

A MAINTENANCE METHOD FOR THE EXHAUST VALVES ON THE ALPHA-TIGHT HOT CELL UNDER A VENTILATING CONDITION

YASUTAKA MIZUKOSHI, NAOYA KUSHIDA
Japan Atomic Energy Agency (JAEA)
4002 Narita-cho, O-arai-machi, Ibaraki-ken, Japan

ABSTRACT

Alpha-tight hot cells are located at the Fuels Monitoring Facility, Oarai Research and Development Center, Japan Atomic Energy Agency. These cells have a containment capability for nuclear materials. A safe and efficient maintenance method for the exhaust valves under a ventilating condition has been developed.

Conventionally, when exhaust valve maintenance work is done for the hot cell, it is necessary to stop the ventilation during the work. From prior experiences, it is known that this work involves large risk to workers due to the long time needed, and much cost, and produces much radiation waste. Therefore, a new method of valve maintenance under a ventilating condition was desired to reduce those items.

A provisional exhaust system to maintain the negative pressure in each hot cell without stopping the existing exhaust system operation was installed for use during maintenance of these valves. This led to reductions of the work period, cost, and generated radiation waste volume of 1/3, 3/5, and 1/4, respectively, compared to the conventional method.

1. Introduction

The Fuel Monitoring Facility (FMF) is located adjacent to the experimental fast reactor, JOYO, at the Oarai Research and Development Center of the Japan Atomic Energy Agency. This facility is part of the hot cell complex for examination of assemblies from fast reactors. A photograph of the FMF exterior is shown in Fig.1.

Both non-destructive examinations of fuel assemblies and destructive examinations on fuel pins can be carried out in the FMF. In order to examine MOX (mixed oxide) fuel pellets containing plutonium, alpha-tight hot cells have been utilized in the FMF.

In this study, the maintenance method for the exhaust automatic control valves on the alpha-tight hot cells under a ventilating condition was established.



Fig.1 Photo of the FMF exterior

2. Outline of the FMF and the metallography cell

The fuel assemblies and other subassemblies are carried into the FMF from the reactors. The building plan of the first floor is shown in Fig.2. Non-destructive examinations on these subassemblies and some destructive examinations on fuel pins are carried out in the examination cell and the No.2 examination cell. The major destructive examinations like microscopic observations of the fuel pellets are conducted in the metallography cell which is one of the alpha-tight hot cells.

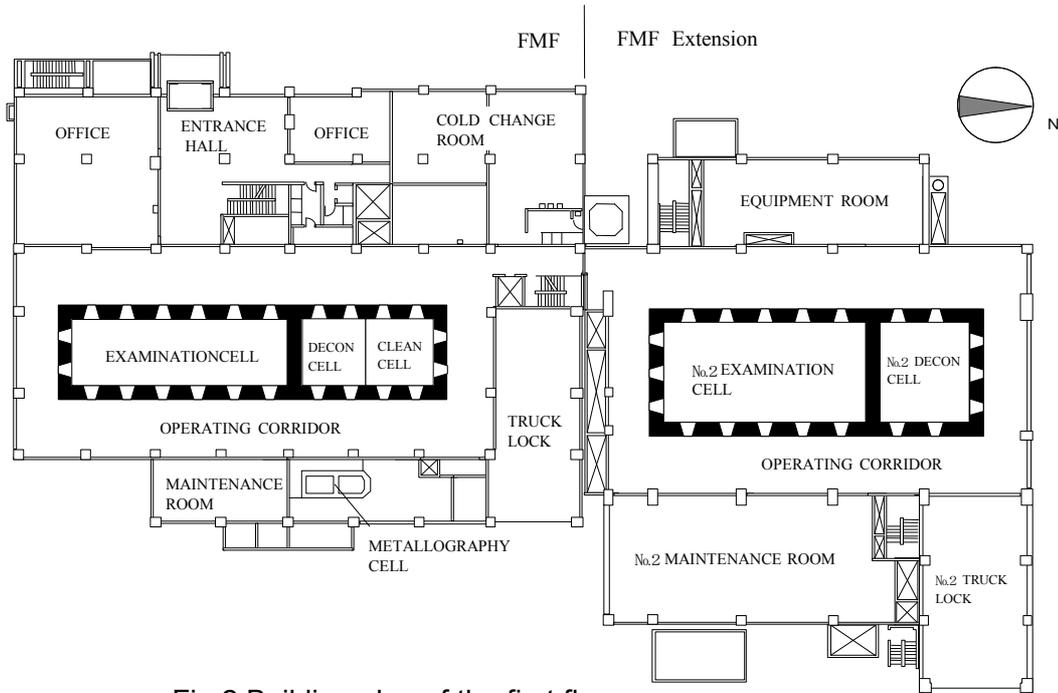


Fig.2 Building plan of the first floor

The sectional plan and outline of the metallography cell are shown in Figs.3 and 4. The metallography cell is used for microscopic observations and analyses of fuels and cladding materials. The metallography cell is 2.43 m long, 1.68 m wide and 1.7 m high. It has 350-mm-thick iron walls and it is kept with a nitrogen atmosphere in order to allow examination of irradiated fuel pellets. Additionally, the cell is lined with 3-mm-thick stainless steel plates to allow for handling of plutonium-containing MOX fuel pellets. Dose rate of the cell is very high because the fission products released from the fuel pellets adhere to its inner surface.

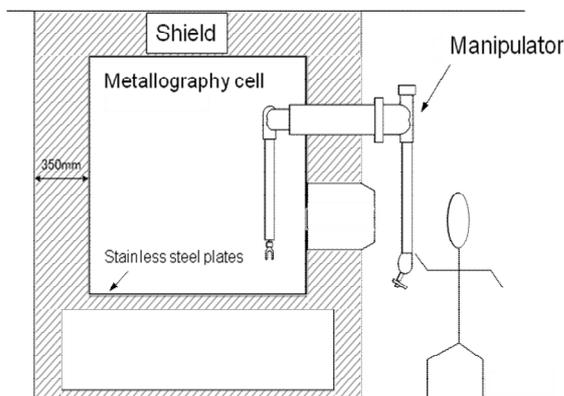


Fig.3 Sectional plan of the metallography cell



Fig.4 Photo of the operating corridor of the metallography cell

3. Establishment of maintenance method of exhaust valves

The exhaust system of the metallography cell is shown in Fig.5. These systems run continuously 24 h/day, 365 days per year since 1978. The exhaust automatic control valves are the most important instrument in the exhaust system which keeps the negative pressure of the hot cell and they are located behind the exhaust filter. Their prolonged use under severe conditions leads to wear and deformation of the rubber seals in these valves.

In the case of the conventional maintenance method, it is necessary to stop the ventilation during maintenance work to replace the exhaust automatic control valves. As well as the risk to workers, this involves much time and cost. Therefore, over the past 25 years, these valves have not been replaced with new ones. So, an innovative maintenance method for the exhaust valves while maintaining the ventilation condition was considered.

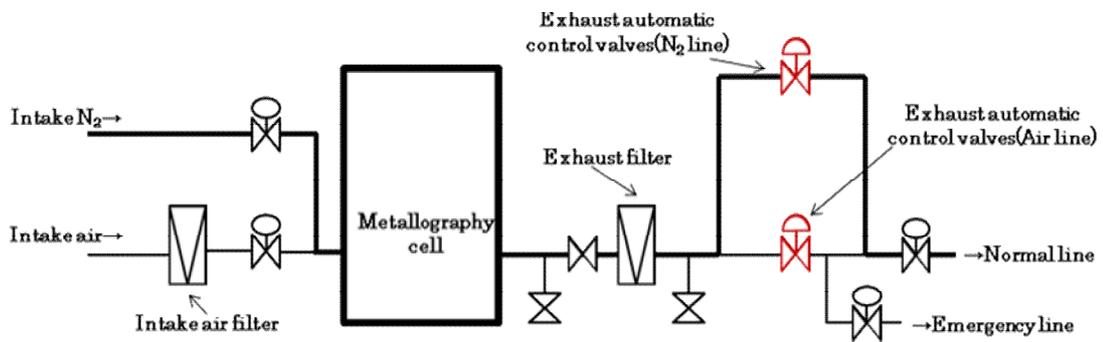


Fig.5 Exhaust system of the metallography cell

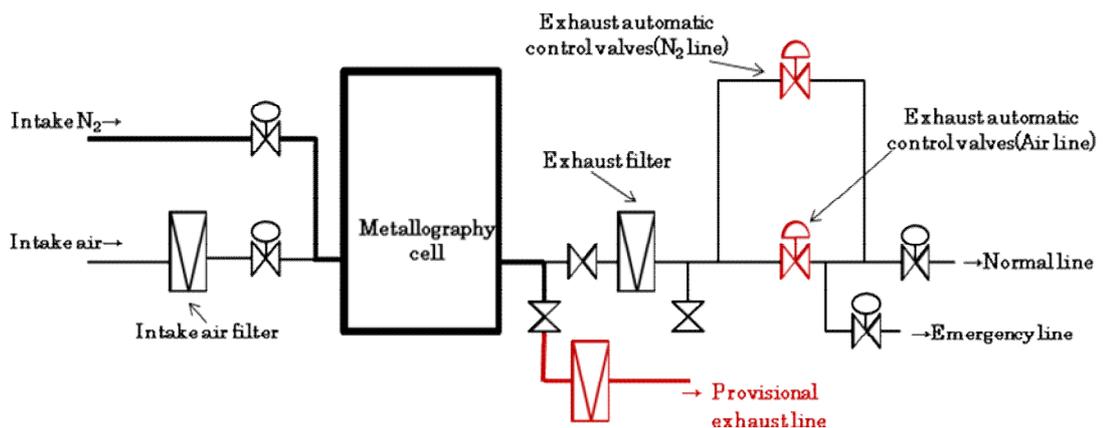


Fig.6 Provisional exhaust system of the metallography cell

In order to keep the negative pressure in the metallographic cell during maintenance and/or replacement of the exhaust automatic control valves, the provisional exhaust line was prepared for use instead of the original exhaust line. Fig.6 shows the provisional exhaust system. The provisional exhaust line was connected to the line between the hot metallography cell and the exhaust filter. While the metallographic cell was operating using the provisional exhaust system, the exhaust automatic control valves were replaced with new ones under the radiological work. Fig.7 shows the scene when maintenance work was conducted on the exhaust automatic control valves. The method makes it possible to keep the negative pressure in the hot cell without stopping the exhaust system operation.



Fig.7 Scene showing maintenance work of the exhaust automatic control valves

4. Conclusion

The maintenance method for exhaust automatic control valves on alpha-tight hot cells under the ventilating condition was established using the provisional exhaust system. Implementation of this method led to reductions of work period, costs and generated radiation waste volume with maintenance of 1/3, 3/5 and 1/4, respectively.

AN INTEGRATED TOOL TO REPACK, CHARACTERISE AND RECYCLE OLD U/Pu-BASED COMPOUNDS IN THE LEFCA FACILITY

F. MAZAUDIER

CEA Cadarache, DEN/DEC
F-13108 Saint Paul Lez Durance, France
<mailto:fabrice.mazaudier@cea.fr>

ABSTRACT

Since the late 50s, R&D in the field of nuclear fuel has required implementing various solid Pu-based compounds in meso-scale amounts (10^0 - 10^3 g) and in specific physical or chemical forms. Materials resulting from these activities have since been identified and inventoried in a number civil research facilities in France and abroad. Several relevant safety issues have been raised for a number of specific unused nuclear materials. As a part of the decommissioning and clean-up programmes conducted by the CEA, the LEFCA has been committed to studying, designing, building and operating (with authorisation from the French Nuclear Safety Authority, ASN) a specific semi-industrial tool to manage storage containers and recycle materials addressing specific safety issues. This paper describes the LEFCA-MEX project to be conducted in a largely refurbished facility. This project sets out to answer these specific safety issues in this new field activity raising long-term and sustainable concerns.

1. Introduction

The MEX¹ project was set up in the LEFCA² in 2007 within the framework of a wider programme of cleaning up, dismantling and decommissioning old CEA³ facilities (DADN/MATSE Project). Its target is to recover and manage old storage containers and repack or recycle old unused U/Pu-based compounds so they meet the current regulatory requirements. The inventory includes hundred of containers with old U-based or Pu-based fuels (sometimes 50 years' old), as well as uranyl nitrate acid solutions from various experimental facilities. As these objects do not meet the current safety criteria for interim storage or transportation, specific treatments are required. This project partially answers the issue of managing unused nuclear fuel or compounds through the design, the construction and qualification of an integrated tool. This tool will be used to meet our own requirements, but may also be used for other international R&D laboratories.

2. Refurbished LEFCA facility [1, 2]

The LEFCA is an alpha Pu laboratory. This facility was built in 1981 and started using nuclear materials in 1984. The building has three levels and an overall surface of 2,700 m². It includes 13 hot cells. Each cell is more than 100 m². Three cells are devoted to facility operations like waste management and nuclear material measurements. Ten of them are dedicated to R&D activities involving fuel studies, mainly on actinide-based oxide ceramics (U, Pu, Am). In each hot cell, the nuclear materials are handled in glove boxes operating under an inert gas (N₂, max 200 ppm O₂) for safety reasons, e.g. pyrophoric Pu-based powders like carbide or nitride. 100% Am-based fuels can also be produced in small amounts in a specific shielded glove box. More than 70 glove boxes are currently in operation.

All material science technologies and more than 100 experimental devices are available for R&D and facility management.

The LEFCA facility is equipped with the necessary powder metallurgy technologies (BET, granulometry, grinding machine, powder blender, uniaxial press, high-temperature furnace,

¹ A French abbreviation for "Matière EXotique".

² Laboratoire d'Etudes et de Fabrications expérimentales de Combustibles Avancés

³ Commissariat à l'Énergie Atomique et aux Énergies Alternatives.

(carbothermic reduction), metal and alumina sintering furnaces) to elaborate oxide, carbide and nitride ceramics. Furthermore, a number of analytical tools (LECO[®] (C, S, N, O) analysers, TGA-DTA, dilatometer, MS, and DSC) and characterisation means (OM, SEM, EPMA, XRD, HT-XRD, mechanical testing devices, and thermal testing devices (e.g. laser flash method, drop calorimeter) are available and used in the programmes. The LEFCA laboratory also has specific technical tools to manufacture (welding bench, micro-TIG device, etc.) and inspect (X-ray) experimental fuel rods and sub-assemblies for analytical irradiation experiments. To manage nuclear material and waste, two nuclear measurement stations using γ -scanning and neutron counting are currently operational, with one having been upgraded in 2010.

The R&D staff – 35 people and 10 students/y – perform high-level scientific studies on basic and innovative fuels within the framework of the third and fourth generation nuclear systems (MOX [3-4], Cr-doped MOX [5], co-converted powder based fuels, carbides [6], nitrides [7], Am-bearing ceramics [8-9]). In connection with the hot laboratory, there is also a special training facility called the "Plutonium school" with highly-specialised employees who provide expert training on the implementation of plutonium and Pu fuels (2000 trainees since 1987).

In order to meet the latest safety requirements and the challenging R&D targets, a large refurbishment programme was launched in 2005 and will end in 2010. This programme includes the reinforcement of the building to meet seismic requirements, improvement of building fire resistance, the dismantling of old gloves boxes which are no longer in operation, and replacement of the control devices such as criticality accident and contamination detectors.

This work was carried out by laboratory staff at the LEFCA facility which is now ready for the next decade in terms of nuclear safety, quality and technical needs to meet new R&D challenges in the field of nuclear energy.

And now, the LEFCA facility is also devoted to the management of old unused nuclear fuel and their packaging, a new field of activity detailed in this paper.

3. Nuclear material inventory: technical and regulatory requirements

A fresh fuel or material (in contrast to irradiated material or spent fuel), without any particular use (but not waste) that does not meet – in its current state – the updated specifications for long-term interim storage or public transportation, is qualified as an "exotic" material (MEX). It can be a plutonium-based and/or uranium-based material enriched in uranium-235 with at least one of the following characteristics: i) identification or traceability uncertainties, ii) specific radiolysis/thermolysis risk (sorbed water on powdered material or plastic conditioning material) including the potential consequences of hydrogen in containers, iii) problem of excess reactivity (e.g. pyrophoricity), iv) cannot be recovered (orphan material, worth transferring to a waste outlet), v) requiring a specific physicochemical treatment, or vi) packaging weakness, defect or degradation.

The MEX project involves analysing the inventory to process at the LEFCA laboratory, which currently includes about 100 containers of solid U/Pu-based (60) material – oxides (PuO_2 or $(\text{U,Pu})\text{O}_2$), carbides ($(\text{U,Pu})\text{C}$, PuC), nitride ($(\text{U,Pu})\text{N}$), metallic or intermetallic compounds (PuAl , UPuFe), fluoride (PuF_4) – and about 40 "bouteillons" (plastic bottles made of High Density Poly Ethylene, HDPE) containing nitric acid solutions of uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2 = \text{"UN"}$) enriched in uranium-235.

