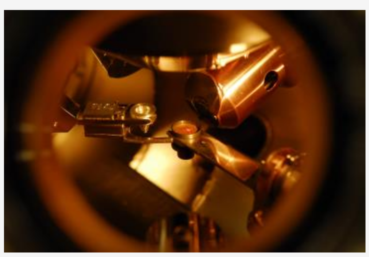
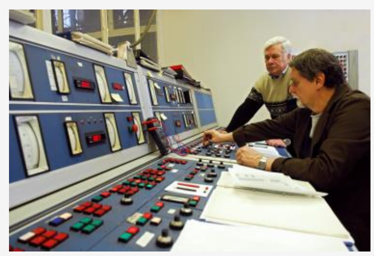
Hungarian Academy of Sciences
Centre for Energy Research

Progress Report on Research Activities





2012

HUNGARIAN ACADEMY OF SCIENCES
CENTRE FOR ENERGY RESEARCH

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PROGRESS REPORT ON RESEARCH ACTIVITIES IN 2012

Dear Reader,

Welcome to the first Progress Report of the Centre for Energy Research, Hungarian Academy of Sciences. From January 1, 2012, the Institute of Isotopes joined the KFKI Atomic Energy Research Institute in the framework of a major reorganisation of the institute network of the Hungarian Academy of Sciences. The merging of the two institutes was carried out without substantial difficulties, however, it was a good argument to reconsider their strategies.

As far as nuclear energy R&D&I is concerned, the strategy has remained unchanged. It consists of three basic elements, namely

- to provide the scientific background for the extended safe operation of the Paks NPP units,
- to participate in the preparation of constructing new nuclear units in Hungary, and
- to contribute to the international efforts related to the closure of the fuel cycle and the development of the new generation of power reactors.

Concentrating human resources and infrastructures to these challenges is the most important duty of the management. Hopefully, the proposed Hungarian national nuclear R&D program will start rather soon and it will decisively influence the activities of the research centre. The establishing of a strong nuclear cooperation among the nuclear research centres of the Visegrád 4 countries aiming at the construction of a Generation 4 reactor also requires a strong governmental support. Additionally one can mention that the merging of institutes led to a situation when a great part of the national knowledge base on nuclear safety and security is concentrated in the same institution and the synergies can be utilized.

As far as the Institute of Isotopes is concerned, a new strategy was elaborated in 2012. The objective was to establish an R&D&I institute for national energy strategy, comparative analysis of using various energy resources, R&D concerning selected versions of environmental friendly energies, energy storage, etc. The elaboration of the strategy required a lot of internal discussions and finally the strategy was accepted by the Hungarian Academy of Sciences. As a consequence, the name of Institute of Isotopes was changed to Institute for Energy Security and Environmental Safety (valid from January 1, 2013).

The R&D&I projects of the research centre have been continued in 2013, basically in the same way as it was common in the former KFKI Atomic Energy Research Institute. The Progress Report presents the results of various projects in a uniform manner. I hope you will find interesting to get acquainted with the results presented in the Progress Report.

János Gadó
Director General

I. GENERATION IV REACTORS

TRANSIENT ANALYSIS OF GAS FAST REACTORS WITH CATHARE CODE

Gusztáv Mayer, Antal Takács

Objective

In the frame of GIF (Generation IV International Forum) three fast reactor types were selected for future development. Fast reactors have the unique ability to generate their own fuel and they are able to burn minor actinides. The high outlet temperature of the helium coolant used in the GFR (Gas Fast Reactor) system makes it possible to deliver electricity, hydrogen, or process heat with high efficiency. Since no helium-cooled fast reactor has ever been built, a necessary step is needed for the building of the large scale GFR system. Hungary, Slovakia and the Czech Republic founded a consortium aiming to build the 75MW ALLEGRO as a demonstrator of the 2400MW GFR system. It is essential even in the design phase of ALLEGRO to justify that all the safety requirements are satisfied.

Methods

The Thermohydraulics Department of MTA EK participates in the European projects with thermohydraulic calculations of ALLERGO and of GFR, using the French CATHARE thermohydraulic code. The CATHARE code has been fully validated against Pressurized Water Reactor (PWR) types in the past, and it is currently being validated against gas cooled fast reactor types. In order to prove the ability of modelling gas fast reactors with CATHARE, a summary of the literature of CATHARE validation against measurement data was compiled. The unique challenge of gas fast reactor systems is their low thermal inertia; therefore it is important to know how to increase the grace time before core degradation in design extension conditions. In order to illustrate this, we performed CATHARE calculations emphasizing the importance of nitrogen injection in beyond design conditions. Finally a study was conducted to compare the management of incidents for LOCA scenarios in a GFR and in ALLEGRO.

Results

Based on the measurements carried out at the HEFUS helium loop test facility (Brasimone, Italy) an international code validation was performed and the following conclusion can be drawn [1]. The CATHARE code can describe the steady-state and transient processes with relatively good accuracy at the investigated plant conditions. MTA EK performed CATHARE calculations for ALLEGRO in beyond design condition. A 3 inch LOCA scenario aggravated by a total blackout was calculated. It was found that the pressure loss coefficient of the nitrogen accumulator line is an important parameter and the degradation of the core can be delayed by decreasing its value. The results showed that the core damage can be avoided even at 3 inch break size, viz. the peak cladding temperature does not exceed the melting point if the pressure loss coefficient of the nitrogen injection line is sufficiently small. The DHR (Decay Heat Removal) strategies during LOCA were discussed. It was found that the treatment of LOCA scenarios is similar for GFR and for ALLEGRO, and it was also concluded that the question of nitrogen injection should be analyzed more in detail for ALLEGRO.

Remaining work

In the frame of the GoFastR project a tentative list of transients was compiled for ALLEGRO transient analysis. We have to extend this list with further cases and we have to justify by calculations that all the safety criteria are fulfilled. There are further technical questions to be answered, for instance the rotation speed of the primary blowers has to be determined after a LOCA scenario in medium backup pressure or the opening pressure of nitrogen tanks in case of beyond design conditions.

Related publication

[1] M. Polidori, P. Meloni, K. Mikityuk, E. Bubelis, M. Schikorr, G. Geffraye, F. Bentivoglio, N. Tauveron, G. Mayer, E. Geus, O. Frybort: *Thermal-hydraulic codes benchmark for gas-cooled fast reactor systems based on HEFUS3 experimental data*, Proceedings of ICAPP 2013. Jeju Island, Korea, April 14-18, (2013)

FINANCING OF THE PROCESSING AND DISPOSAL OF RADIOACTIVE WASTES, THE CLOSING OF THE NUCLEAR FUEL CYCLE AND THE DECOMMISSIONING OF THE NUCLEAR FACILITIES – ANALYSIS OF THE PRACTICE OF CERTAIN COUNTRIES

Anikó Földi, Kinga Gaál, Zsófia Kókai, Tamás Pázmándi, Péter Szántó, Péter Zagyvai, Balázs Zábori

Objective

The processing and disposal of radioactive wastes, the closing of the nuclear fuel cycle and the decommissioning of the nuclear facilities were examined from economical aspects.

Methods

As of 1 January 1998, the Act CXVI of 1996 on Atomic Energy established the Central Nuclear Financial Fund in Hungary. Decision about new nuclear power plant units at Paks site and the financing of the fuel cycle closure demand to review the operational framework of this fund. In this study the processing and disposal of radioactive wastes, the closing of the nuclear fuel cycle and the decommissioning of the nuclear facilities were examined from economical aspects. The financing solutions of these activities were assayed for five countries (the Czech Republic, Finland, Canada, Spain and Sweden) that have significant nuclear energy potential.

Results

Similarly to the Hungarian practice, the studied countries also created their own central nuclear financial funds but there are obvious differences in their operation.

The legal and organizational structure of these countries, the operational rules of the funds, the handling of some special problems and the availability of required assets were reviewed in every chapter. In the final chapter the examples of the good practices were discussed in order to advise how it is possible to put these elements into the Hungarian practice.

Remaining work

The studies should be extended to other countries. Strengthening of international relationships will be suggested.

Related publications

[1] A. Földi, K. Gaál, Zs. Kókai, T. Pázmándi, P. Szántó, P. Zagyvai, B. Zábori: *Financing of the processing and disposal of radioactive wastes, the closing of the nuclear fuel cycle and the decommissioning of the nuclear facilities – analysis of the practice of certain countries (in Hungarian),* Centre for Energy Research, EK-SVL-2012-254-01-01-00 (2012)

PARTICIPATION IN THE EU PROJECT GOFASTR

István Farkas, Tatiana Farkas, Gusztáv Mayer, Antal Takács, Iván Tóth

Objective

The aim of the GoFastR project is to demonstrate the viability of the basic designs of the gas cooled fast reactor (GFR) including the core and fuel subassemblies, the GFR-specific safety systems, the balance of plant and the containment concept. The project focus is both on GFR in general and its first demonstrator, the 75 MW ALLEGRO reactor. MTA EK contributed to the project partly by performing calculations for the design of the experimental fuel assemblies and by the analysis of the transient behaviour of GFR and ALLEGRO.

