG, G. TANGUY, M. SOUROUILLE, S. WOIGNER, M. SENOO, T. BANBA, K. KURAMOTO, T. YAMAGUCHI, K. SHIMIZU, C. FILLET, N. JACQUET-FRANCILLON, J. GODARD, J.L. DUSSOSSOY, F. PACAUD, J.G. CHARBONNEL – “*Examination and testing of an active glass sample produced by COGEMA*” – Materials Research Society Symposium Proceedings Vol.353 – 1995
6. D. MATHIEU, R. PHAN TAN LUU, “*NEMROD software package*” – LPRAI Marseille
7. F. PLAS, Z. ANDRIAMBOLOLONA – “*Exposé de l'ANDRA*” – in CEA-VALRHO summer session Proceedings “*Glass – Scientific research for high performance containment*” – Méjannes-le-Clap – August 31<sup>st</sup> – September 7<sup>th</sup> 1997.
8. J.M. BART, J.G. CHARBONNEL, S. PEUGET, V. BROUDIC, C. JEGOU, T. ADVOCAT – “*A new research facility devoted to highly radioactive materials*” – Atalante 2000 – Avignon, France – October 2000
9. E. NICAISE, C. VEYER, S. GOETGHEBEUR, P. HRMA, E.V. MORREY, G.L. SMITH, J.D. VIENNA, J.L. DUSSOSSOY, C. LADIRAT, A. LEDOUX, M. PUYOU – “*Hanford high-level waste processing in a cold-crucible melter: test results obtained in the framework of the TWRS-P contract*” – WM'99 – Tucson – 1999
10. C. LADIRAT, C. FILLET, R. DO QUANG, C. VEYER, G. MEHLMAN, T. FLAMENT – “*The cold-crucible melter: a key technology for the DOE cleanup effort.*” - WM'01 – Tucson – 2001
11. T. ADVOCAT, G. LETURCQ, J. LACOMBE, G. BERGER, R.A. DAY, K. HART, E. VERNAZ, A. BONNETIER – “*Alteration of cold-crucible melter titanate-based ceramics: comparison with hot-pressed titanate-based ceramic.*” – Scientific Basis for nuclear waste management XX – Boston – December 2-6, 1996
12. T. ADVOCAT, C. FILLET, J. MARILLET, G. LETURCQ, J.M. BOUBALS, A. BONNETIER – “*Nd-doped zirconolite ceramic and glass ceramic synthesized by melting and controlled cooling.*” - Scientific Basis for nuclear waste management XXI – Davos, Switzerland – September 28-October 3, 1997
13. P. LOISEAU, D. CAURANT, N. BAFFIER, C. FILLET – “*Neodymium partitioning in zirconolite-based glass-ceramics designed for minor actinides immobilization*”- Atalante 2000 – Avignon, France – October 2000
14. P. LOISEAU, I. TOUET, D. CAURANT, Y. DEXTRE, C. FILLET – “*Characterization of the microstructure of zirconolite-based glass-ceramics.*” - Atalante 2000 – Avignon, France – October 2000
15. G. LETURCQ, T. ADVOCAT, P.J. McGLINN, K. HART – “*Intrinsic kinetic parameters controlling the long-term chemical durability of zirconolite-based ceramics and glass-ceramics.*” Atalante 2000 – Avignon, France – October 2000