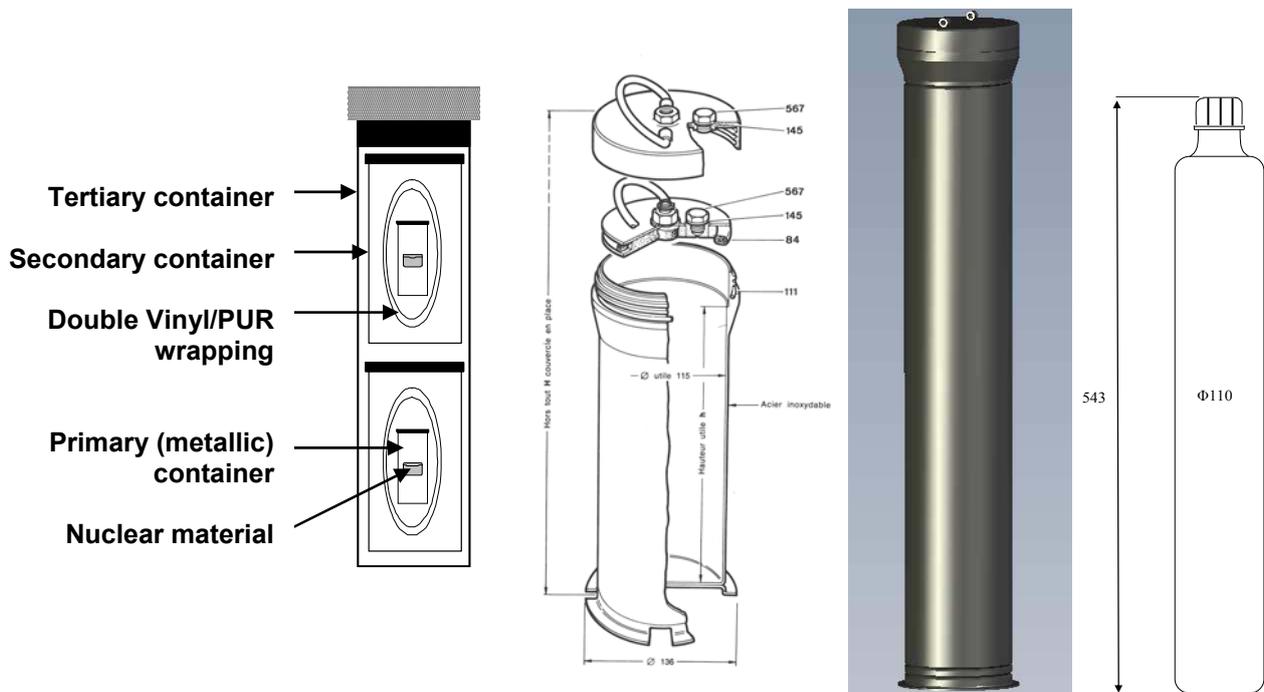


Figure 1: Principle of conditioning Pu-based materials, Tertiary stainless steel containers (2.5 mm thickness wall), Uranyl Nitrate "bouteillon" (HDPE)

These exotic materials are distinguished by their large quantities and a broad range of chemical and physical forms, including solid material that can be mixed in the same container and that can already be several decades' old.

Generally speaking, the treatment of such old material is defined upon delivery of the containers to the LEFCA facility before being transferred to the new interim storage facility called MAGENTA, in the Cadarache centre [10].

The treatment principle involves two main phases after the delivery and storage phase: the containers are first opened in two new glove boxes (further description given in this document). The material is then "depackaged" before undergoing nuclear measurements followed by a specific treatment: physicochemical (e.g. oxidation in newly-designed equipment) or other.

Uranyl nitrate is subjected to a different type of treatment: after delivery and storage, it is reconditioned in glove boxes and a sample is taken for in-depth radiochemical analysis.

The MEX project has been organised into two phases:

- 1) A development phase to analyse and specify the technical and regulatory requirements, as well as to define, design, develop, build and qualify the new tools and processes (two glove boxes for cutting up and opening containers + one oxidation furnace), and to obtain the necessary operating licenses.
- 2) The treatment of the exotic materials (production stage), involving simultaneous development and qualification actions to meet any new requirements or programme changes.

The development phase of the MEX project is divided into 6 interdependent tasks and 1 operational management task. The six main tasks concern:

- 1) Safety analysis and nuclear material management,
- 2) Uranyl nitrate (liquid form) management,
- 3) Solid material management,
- 4) Development of physicochemical treatment processes and methods (oxidation, calcination, etc.),
- 5) Infrastructure changes,

- 6) Engineering involving issues such as production-like management and organisation (processes, stages and phases, quality assurance and control, traceability, performance, cost and resources, lead times, and hazards).

4. Safety & regulatory issues, safeguards and nuclear material management

4.1. Introduction

Exotic materials will be sent to the LEFCA laboratory for treatment intended to make them comply with the current management rules (implementation, transport and interim storage) and safety requirements. An inherent characteristic of this type of activity – recovering and retreating old unused nuclear material – involves a safety assessment and demonstration, which raises sharp technical issues. These issues mainly concern four themes: criticality risk management, operational dosimetry, management of objects with a risk of radiolysis, and of potentially pyrophoric objects (carbides, nitrides and metals). Three safety reports are drafted to meet three licensing requirements (in liaison with ASN): the first for the delivery and treatment of uranyl nitrate, a second for the delivery and interim storage of solid material containers, and a third for the treatment of these materials, mainly focusing on technical operations in a hot cell largely dedicated to this project.

Inventory control (nuclear material and waste management: accountancy and physical tracking) is a strict regulatory requirement for which a specific procedure is recommended.

Another concern involves analysing the occupational hazards and safety risks, factors which are taken into account as early as tool design right up to the treatment operations.

4.2. Criticality safety

For safe handling of uranium and plutonium compounds, nuclear criticality safety is implemented.

For the uranyl nitrate bouteillons management, criticality safety control is demonstrated through control of the geometry components of the devoted equipment. By design, the process (detailed in a specific section) developed to repack and sample UN can only involve one bouteille at a time. The solution is pumped into a new bouteille, with both being held in a vertical position according to a pre-determined geometry and a minimum distance imposed by design. A sub-critical retention device (inclined glove box base) will be implemented to protect against any failure or leakage into the glove box. In the case of accidental spillage, the liquid will be recovered by pumping.

There are solid materials whose reconditioning plastics, efficient neutron moderators, must be explicitly taken into account with respect to the criticality safety (mass and moderation control) in the hot cell and the devoted glove box. Demonstration is based on the permissible moderating mass limits in relation to the fissile mass contained in each container, including predefined management methods.

Specific calculations were performed to increase the number of vertical stacking cells in the storage room to be able to stack UN bouteillons or solid material containers indifferently.

4.3. Nuclear material management (accountance, control and tracking)

Inspections will be conducted on solid materials by means of neutron counting and gamma scanning within the regulatory deadlines. This will be performed on primary and/or secondary containers extracted from tertiary containers (figure 1). This procedure will make it possible to improve our knowledge of the different objects contained within. Nuclear material in uranyl nitrate will be controlled according to the available knowledge of the product's net mass, the liquid density, concentration (gU/L) and isotopic composition (U235/U). This will be done analytically on all samples.

To control material contained in glove boxes, the design of new equipment has been focusing on minimising blind corners and other inaccessible areas, as well as being able to carry out frequent and thorough cleaning while in use.

In terms of generated waste and any nuclear material it may contain, the principle of inventory control is based on additional traceability focusing on this specific retreatment activity to ensure optimal physical tracking.

4.4. Radiolysis effect and hydrogen generation

Some of the containers to be sent to the LEFCA laboratory might contain hydrogen as a result of the decomposition of sorbed water on powdered materials in addition to the degradation of plastic conditioning materials, under the effect of radiations.

Specific measures will be implemented to manage all of these containers and materials risking radiolysis, including explosiveness and contamination tests of gas covers in transport casks (TNBGC). Containers will also be opened in nitrogen-inerted glove boxes. We have chosen a special horizontal abrasive disk cutting machine, to open containers with solid material that may have become oval-shaped due to explosion.

Solid materials (powdered oxides) with a radiolysis risk will then be calcined at high temperature (at least 950°C) to minimize sorbed water content prior to future interim storage.

4.5. Radiological protection

To reduce the dosimetry cost at a level as low as possible (application of the ALARA principle) before defining the treatment procedures and designing the glove boxes used for the treatment of solid material containers, an in-depth study was conducted on the basis of facility data and feedback on comparable activities. Though neutron dosimetry is to be taken into account, it is not a design-basis factor. The gamma dosimetry of Am is the main parameter for design. Specific measures will be implemented for equipment (lead glass, seals in front of glove ports, metal parts on glove boxes, remote tools), as will numerous operational and organisation measures. Preliminary calculations have shown that operator doses fall within the regulatory limits, without any evident or large deviation in relation to the usual dose levels at the LEFCA facility. An ALARA study is currently underway which focuses on higher dose-emitting objects and materials containing high levels of americium.

4.6. Oxidation hazards: pyrophoricity, breakaway kinetics and exothermicity

Managing the oxidation of carbide or nitride nuclear fuel is one of the main issues underlying i) the safety risk analysis of back-end needs to reprocess scrap and spent fuel (via the Purex process), ii) the regulatory requirements for safe storage, and, iii) standard handling aspects in R&D hotlabs. The oxidation of mixed (U,Pu) carbide fuel, which is sizing the issue, was studied [11]. The overall oxidation reaction is generally described as:



in which M = (U,Pu), usually with 80 at.% U and 20 at.% Pu. The reactant carbide MC_x is assumed to be a two-phase mixture of monocarbide MC (90 wt.%) and sesquicarbide M_2C_3 (10 wt.%), without any free carbon.

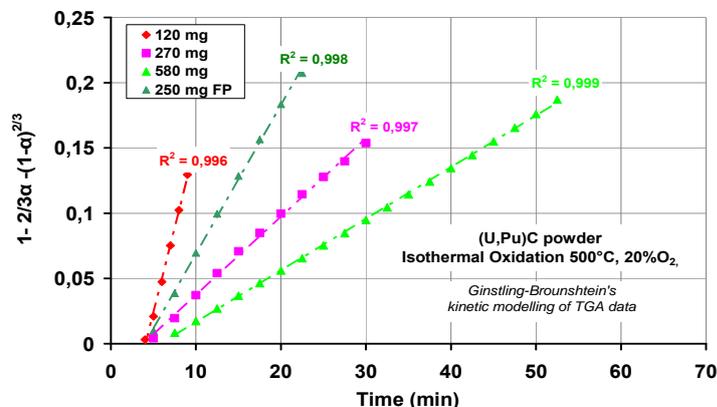


Figure 2: Modelling of the experimental data (UPuC powder oxidation at 500°C)

The kinetic treatment and modelling of isothermal TGA data (figure 2) proved that the apparent activation energy is low (≈ 25 kJ/mol) and definitely confirms the slight effect of temperature on the oxidation rate. Gas diffusion was assumed to play a major role in the oxidation process of powdered samples.

In our experiments, the oxidation of mixed (U,Pu)C carbide (porous and powdered samples) did not show any intrinsic capacity to self-sustain regardless of the temperature or the oxygen content: spontaneous and uncontrolled oxidation was never observed. However, heating is required to complete oxidation. The oxidation process does not show any unwanted kinetic transitions.

The oxidation products are always low-density finely-divided oxide powder tending to slow down oxidation: no protective oxide layer was observed on the samples.

Let us consider the fire triangle (figure 3) to illustrate the safety principle applied: the oxidation reaction is possible when all three points of the triangle are involved.

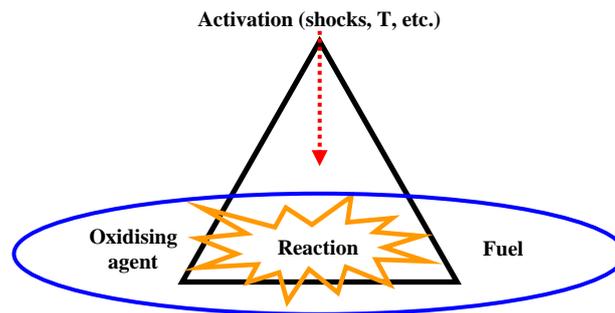


Figure 3: Fire or oxidation triangle

The chemical reaction of oxidation is impossible without any activation (heat, shocks, etc.), fuel (considering (U,Pu)C only as a "chemical" fuel) or oxygen.

The safety principle consists in avoiding that fuel and oxygen be put together without total control over at least one corner of the triangle.

At room temperature in standard N_2 -inerted glove-boxes (≈ 10 -100 ppm O_2), handling does not represent any hazard in terms of sudden and uncontrolled oxidation.

As a general rule, managing oxidation at high temperature (2 corners controlled: activation and fuel) during the conversion process will be based on oxygen availability.

4.7. Ergonomics, handling and human & organisational factors

Ergonomic issues were incorporated into the design of new equipment, which will also help better manage the steady flow of transport casks and containers into the facility. Qualified operators were consulted during the development phase and devices designed to minimise loads during handling (specific tools will be implemented). Human & organisational factors were analysed in collaboration with an expert.

Dedicated production management resources with the appropriate methods will be deployed to ensure the permanent operational monitoring of all safety and security issues.

5. Hot cells, tools and processes involved

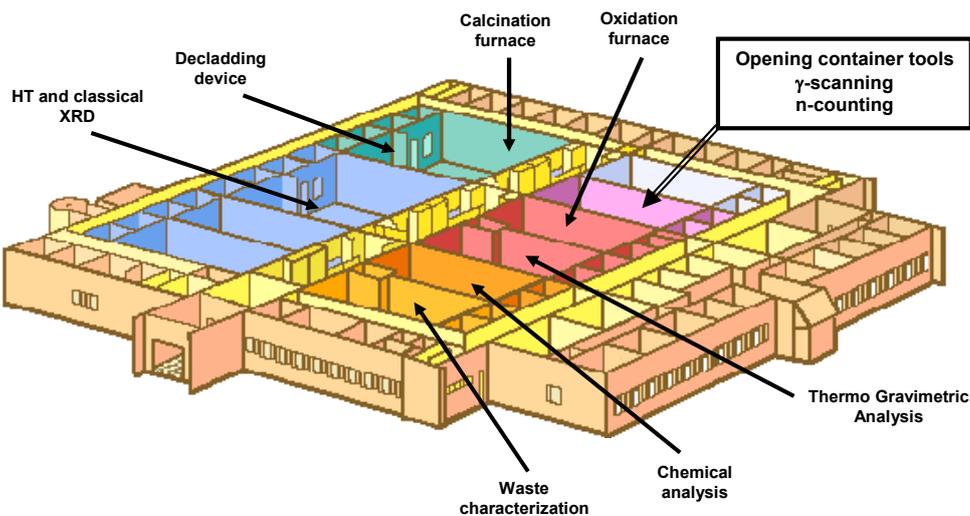


Figure 4: LEFCA hot cells to be used in the project

The MEX project has a major impact on the LEFCA facility (figure 4) – as will be seen through the description of the tool, methods and processes – since a hot cell is entirely devoted to technological operations on containers (hot cell #2) so as to check and examine the items, and all the technical and safety issues raised.

5.1. Transport cask management and container storage

The transport casks (TNBGC) are delivered to the front of the truck bay on the facility ground floor. They are unloaded and stored before treatment in a dedicated area in relation to their criticality safety index. Acceptance tests will be performed on cover gas samples taken from these transport casks. This test will be used to confirm container integrity, the absence of any internal contamination, and the absence of an explosive atmosphere due to hydrogen produced by radiolysis. This test will be performed with a special integrated gas analyser to control the contamination level in the gaseous sample and its explosive nature (via an explosimeter).

When the test is negative (no contamination or explosive atmosphere), the transport cask can be opened, the container can be removed, and the surface contamination can be checked. Each container is then placed in storage packaging according to its size and then transferred to the storage facility pending treatment.

A specific management procedure is applied in the event a transport cask fails this test (presence of an explosive atmosphere and/or contamination).

5.2. Glove box for the treatment of uranyl nitrate containers

Liquid uranyl nitrate must be reconditioned in new bottles and samples must be taken for radiochemical and chemical analysis (U concentrations and isotopes, H^+ and NO_3^- , halides, and other metallic impurities, etc.).

A special glove box has been designed and built (UN glove box). This UN glove box contains a three points orbital tool cutting machine to open vertically-positioned containers in a semi-automatic way to access the bottle.

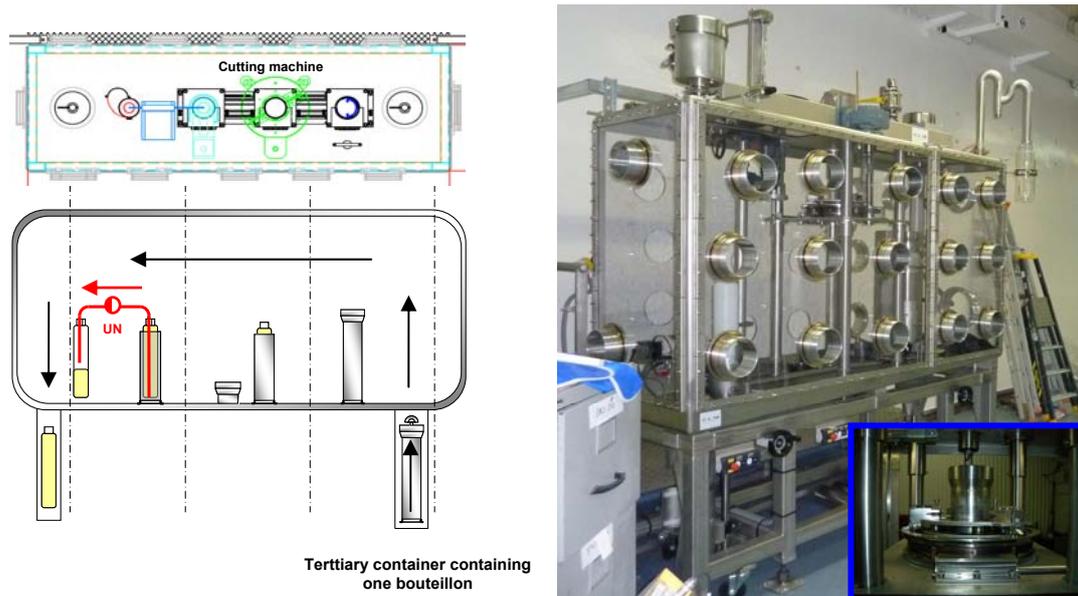


Figure 5: Schematic diagram of UN glove box (top view and general functional diagram), the UN glove box in cell# 2 and the cutting machine (inset photo)

The bouteillon is then perforated to insert the suction pipe and nozzle to extract the liquid. The UN solution is then transferred into a new bouteillon (duration < 15 minutes) using a peristaltic pump which is also used to take a sample for the analytical needs. This pump can be used to recover any UN liquid at the bottom of the glove box which is inclined at a specific angle to create a sub-critical retention.