Methods

For design purposes the Computational Fluid Dynamics code FLUENT was used, while the transient analysis of the GFR and ALLEGRO systems was performed by the CATHARE code. A series of benchmark calculations were run in order to validate the applied computer codes for the circumstances of gas cooled reactors.

Results

Different benchmark cases have been calculated for the German L-STAR facility with the aim to validate the FLUENT code with respect to prediction of core pressure drop and heat transfer. Analysis of the effect of the applied turbulence model pointed out that application of the k-ε model gives insufficient results, while the Reynolds Stress turbulence model permits to describe the flow structure dominated by secondary flows. Results obtained by using first and second order numerical schemes were similar indicating that the resolution of the numerical mesh was adequate. Comparison of the numerical meshes of the different participants demonstrated the high quality of the mesh developed by MTA EK. In spite of that, the pressure drop of the test section was generally overestimated by most CFD tools and this was true for the heater rod temperatures as well. It was suggested that consideration of radiation effects might be necessary for proper prediction of wall to air heat transfer [3].

Within the transient analysis work package most of the MTA EK activity was concentrated on the ALLEGRO reactor. The results of the steady state benchmark cases indicate an excellent agreement between results of the SIM and the CATHARE codes. In the transient benchmark, investigating the ALLEGRO behaviour following an unprotected loss of flow accident, the agreement was also satisfactory: the differences between the results are mainly caused by different assumptions for the thermal inertias in the various sections of the primary cooling circuit and by slightly different coolant flow redistribution between the core and the core bypass flows during the simulated transient [1].

From the list of design basis accidents MTA EK was responsible for the analysis of consequences of loss of heat sink (LOHS) and loss of off-site power (LOOP). The LOHS transient necessitated the introduction of a new safety signal in order to avoid boiling and consequent pressure increase in the secondary circuit. With the new signal introduced it could be shown that both the LOHS and the LOOP transients fulfilled the acceptance criterion, even taking into account the most adverse single failures [1]. Analysis of the transient caused by a secondary circuit break was also started, but aborted early in the transient due to CATHARE modelling problems. MTA EK cooperates with the French CEA on the resolution of the problem.

CFD analysis results for the ALLEGRO experimental subassembly performed by the FLUENT code were documented [2]. It was shown that the thermal shield with the original design geometry is very effective in protecting the wrapper from the high temperature in the assembly. The maximum wrapper temperature remained in all cases below 270 °C. Increasing the width of the thermal shield practically did not affect the wrapper temperatures, while it increases the pressure drop in the bypass channel. The effectiveness of the thermal shield is mainly due to the poor conductivity of the static helium, which is used as a filler gas in the thermal shield. The two determining ways of heat transfer through the thermal barrier are natural convection and heat conduction through baffles; taking into account radiation changes only slightly the temperature distribution.

Remaining work

The EU project GoFastR has come to an end. Further work at MTA EK will be performed within the ALLEGRO Consortium, its aim being to finalize the design of the ALLEGRO reactor, prepare a safety analysis report and, ultimately, proceed to its licensing. In this framework the safety analysis cases have to be completed. As shown by the results produced in the GoFastR project, further effort is needed to reduce uncertainties implied in code analyses both with systems and CFD codes.

Related publications

[1] K. Mikityuk et al.: *ALLEGRO transient analysis,* GoFastR Deliverable D 1.4-4 (March 2013)

[2] T. Farkas and I. Farkas: *Design of an experimental ceramic fuel S/A loaded in the MOX core (CFD FLUENT analysis)*, AEKI-THL-2010-422/02/M0 (2012)

[3] R. Krüssmann et al.: *L-STAR benchmark results,* GoFastR Deliverable D 1.5-4 (February 2013)

REACTOR PHYSICS INVESTIGATION OF SODIUM COOLED FAST SPECTRUM REACTOR CONCEPTS

András Keresztúri, Ádám Tóta, István Pataki

Objective

The generic long term goal of the presented activity is the comparative evaluation of the different fast reactor concepts by using own reactor physics calculations. The two most important standpoints of the comparison are the safety aspects and the isotopic inventory correspondence to the sustainable development requirement. Various fast spectrum reactors concepts found in literature had to be calculated and evaluated.

Methods

Cross section generation by using the ECCO spectral transport code, subsequent 3D core design calculations with the KIKO3DMG code.

Results

In 2012 - according to the project plans - the safety aspects of 4 Sodium cooled fast spectrum reactor concepts – defined in the frame of the OECD NEA WPRS cooperation - have been investigated. The investigations were focusing on the following safety related characteristics influencing the reactor physics and the dynamic behaviour of the core:

- Temperature reactivity coefficients
- Void coefficient
- Power peaking factors
- Shut down reactivity at different operational states of the reactor
- The worth of the absorber rods influencing consequences of the failures of their motion

In the Table, the safety related characteristics of the sodium cooled fast reactors calculated by KIKO3DMG code are presented, moreover, it shows their isotopic transmutation capability, namely the conversion ratios. From the presented results it can be concluded that the most promising concept is the large core consisting of carbide fuel. The strong Doppler feedback can compensate the positive void reactivity, the worth of the single control rod is small enough – leading to less sever consequences in case of its uncontrolled movement – especially in comparison to the small cores, while the shut down conditions are always met. The conversion ratio is also the most advantageous for this core, significantly larger than 1. Although this core is operating at a little bit higher temperature than the oxide core, the melting point of the pellets is relatively high and additionally - in contrast to the oxide fuel – chemical interaction between the pellet and the cladding cannot be observed. It is also worth mentioning that – according to our calculations and the literature data - the void effect of the lead cooled fast reactors can be close to zero.

	Large carbide fuel core (3600 MWth)	Large oxide fuel core (3600 MWth)	Medium metallic fuel core (1000 MWth)	Medium oxide fuel core (1000 MWth)
βeff	0.405%	0.393%	0.366%	0.357%
Doppler constant ($)	-2.79	-2.42	-1.06	-2.31
Sodium void worth ($)	5.73	5.19	5.06	4.87
Control rod group worth ($)	0.28	0.24	1.35	1.25
Shut down k-eff	0.95458	0.96371	0.83130	0.81941
BR (Breeding Ratio)	1.15	1.082	0.79	0.84

Related publication

[1] Á. Tóta, I. Pataki, A. Keresztúri: *Calculation of Sodium Cooled Fast Reactor Concepts, Preliminary results of an OECD NEA benchmark calculation*, presented at the International Conference on Fast Reactors and Related Fuel Cycles, Safe Technologies and Sustainable Scenarios (FR13), ID: IAEA-CN-199/167, Paris, 2013

SUPERCRITICAL WATER REACTOR – FUEL QUALIFICATION TEST

Csaba Maráczy, György Hegyi, Gábor Hordósy, István Trosztel, Péter Vértes

Objective

The aim of the SCWR-FQT (Supercritical Water Reactor - Fuel Qualification Test) Euratom-China parallel project is to design an experimental facility for qualification of fuel for the supercritical water-cooled reactor. The facility is intended to be operated in the LVR-15 research reactor in the Czech Republic. This reactor enables to replace one of its assemblies with a pressurized tube containing a four rod fuel bundle, which shall be connected with coolant pumps, safety and auxiliary systems to simulate a supercritical water environment. All necessary documents required by the Czech regulator for licensing of the FQT facility shall be the outcome of this project. Our institute is participating in the 3D steady state and 3D transient analysis of LVR-15 with the fuelled loop.

Methods

- Monte Carlo neutron transport calculations.
- Isotopic inventory calculations.
- 3-D coupled neutronic-thermohydraulic calculations of LVR-15 with the FQT facility.

Results

3-D coupled neutronics-thermohydraulics calculations of LVR-15 with the FQT facility were applied to determine the power of the tested fuel rods during irradiation. Conservatively calculated enveloping parameters (e.g. reactivity coefficients) were determined for the safety analysis. The gamma heating of the thick pressurized tube of the FQT facility evaluated with the help of the MCNP Monte Carlo code resulted in significant difference in the temperature distribution of the coolant compared to the case of omitting it. The temperature distribution along the zigzag path of the coolant was calculated by the coupled neutronic-thermalhydraulic KARATE code system. Figure 1 shows the calculated results. The active height of fuel rods is between 0 and 60 cm. Above it the heat exchange between the flow paths was calculated.