Glove box qualification involved a number of expert operators and aimed at validating the nominal operating conditions and related performance levels, in addition to its operation in incident conditions. Maintenance tests were also performed on the cutting tool.

The UN glove box is installed in a specially-refurbished hot cell #2 ready to host this equipment and treatment operations.

5.3. Glove box for the treatment of solid material containers

A specially designed and developed glove box will be used to open containers holding solid exotic materials, to extract the contents (primary and secondary containers) and to unwrap nuclear materials. Currently being built, this glove box is expected to be delivered and qualified in 2011. This glove box will also be installed in the refurbished hot cell #2.

The primary and secondary containers will be opened and removed semi-automatically in this glove box using a special horizontal abrasive disk cutting machine (cutting of horizontally-positioned containers, see Figure 6). This cutting machine has a rotating disc with controlled progression and counter-rotation of the container inserted in mobile jaws. The machine can cut containers into several sections. A manual piston pushing tool is used to remove the primary and secondary stuck containers.

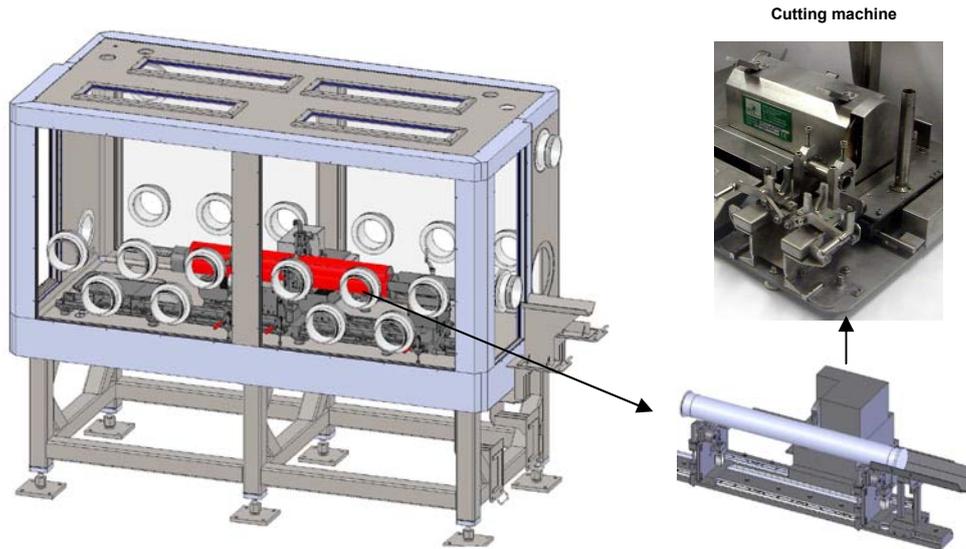


Figure 6: Glove box for solid material containers; abrasive orbital cutting tool, cutting machine (inset photos)

Abrasive cutting disk requires a lubricant. A non-flammable liquid lubricant was chosen as the best compromise between the safety requirements limiting the fire hazards, controlling the quantity of hydrogen in the glove box, and the simplified management of cutting sludge possibly contaminated by plutonium. The glove box is shielded against gamma radiation by means of lead glass (20 mm equivalent to 3 mm of lead), by stainless steel sections, and by seals on the glove ports. These measures protect operators and people in the vicinity of the glove box which will contain Am-bearing nuclear material. This new glove box is connected to an existing glove box (No 210) via a tunnel, which will be used for more complex operations on the material (sorting, partitioning and batch preparation).

5.4. Layout of a hot cell for container treatment

Hot cell #2 was entirely refurbished to host for two glove boxes dedicated to the technical treatment of containers: the UN glove box, and the exotic material glove box which is connected to glove box No. 210.

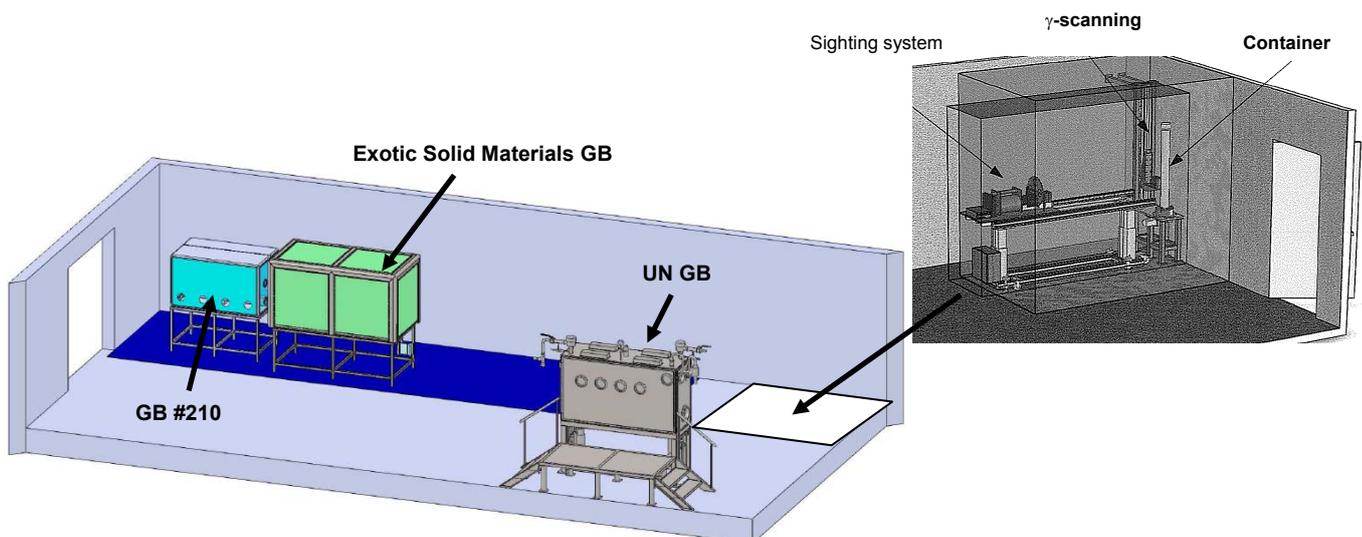


Figure 7: Hot cell #2 devoted to the technical treatment of containers and for nuclear measurements

In principle, all of the containers will first transit through this cell before returning to the storage room of the LEFCA facility. They will undergo specific treatment or transport at a later date.

The recently-upgraded γ -n counting station is also installed in this hot cell. This station will mainly be used during the first stage involved in the treatment of solid material containers in order to meet regulatory requirements governing the quantitative assaying and qualitative characterisation of nuclear material.

Hot cell # 2 will be subject to a very specific safety management procedure. There will be a criticality unit and geometry control for the 'UN glove box' side of the cell, and another criticality unit for the other side of the hot cell which will be managed in terms of mass/moderation, including the possibility of implementing different types of conditions.

5.5. Oxide conversion process and furnace [11]

The oxidation process determined for the total conversion of mixed (U,Pu)C into oxides involves isothermal oxidation above $T = 600^{\circ}\text{C}$, in a high-oxygen content atmospheres, carried out with pre- and post-inerting steps following the reaction described in § 4.6.

The relevance of choosing a relatively high temperature oxidation treatment is a compromise between the performance, efficiency, safety, and the oxide product specifications, to reduce the carbon content as much as reasonably achievable, and to obtain a real recyclable powder.

The reaction – whose activation is imposed at high temperature – will be controlled by the overall oxidation rate which cannot exceed the rate at which the oxidising agent is consumed in contact with the fuel. The kinetics is controlled by the oxidising gas flow rate which is adapted in relation to the actual reactivity so as to prevent any sudden transition and the accumulation of oxygen. CO_2 variations at high temperature help dissipate the energy and prevent the formation of an adherent layer.

Oxide conversion will be performed in a multi-purpose (sintering, oxidation, calcination) tubular alumina furnace. The oxidising furnace and related glove box No. 311 are installed in hot cell # 3 (figure 8). This is a horizontal tubular furnace made by AET in 1996 and originally designed for oxidising or reducing sintering. The furnace design was entirely reviewed.



Figure 8: Oxidising furnace and gas analysers (O_2 , CO_2), stainless boat on loading train

The reaction is monitored through the continuous analysis of O_2 and CO_2 upstream and downstream of the reactor (electrochemical and paramagnetic sensors for O_2 , FTIR for CO_2)

measurements) and through the controlled supply of oxygen. To manage exothermicity and any abnormal events, sensors (temperatures, pressure, cooling system flow) and feedback actuators have been implemented on the oxygen availability. Weight gain measurements and XRD-controlled samples will be used to check the efficiency of the oxidation treatment. The performance objective is to be able to oxidise up to 200 g per batch. R&D will be required for other reactive forms, nitrides and divided metallic forms.

5.6. Other equipment (Calcination furnace, X-ray radiography, decladding device, TGA)

Other equipment will be used for the retreatment of materials: a calcination furnace for powders with a risk of radiolysis and a glove box for pin decladding operations (in order to optimise the available storage space).

X-ray diffraction (XRD) and thermogravimetric analysis (TGA) will be used for refined characterisations and/or quality control.

6. Operational aspects of treatment

6.1. Uranyl nitrate treatment

To optimise the available storage capacity, the containers of UN will be treated one by one in the UN glove box per campaign according to batch series. Each series will involve determined transport operations of 4 transport casks, each housing a container of uranyl nitrate.

6.2. Treatment of solid material

The treatment principle for internal containers holding solid exotic materials involves two stages after the acceptance and delivery, i.e. stage: 1) storage followed by the technical treatment of the containers in the cell #2, and 2) physicochemical treatment adapted to the different reconditioned objects in the containers sorted into types.

Exotic solids: Reconditioning, Treatment & Characterisation

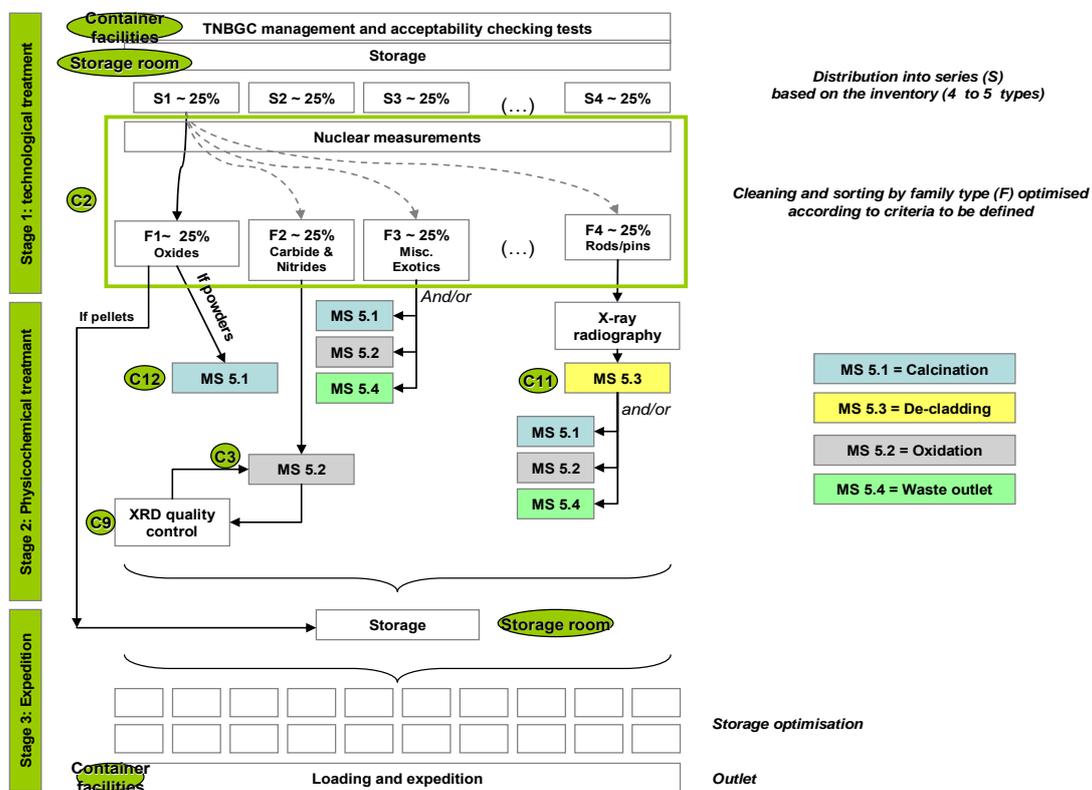


Figure 9: Flow diagram (principles)

6.2.1. Stage 1: Technical treatment of containers

This stage has been divided into 4 series of n containers. Each S series will be sorted in order to feed four family type of containers, i.e. 4 predefined types, corresponding to typical cases (oxides, carbide/nitrides, rods/pins, miscellaneous). Each series involves two phases:

- 1) Management of the transport casks (several transport operations) and storage of containers,
- 2) Technical treatment.

The containers of exotic materials must first be opened, the primary and secondary containers must be removed in the solid material glove box, and the materials must be sorted in glove box No. 210, before being reconditioned per type/level of complexity with respect to the subsequent treatment or management method.

One of the objectives is to improve/review the conditioning and knowledge of materials so as to start preparing the physicochemical treatment operations.

6.2.2. Stage 2: Physicochemical treatment

Depending on the chemical nature of the material or the issues raised, the materials will be: i) characterised or analysed (type of alloy, impurity content, etc.), ii) calcined at high temperature to minimise the quantity of sorbed water and volatile organic material and thus the risk of radiolysis (oxide powders), iii) oxidised by isothermal treatment (potentially pyrophoric material such as U or Pu carbides/ nitrides or divided metallic forms), or iv) decladded (rods and pins) for thermal treatment. Materials brought into conformity will then be reconditioned and transferred to an appropriate outlet or to a waste disposal site if they cannot be recovered/recycled.

The second stage is thus divided into 4 phases: calcination, oxidation, decladding and management of non-recoverable material.

The table below indicates the maximum 'volume' of work resulting from the overall treatment of 60 containers of solid exotic materials.

	"Volume"	Room/ Equipment
Transport cask acceptance	40	Storage room facilities
Container opening	60	C#2 Glove boxes for solid exotic material
γ -n counting	400 countings	C#2 / γ -n station
Calcination	20 treatments (batch : 1 kg of material)	C#12 / 1201 furnace
Oxidation	100 to 200 treatments (batch : 100 or 200 g)	C#3 / 311 furnace
Decladding	50 objects	C#11 / 1108 glove box
X-ray diffraction	100 to 200 analyses	C#9 / XRD
Thermogravimetric analysis	20 analyses	C#4 / TGA

Table 1: Volume of work for the treatment of solid materials

6.3. Determining the best treatment scenario and typical resources

A matrix-type organisation has been implemented to help to determine the treatment methods and optimal treatment scenario. This includes a project risk assessment and a 'failure modes and effects analysis' (FMEA) for the technologies and processes.

Approved and specifically-qualified resources will be employed to operate the treatment tool, from the management of the transport casks and containers up to the handling of nuclear material in glove boxes and including general operations (nuclear materials measurements, waste management, etc.).

The responsibility and tracking of production, as well as the continuous improvement of methods, traceability, and the continuous management of safety, security and radiation protection issues will be entrusted to a production supervisor and a devoted security manager with a technician specialised in radiation protection.

A support engineer will be responsible for aspects such as project management, physicochemical studies, process development, drafting reports and defining new requirements, whereas a physicochemical technician will be responsible for analytical tests.

7. Conclusion

The LEFCA-MEX Project target is to manage storage containers and reprocess old U/Pu-based materials (and also Uranyl Nitrate aqueous solutions) addressing specific and complex safety issues. An integrated tool has been built to answer the questions.

This new field activity with long-term and sustainable concerns, will take place during at least 5 years, in a in-depth refurbished LEFCA facility, ready for the next decade and the main challenges on nuclear fuel, R&D for future systems, recycling and compliance of old materials.

8. References

- [1] Upgrading of the LEFCA experimental facility for the study of next generation nuclear fuels, J.P. Coulon, F. Boussard, Proc. of the HotLab 2008 Conference, Sept. 2008, Sellafield, UK.
- [2] <http://www-cadarache.cea.fr/fr/entreprises/projets/lefca/>
- [3] A mechanistic approach of the sintering of nuclear fuel ceramics, Materials Chemistry and Physics, Volume 67, Issues 1-3, 15 January 2001, Pages 120-132, J. L  chelle, R. Boyer, M. Trotabas.
- [4] Characterisation of plutonium distribution in MIMAS MOX by image analysis, Journal of Nuclear Materials, Volume 375, Issue 1, 30 March 2008, Pages 86-94, G. Oudinet, I. Munoz-Viallard, L. Afore, M.J. Gotta, J.M. Becker, G. Chiarelli, R. Castelli.
- [5] Influence de l'adjuvant de frittage, Cr₂O₃, sur l'homog  nisation de la r  partition en plutonium au sein d'une pastille MOX h  t  rog  ne", A. Pieragnoli, PhD Thesis, 2008, Limoges ENSCI.
- [6] Direct carbothermic reduction of actinide oxalates: Example of Nd(III) oxalate-carbon mixtures conversion, Journal of Nuclear Materials, Volume 385, Issue 1, 15 March 2009, Pages 186-188, A. Handschuh, S. Dubois, S. Vaudez, S. Grandjean, G. Leturcq, F. Abraham.
- [7] Experimental assessment of thermophysical properties of (Pu, Zr)N, Journal of Nuclear Materials, Volume 344, Issues 1-3, 1 September 2005, Pages 186-190, V. Basini, J.P. Ottaviani, J.C. Richaud, M. Streit, F. Ingold.
- [8] Plutonium and americium monazite materials: Solid state synthesis and X-ray diffraction study, Journal of Nuclear Materials, Volume 366, Issues 1-2, 30 June 2007, Pages 52-57, D. Bregiroux, R. Belin, P. Valenza, F. Audubert, D. Bernache-Assollant.
- [9] Synthesis and Rietveld structure refinement of americium pyrochlore Am₂Zr₂O₇, Journal of Alloys and Compounds, Volume 448, Issues 1-2, 10 January 2008, Pages 321-324, R.C. Belin, P.J. Valenza, P.E. Raison, M. Tillard.
- [10] <http://www-cadarache.cea.fr/fr/entreprises/projets/magenta/>
- [11] On the oxidation of (U,Pu)C fuel - Experimental and kinetic aspects, practical issues, F. Mazaudier, C. Tamani, A. Galerie, Y. Marc, Journal of Nuclear Materials, 2010. To be published.

SET OF DEVELOPMENTS FOR STUDY INTO SURFACE DEPOSIT QUANTITATIVE COMPOSITION DISTRIBUTION WITH HEIGHT OF FUEL PIN ZIRCONIUM CLADDINGS FROM WATER-COOLED NUCLEAR REACTORS AFTER OPERATION

I.M. SMIRNOVA, V.D. RISOVANY

*JSC "SSC RIAR"
Dimitrovgrad 433510 – Russia*

Procedural developments to obtain reliable deposits samples from Zr-alloy cladding regions of spent fuel pins for the purpose of highly accurate identification of their quantitative chemical composition and determination of the deposit elements distribution with the fuel pin height are presented. A device designed for consecutive removal of deposits at the required fuel pin height level retaining the item integrity is described. Composition of chemical agent solution, temperature and time mode of deposit removal, metrological characteristics of the analytical deposit analysis procedure are presented. A possibility of successful application of these developments is presented.

Based on the experience of water-cooled NPPs, deposits on the fuel pin claddings in different types of reactors can effect the fuel pin cladding material characteristics to a greater or lesser degree. Mechanism of the cladding local fracture under deposits is not investigated enough and studies into chemical composition of deposits, specifically in the places of defect formation, are important for solving this material science problem.

The report presents procedural developments that allow the obtaining of reliable, detailed and precise data on the distribution of deposited elements with the fuel pin height. The developments include a method of removing surface deposits using chemical agents and a device for performing this operation, adjustment of a serial spectrometer with inductively-coupled plasma for handling radioactive materials and a procedure for performing quantitative elemental analysis of deposits using atomic-emission spectrometry with inductively-coupled plasma (ICP-AES).

Unlike a widely used mechanical method of deposit removal, a chemical method allows the elimination of all drawbacks that complicate or devaluate the following quantitative analysis of samples. Among these drawbacks are impossibility to remove deposits tightly coupled with the surface or those from fine pores and pits; ingress of Zr oxide film or scraper/brush material into samples; inevitable averaging of the analysis results due to a need for taking a sample from quite a large surface area of the cladding to obtain a representative weight portion given thin deposit layers, impossibility of performing the work in a hot cell with rarefaction in case of deposit layer thickness not exceeding very few micrometers.

RIAR has developed and implemented a method of removing deposits from the fuel pin Zr cladding surface using a water solution of mineral acids effective both in case of very thin deposits (several micrometers) on the fuel pin claddings and significantly thick deposits (300 μm and more) [1]. The solution composition was developed after experimental investigations based on the reference data on the state (suspended state, colloidal state, solution) of impurities present in the coolant, composition and possible forms of deposits on the fuel pin claddings. The solution composition, temperature and time mode allow total conversion of all deposits into a homogeneous solution [2] without fracture of the fuel pin cladding material (Zr alloys of various chemical composition) and surface layer of Zr oxide. One of the advantages of the chemical method is that removal and dissolu-

tion of deposits are included into one procedure which significantly simplifies a process of sample preparation for its analysis using ICP-AES (samples are introduced into discharge in a form of solution aerosols) and reduces its error.

Conversion of surface deposits into solution is optimized in relation of decayed deposit quantity to acid solution volume, as well as in temperature and time mode. The process is the most effective at a solution temperature of 50...90 °C and during 10...30 min depending on the deposit layer thickness.

Completeness of the deposit removal using the proposed solution, including open tangential cracks of Zr oxide, except for visual inspection (fig.1, 2) is confirmed by the absence of deposit elements in renewed solution portions and examinations using SEM and X-ray spectrum microanalysis [3].

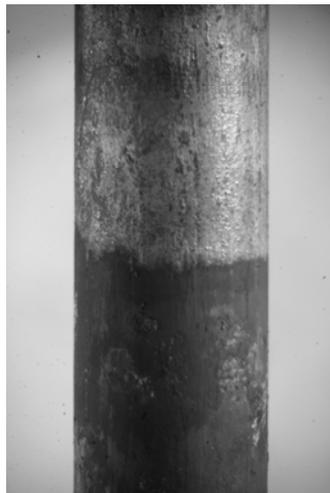


Fig. 1. View of the VK-50 fuel pin cladding (a burnup of 18,7 MWday/kgU for an operation period of 17,616h) with an interface between the region not treated by chemical agents (lower part of the photo) and the region after removal of surface deposits (upper part of the photo)

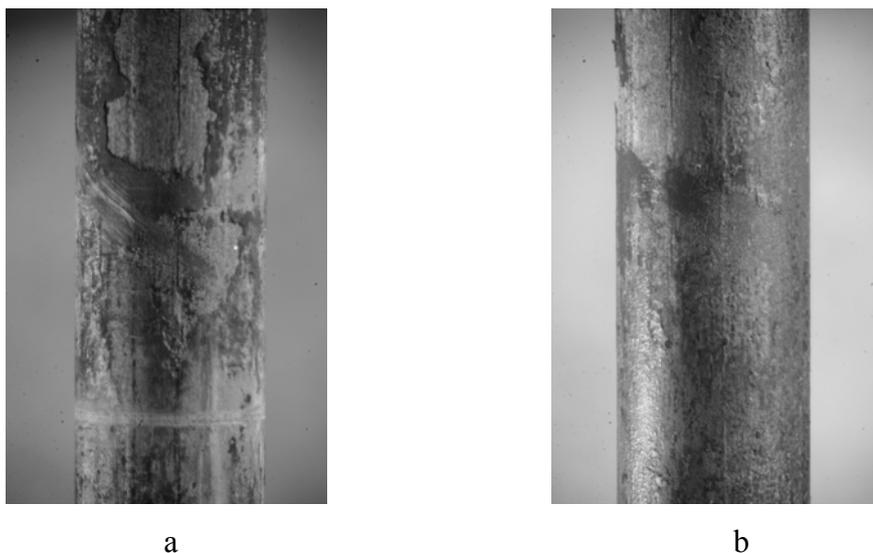


Fig. 2. View of the VK-50 fuel pin cladding area (a burnup of 18,7 MWday/kgU for an operation period of 17,616 ч, distance from the lower plug of the fuel pin is 1000 mm): a – prior to deposit removal; b – after deposit removal

Insignificant effect of the proposed solution of chemical agents on the fuel pin cladding material and Zr oxide surface layer is identified during multiple experiments simulating deposit removal process, including the cladding specimens after operation.

Integrity of the item and cladding material is confirmed by additional investigations using pulsed eddy current defectoscopy which allows the revealing of defects in the cladding integrity $0,005 \text{ mm}^3$ in volume, $20 \text{ }\mu\text{m}$ in depth and more [4]. An example is found in evaluation of the VVER-1000 irradiated fuel pin surface state after deposit removal carried out using pulsed eddy current defectoscopy. The results of the eddy current scanning showed the absence of abnormal responses in those areas of the fuel pin where deposits were removed (fig. 3).

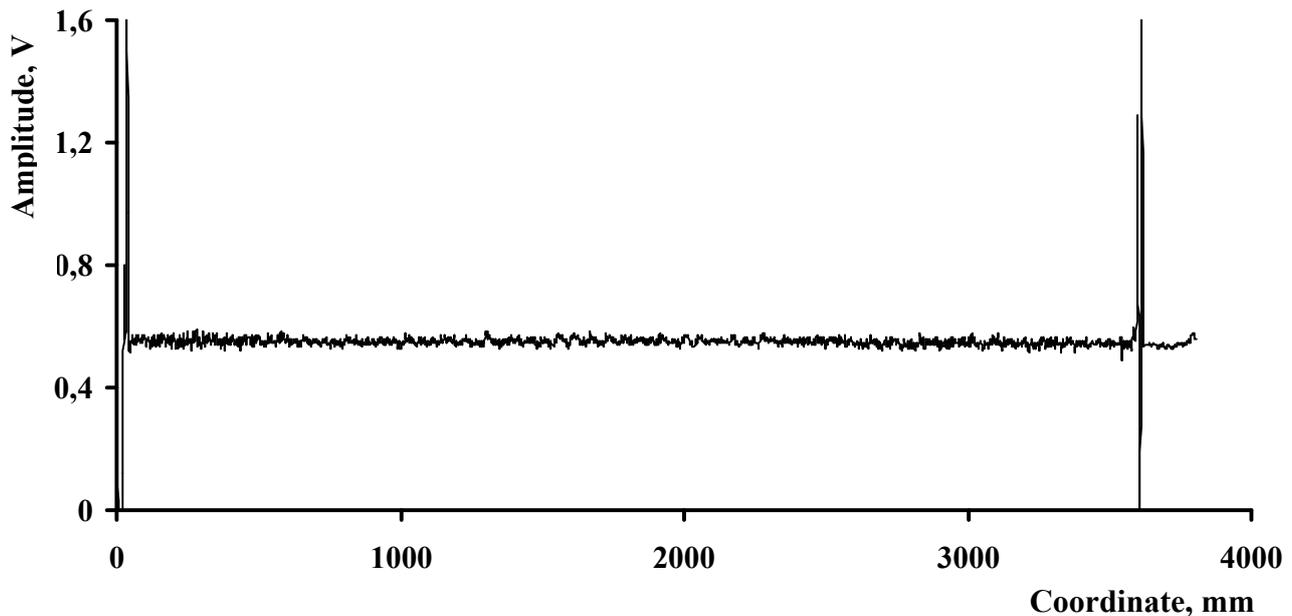
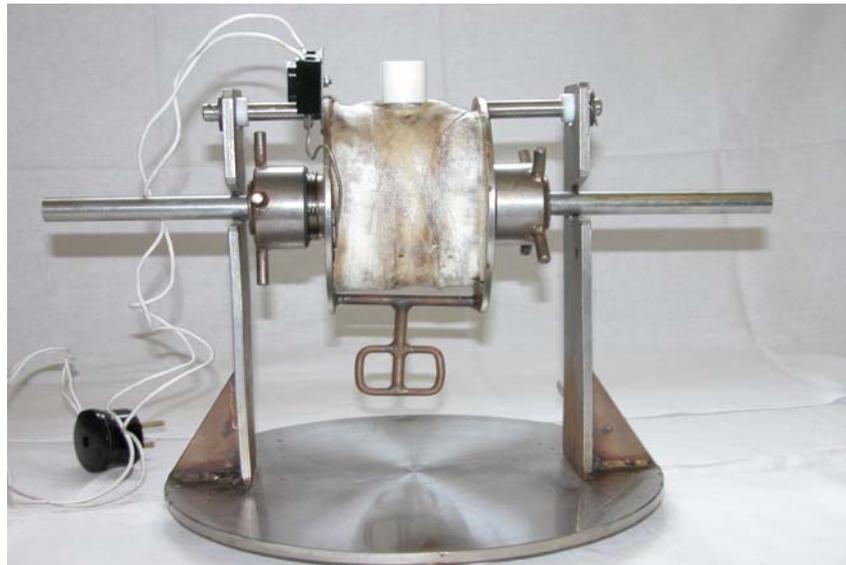


Fig. 3. Eddy-current diagram for the VVER-1000 fuel pin on the cladding areas of which the deposit was removed using the developed method.

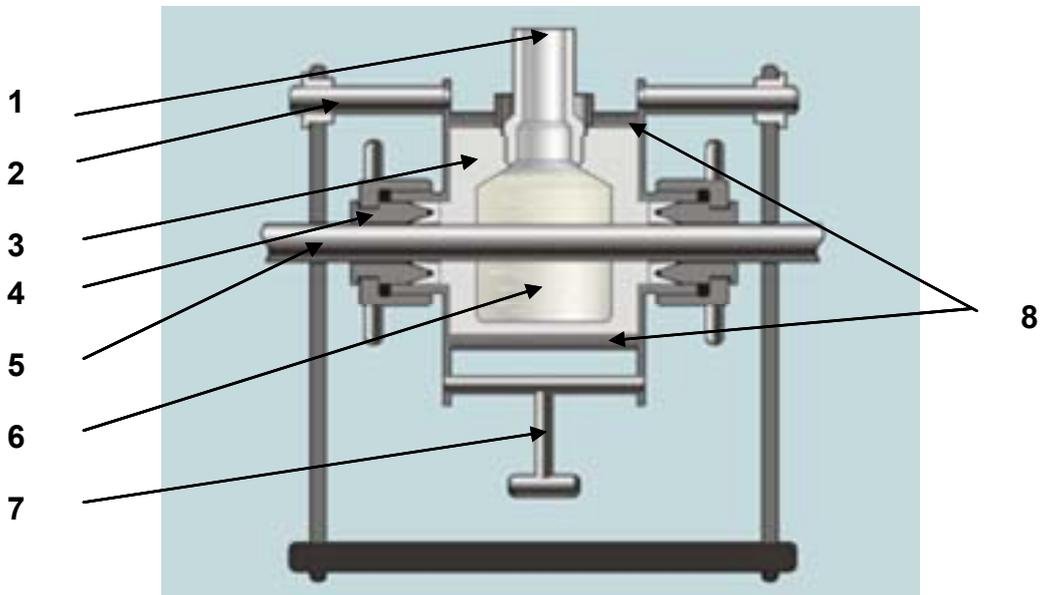
Complete dissolution of deposits is confirmed experimentally. At first, deposits containing hardly soluble iron compounds - FeO , $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, Fe_3O_4 were dissolved by the developed method of deposit removal, then the solution passed through 7 membrane filters of different porosity: $3,0 \text{ }\mu\text{m}$, $2,0 \text{ }\mu\text{m}$, $1,0 \text{ }\mu\text{m}$, $0,8 \text{ }\mu\text{m}$, $0,6 \text{ }\mu\text{m}$, $0,4 \text{ }\mu\text{m}$ and $0,2 \text{ }\mu\text{m}$. Analysis of the solution after its filtering confirmed its similarity to the initial one (prior to filtering) in the content of deposit elements which is evident of the conversion of all deposit elements using the proposed solution of chemical agents into dissolved forms.

A set of developments includes a device for deposit removal from the cladding areas up to 47 mm long performed in hot cells consecutively with the entire height of fuel pins of different sections [5].

The device incorporates a chamber outside which a heater is installed (fig. 4). The chamber is made of fluoroplastic that allows the heating up to 90°C and use of chemical agents. Openings in the chamber faces which are equipped with sealing arrangements allow the free movement of a fuel pin inside the chamber in any direction and the leak-tight placement at a set coordinate. In so doing, a fuel pin is placed horizontally relative to its axis, while the coaxial arrangement of the openings in the chamber faces prevents fuel pin deformation during its movement.



a



b

Fig.4. Photo (a) and layout (b) of the device for deposit removal from the fuel pin cladding surface: 1 – opening in the lateral surface of the chamber, 2 – rotating device, 3 – chamber, 4 – sealing arrangements, 5 – fuel pin, 6 – working volume of the chamber, 7 – handler, 8 – heater

Opening in the lateral surface of the chamber is designed for filling of the chamber with a solution of chemical agents and its further elimination upon completion of the deposit removal. The solution volume is provided so that the fuel pin cladding surface is completely immersed in the solution inside the working volume of the chamber. Upon completion of the deposit removal, spent solution is removed from the chamber working volume by rotating with a handler and by rotating device about the horizontal axis. After the deposit removal, the fuel pin cladding area under analysis is washed using distilled water, sealing arrangements are loosened and fuel pin is displaced in a set direction up to the next required coordinate.

The deposit removal process carried out in hot cells allows the performance of investigations without any limitations in radionuclide activity, while preparation (weighing, dissolution and dilution) of a sample for chemical analysis during mechanical removal of deposits is conducted in glove boxes

which results in significant limitations in radionuclide activity and, therefore, limitations in mass of deposit samples, reduces accuracy and increases error of the analysis.

Fuel pin purified from deposits completely or partially using the proposed method is further suitable for the material ICP testing, while solutions are used for quantitative analysis of chemical composition of deposits by ICP-AES. This method of analysis is highly sensitive, multi-elemental, effective and flexible which allows the obtaining of reproducible results with low absolute error when determining both micro- and macro-concentrations of elements in objects different in their composition [6-8]. Based on this method and deposit removal process, a procedure for quantitative chemical analysis was developed and metrologically certified [9]. With mastered methods of sample preparation, calibration, concentration measurements and introduction of corrections for systematic factors of influence, high sensitivity of the method allowed the achievement of high accuracy of the procedure and maximum low detection limits (DL) of controlled elements (Table 1).

Table 1

Analytical lines of controlled elements and detection limits

Element	λ^* , nm	DL, ng/cm ³	Element	λ^* , nm	DL, ng/cm ³
Fe	259,940	0,010	Co	228,616	40,000
Cr	205,552	1,000	Ca	393,366	0,050
Cu	324,754	0,010	Mg	278,553	0,049
Ni	231,604	3,300	Si	251,611	10,000
Mn	257,610	0,800	Na	589,592	8,300
Zn	213,856	0,600	Al	396,152	18,800
Zr	339,198	0,010	Mo	202,203	0,700
Nb	269,706	10,800	K	766,491	159,000
Sn	189,926	0,700	B	208,959	10,000
U	302,221	1,000	Eu	381,967	1,000
Ti	190,930	3,000			

*Wave length of analytical line.

Detection limits are assessed using the following ratio

$$DL = 3 \sigma_{\text{backgr}} \text{BEC},$$

where σ_{backgr} – relative standard deviation of background intensity ;

BEC – element concentration providing an analytical signal equivalent to the background (background equivalent concentration) [7, 10].

Relative measurement error for most controlled elements ranges within 1.7...5%. The method sensitivity and accuracy of the analysis allows the identification of the deposit ultimate composition from a small area of the fuel pin surface (tens of square centimeters) even in case of the deposit layer thickness of very few micrometers that was earlier impossible using the mechanical method of deposit removal and less sensitive methods of analysis.