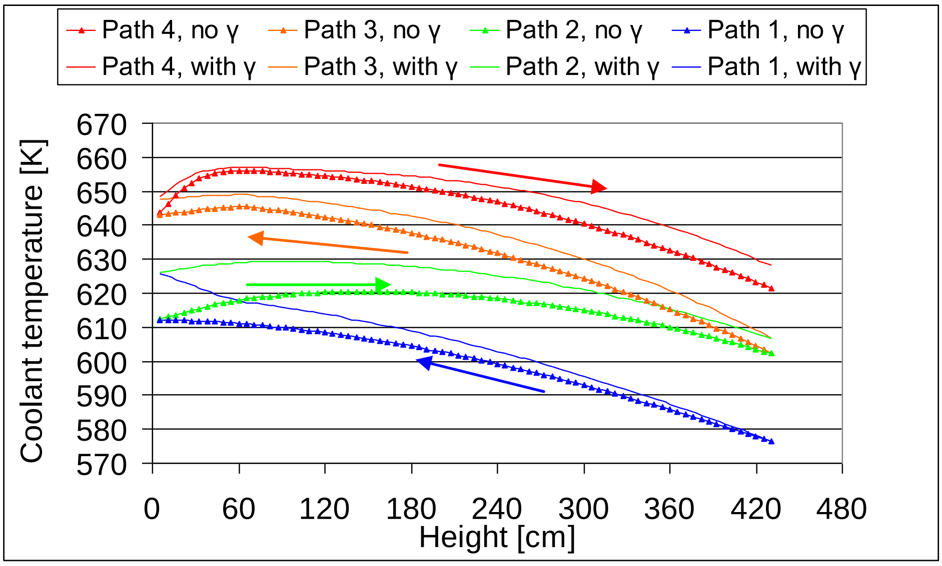

Figure 1: Coolant temperature distribution along the height of the SCWR-FQT section in the LVR-15 research reactor

Remaining work

- Developing the KIKO3D-ATHLET model of LVR-15 with the SCWR-FQT section.
- RIA (Reactivity Initiated Accident) analysis with the KIKO3D-ATHLET coupled dynamic code.

Related publication

[1] D.C. Visser, A. Shams, A. Kiss, T. Vágó, A. Brolly, Gy. Hegyi, G. Hordósy, Cs. Maráczy, P. Vértes, O. Frybort, P. Dostal, A. Vojacek: *Analyses of normal operation, Interim report after year 1*, SCWR-FQT (Contract Number: 269908) Deliverable E2.1

THE SAFETY OF THE HPLWR REACTOR

András Keresztúri, IstvánTrosztel, György Hegyi

Objective

The generic aim of the presented activity is to establish the safety of the High Performance Light Water Reactor (HPLWR) concept - cooled by supercritical water - by specifying the appropriate safety system design. The transients caused by the relevant limiting initial events had to be simulated in an iterative way by using different variants of the safety system parameters (capacity, set point, velocity, etc.). The final goal of the calculations was to evaluate the different variants and to select the most effective combination and parameters of the safety systems.

Methods

The task was solved in the following steps:

- Mapping of the different solutions and variants of the safety and control systems, their possible parameter range using also the recommendations found in the literature
- Simulation of the different type of transients and accidents by using various solutions and parameters of the safety and control systems
- Recommendation for the appropriate configuration and parameters of the safety systems

Results

Besides the reactivity initiating events – investigated already in 2011 -, the following initiating events were analyzed:

- Large LOCA (Loss of Coolant Accident) in the cold leg
- Medium size LOCA in the cold leg
- Small break LOCA in the cold leg
- Large LOCA in the hot leg
- Station black out which covers also the turbine trip
- Main circulation pump trip

By solving the task to find the appropriate configuration and parameters of the safety systems, the starting point was our preparatory study, which was mapping the different foreseen solutions applied in the supercritical and boiling water reactors in the literature. The corresponding report of the project is proposing a new preliminary concrete configuration and estimates its parameters. The cold leg small break LOCA analysis proves that, thanks to the lack of the phase transition, safety system actuation is not necessary for satisfying the acceptance criteria. On the other hand, it was found that the most severe accident is the Large Break LOCA requiring the actuation of all the systems and with the largest capacities. Therefore, the analysis of this event was performed by supposing several safety system variants. It turned out that the passive emergency core cooling system of the preliminary concept cannot inject enough amount of coolant into the core, moreover, the injection positions finally had to be selected in a more sophisticated way. Nevertheless, the analyses based on the preliminary concept proved useful for finding the appropriate, improved solution which assures the fulfilment not only for the Large Break LOCA but also for the further events of the above list.

Remaining work

There is no remaining work.

Related publication

[1] I. Trosztel, A. Keresztúri: *The potential safety and control systems of the HLWR (High Performance Light Water Reactor), Analyses of the abnormal and normal operation events by using the ATHLET code*, CER internal research report, AEKI-RAL-2009-219/08-M0, 2012.

UNCERTAINTIES OF THE CALCULATED REACTIVITY TYPE PARAMETERS OF SODIUM COOLED FAST REACTORS

András Keresztúri, Ádám Tóta, István Pataki, István Panka

Objective

Best estimate codes without knowledge of uncertainties can not be used for safety evaluation. Originally, in the frame of the OECD NEA Uncertainty Analysis in Best-Estimate Modeling (UAM) cooperation, the final objective was to determine the uncertainty of the light water reactorcalculations, but in 2012 the activity has been supplemented with the corresponding investigations of 4 Sodium fast reactor concepts.

Methods

Concerning the statistical method, basically the algorithm elaborated in 2009 was used. At the first step, a sampling procedure for the selected isotopes and cross sections, and also for the relevant technological data is performed many times and subsequently, the elaborated statistical methodology is applied. Finally, one can get the estimated standard deviations and /or correlation matrices both for the reactivity type parameters. Concerning the correlations of the input data for the subsequent steps of the calculations, the sampling method is based on the modified Cholesky decomposition algorithm.

Results

For a medium type oxide fuel core, the following results – namely the maximum and minimum values characterizing the 95 % probability content with 97 % confidence level, standard deviations - were obtained.

	k-eff rods out	Beff	Worth of all CRs $	Void Δρ	Void $	Doppler Δρ	Doppler $
max	1.0920	0.363%	73.4274	0.0230	6.4955	-0.0050	-2.0163
min	0.9927	0.351%	66.8174	0.0117	3.2630	-0.0063	-2.5399
aver.	1.0332	0.358%	70.1664	0.0173	4.8368	-0.0057	-2.3021
st. dev.	0.0187	0.002%	1.1953	0.0026	0.7311	0.0003	0.0999
rel. st. dev.	1.81%	0.66%	1.70%	14.96%	15.11%	4.42%	4.34%

Related publication

[1] Á. Tóta, I. Pataki, A. Keresztúri, I. Panka: *First results of the uncertainty analysis of the WPRS Sodium-Cooled Fast Reactor Benchmark calculations*, presented on the Third Meeting of the Sodium-Cooled Fast Reactor Benchmark Task Force (SFR-TF) of Working Party on Scientific Issues of Reactor Systems (WPRS) of OECD, 19 February 2013, Paris

II. Research Related to NPPs

ESTABLISHMENT OF A REGIONAL CENTER OF COMPETENCE FOR VVER TECHNOLOGY AND NUCLEAR APPLICATIONS (CORONA)

János Sebestyén Jánosy

Objective

CORONA is an international project financed by ***EURATOM***. This project is led by the ***Kozloduj Training Centre*** in Bulgaria, there are ten other participants: ***Fortum*** (Finland), ***INRNE*** (Bulgaria), ***JRC*** (Belgium), ***Mephi*** (Russia), ***REZ*** (Czech), ***PM Gmbh*** (Austria), ***Risk Eng.*** (Bulgaria), ***Technatom*** (Spain) ***Slavutich LLC*** (Ukraine) and ***our Institute – CER HAS.*** There are eight working groups organized by the parties. Our Institute participates in four of them.

The essence of the project is to provide a special purpose structure for training and qualification of personnel for serving VVER technology as one of nuclear power options used in EU. Such approach should allow unifying existing VVER related training schemes according to IAEA standards and commonly accepted criteria recognized in EU. The structure is based on three general pillars:

1) training schemes for VVER nuclear professionals; for non-nuclear specialists and subcontractors, involved in nuclear sector; for students;
2) VVER related knowledge management system, which will accumulate information regarding design data, operational experience, training materials, etc.;
3) specialized regional training center for supporting VVER customers with theoretical and practical training sessions, training materials and general and special assignment training tools and facilities.