A list of controlled elements (Table 1) was conditioned by a degree of their effect on the formation of deposit layers and change in properties of the fuel pin cladding material, as well as by technical features of the spectrometer.

Serial spectrometer "Spectroflame Modula S" (Germany) of standard configuration is not intended for handling radioactive materials. However, its adjustment (installation and connection of the exhaust system to a special vent system; use of disposable plastic container as a drain device with fur-

ther liquid removal to the special vent system together with multiple dilution of sample solution) made it possible to use it as a reliable tool for investigation of materials after irradiation.

The ICP-AES method is relative, i.e. it requires preliminary precise calibration using standard samples for each controlled element on which the validity of the analysis results depends significantly. For this method, calibration charts are linear ranging within 4-6 orders [6, 8,10]. However, in case of the deposit analysis, breakdown of calibration charts into two sub-ranges turned out to be the most preferable: from detection limits up to $1 \mu\text{g}/\text{cm}^3$ and from $1 \mu\text{g}/\text{cm}^3$ up to the maximum controlled concentration for each element. Random error of calibration characteristics is significantly reduced with such optimization of graduation near a value of $1 \mu\text{g}/\text{cm}^3$.

Synthetic solutions of individual elements based on standard samples of composition of metal and non-metal ion water solutions are used as calibration solutions. When preparing calibration solutions, composition, acidity of the analyzed sample solutions and all preparation operations (including dilution) to eliminate differences in their physical-chemical properties and prevent significant systematic errors are taken into account.

When developing the procedure, selection of analytical lines of controlled elements is the most important. A selected line should be free from direct or partial overlap from other lines and at the same time be sensitive enough (Table 1). Spectra of these elements in the region of selected lines were preliminary investigated. The spectra were obtained by consecutive introducing into plasma of the following: water (distilled water after filtering through columns with ion-exchange resin); water solution of the identified element with a concentration of $0.1 \mu\text{g}/\text{cm}^3$; acid solution to remove deposits with a concentration of the identified element equal to $0.1 \mu\text{g}/\text{cm}^3$. The analysis of the obtained spectra showed that background radiation doesn't influence significantly on the intensity of analytical lines of deposit elements even in the low concentration region.

During metrological certification of the procedure, the following main characteristics of measurement error were identified for all controlled elements: combined standard uncertainty σ_s for single- and triple measurements; effective number of degrees of freedom f_{eff} corresponding to uncertainties; ranges of absolute Δ and relative error with confidence probability $P=0,95$ for five points for each element. Metrological characteristics of Fe concentration measurement error are given as an example in Table 2.

Table 2

Main error characteristics for Fe at single and triple measurements based on the quantitative analysis procedure

Error characteristic	Points within the range of measured concentration values for which the analysis errors are calculated, $\mu\text{g}/\text{cm}^3$				
	0,1	0,5	1,0	50	100
$\sigma_s(1), \mu\text{g}/\text{cm}^3$	0,0015	0,0067	0,0119	0,60	1,28
$\sigma_s(1), \%$	1,518	1,337	1,188	1,19	1,28
f_{eff}	14	16	12	12	15
$\sigma_s(3), \mu\text{g}/\text{cm}^3$	0,0013	0,0062	0,0118	0,59	1,22
$\sigma_s(3), \%$	1,304	1,236	1,185	1,19	1,22
f_{eff}	16	14	12	12	13
$\delta(1), \%$	5,877	2,834	2,589	2,60	2,73
$\Delta(1), \mu\text{g}/\text{cm}^3$	0,0059	0,0142	0,0259	1,30	2,73
$\delta(3), \%$	5,385	2,651	2,581	2,58	2,63
$\Delta(3), \mu\text{g}/\text{cm}^3$	0,0054	0,0133	0,0258	1,29	2,63

Within the framework of the agreed and research work using the described set of developments, studies into composition and distribution of deposit elements with height of the RBMK-1000, VVER-1000 and VK-50 fuel pin claddings were performed.

Distribution of Fe as the basic element of deposits and Cu as an element inducing corrosion of the claddings of the RBMK-1000 FA pins spent at the Leningrad NPP are given as examples in figures 5, 6.

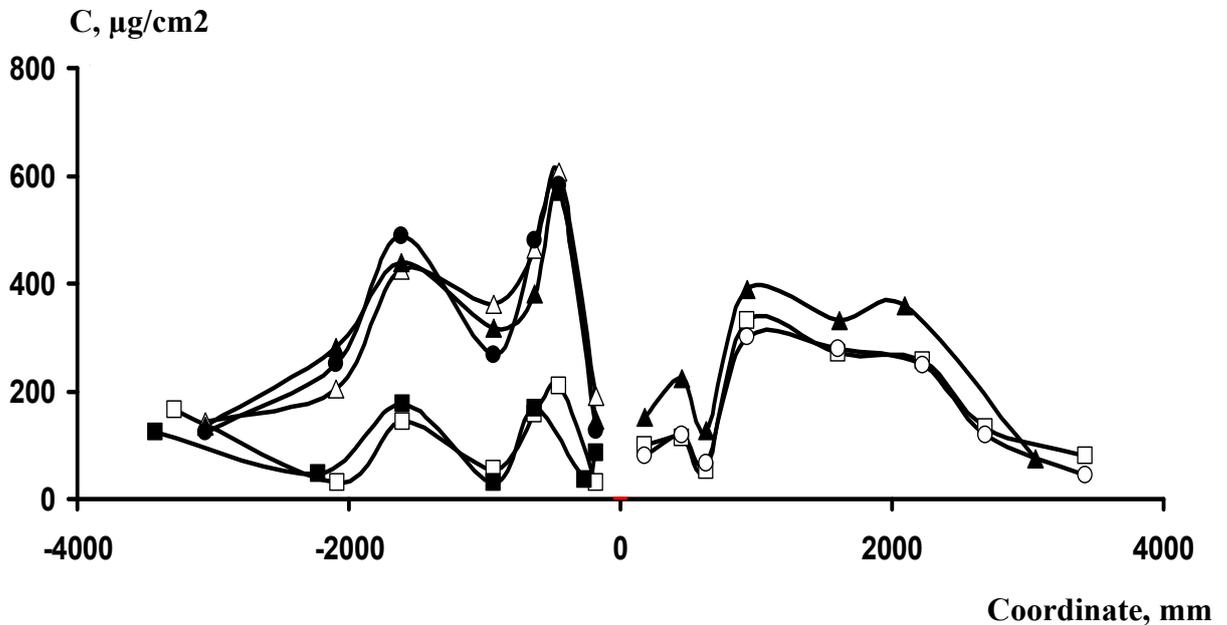


Fig. 5. Content of Fe on the fuel pin claddings with the FA height: 1H (Δ) (generated power of 2830 MWday/FA); 2H (\bullet) (generated power of 2869 MWday/FA); 5H and 5B (\blacktriangle) (generated power of 1608 MWday/FA); 3H (\blacksquare) (generated power of 2745 MWday/FA); 2B (\circ) and 2H-1B (\square) (generated power of 2838 MWday/FA)

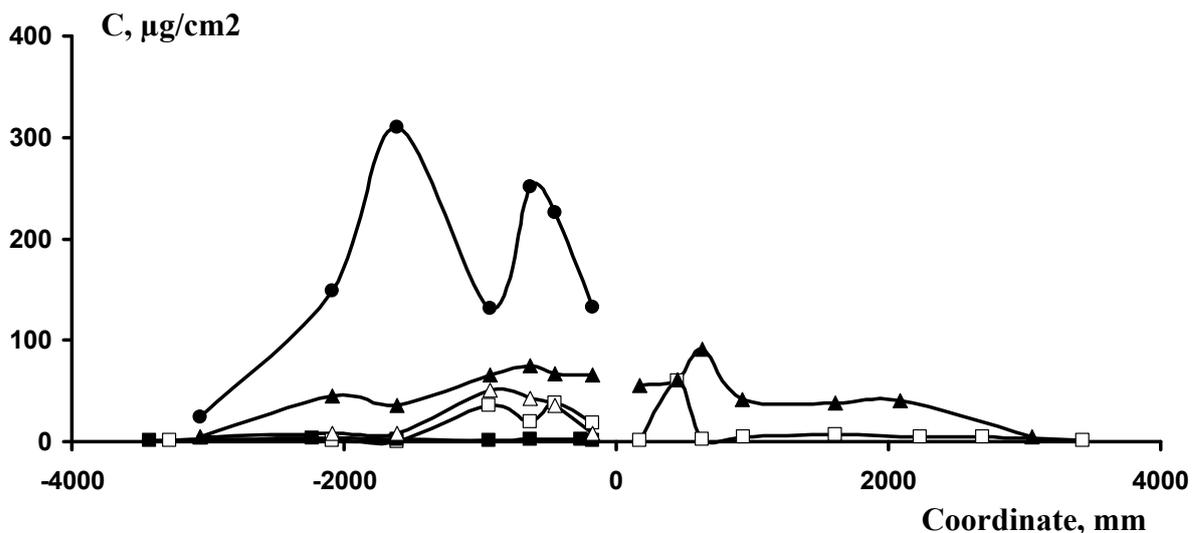


Fig. 6. Content of Cu on the fuel pin claddings with the FA height: 1H (Δ) (generated power of 2830 MWday/FA); 2H (\bullet) (generated power of 2869 MWday/FA); 5H and 5B (\blacktriangle) (generated power of 1608 MWday/FA); 3H (\blacksquare) (generated power of 2745 MWday/FA); 1B (\circ) and 2H (generated power of 2838 MWday/FA)

In this case, the deposits were removed between spacer grids from the fuel pin cladding areas 80 mm long. Coordinates of the examined areas (distance from the fuel pin plug to the center of the examined area) were fixed with an error of ± 10 mm using optical inspection system RVP-506. Positive values along the X-axis correspond to the coordinate of the fuel pin from the FA upper bundle, while negative – from the FA lower bundle. Numbering of fuel pins is conventional; index "H" refers to the lower fuel pin bundle and "B" – to the upper one. The investigation results are presented as a content of elements on a unit of the fuel pin cladding surface area ($\mu\text{g}/\text{cm}^2$) in order to enhance informativity. Calculation was carried out based on the volume of chemical solution used for deposit removal and on the cladding surface area under examination.

Thus, the above-described developments allow the highly accurate (relative error of analysis for most elements is 1.7–5 %) analytical control of the ultimate composition of deposits on Zr claddings of the fuel pins from water-cooled nuclear reactors after operation without any significant limitations in radionuclide activity, from any fixed sections along the fuel pin height, retaining integrity of the product, cladding material and Zr oxide surface layer and with maximum low detection limits.

The investigation results obtained using these developments can be used for study into mechanisms of the fuel pin cladding material damage, optimization of the reactor water chemistry, effective use of calculation methods to reveal and forecast the deposit formation processes.

References

1. Pat. 2263161. MPK⁷ C23G /12. Method of production of deposit samples from Zr fuel pin cladding surface for quantitative analysis/ Smirnova I.M., Kuchkina I.N., Lyadov G.D., Markov D.V.// Bulletin of Inventions, Useful Models, 2005. No. 30. P. 725.
2. Smirnova I.M., Kuchkina I.N. Application of ICP-AES for identification of factors influencing the accumulation of coolant impurities in deposits on fuel pins from the VK-50 reactor facility / Collection of abstracts of the XVIII Ural Conference on Spectroscopy, Novouralsk, September 10-14, 2007. – Ekaterinburg: Edited by "Analytics and Control", 2007. P. 41–42.
3. Smirnova I.M., Filyakin G.V., Kuzmin S.V. Post-irradiation examinations of deposits on the RBMK fuel pin claddings // Atomnaya Energiya, 2008. Vol. 105. Ed. 2. P. 113–115.
4. Pavlov S.V., Sukhih A.V., Sagalov S.S. Eddy-current methods of control in reactor material science. – Dimitrovgrad: JSC "SSC RIAR", 2010. P. 216.
5. Pat. 55371. MPK⁷ C23G 3/00. Device for removal of surface deposits from long products/ Smirnova I.M., Kuchkina I.N., Markov D.V., Neugodnikov D.S.// Bulletin of Inventions, Useful Models, 2006. No. 22. P. 918.
6. Chudinov E.G. Atomic-emission analysis with inductive plasma. Results of Science and Technology. Analytical Chemistry. – M.: VINITI, 1990. Vol.2.
7. Pupyshev A.A., Danilova D.A. Atomic-emission spectral analysis with inductively coupled plasma and a Grimm-type glow discharge. – Ekaterinburg: State Educational Institution of Higher Professional Education Ural State Technical University –Ural Polytechnical Institute, 2002. P.202.
8. M. Thompson, J. N. Walsh. Handbook of Inductively Coupled Plasma Spectrometry. Translation from English. – M.: Nedra, 1988. P.288.
9. Smirnova I.M., Kusnir Yu.A. Metrological aspects of analysis of the surface deposits on the claddings of water-cooled reactor fuel pins using atomic-emission spectrometry with inductively coupled plasma.// RIAR Proceedings, 2007. Ed. 1. P.53–60.
10. Boss C.B. Concept, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry / C.B. Boss, K.J. Fredeen. – Perkin Elmer, 1997.

STUDYING HELIUM ACCUMULATION IN AUSTENITIC STEELS FOR EVALUATING RADIATION DAMAGE IN INTERNALS OF WATER-MODERATED WATER-COOLED POWER REACTORS

S.V. BELOZEROV, V.S. NEUSTROEV, V.K. SHAMARDIN
JSC SSC RIAR
Dimitrovgrad-10, 433510 – Russian Federation

ABSTRACT

The accumulation of helium in austenitic steels upon the irradiation in research and power reactors has been studied. It has been shown that the application of a high-sensitive mass-spectrometer method of determining integral accumulation of helium makes it possible to obtain reliable correlation dependences between the content of helium in the irradiated steel and the damaging dose.

1. Introduction

At present, the major part of the electric power generated in the Russian Federation at atomic power plants is due to reactors of the WWER (water-moderated water-cooled power reactor) type. The age of many of these reactors built in 1970–1980s approaches their service life (about 30 years) established on the basis of a limited database for the properties of structural materials used in these reactors after irradiation available in those years. The substantiation of a prolonged (30 years) designed service life of WWP nuclear reactors and its prolongation by 10–15 years or greater requires the knowledge of the laws that govern changes in the structure and properties of structural materials irradiated by neutrons under the conditions characteristic of the internals of these reactors, first of all, of the reflection shield. The major part of the nonremovable internals of these reactors is made from steel in the austenitized state.

The neutron-physics calculations carried out at the FSUE OKB GIDROPRESS show that the maximum neutron-induced damaging dose expressed in displacements per atom (dpa) in some regions of the reflection shield after a 30-year operation will reach approximately 75 dpa and with the planned increase in the service life of a reactor to 60 years it may reach 100 dpa or greater. Thus, for the development of model concepts concerning changes in the properties of materials used in internals during the in-core irradiation to such significant damaging doses there is required a reliable determination of, first of all, the damaging dose in materials science experiments on the irradiation of materials and studying their properties.

In the majority of cases, the estimation of the damaging dose in the positions used for the irradiation of the materials investigated is carried out based on the calculated or experimentally measured value of the fluence of neutrons with an energy of more than 0.1 MeV. In such calculations, there are used a sufficiently large number of quantities (nuclear-reaction cross sections, flux density, spectral composition of the neutron radiation, etc.); the errors in the determination of these can introduce an essential uncertainty into the final value of the calculated damaging dose. This is important both for the nontrivial conditions of irradiating materials in research reactors (complex geometry of the irradiating device, the heterogeneity of the material, etc.) and for the conditions of irradiation of materials in power reactors. At the same time in a number of works [1–4] there is noted a correlation between the values of the damaging dose and of the integral accumulation of helium in the irradiated material.

Most substantially, the dependences of the accumulation of helium on the damaging dose are manifested for austenitic steels (which contain a significant amount of nickel) during irradiation in those positions which are characterized by the high density of the thermal-

neutron flux (Fig. 1). The maximum rate of helium accumulation in steel during in-core irradiation in these works [1–4] ($K=C(\text{He})/D=51$ appm/dpa) is characteristic of steel irradiated in the mixed spectrum of a high-flux isotope reactor (HFIR) in the position of a peripheral target, whereas the irradiation in the same reactor in the position of the reflector (with a hafnium shield for decreasing the thermalneutron flux) leads to a sharp decrease in the rate of helium accumulation ($K=7.5$ appm/dpa). The rate of helium accumulation in steel 316 during irradiation in a light-water power reactor of the PWR type (bolt of the reflection shield, the central plane of the core) is about 15 appm/dpa. A substantially lower rate of helium accumulation ($K=0.32$ appm/dpa) is observed during irradiation of an iron–chromium–nickel alloy (15.5% Ni) in a fast-neutron reactor EBR-II.

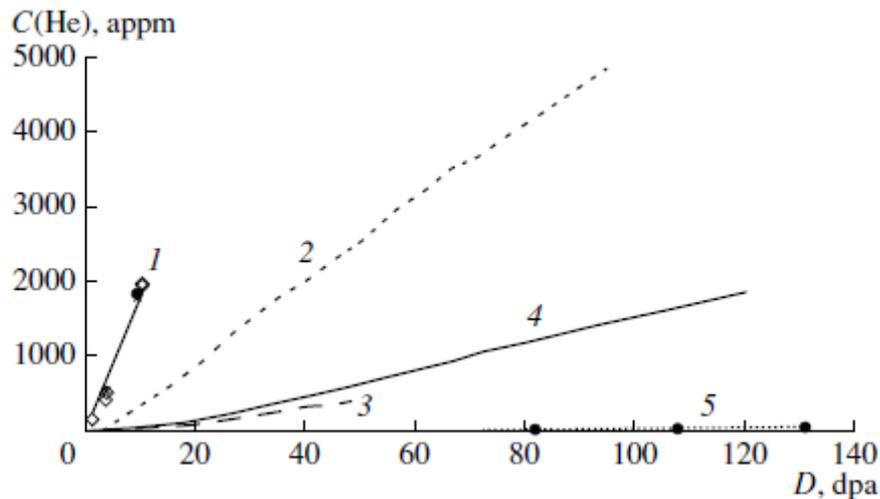


Fig 1. Calculated dependences of the accumulation of helium on the damage dose: (1) steels 304 and 316, accelerator LANSCE [3]; (2) reactor HFIR, the irradiation position corresponding to a peripheral target [1]; (3) reactor HFIR, the irradiation position corresponding to the reflector [1]; (4) steel 316, the irradiation position corresponding to a bolt of the reflection shield of a PWR reactor [2]; and (5) an Fe-15Cr-15Ni alloy, an EBR-II reactor [2].

Thus, the determination of the accumulation of helium in austenitic steel during in-core irradiation not only can serve as an indicator of the damaging dose, but also characterizes the conditions of the material irradiation from the viewpoint of the spectral composition of the neutron radiation. A similar approach has been realized, for example, in the standard test method for the analysis of the fluence monitors based on helium accumulation [5] realized using highly sensitive helium mass spectrometry [6]. The accumulation of helium in materials irradiated by neutrons is one of the most important factors that can influence the degradation of the physicomechanical properties of structural materials during in-core irradiation [7]. This work is devoted to studying factors that govern the accumulation of helium in corrosion-resistant austenitic steels during irradiation in the research reactors located at the JSC SSC RIAR and also in power reactors depending on the damaging dose and the type of neutron spectra.

2. Experimental

The determination of the integral accumulation of helium in steel samples after in-core irradiation was carried out by mass spectrometry with the application of the method of isotope dilution according to the procedure No. 505 of the list of procedures published in the proceedings of the Research Institute of Atomic Reactors (JSC SSC RIAR) [8]. For the application of the mass-spectrometric method of measuring helium content in irradiated structural materials, there was developed an experimental installation for the extraction and

analysis of radiogenic gases on the base of a commercial MI1201 mass spectrometer (Fig. 2).

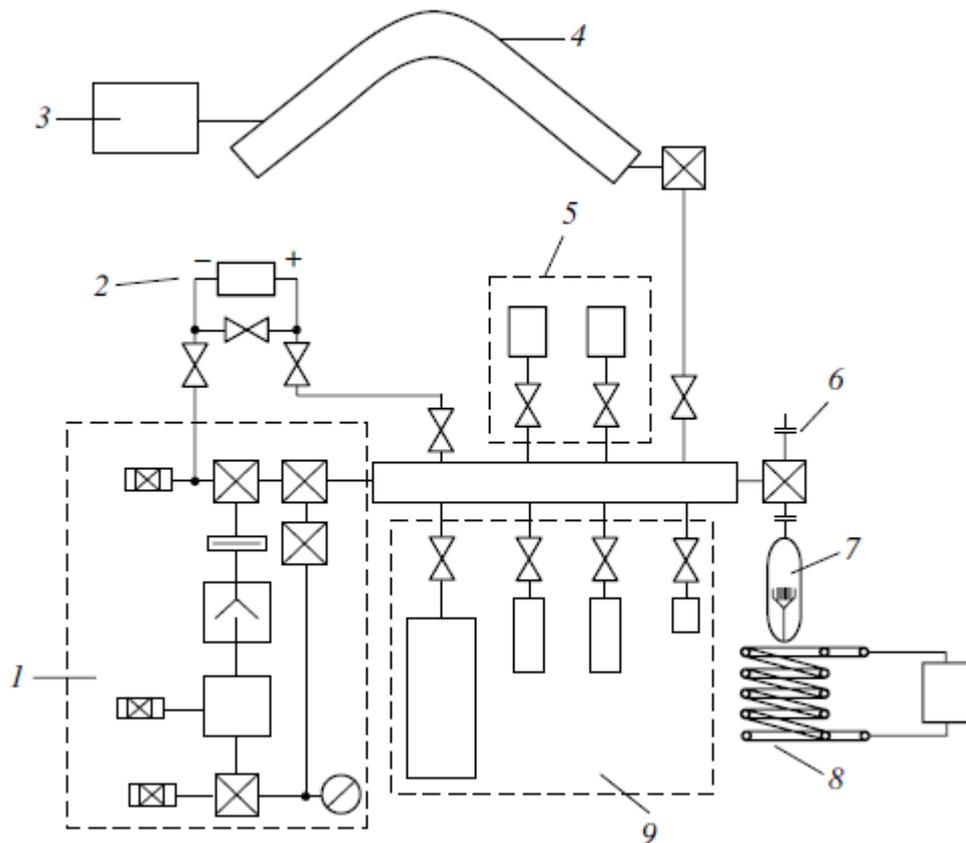


Fig 2. A schematic of an experimental installation for measuring helium content in the irradiated structural materials: (1) vacuum pumps and the system for measuring vacuum; (2) pressure gage of marker; (3) automated measuring-controlling system of the mass-spectrometer; (4) MI1201 mass-spectrometer; (5) ampoules with a marker and control mixture; (6) lock of loading sample; (7) chamber for sample; (8) high-frequency inductor; (9) system of calibrated volumes.

The modernization of the measuring system with the application of a volumetric calibration and quasi-static regime of helium pumping out made it possible to increase the sensitivity of measurements by three orders of magnitude in comparison with the normal mode of measurements using this spectrometer. The confidence limits of the error in the results of measurements of the molar fraction of ^4He isotope (with a confidence probability of 0.95) that were established as a result of a metrological certification of the procedure were 6–9% in the range of helium concentrations in the sample from 10^{-9} to $5 \cdot 10^{-7}$ mol. The procedure makes it possible to determine helium concentrations above 1 appm in steel samples 5–50 mg in weight [9]. It also permits a qualitative analysis of the content of other radiogenic gases (hydrogen, tritium) in the samples of the irradiated materials.

3. Results

To estimate the influence of the neutron spectrum on the accumulation of helium in austenitic steels irradiated to comparable damaging doses (on the order of 15 dpa), the irradiation (using neutron spectra differing in thermal components) and subsequent study of the accumulation of helium in samples of steels of several different compositions have been carried out in research reactors of different types (located in the Research Institute of Atomic Reactors) and also in power reactors of the WWER type.

3.1. Accumulation of Helium during Irradiation of Steel by Thermal Neutrons

For our studies, we used samples of steels of the Cr17-Ni13-Mo3 and Cr18-Ni10 grades. The irradiation of the samples was carried out in the high-temperature experimental irradiation channel No. 4 of the SM reactor. The samples were placed in zirconium pipes of the irradiation device (ID) on eight floors along the height of the reactor core (~400 mm). The samples on the four lower floors, which were located below the central plane of the core, were protected by cylindrical hafnium shields placed directly on the samples (Fig. 3). The average temperature of the shielded samples over the exposure time was 302 ± 10 °C; the temperature of the unshielded samples was 299 ± 10 °C.

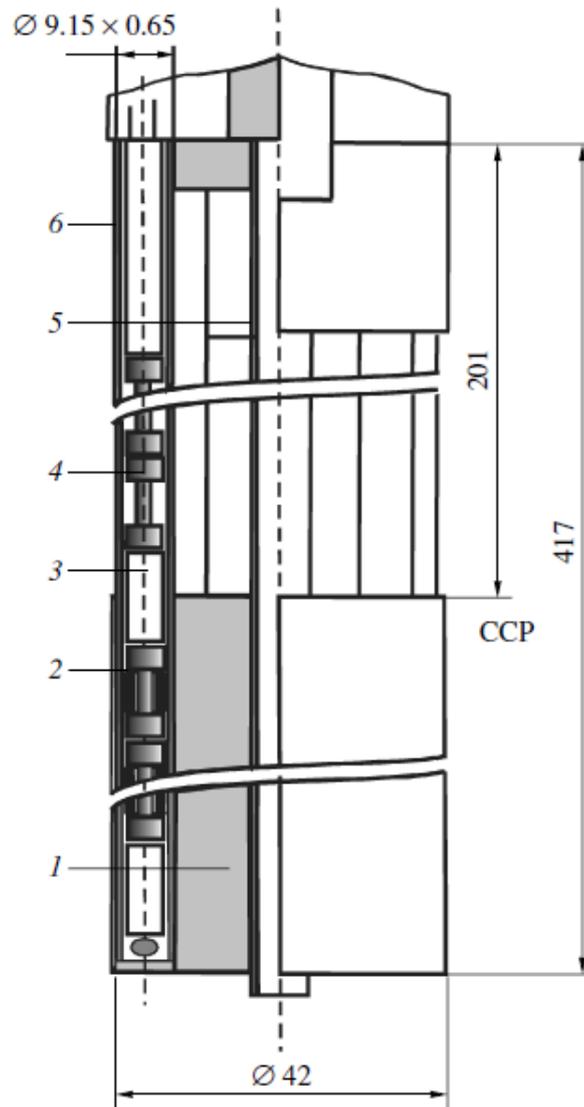


Fig 3. Device for irradiating samples (schematic): (1) steel cylindrical block; (2) hafnium shield; (3) spacer; (4) steel sample; (5) central zirconium pipe; (6) peripheral zirconium pipe. CCP = core central plane.

In the central tube of the ID, ampoules with neutron activation detectors (NADs) for monitoring neutron flux were placed. As can be seen from Fig. 4, the shielding of the samples significantly changed the thermal part of the neutron spectrum during in-core irradiation. The irradiation of the samples was conducted in two stages. After the end of stage 1, partial unloading of the samples and detectors of the neutron fluence from the reactor was conducted. For each stage, the content of helium in the samples located along the height of the ID was calculated and measured.

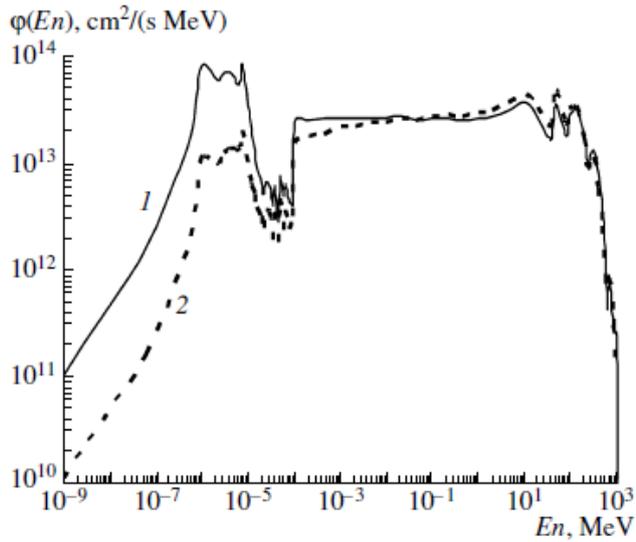


Fig 4. Differential energy spectrum of neutrons in the experimental channel No.4 of an SM reactor: (1) unshielded spectrum; (2) shielded spectrum.

It follows from Fig. 5 that the content of helium in the samples of steels irradiated in the complete spectrum (with the unshielded thermal component) exceeds the content of helium in the samples irradiated using the shielded spectrum (without the thermal component) by more than an order of magnitude. In this case, there is observed a correlation between the calculated data and results of measurements. The difference between the helium content determined by calculation and experimental methods in the samples irradiated in the complete spectrum does not exceed 5%; in the samples irradiated in the shielded spectrum, it reaches 20% after the first stage and 40% after the second stage of irradiation. An increase in this difference with time can be connected with a change in the contribution to the accumulation of helium from the reactions of the fast and thermal neutrons because of the “burning out” of the absorbing shields.

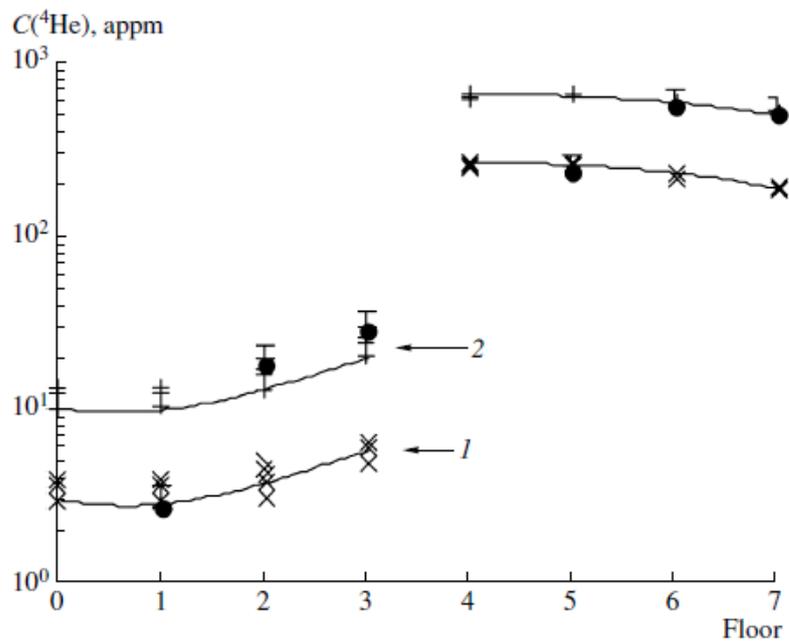


Fig 5. Distribution of helium accumulated in steel along the height of the device for the irradiation of samples: (1) stage I of irradiation; (2) stage II of irradiation; (•) results of measurements.

The rate of helium accumulation in steels in the range of damaging dose of 4–15.6 dpa was 53 ± 4 appm/dpa for the samples irradiated in the complete spectrum and 1.8 ± 0.7 appm/dpa in the shielded spectrum (Fig. 6).

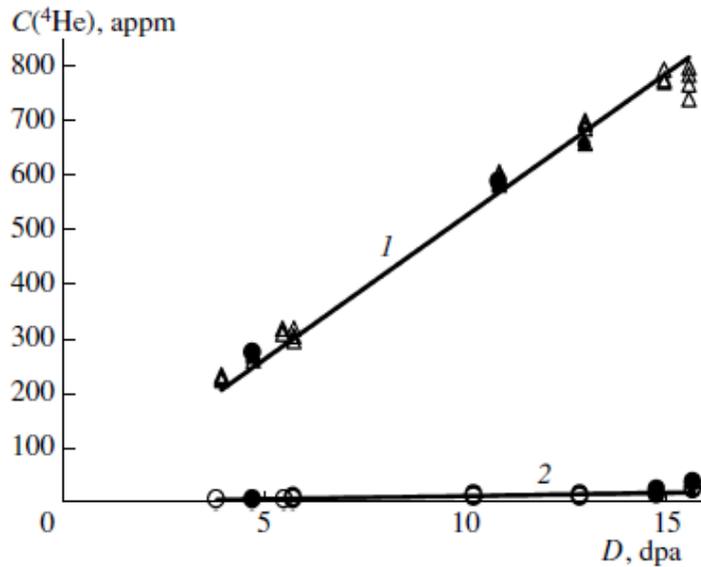


Fig 6. Dependence of the accumulation of helium in steel samples on the damaging dose: (1) total spectrum; (2) shielded spectrum; (•) results of measurements.

3.2. Accumulation of Helium upon Irradiation with Fast Neutrons

To determine the rate of helium accumulation in the corrosion-resistant steel during irradiation in a neutron spectrum without a thermal component, we carried out the irradiation of the samples of steel Cr18-Ni10 in the research reactor BOR-60 in which the neutron flux virtually does not contain thermal neutrons. The temperature of irradiation was from 320 to 340°C. The fluence of fast neutrons ($E > 0.1$ MeV) for the samples irradiated at different heights in the irradiating device was from $3 \cdot 10^{22}$ to $1.6 \cdot 10^{23}$ cm^{-2} . As follows from the data shown in Fig. 7, the rate of helium accumulation in steel Cr18-Ni10 during irradiation in the BOR-60 reactor by rapid neutrons does not exceed 1 appm/dpa, which corresponds to previously published calculation data about the accumulation of helium in steel during irradiation by fast neutrons [2].

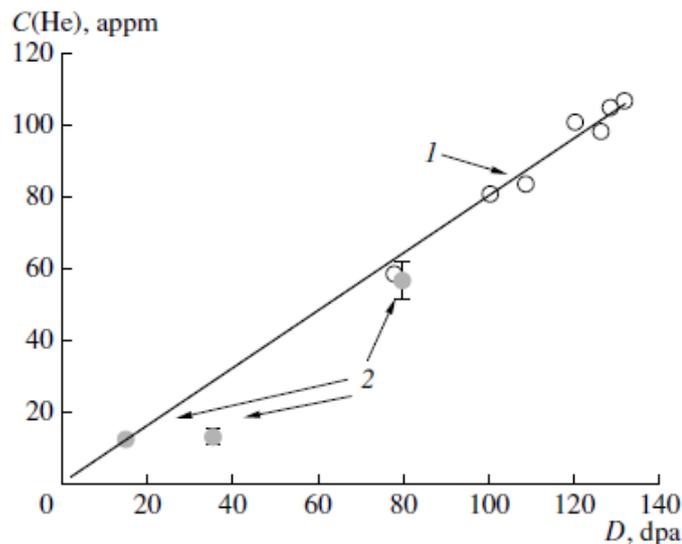


Fig 7. Dependence of the accumulation of helium in steel on the damaging dose: (1) calculated data for the Fe-15Cr-45.3Ni alloy (EBR-II); (2) results of measurements for the Cr18-Ni10 steel (BOR-60).

3.3. Accumulation of Helium in Steel during Irradiation in Power Reactors

To estimate the rate of helium accumulation in the materials used in the internals of reactors of the WWER type depending on the damaging dose, the following measurements of the integral accumulation of helium were carried out:

— in samples of steel C0.08-Cr18-Ni10-Ti cut out from the guide channel of the fuel assembly of the WWER-1000 reactor irradiated at a distance of 100–150 mm from the reflection shield of the reactor for a period of five years in the range of damaging doses from 0.2 to 15 dpa at temperatures 285–310°C;

— in samples of steel C0.06-Cr18-Ni10-Ti cut out from the spacer grids of the working cassettes of the WWER-440 reactor irradiated to a damaging dose of 7–20 dpa at temperatures of ~300°C. The values of the damaging doses for these samples were evaluated from the data on the distribution of the activity of the ^{54}Mn and ^{60}Co nuclides along the guiding channels and fuel assemblies of the WWP reactors obtained both by the calculation and experimental methods.