The wider objective of the project is to implement the Council Conclusions of 1 - 2 December, 2008 related to skills in the nuclear field: new skills and competences are needed in the context of the Nuclear Renaissance and to fulfill obligations under Article 7 of the COUNCIL DIRECTIVE (EURATOM) establishing a Community framework for the nuclear safety of nuclear installations. The specific objectives of the project are:

- enhancing safety and performance of nuclear installations with VVER technology through specialized initial and continuous training of personnel involved;
- keeping the adequate level of safety culture;
- contributing to the development of Knowledge Management System for VVER technology;
- preserving and further developing nuclear competencies, skills and knowledge related to VVER technology, as a technology used in the EU.

Methods

Our Institute has no significant direct experience in teaching personnel for the nuclear power plants. Our contribution to the CORONA project can be based on the following:

- - experience in teaching nuclear engineers at the Budapest Technical University for evaluating safety of Nuclear Power Plants,
- - experience in teaching nuclear engineers at the Budapest Technical and Economic University for evaluating reactivity induced accidents,
- - experience to use the full-scope replica simulator for Reactor Protection System and other Instrumentation and Control refurbishment projects.

The methodology of these training courses and the experience of simulator usage can be embedded into the training courses worked out by the CORONA project.

Results

The Corona project started in 2011 year and proceeds according to well established and internationally approved time schedule. In 2012 the results of the Working Package 1 and 2 have been already submitted.

Remaining work

All working packages are proceeding according to the time schedule. The software (intranet) for the project and the results of the Working Packages 3 and 4 are commencing in 2013.

Related publication

All the project documents are to be submitted to the ***EURATOM*** for further investigations and suggestions.

Effect of Manufacturing on the Stress State of a Reactor Pressure Vessel Cladding

Tamás Fekete, Levente Tatár, Dániel Antók, Péter Tóth

Objective

The Reactor Pressure Vessel (RPV) is one of the most important components for safety and lifetime of an NPP unit, accidental damage of which may cause severe environmental issues. The most important function of the RPV is the maintenance of pressure and temperature conditions, which are necessary for controlled power generation during operation, heating-up and cooling-down of the reactor, cooling-down of the core under emergency conditions and preventing release of radioactive materials into the containment. This requirement means that the vessel should keep its integrity during all possible modes of operation. RPV-s have large cross-sections (e.g.: VVER-440: 149 mm wall thickness with 3800 mm diameter), work at elevated temperatures (≈270 – 290 °C) and high pressures (≈12.2 MPa). The vessels are manufactured from ferritic steels cladded with austenitic anti-corrosion layer from inside. The thermal-physical properties (thermal expansion and thermal conduction coefficient) of cladding significantly differ from the those of low-alloyed base metal and weld seam, therefore, during cooling down and heating up the vessel, significant compatibility stresses may arise on the interface of the cladding and base material. This effect is modelled usually by stress-free temperature of cladding, assuming the same temperature as the operating temperature of corresponding component in engineering practice. The stress fields in RPV's are complex, caused by complexity of the pressure vessel geometry itself, by complex thermal fields through the wall thickness and the different thermal-physical properties of structural materials. The main goal of the study was to assess the compatibility stresses arising in the cladding at operating temperature, taking into account elastic-plastic properties of the structural materials and the effect of last heat treating and first hydrotest of the RPV.

Methods

The methodology of calculations was developed at MTA EK, using elastic-plastic material models of structural materials. Flow curves of materials – describing real elastic-plastic deformation behaviour of the cladding and of the base material – were developed from tensile test results performed at MTA EK in the frame of earlier projects. Coupled (thermo-mechanical) axial symmetric finite element models were elaborated for the RPV geometry. Large deformation plasticity theory was used to model effects of geometrical and material nonlinearities that are present in the system during cooling phase of last technological heat treating and first hydrotest. Applied thermal and pressure boundary conditions can be seen in Figure 1. (left). Numerical calculations were performed by using the Msc.MARC FEM code with updated Lagrange procedure. The study was performed applying real flow curves of structural materials to see the influence of real flow properties of the cladding on compatibility stresses.

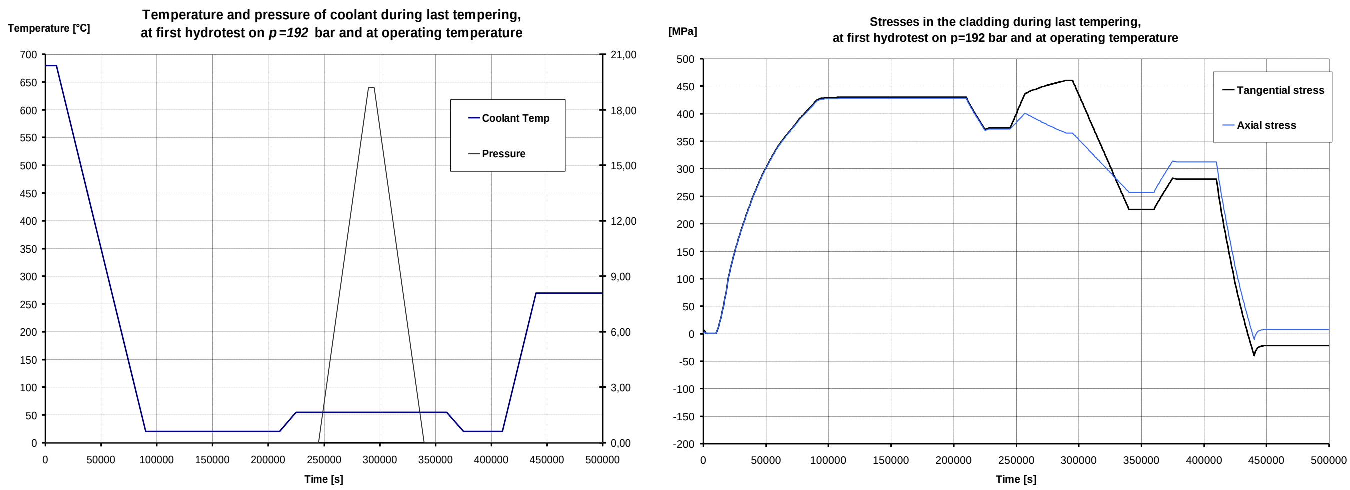

Figure 1: Boundary conditions and calculated stress components arising in the cladding

Results

Results show that the last technological heat treating during manufacturing and the first hydrotest of the RPV can slightly reduce compatibility stresses arising in the cladding at operating temperature in tangential direction (Fig. 1, right, at 500 000 s). This is because hardening of cladding is high during first stage of plastic deformation.

Related publication

[1] Fekete T., Tatár L., Antók, D., Tóth P.: *Foundations of p-T Limit Curves. Analyses assessing influence of real elastic-plastic behaviour of cladding on p-T Limit Curves.* Project report, MTA EK report, Budapest, July 2012 (in Hungarian)

PTS ANALYSIS OF PAKS NPP REACTOR PRESSURE VESSELS

TAMÁS FEKETE, GYÖRGY ÉZSÖL, ATTILA GUBA, LEVENTE TATÁR,
DÁNIEL ANTÓK, PÉTER TÓTH

Objective

PTS (Pressurised Thermal Shock) phenomenon can occur when in some accidental situations extra quantity of cooling water flows into the reactor pressure vessel (RPV), cooling it excessively. RPV-s have large cross-sections (e.g.: VVER-440: 149 mm wall thickness with 3800 mm diameter), work at elevated temperatures (≈270 – 290 °C) and high pressures (≈12.2 MPa). A PTS event can cause a dangerous situation regarding the integrity of RPV-s, as high thermal gradient develops in the vessel, causing high thermal stresses, which are superposed to stresses originating from internal pressure. The thermal and stress fields in RPV's are very complex, caused partly by complexity of the pressure vessel itself and partly by complex thermal loadings. The main goal of this study was to assess the feasible lifetime of the RPV-s of Paks NPP from PTS point of view.

Methods

The methodology of calculations was developed at Hungarian Academy of Sciences Centre for Energy Research. Two thermal hydraulic transients were selected from previous beyond design base accident (BDBA) calculations, which caused most severe cooling during the system thermal hydraulic analyses. System thermal hydraulic calculations were performed by using RELAP5 Ver3.3. During structural integrity analyses, 3D temperature field and linear elastic stress field calculations were performed with finite element methodology for the lower cylindrical part of the vessel. Coupled (thermo-mechanical) finite element models were elaborated for the RPV geometry. Numerical calculations were performed by using the Msc.MARC FEM code. Fracture mechanics calculations were based on linear elastic fracture mechanics (LEFM).