From the results of measurements of helium accumulation in steel Cr18-Ni10-Ti-type shown in Fig. 8, we can suppose that the accumulation of helium is proportional to the damaging dose and to determine the rate of accumulation as being equal to 5.4 appm/dpa, assuming that no helium was present in the steel before the irradiation. The rate of accumulation was obtained without taking into account the result of measurement (content of helium at a level of 180 appm) for the damaging dose of 20.7 dpa, since the maximum content of helium is almost two times greater than the estimate of the helium accumulation made on the basis of the extrapolation of the dependence proposed, which, apparently, is connected with the influence of some disregarded factors on the results of measurements. The deviation of the results of measurements can also be caused by an error in the determination of the damaging dose when using correlation dependences of this quantity on the activity of the ^{54}Mn and ^{60}Co nuclides in the irradiated steel.

The results obtained agree satisfactorily with the data of [10] which show that the helium accumulation in cold-deformed steel 316 with an Ni content of 13% does not exceed 70 appm during irradiation in a PWR power reactor to a damaging dose of approximately 20 dpa. For refining the parameters of the dependence at large damaging doses, additional studies of the accumulation of helium at the damaging doses of 20 dpa and greater are required.

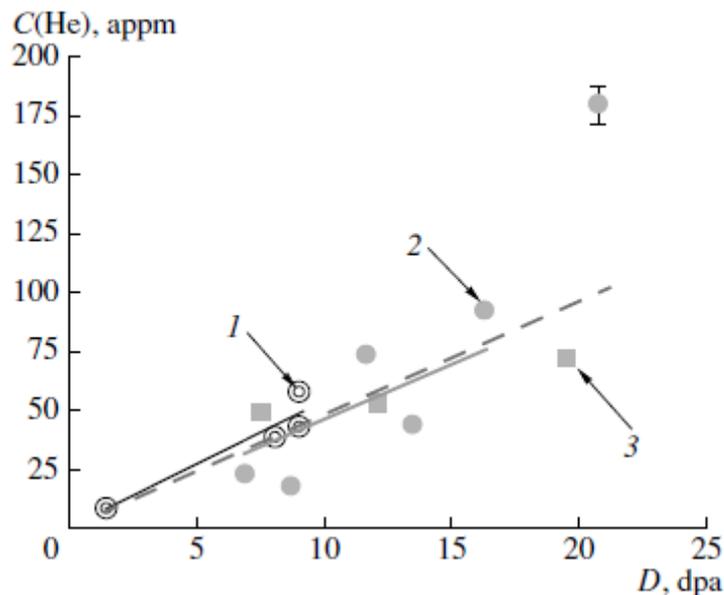


Fig 8. Accumulation of helium in steel Cr18-Ni10-Ti depending on the damaging dose: (1) results of measurements for the WWER-1000 reactor; (2) results of measurements for the WWER-440 reactor; (3) results for steel 316 irradiated in the PWR reactor [10].

4. Conclusions

1) Basic factors that govern the accumulation of helium in austenitic steels during irradiation in research reactors of the SM and BOR-60 type have been established depending on the damaging dose and the type of the neutron spectrum. It is shown that the rate of helium accumulation in steels of the Cr18-Ni10 and Cr17-Ni13-M3-type in the range of damaging doses of 4–15.6 dpa during irradiation in the reactor of the SM type was 53 ± 4 appm/dpa, which is comparable with the rate of helium accumulation in steels of analogous class during irradiation in reactors of the HFIR type. The shielding of the thermal part of the neutron spectrum during irradiation of these steels in the SM reactor under the analogous (with respect to the unshielded samples of steel) temperature–dose irradiation conditions leads to a significant decrease in the rate of helium accumulation (to 1.8 ± 0.7 appm/dpa), which made it possible to experimentally confirm (in this range of damaging doses) the well-known concept of the preferred generation of radiogenic helium in nickel-containing materials under the action of the thermal part of the neutron spectrum. The substantially lower rate of helium accumulation, whose magnitude does not exceed 1 appm/dpa, is noted in steel of the Cr18-Ni10-type during irradiation in the BOR-60 reactor, which is also comparable with the known experimental and calculated estimations of the accumulation of helium during irradiation of austenitic steels in fast-neutron reactors [12, 13].

2) Experimental estimations of the rate of helium accumulation in steels of the C0.06-Cr18-Ni10-Ti-type during irradiation in WWER reactors have been carried out. The accumulation of helium is proportional to the damaging dose, and its rate (5.4 appm/dpa) is higher than during irradiation of steels of this class in fast-neutron reactors, but is substantially lower than the rate of helium accumulation in these materials upon the irradiation in research high-flux reactors with a large contribution of the thermal part of the neutron spectrum. To confirm the suggested dependence of helium accumulation in austenitic steels or reveal possible deviations from the proposed dependence during irradiation in power reactors, an experimental determination of the integral accumulation of helium at higher damaging doses (greater than 20 dpa) is required.

3) The possibility of the application of the developed mass-spectrometric methods of determining helium content in irradiated materials for conducting precision simulation experiments in research and power reactors for studying irradiation of materials of internals of WWER reactors is substantiated. The use of the high-sensitive experimental method of determining integral accumulation of helium proposed makes it possible to obtain reliable correlation dependences between the content of helium in the irradiated steel and the magnitude of the damaging dose. The use of this procedure also makes it possible to correctly perform reactor experiments on the study of the role of helium in the processes of swelling-up and strengthening of structural materials and, first of all, austenitic steels, during the in-core irradiation.

References

1. F. A. Garner and L. R. Greenwood, "Neutron Irradiation Effects in Fusion or Spallation Structural Materials: Some Recent Insights Related to Neutron Spectra," *Radiat. Eff. Defects Solids* 144, 251–286 (1998).
2. F. A. Garner, L. R. Greenwood, and B. M. Oliver, "A Reevaluation of Helium/Dpa and Hydrogen/Dpa Ratios for Fast Reactor and Thermal Reactor Data Used in Fission–Fusion Correlations," *J. Nucl. Mater.* 22, 208 (1996).
3. B. M. Oliver, F. A. Garner, S. A. Maloy, et al., "Retention of Very High Levels of Helium and Hydrogen Generated in Various Structural Alloys by 800 MeV Protons and Spallation Neutrons," in *Proc. 20th Int. Symposium on Effects of Radiation on Materials* (West Conshohocken, PA, 2002).
4. Ph. Dubuisson, J.-P. Massoud, and N. de Mathan, et al. "Behavior under Neutron Irradiation of Austenitic Stainless Steels (Representative of French Core Internals) Irradiated in Bor-60 and SM Reactors," in *Sixth Russian Conf. on Reactor Material Science: Abstracts of Papers*, GNTS NIIAR, Dimitrovgrad, 2000), pp.312.

5. ASTM E 910-95 (E 706 IIC), "Standard Test Method for Application and Analysis of Helium Accumulation Influence Monitors for Reactor Vessel Surveillance" in *Annual Book of ASTM Standards*, Vol. 12.02, pp. 490–500 (1995).
6. H. Farrar IV and B. M. Oliver, "A Mass Spectrometer System to Determine Very Low Levels of Helium in Small Solid and Liquid Samples," *J. Vac. Science Techn. A4*, 1740 (1986).
7. A. G. Zaluzhnyi, Yu. N. Sokurskii, and V. N. Tebus, *Helium in Reactor Materials* (Energoatomizdat, Moscow, 1988) [in Russian].
8. S. V. Belozerov, "Determination of Helium Content in Irradiated Construction Materials by Mass-Spectrometer Method," in *Sb. Trudov FGUP GNTs RF NIIAR* (Dimitrovgrad, 2003), No. 2, pp. 68–78.
9. S. V. Belozerov, "Accumulation of Helium in Steel and Beryllium upon Irradiation in Research Reactors," PhD Thesis (Ul'yanovsk, 2005).
10. F. A. Garner, D. J. Edwards, S. M. Bruemmer, et al., "Recent Developments Concerning Potential Void Swelling of PWR Internals Constructed from Austenitic Stainless Steels," in *Proc. 6th Russian Conf. on Reactor Material Science*, (MINATOM, Dimitrovgrad, 2000), Vol. 3, Part 1, pp. 3–21.
11. V. S. Neustroev, Z. E. Ostrovsky, and V. K. Shamardin, "Investigation of Radiation Phenomena in Austenitic Stainless Steel for Extension of WWER Service Life Internals," in *Proc. of European Commission Meeting on Embrittlement and Mechanistic Interpretation of Reactor Pressure Vessel and Internal Materials* (European Communities, 2005), pp. 221–235.
12. D. J. Edwards, E. P. Simonen, F. A. Garner, et al., "Influence of Irradiation Temperature and Dose Gradients on the Microstructural Evolution in Neutron-Irradiated 316 SS," *J. Nucl. Mater.* 317, 32–45 (2003).
13. F. A. Garner, D. J. Edwards, S. M. Bruemmer, et al., "Recent Developments Concerning Potential Void Swelling of PWR Internals Constructed from Austenitic Stainless Steel," in *Proc. Intern. Symp. on Contribution of Materials Investigation to the Resolution of Problems Encountered in Pressurized Water Reactors*, (Fontenvraud, 2002), Vol. 1, pp. 393–404.

Renewal of the shielded Electron Probe Microanalyser (EPMA) in the CEA LECA-STAR hot laboratory: safety and technical improvements

HOTLAB 2010 - September 06-10 - Dimitrovgrad, Russia

J. LAMONTAGNE*, Th. BLAY, P. NAVARRA
 Commissariat à l'Énergie Atomique
 CEA/DEN/DEC
 F-13108 St Paul Lez Durance, France
 E-Mail : jerome.lamontagne@cea.fr



énergie atomique • énergies alternatives

DIRECTION de l'ÉNERGIE NUCLÉAIRE
 DÉPARTEMENT D'ÉTUDES
 DES COMBUSTIBLES
 CENTRE de CADARACHE

Context: For more than 30 years, CEA LECA-STAR hot laboratory performs microanalyses examinations on irradiated nuclear fuel using an EPMA. This equipment allows the characterisation of the elemental composition and its spatial distribution by wavelength dispersive X-ray spectroscopy (WDS). The last EPMA CAMECA CAMEBAX aged over 25 years has been replaced this year by a CAMECA SX100R which is dedicated to the investigation of highly radioactive samples including irradiated fuel. For the EPMA renewal project, the feedback from the CAMEBAX has been used. The studies have been focused specifically on the improvement of 3 major aspects. The first one was to improve safety of the EPMA. Special attention was focused to guaranty the extraction of an irradiated sample from the EPMA under all circumstances (regardless of loss of fluid or electricity...). Secondly, from an analytical point of view, the accuracy of the results had to be improved. In particular, the design of the shielding was optimised in order to reduce more efficiently the radioactive background coming from the irradiated sample. Thirdly, the microprobe accessibility for the maintenance operations in the hot cell was facilitated. Preliminary results of microanalysis obtained with this new EPMA illustrate improvements in terms of reliability and accuracy when compared with results obtained with the previous device.

LECA-STAR

Microanalysis Laboratory

Transfer to microanalysis Laboratory by a pneumatic transfer

Devices presented in the dedicated hot cell without the removable shielded wall

- Shielded EPMA SX100R (CAMECA)
- Shielded SEM XL 30 (FEI)
- Shielded SIMS 6f (CAMECA)
- Shielded μ XRD (GE)

Metallographic facility

Samples preparation

Microscopic observations

Main steps for the renewal of the EPMA

- Dismantling of the old CAMEBAX EPMA
- Modification of the dedicated cell and ergonomic improvements
- Manufacturing and tests under real conditions in the factory

Installation in the dedicated hot cell (schematic top view)

- EPMA (without electronic part and control panel) and glove box inside the hot cell
- Sample always inside the glove box or in the airlock or in the EPMA to avoid cell contamination
- EPMA out of the glove box in order to facilitate the maintenance actions

Labels: Double shielded door, Concrete wall, EPMA, Airlock, Glove box, Removable shielded wall

Main characteristics

EPMA SX100R (CAMECA):
 • 4 spectrometers (sin θ range: 25000 \rightarrow 81000) with the configuration below:

	SP 1	SP 2	SP 3	SP 4
Pressure	Low Pressure	High Pressure	Low Pressure	High Pressure
Type of crystals	PET TAP PC1 Quartz <1011>	LIF PET	LIF PC1 TAP PC2	LIF <220> PET

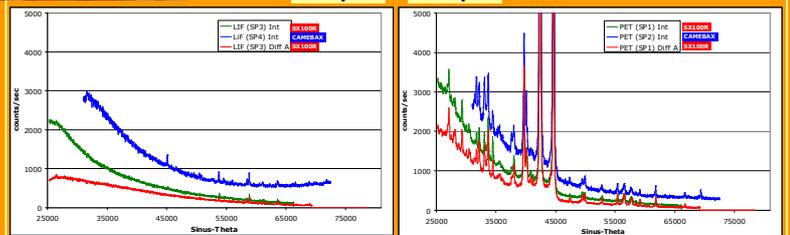
- Gun W or LaB6
- High voltage until 30 KV
- Gas in the counters: Argon/CH₄
- Optimised shielding in DENAL® (tungsten alloy material with high density)
- Pumping: 3 pumps (primary, turbo-molecular and ion for the gun)
- Anticontamination system (Cold plate cooled with liquid nitrogen and O₂ jet)



SX100R vs. CAMEBAX: comparison of results

Acquisition of spectrums on a highly irradiated nuclear fuel

Highlight of the drastic reduction of the radioactive background



- Substantial reduction of the radioactive background provided by the optimized shielding
- Significant reduction of the radioactive background due to the Automatic Differential mode but less pronounced than the contribution of the optimized shielding
- Total factor reduction of the radioactive background: from 2.4 to 7.2 depending on the crystal and the sin θ position

SX100R vs. CAMEBAX: improvements

Safety

The principal rules for an efficient nuclearisation:

- To be able to recover the sample in any position in the glove box
- To provide the sample extraction from the EPMA in any situation
- No contamination of the cell

Sample transit from the glove box to the EPMA

Airlock (Top view)

Manual connexion possibility
 (in case of loss of electricity, fluid...)

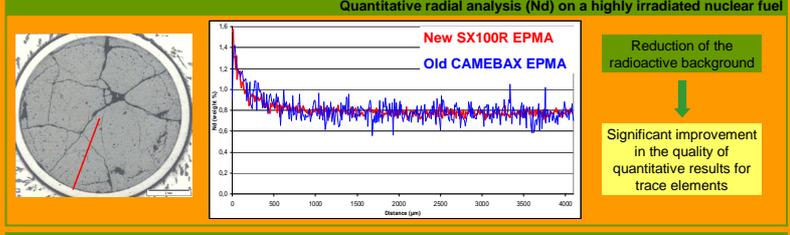
Shielding

In order to reduce more efficiently the radioactive background coming from the irradiated sample:

- The design of the shielding in the spectrometers is optimised (around the counters and in the entrance of the spectrometers)
- The material used for the shielding in the spectrometers is a tungsten alloy material DENAL®
- The sample stage in the analysis chamber is made with a 80 kg DENAL block

Labels: Denal shielding, Sample, Denal shielding (80 kg), counter, Spectrometer

Sample stage in the analysis chamber



Others features tested on highly irradiated nuclear fuels

SEM images (secondary and backscattered electrons, absorbed current)

X-ray mapping

Labels: Beam mapping (W), Stage movement (W)

Superior SEM and X-ray imaging expected with a higher lateral resolution (LaB₆ gun) to be tested

In June 2007, the shielded EPMA renewal project began with a contract between CEA and CAMECA. From January 2009 to May 2009, the CEA achieved the dismantling of the old EPMA and the modification of the dedicated hot cell. In June 2009, the new one (SX100R) was delivered in the LECA-STAR facility. The renewal work has been completed in November 2009. Since January 2010, the EPMA experimental activities programs have resumed with safety and analytical capabilities improved.

PIE Facilities for local and regional requirements

G. Ruggirello, ruggirel@cnea.gov.ar

Argentina has covered a wide range of activities concerning PIE and Visual Inspection of Fuel Elements and Internal Reactor components since more than 40 years ago, to support the operation of our two PHWR NPP and one 10 MW Research Reactor. Therefore, several facilities were implemented and others are under construction to perform these activities in the LAPEP laboratories, located at the Ezeiza Atomic Center, which are the following:

- One line of lead shielded Hot Cells (CELCA laboratory) for physical testing that includes an Optical metallographic bench and a SEM.
- One line of concrete Hot Cells for disassembling and conditioning of spent fuel elements.
- One pool for reception and handling of the spent fuel elements.
- One decontamination room for waste treatment, maintenance and decommissioning of small components.
- One line of Analytical Hot Cells for development of techniques concerning to the dissolution and separation of radio nuclides from nuclear materials samples.

All of that is complemented with the facilities for inspections and sample preparation at the SFP in the NPPs. Nowadays, within the framework of a new impulse for the nuclear activities in the region, such as the construction of new NPPs, RRs, radioisotopes production, development of new materials and waste treatment, the use of the PIE facilities is consistently growing, so that LAPEP laboratories are becoming a key center for testing radioactive materials in South America.

USERS:



Atucha I and II, PHWR NPPs



Embalse NPP, CANDU 6



RA-3 Research reactor MTR 10MW

APPLICATIONS:

- Periodic controls by Visual Inspection and NDE in SFP bay
- Control of design improvements and base materials changes
- Development of different MTR nuclear materials



SFP bay station for FE and internal samples visual inspection and metrologies
 J.M. Frediani CN Atucha1 frediani@na-sa.com.ar
 R. Perez CN Atucha1 perez@na-sa.com.ar



Improved FE by U mass increasing and the use of LEU for Bu extension from 7,5 to 12,3 GWd/tonU. FE defect characterization and evaluation of the cause of the failure. Fuel performance confirmation.

"Fifth International Conference on CANDU Fuel (1997) Nuclear Fuel Performance in Embalse NPP, Design Optimizations and Manufacturing Improvements". Fuel Engineering Department. IEC-CN-CNEA



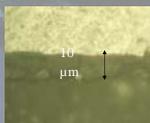
Fuel Element:



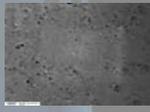
PIE of MTR fuel plates for nuclear material assessment. Assistance to the enrichment reduction program in cooperation with ANL "Post-irradiation examination of U₃Si₂-Al fuel element manufactured and irradiated in Argentina"; 2002 International RERTR Meeting

Structural and Internal Reactor Components:

- Surveillance program of RPV in Atucha I and II
- Monitoring of pressure tubes integrity in Embalse
- Internal components behavior: control of cooling channels, control-rod, guide tubes, etc
- Characterization of diverse materials for the PSI and ISI programs



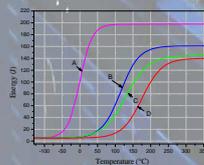
Oxide layer measurement by OM



Submicron fission gas bubbles distribution in disperse MTR fuel element (by SEM)



Impact Test



Surveillance program of RPV Impact energy transition curve.

- A - Non irradiated material, T41J : -25 °C
 - B - Low irradiation level, 0,048 dpa, T41J : 83°C
 - C - Medium irradiation level, 0,078 dpa, T41J : 95°C
 - D - High irradiation level, 0,1135 dpa, T41J : 147°C
- IAEA reference material JF (round robin test)
 Iorio A.F., Chomik E. iorio@cae.cnea.gov.ar



Instrumented Charpy pendulum



ACAD machine to tailor the tensile samples from tubes and sheets



Environmental chamber for universal tensile test at different temperatures

COMPLEMENTARY LABORATORIES:



RADIOCHEMICAL HOT CELLS (LFR)

To supports the R&D groups for faster and more reliable chemical analysis. Sample dissolution, radiochemical analysis and burn-up determination for fuel materials.
 Lead shielded tight box for sample dissolution and dilution
 Glove boxes for cation analysis by ICP - MS
 Burn-up determination
 J. Vaccaro, M. Falcon, et al vaccaro@cae.cnea.gov.ar



LABORATORY FOR SPECIAL ALLOYS DEVELOPMENT (LMFAE)

To supports zirconium metallurgy: fuel element cladding, pressure and calandria tubes for CNE and shroud tube and guide tube for CNAI
 Optical Microscope, Scanning, EDS, EBDS
 X ray diffractometer, Sample preparation for metallographic and TEM
 Thermo gravimetric balance, Thermal differential analysis
 Thermal treatment under vacuum
 Universal tensile testing machine, Hydrogen contents (LECO)



CELCA HOT CELLS Intervention area, Transferring radioactive samples into cells and dry storage vaults

'Hydrogen in Zircaloy-4: Effects of the Neutron Irradiation on the Hydride Formation'. Journal of Materials Science
 'Hydrogen determinations in a Zirconium based alloy with a DSC'. 'Hydride phase dissolution enthalpy in neutron irradiated Zircaloy-4'.
 Journal of Nuclear Materials, Elsevier Science. P. Vizcaino, A. D. Banchik, et al vizcaino@cae.cnea.gov.ar

IMPLEMENTATION OF RECONSTITUTION TECHNIQUE FOR SURVEILLANCE TESTS AT KIEV INSTITUTE FOR NUCLEAR RESEARCH

L. CHYRKO, V. REVKA, Yu. CHAIKOVSKY, S. KOVBASENKO,
Yu. GULCHUK, V. OTSALUK

*Radiation Material Science Department, Institute for Nuclear Research
47 Nauki avenue, 03028, Kiev – Ukraine*

ABSTRACT

This paper reviews an application of the reconstitution technique for surveillance tests that was implemented at Kiev Institute for Nuclear Research last year. In the WWER-1000 surveillance program the Charpy V-notch and pre-cracked Charpy specimens are used to estimate the radiation embrittlement rate of reactor pressure vessel materials. However a large scatter of the neutron fluence values for the specimen sets does not meet the regulatory requirements to get a reliable estimation. An application of the reconstitution technique allows us to resolve this issue.

The reconstitution technique is based on the electron beam welding. An electric discharge machine is used to prepare inserts, end tabs and notches on the reconstituted specimens. A servo hydraulic testing machine is used to pre-crack the specimens. In the paper the Charpy impact and fracture toughness test data are presented for reference and reconstituted surveillance specimens in unirradiated condition. The Charpy impact tests demonstrated the statistically similar Charpy energy curves for the standard and reconstituted Charpy V-notch specimen sets. Fracture toughness test results have shown the reference temperatures T_0 for the standards and reconstituted specimens is practically the same.

1. Introduction

The reconstitution technique is being applied in the material science labs for more than 20 years. However over the last ten years the higher safety requirements for nuclear power plants under operation has led to the increased demands for the reconstitution [1]. Furthermore a direct fracture toughness estimation using small pre-cracked Charpy specimens to reliably predict a state of RPV materials has also increased the necessity of the reconstitution.

An application of the reconstitution technique for Ukrainian NPPs is caused by additional reasons. According to the national regulatory requirements a scatter of the neutron fluence values for the surveillance specimen sets designed to evaluate the RPV metal radiation embrittlement rate should not exceed 10 %. However the disadvantages in the surveillance assembly design have led to the large scatter of the neutron fluence values (35 % and more). An application of the reconstitution technique allows us to resolve this issue.

Using the reconstitution technique it is possible to select the appropriate specimen sets for the reliable estimation of radiation embrittlement rate according to the regulatory requirements. Another important advantage for reconstitution is a possibility to estimate the DBTT radiation shift for a higher neutron fluence using the reconstituted specimens in comparison to the standard specimen test data for the same surveillance set.

In this paper an application of the reconstitution technique for the WWER-1000 RPV base metal is considered using unirradiated Charpy V-notch and pre-cracked Charpy specimens.

2. Materials and reconstitution technique

The material under study is a 15Kh2NMFA-A grade steel which used for WWER-1000 reactor pressure vessel manufacture. Specimens for the tests were cut of the unit D7. The analysis of the chemical composition was carried out by means of the optical emission spectrometer GDS-500A LECO (USA). Measurements and results processing were realized in line with the standard GOST 18895-97. The chemical composition is presented in Table. 1.

C	Si	Mn	Cr	Ni	Mo	Cu	S	P	V
0.17	0.29	0.47	2.24	1.34	0.51	0.05	0.01	0.01	0.09

Table 1: Chemical composition of 15Kh2NMFA-A steel in % wt

The reconstitution technology is based on electron beam welding. The equipment for the EBW technology was designed and manufactured at Institute of Nuclear Research Rez (Czech Republic). The reconstitution of Charpy specimens was performed at the following welding parameters: $U_{ACC} = 50$ kV, $I_W = 35$ mA, $I_F = 553$ mA and 10 mm/s welding rate. Applying such welding parameters gives the width of welds of 1.5 – 2.0 mm (Fig. 1). A length of the inserts for the reconstituted specimens was 17 mm.

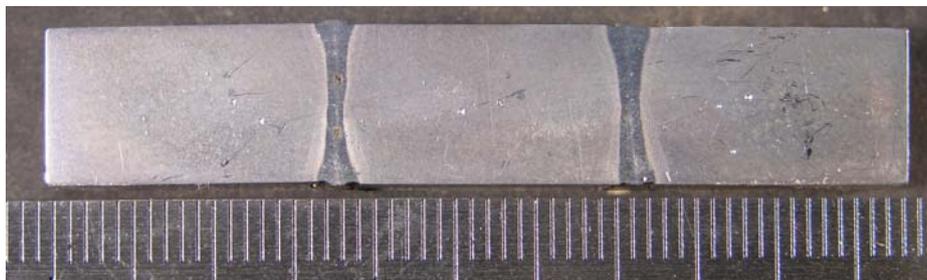


Fig 1. Reconstituted Charpy size (10x10x55 mm) specimen with an insert of 17 mm length

For the qualification of the reconstitution technology the mechanical test and metallographic study were performed. The static bend test has shown the strength of welded joints is high enough to sustain a 34 kN load at the room temperature without fracture. The temperature measurements of inserts during the welding process have shown the temperature does not exceed 180°C on the distance of 5 mm from the weld joints so the overheating of the inserts is not revealed. Metallographic study of weld metal and HAZ obtained at the optimized welding parameters revealed the structures typical for the weld joints obtained at EBW. The results of hardness measurements have shown there is no influence of the EBW process on the material properties in the central part of inserts.

In order to completely renew the Charpy specimens from the tested halves the mechanical notches were made on the reconstituted specimens with the same orientation as for standard specimens. For this purpose an electric discharge machine with a remote control was used. Also this equipment was applied to prepare inserts, end tabs and remove the protrusions of welds on the surface of reconstituted specimens that is appeared after the EBW process.

3. Results and discussion

3.1 Charpy impact test data

Charpy impact tests are performed using a KMD-30 pendulum impact tester with a capacity of 300 Joules in line with the requirements of GOST 9454-78 [2] (this Russian standards conforms with EN-10045-2) and PNAE G-7-002-86 [3] both for standard and reconstituted Charpy V-notch specimens. The specimen orientation was T-S according to the standard ASTM E399. An impact velocity was 5.6 m/s.

The test temperatures were chosen in such way to test the most of specimens at the temperatures corresponding to the specified levels of impact energy in the transition range and the upper shelf energy (USE). The percent shear area was defined remotely in accordance with the ASTM E23 standard [4] comparing it with the graduated diagrams. The temperature index T_{KI} corresponds to the specified levels of impact energy that depends on material yield strength according to PNAE G-7-002-86. In this study the level of 47.2 Joules are used to determine the temperature T_{KI} .

The processing of the Charpy impact test data for reconstituted as well as standard specimens was carried out in line with the requirement of PNAE G-7-002-86. The temperature dependence of impact energy has been fitted by the hyperbolic tangent function. The upper shelf energy was estimated as an average value for the specimens with 100 % shear area on the fracture surface. The lower shelf energy for the Charpy curve was chosen as zero.

Charpy impact test results are shown in fig. 2 for standard (reference) and reconstituted specimens. There is a good agreement between the USE values before and after reconstitution. The upper shelf energy is 203 J and 206 J for standard and reconstituted specimens accordingly.

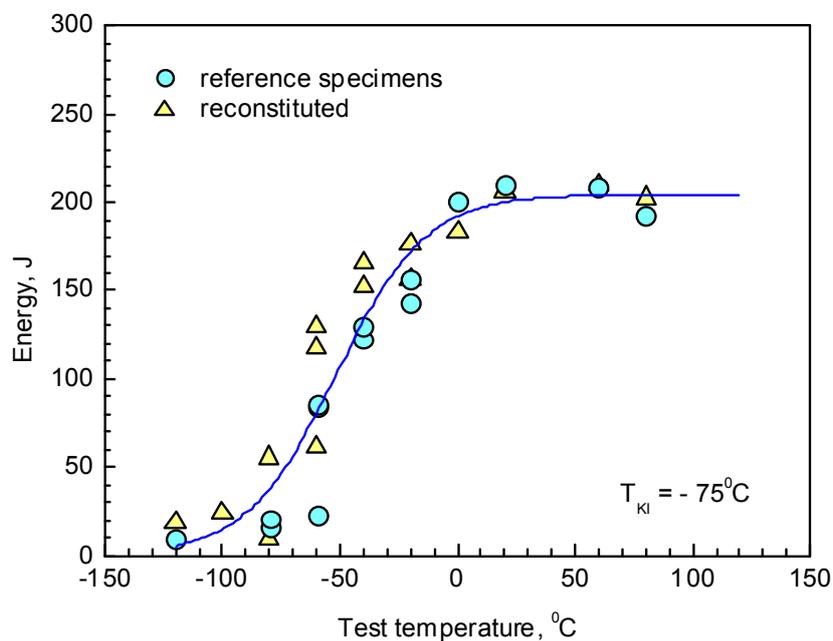


Fig 2. Temperature dependence of impact energy for reference and reconstituted specimens

However there is some difference in the transition temperature for the standard ($T_{KI} = -67^{\circ}\text{C}$) and reconstituted ($T_{KI} = -81^{\circ}\text{C}$) specimen sets. In order to compare Charpy curves for two specimen sets the Chow test was applied [5]. The Chow test allows determining if there is the statistically significant discrepancy in the plotted regression lines. To verify the significance of Chow test the F-statistics is used in the most cases. The statistical analysis showed that the results of two test runs are possible to combine at the

level of significance $\alpha = 0.05$ and the corresponding Charpy curves should be considered as uniform.

3.2 Fracture toughness test data

The static fracture toughness tests were performed using a servo electric testing machine Instron 1362 (100 kN load capacity and 100 mm stroke) retrofitted with 8500 digital controller. The pre-cracked Charpy V-notch (PCVN) specimens with T-S orientation were tested using a static 3-point bend test method. The tests were performed in the position control mode. A testing rate was 0.5 mm/min. The fracture toughness test data analysis was performed according to the Master curve approach and a standard ASTM 1921-05 [6]. In order to obtain the plastic component of J - integral the load-line displacement measurement was used.

The pre-cracking of the fracture mechanics specimens was performed using servo hydraulic testing system with a load capacity of 50 kN. The test frequency was 20 Hz. Stress ratio, R , was 0.1 and the maximum load per cycle was 3.3 kN. Maximum stress intensity factor for the last 0,6 mm fatigue crack was $\sim 16 \text{ MPa}\sqrt{\text{m}}$. The pre-cracking was performing at room temperature. Finish sharpening to produce the last 0.6 mm of crack growth had taken 60000 - 120000 cycles.

Fracture toughness test results are shown in fig. 3 for regular and reconstituted specimens. The reference temperature for the regular specimens ($T_0 = -153^\circ\text{C}$) is practically the same as for the reconstituted specimens ($T_0 = -158^\circ\text{C}$). A difference is 5°C only. However it has been found that a scatter of K_{Jc} values after the reconstitution is higher in comparison to the regular specimen test data.

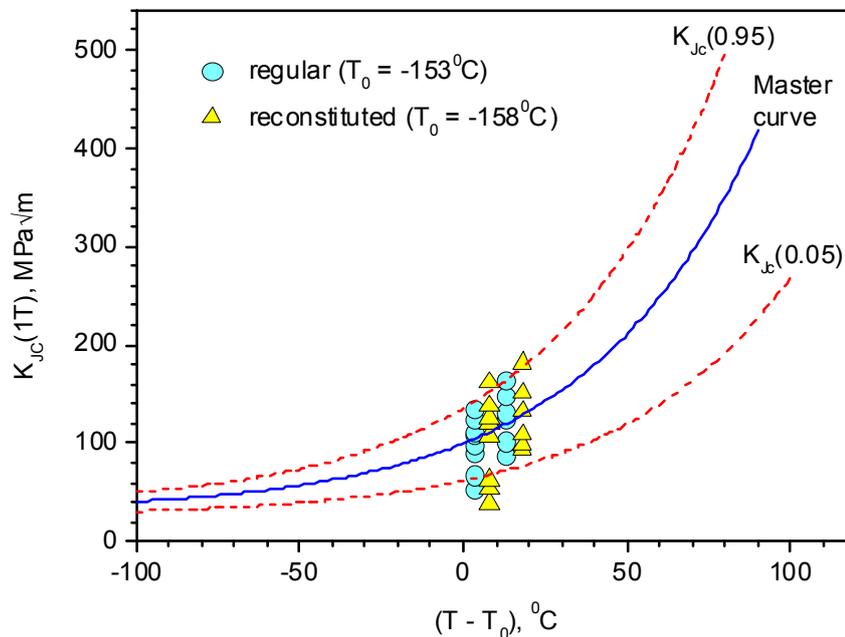


Fig 3. Master curve and 5 % and 95 % tolerant bounds for standard and reconstituted specimens

4. Summary

In this paper an application of the reconstitution technique for the WWER-1000 RPV base metal is presented using unirradiated Charpy V-notch and pre-cracked Charpy specimens. The following conclusions can be drawn:

- Charpy impact test results have shown there is a good agreement between the upper shelf energy values for specimen sets before and after reconstitution. In addition it has been found the difference between the Charpy curves for standard and reconstituted specimens is not statistically significant.
- Master curve analysis has shown the reference temperature for the regular specimens ($T_0 = -153^{\circ}\text{C}$) is practically the same as for the reconstituted ones ($T_0 = -158^{\circ}\text{C}$). However it has been revealed that a scatter of K_{Jc} values after the reconstitution is higher in comparison to the regular specimen test data.

5. References

-
1. E. van Walle, M. Scibetta, M. Valo, H.-W. Viehrig, H. Richter, T. Atkins, M. Wootton, E. Keim, L. Debarberis, M. Horsten, "RESQUE: Reconstitution Techniques Qualification & Evaluation to Study Ageing Phenomena of Nuclear Pressure Vessel Materials", Small Specimen Test Techniques: Fourth Volume, ASTM STP 1418, M. Sokolov, J. Landes and G. Lucas, Eds., ASTM International, West Conshohocken, PA, 2002
 2. GOST 9454 Metals. Impact bend test method at lower, room and elevated temperatures. – M.: Standards Publisher, 1982. – 12 p.
 3. PNAE G-7-002-86 Standards for calculations of nuclear energetic facilities and pipes strength. – M.: Energoatomizdat, 1989. – 524 p
 4. ASTM E23-05 Standard Test Methods for Notched Bar Impact Testing of Metallic Materials. Annual Book of ASTM Standards, Volume 03.01, 2005.
 5. Magnus Ya.P., Katyshev P.K., Peresetsky A.A. Econometrics. Primary course. – M: Cause, 2004. – 576 p.
 6. E1921-05 Standard Test Method for Determination of Reference Temperature, T_0 , for Ferritic Steels in the Transition Range. Annual Book of ASTM Standards, Volume 03.01, 2005