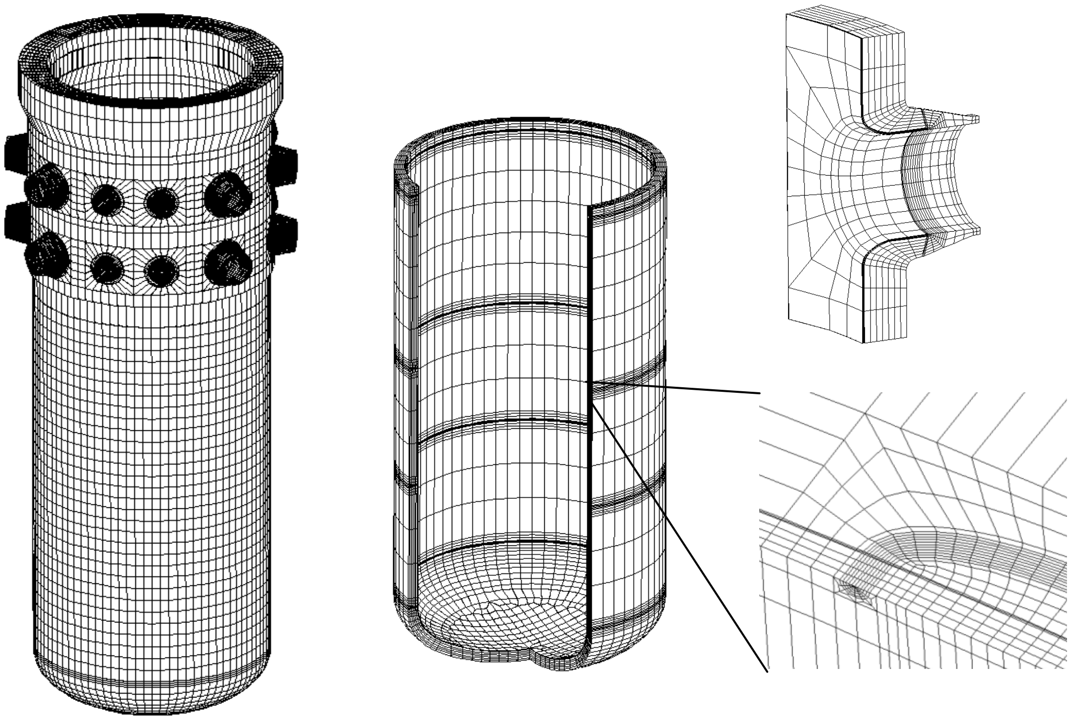

Figure 1: Boundary conditions and calculated stress components arising in the cladding

Results

Computations were made with 3D FEM models of the RPVs. Computed results show that feasible lifetime of RPVs can be extended safely up to the planned 'extended lifetime' from PTS point of view.

Application of Miniature Specimens to Ageing Monitoring of Pressure Vessels and Pipes

Ákos Horváth, Tamás Fekete, Attila Kovács, István Nagy, Levente Tatár, Péter Tóth

Objective

Existing VVER 440 type nuclear power generation units in Hungary will reach their 30th operational year. At the time of further operation, the ageing mechanisms can exert observable influence on mechanical properties of various structural materials built into the primary circuits of the units. Reactor pressure vessels have extensive surveillance programmes in order to monitor ageing of their structural materials, but other pressure vessels and components of the primary circuits have no similar programmes for ageing monitoring. The aim of the project is to develop feasible monitoring technology to assess the ageing state of various equipment and steel pipes installed in the primary circuits of VVER 440 Nuclear Power Plants.

Methods

The methodology of proposed assessment technology was developed by MTA EK and Bay Zoltán Nonprofit Ltd. for Applied Research. The main problem of the measurement technology is that –because of the lack of surveillance programme – the components of the primary circuits have no prepared specimens for ageing monitoring (except the reactor pressure vessel). The problem of specimen preparation from operating equipment had therefore been taken into consideration. Because of the very limited amount of materials foreseen for testing purposes, various measurement technologies (e.g. tensile tests, Charpy tests) based on miniaturised specimens were carefully analysed and examined. Tensile tests based on miniature flat specimens have been proposed for measurements on cut samples from real equipment. The adequacy of the proposed test methodology had been demonstrated on model equipment. The photo of a cut sample is presented in Fig. 1, photos of tensile specimens in original state and after test are presented in Fig. 2.

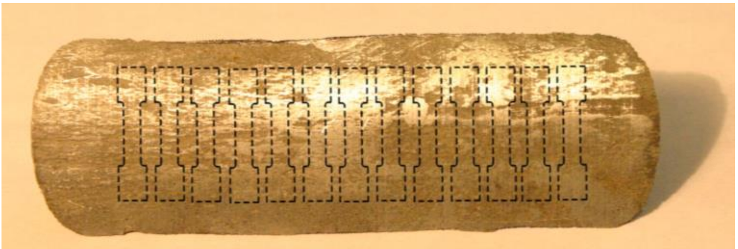

Figure 1: Cut sample with contour of flat tensile specimens

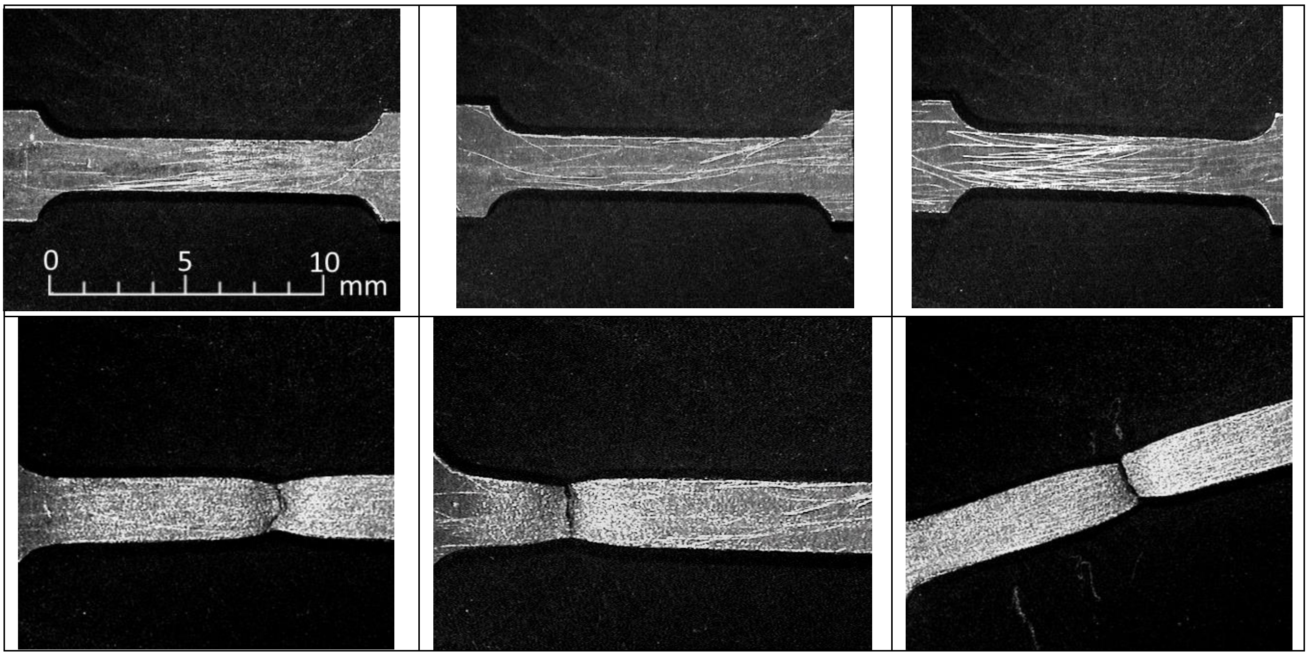

Figure 2: Tensile specimens before/after the test

Results

The results show that the proposed testing methodology based on miniature flat tensile specimens can be applied for ageing monitoring of structural materials built into various constituents of the primary circuits of VVER 440 NPPs.

TECHNICAL BASIS OF LEGISLATION RELATED TO CLEARANCE LEVELS WITH RESPECT TO DECOMMISSIONING OF NUCLEAR FACILITIES – SUMMARY OF A 4-YEAR WORKING PERIOD

Tamás Pázmándi and Péter Zagyvai

Objectives

Clearance of slightly radiocontaminated material originating from the dismantling of nuclear facilities is one of the key issues of radioactive waste management and decommissioning. The mitigation of manageable and disposable radioactive waste resulting in the generation of traditional waste and/or recyclable and reusable equipment, materials and buildings is an important economical driving force that is closely related to the legal (regulatory) and altogether scientific process of clearance. The existing national regulations on clearance were deemed to require revision and update, thus in 2009 the Hungarian Atomic Energy Authority (HAEA) invited three Technical Support Organizations (TSO) for a four-year-long research project. The original team comprised the Atomic Energy Research Institute together with the National Research Institute for Radiobiology and Radiohygiene (NRIRR) and the Institute of Nuclear Techniques of Budapest University of Technology and Economics (BUTE INT). (After the third year INT withdrew from the project.) The final goal was the compilation of a detailed guidance for facilitating clearance in nuclear decommissioning with appropriate practical appendices, thus providing sufficient technical basis for the renewal of the legislative documentation.

Methods

In the first three years the contributing projects of the three cooperating partner institutes were realized separately but they followed a common thread approved by HAEA. Evaluation of existing international guidance and Hungarian legislation as well as analysis of several practical cases (experience obtained from recent clearance procedures in Hungary, potential role of clearance in the decommissioning plans of operating Hungarian nuclear facilities etc.) were presented in the research reports. Detailed analysis of exposure scenarios applicable for conditional and unconditional clearance procedures were also presented and methodology of developing appropriate reference levels – in addition to the selection of them from international compilations - was described in details. During the final year of the project, experts of NRIRR and MTA EK elaborated a draft guidance *"Clearance procedure for bulk amount of waste originating from the decommissioning of nuclear facilities"* accompanied by two appendices: *„Clearance scenarios"* and *„Measurement methods for the assessment of radiocontamination of clearable waste"*.

In general, the waste/clearance index (WI/CI) method has been confirmed to distinguish between clearable and disposable waste:

$$WI / CI = \sum_i \frac{c_i}{RL_i}$$

In the equation c_i denotes the activity concentration [Bq/kg] or [Bq/m²] of radionuclide *i* in a well-defined waste stream, RL_i is the reference (clearance) level as related to a committed effective dose of 10 μSv/year considering the least favourable but realistic exposure route from the cleared material to the most sensitive reference person. The set of reference levels are generally divided into two main categories: the "moderate" and the "bulk" amounts of waste, the limit between them is the order of 1 t. Thus decommissioning waste will mostly belong to the "bulk" category the RL of which is generally smaller than those of the "moderate" waste by two – three orders of magnitude. In the group of "bulk" levels four sub-categories of clearance levels (CL) can be distinguished:

- CL for metals (steel etc.) for recycling, reuse and dumping to non-radioactive disposal sites [Bq/kg];
- CL for building rubble considering recycling, reuse and dumping [Bq/kg];
- CL for other types of material [Bq/kg];
- CL for the remaining parts (buildings, equipment, soil etc.) of the controlled area of the facility [Bq/m²].

Results

The draft guidance consists of the following main chapters: Introduction; Definitions; Recommendations. The last one is further divided into two sub-chapters: general recommendations (the legal process of decommissioning, categories of potential radioactive wastes, characterization of clearable wastes, options of clearance) and topical recommendations (practical accomplishment of clearance, documentation, archiving, contacts).

In Appendix I several examples are presented for typical scenarios of dose consequence calculations to be included in the safety case of the clearance process. Scenarios are described

- for building rubble and reusable buildings and sites;
- for landfill and traditional waste disposal;
- for metal recycling.

Exposure calculations are presented for the following pathways:

- Internal exposure via inhalation of dust;
- Internal exposure via inadvertent ingestion;
- External exposure from contaminated materials and surfaces;
- Immersion (skin dose) from dispersed dust.

Appendix II describes practical measurement methods applicable for the determination of radioactive contamination of clearable materials. Sampling methods and sample types as well as the applicability of scaling factors are discussed; then main features and characteristic detection limits are presented for gamma spectrometry, alpha spectrometry, measurement of medium- and high beta emitters and finally methodology of some difficult-to-measure (DTM) nuclides are given.

Remaining work

In addition to the „trinity" of radioactive waste categories (low-, intermediate and high level waste, LLW, ILW, HLW), several European countries with considerable nuclear industry (e.g. France and Sweden) apply further waste classification terms like „very low level waste (VLLW)" and/or „very short lived waste" (VSLW). Legal and practical aspects of introducing these categories in Hungary should be considered on the basis of the findings and analyses of this concluding project.

Another favourable continuation of this project can be the compilation of „best practices" of clearance procedures in Hungary by comparing the appropriate elements of this guidance and the actual accomplishment of design, calculations and assessments. The results will then be summarized in recommendations for possible amendments of the legislative and regulatory framework.

Related publication

[1] L. Juhász, T. Pázmándi, P. Zagyvai: "*Clearance procedure for bulk amount of waste originating from the decommissioning of nuclear facilities*", Draft guidance for the Hungarian Atomic Energy Authority; Appendix I: „*Clearance scenarios*"; Appendix II: „*Measurement methods for the assessment of radiocontamination of clearable waste*", Report OAH/NBI-ABA-04/12 (in Hungarian)

SINAC: SIMULATOR SOFTWARE FOR INTERACTIVE MODELLING OF ENVIRONMENTAL CONSEQUENCES OF NUCLEAR ACCIDENTS – SECOND GENERATION

Tamás Pázmándi, Sándor Deme, Emese Homolya, Edit Láng, István Németh, Péter Szántó

Objective

The SINAC programme system was developed to follow the consequences of radioactive releases of a (hypothetical) nuclear accident. Atmospheric dispersion, plume depletion by dry-out and wash-out, cloudshine and groundshine doses, dose consequences of inhalation and ingestion, early and late health effects are computed by the software. Effects of the introduction of countermeasures are also taken into account.

The SINAC system – developed in AEKI in the 1990's – has gone through a lot of development in the last few years, according to users' needs and to the Hungarian and the international regulations and protocols of radiation protection. Continuous development ensured that the SINAC was used as an interactive expert system in the Hungarian Atomic Energy Authority (HAEA) Centre for Emergency Response, Training and Analysis (CERTA) in the last decades.

The first objective of the work in 2012 was to finish the development of the new SINAC programme; the main task of the past years' development was to create a state-of-the-art software that makes the further developement easier. It was claimed by the user (Hungarian Atomic Energy Agency) in 2012, that the guidelines of the further development for the next years should be defined.

Methods

In the last phase of the programme development the graphical user interface was completed considering users' remarks. A series of tests were performed in order to compare the results of the new and the original programme. After the modernisation of the structure and the user interface of the programme had been finished, the calculation methods and parameters were revised.

Results

The second generation of the SINAC system has basically three separate functions. It handles the input data of calculations, executes the calculations, visualises and savees the results. The programme provides a comfortable and transparent interface to set the parameters of calculations and to visualise the results. The parameters are stored and reloadable for analysing the results. The module responsible for executing the calculations works according to the input data and forwards the output data to the visualisation module. The visualisation module does not only display the calculation results but some of the input data as well. It is possible to save the end results in different formats: binary (raw data), text (tables) and images (maps, charts).

The recommended areas of development in the next four years are meteorology data and methods (advection, dispersion, deposition), dose calculation parameters, radionuclides and countermeasures.

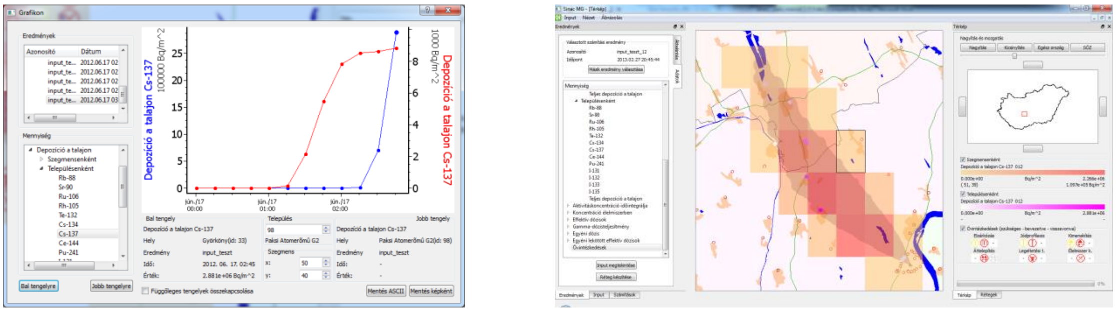

Fig 1: Screenshots from the SINAC

Remaining work

This project has been finished, but in the next four years development of the calculation methods based on the recommendations is to be done in the frame of a new project.

Related publications

[1] S. Deme, E. Homolya, E. Láng, I. Németh, T. Pázmándi, P. Szántó: *Upgrading of the second generation SINAC programme*, EK-SVL-2012-262-02-01-00 (2013)

[2] S. Deme, I. Németh, T. Pázmándi, P. Szántó: *Models of the SINAC programme*, EK-SVL-2012-262-01-01-01 (2013)

[3] S. Deme, I. Németh, T. Pázmándi, P. Szántó: *Testing of the SINAC programme*, EK-SVL-2012-262-01-03-01 (2013)

[4] S. Deme, I. Németh, T. Pázmándi, P. Szántó: *SINAC programme users manual (ver. 1.0.0)*, EK-SVL-2012-262-01-02-01 (2013)

APPLICATION OF NPP AREA MONITORS FOR DETECTION OF RELEASE DUE TO A SEVERE ACCIDENT

Sándor Deme, Edit Láng, Tamás Pázmándi

Objective

The main goal of this work was to develop a method for the detection of radionuclide releases in case of a severe accident.

In case of a severe accident damage in the integrity of the hermetical part of a nuclear power plant (NPP) and release of radioactivity through a wall rupture or leakage (direct release) can be expected. In such case the stack monitoring system gives no information on the emission. At the same time gamma radiation detectors dislocated around NPP buildings (area monitors) are measuring radiation of emitted nuclides. In this study we investigated application of area monitors for the detection of release, bypassing the stack monitoring system.

Methods

The method for the detection of a direct release through a wall rupture or leakage is based on a calculation of gamma radiation field due to stack release and on calculated and measured dose rates in comparison. In order to calculate the dose rate the gamma equivalent of activity concentration in air emitted via stack, air emission volume rate, wind direction and wind speed are necessary. In case of direct release the dose rate measured by area detectors significantly exceeds the calculated one and this means that direct release was also present at that place.

Results

A gamma dose rate meter is part of the stack monitoring system. It is calibrated in 1 MeV photon activity concentration i.e. in photon/sec/m^3 units. Gamma emission rate can be calculated in photon/sec units. This emission appears as a line source starting from the stack in the effective release height, its line activity in photon/m can be calculated considering wind speed. Gamma dose rate of such a line source is shown in Fig 1 as a function of distance from the stack and perpendicular distance from the plume to a monitoring point. The dose rate calculation was performed by Microshield computer code.

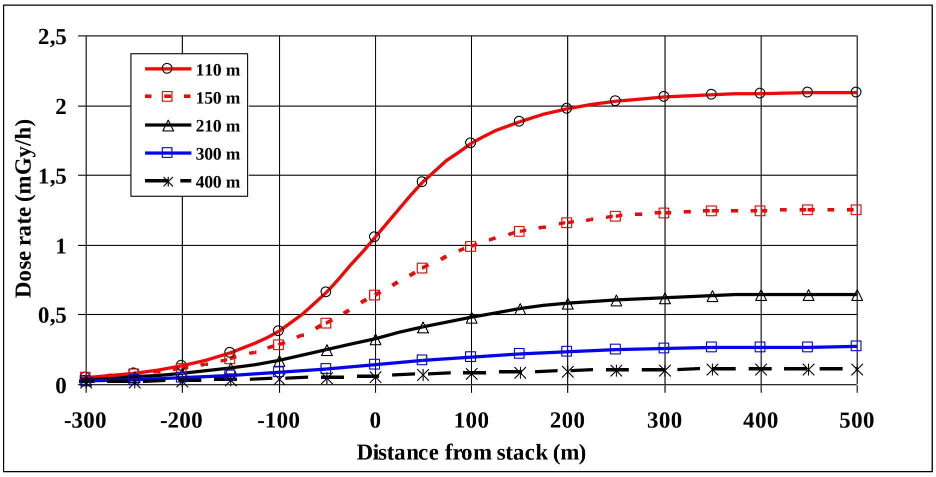

Fig 1: Dose rate of semi-infinite $1\cdot10^{12}$(photon/sec)/m)intensity line source as a function of distance from the stack for 5 different perpendicular distances from the plume

Remaining work

The work performed in 2012 was only the fundamental study on the possibility of indication of non-stack release in case of a severe accident. In the forthcoming years development of the detailed algorithm and computer code is necessary in order to use this method in practice. The final goal is an on-line real time programme for the detection of a non-stack release near ground.

Related publication

[1] S. Deme, E. Láng, T. Pázmándi: *Application of area monitors for detection of release – SUBAKI program code*, EK-TFO-2012-751-04/MO, October 2012

SOFTWARE FOR ESTIMATING MTC IN VVER-440 REACTORS WITHOUT INFLUENCING NORMAL REACTOR OPERATION

Sándor Kiss, Károly Krinizs, József Láz, Sándor Lipcsei

Objective

Moderator temperature coefficient of the reactivity (MTC) is a very important parameter of the fuel load of a nuclear reactor. The power feedback factor together with the Doppler-effect must be negative during the whole fuel cycle and so MTC has to be kept in a controlled range. With traditional methods the MTC measurement can be performed only by changing the reactor state from its normal operation.

On the basis of the global neutron flux fluctuation of the core and the core average of the temperature fluctuation, noise diagnostics allows the estimation of MTC. The basic method was developed, enhanced and applied to the VVER-440 reactor type by our department during the last years. Our aim has been to develop the prototype of a user-friendly programme module based on this method that later can be built into the PAZAR-K noise diagnostics evaluation system as a new module.

Methods

Core average temperature fluctuation was produced as the average of the cold leg temperature noise signals multiplied by transfer functions describing the signal delays and the finite height of the core. Global neutron flux fluctuation was estimated as the average of SPND (Self-power neutron detectors) background detector noise signals after calibration based on in-core SPND signals. Overview and safe handling of a large number of signals and long measurements requires sophisticated user interface elements. The evaluation method requires measurements belonging to the steady state of the reactor. However, long measurements increase the probability of changes of reactor control or other transients that have to be identified and omitted. Another important task of the estimation is signal validation which is now fully controllable by the user through panels displaying auto- and cross power spectral density functions of each signal. Final result is gained by averaging an estimator function over a specific frequency range, which is also displayed and the user is allowed to control it.

Results

A working prototype was created and tested to be built into the PAZAR-K noise diagnostics evaluation system.

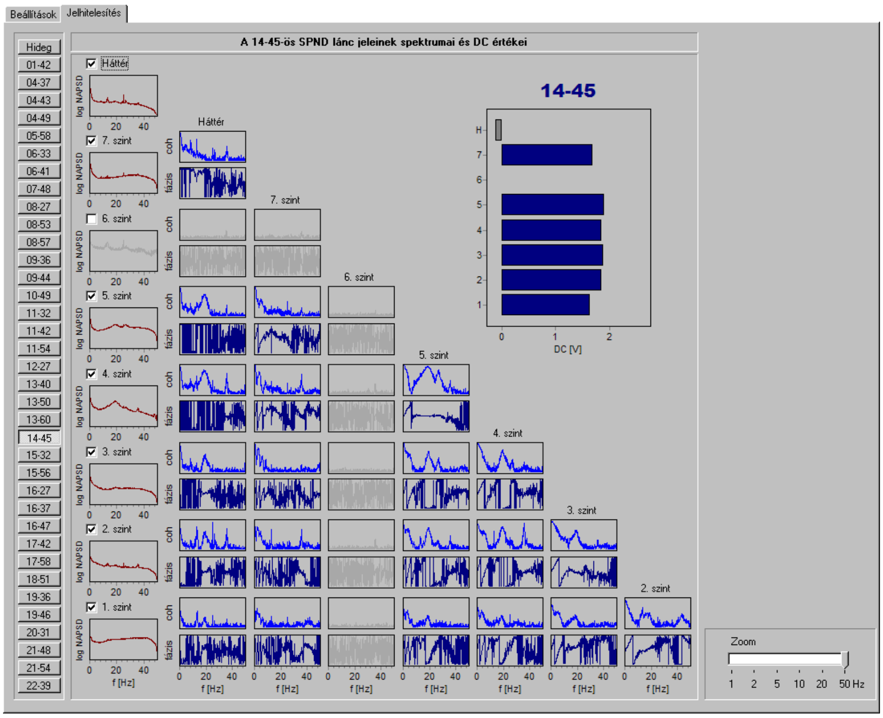

Figure 1: Signal validation panel with auto- and cross spectra of the signals of a selected SPND chain

Most of the evaluations performed during the development of the method in the last years were reproduced to verify and validate the new prototype.

Remaining work

To develop it further and to carry out additional investigations, the programme is planned to be extended to handle cold leg and core outlet temperature measurements, as well. User interface of transient handling has already been developed; it will be built into the prototype in the near future. More development and enhancement of the method itself is planned; if successful, the development results will also be built into the programme.

ACTIVITY RELEASE FROM LEAKING FUEL RODS IN THE DRY STORAGE FACILITY

Zoltán Hózer, Barbara Somfai, Katalin Kulacsy, Mihály Kunstár

Objective

The main objective of the work was the estimation of source terms from leaking fuel rods in the dry interim storage facility to support the licensing of the storage of non-hermetic fuel in the facility.

Methods

Numerical models have been developed to simulate the activity release from the leaking fuel rod during different technological steps of transportation, preparation for storage and incidents in the storage facility. In the calculations 28 radioactive isotopes were tracked during the following operations: removal of assembly from the C-30 container, high temperature drying of the assembly, transportation of the assembly to the storage tube, vacuuming of the storage tube and long term storage in the vertical storage tubes.

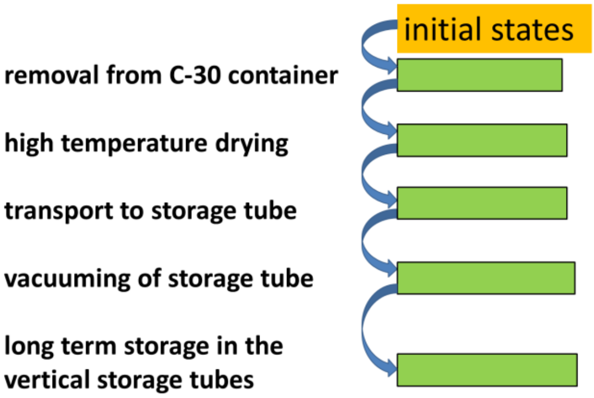

Figure 1: Sequence of activity release calculations in the dry storage facility

Different incident conditions were applied to the above five operations and the releases associated with incidents were determined. The releases during incidents and accidents were calculated in a conservative way: it was supposed that during the event the total activity dissolved in the water inside of the fuel rod would be released.

The models are based on the simulation of physical phenomena and partially on engineering judgement. The dissolution model was based on Paks NPP data. The FUROM code was applied to estimate the diffusion mechanism in the fuel pellets.

Results

Large set of calculated source terms was produced taking into account the following parameters: burnup, position of the defect in the cladding, leakage rate, storage time in the spent fuel pool before transportation to dry facility, efficiency of drying, efficiency of vacuuming and storage time in the vertical tubes. These datasets can be used for the evaluation of environmental releases.

The main conclusions of the calculations were the following:

- The activity dissolved in the water inside of leaking fuel rods can be released in the dry storage facility during different operations and incidents.
- The main source of activity is the dissolution of fuel pellets into the water in the gap between pellets and cladding. The release due to diffusion is negligible due to the low temperature.
- The maximal activity release can take place during the drying of the assemblies. If the drying operation is not successful then vacuuming can lead to maximal release.
- The release during incidents highly depends on the pre-history of the fuel assembly, and its value can be comparable to the release during the drying operation.

Remaining work

Following the calculation of environmental releases, further improvement of the models may be needed in order to reduce the high conservativism applied in the present calculations.

Related publication

[1] Z. Hózer,B. Somfai, K. Kulacsy, M. Kunstár: *Calculation of Source Terms for the Leaking Fuel Rods in the Interim Dry Storage Facility*, EK-FRL-2012-733-01/01-M1

ANALYSES FOR LICENSING A NEW 4.7 % ENRICHED FUEL AND THE RELATED 15 MONTH FUEL CYCLE AT PAKS NPP

András Keresztúri, György Hegyi, Csaba Maráczy, István Panka, Emese Temesvári, Iván Tóth

Objective

In the near future, a new fuel assembly type enriched to 4.7 % is foreseen to be introduced at Paks NPP allowing the introduction of the 15 month equilibrium fuel cycle length. The application of the above assembly essentially modifies the power distributions on all geometry scales; namely the distribution in the fuel pellet, the pin-wise distribution in the assembly. Also the reloading schemes and consequently the assembly-wise power peaking factors are modified to great extent. As a consequence, the relevant part of the Design Basis Analyses – where modified distributions are important - is to be repeated. According to the schedule, in 2012 preparatory works of these analyses had to be carried out.

Methods

Code development, verification, validation, expert assessment

Results

The following tasks were carried out.

- Parameterized few-group constant and response matrix libraries were generated for the KIKO3D and KARATE pin-wise and assembly-wise calculations by using the KARATE spectral modules [1].
- The KARATE code system and the KIKO3D programme were modified according to the new group constant libraries [1].
- Transition and equilibrium cycles were calculated by KARATE for determining the burnup distributions necessary for the further investigations [2].
- The reactor physics frame parameters (conservative bounding values of reactivity coefficients, power peaking factors etc., influencing the safety analysis results) were calculated by KARATE covering the transition and equilibrium cycles [3].
- The methodical problems of the hot channel calculations, originated from the new pin-wise and intra-pellet power distributions were investigated, the intra-pellet distributions were determined for the hot channel and the fuel behaviour codes [4].
- The DBA initiating events in FSAR were surveyed and the relevant ones to be analyzed were selected [5].

The conservative reactivity curves as a function of the average fuel and moderator temperature and density, the boron concentration necessary for the point kinetics model of RELAP were determined by using KARATE [6].

Remaining work

According to the schedule of the project, there is no remaining work.

Related publications

[1] Cs. Maráczy: *Preparation of the few-group constants of the fuel to be applied at Paks NPP enriched to 4.7% and containing 6 gadolinium pins*, EK-RAL-2012-703-01-M0 report, in Hungarian

[2] Gy. Hegyi:*Calculation of the transition and equilibrium cycles for the implementation of the fuel enriched to 4.7% and containing 6 gadolinium pins*, EK-RAL-2012-703-02-M1 report, in Hungarian

[3] E. Temesvári, Gy. Hegyi: *Determination of the frame parameters of the cores consisting of the new fuel enriched to 4.7% and containing 6 gadolinium pins*, EK-RAL-2012-703-03-M4 report, in Hungarian

[4] I. Panka, A. Keresztúri: *Methodology of the hot channel calculations of the cores of the fuel enriched to 4.7% and containing 6 gadolinium pins*, EK-RAL-2012-703-11-M1 report, in Hungarian

[5] A. Keresztúri, I. Tóth: *Completeness of the safety analyses to be applied for cores of the fuel enriched to 4.7% and containing 6 gadolinium pins*, EK-RAL-2012-703-12-M1 report, in Hungarian

ANALYTIC INVESTIGATION OF VARIOUS FLOWS AND HEAT CONDUCTION PROBLEMS

Imre Ferenc Barna

Objective

In our recent study we continued our former activity and analytically investigated various well-known fluid flow and heat conduction equations.

Methods

We investigate fundamental equations, like the Fourier, the Cattaneo heat conduction or the Navier-Stokes equation and try to find new analytic solutions which might give a new insight into the deeper structure and properties of these equations. We usually use the self-similar Ansatz which gives us diffusive (spreading-and-decaying) type of solutions, as a second Ansatz travelling-wave solutions can be examined as well. Such results can illuminate the wave properties of the equations, if they exist.

Results

At first we investigated a generalized and well-known Cattaneo rule [1], with this model we managed to give a new solution of the heat conduction paradox which is an old weak point of the usual Fourier law. The solution of the Fourier heat conduction model is the Gaussian function, which has a strong decay but has an infinite range, therefore includes infinite quick wave propagation nodes as well, which is unphysical.

In a later study we investigated all the mathematical and technical details of this model [2].

In a different work we generalized the self-similar Ansatz to three space dimensions and gave an analytic solution for the Navier-Stokes equation which is also new [3]. The Navier-Stokes equation is one of the most complicated and less known non-linear partial differential equation, attracting attention for more then a century.

This year we went along this way and investigated two such systems as were mentioned above. First we developed a new non-linear heat conduction model which might be interesting describing exotic materials like nano systems [4]. The study is under publication but available on the arxiv server.

Secondly, we coupled the heat conduction mechanism to the problem of a one-dimensional fluid flow and investigated the system, as an interesting feature we applied a different kind of equation of states, (which describes the physical properties of the investigated media) to close the equations. We got a large variety of analytic solutions of a one dimensional system which is fundamental for the further understanding and has not been studied till now. These results are under publication too [5].

Recently, we investigate the compressible 3 dimensional Navier-Stokes equation which is even more complicated than the non-compressible one. We plan to publish our results in late 2013.

Remaining work

Right now some of our results are under publication [3, 4], at the same time now we investigate the compressible 3 dimensional Navier-Stokes equation as well. We plan to study two dimensional flow problems with heat conduction in the future. Such a system was first considered by B. Saltzman and E. N. Lorenz at the beginning of the sixties and leads to the problem of chaotic behaviour of meteorology. Such questions are still very hot and reasonable for studying.

Related publications

[1] I.F. Barna and R. Kersner, "*Heat conduction: a telegraph-type model with self-similar behavior of solutions*" J. Phys. A: Math. Theor. **43**, (2010) 375210

[2] I.F. Barna "*A general telegraph-type model for heat conduction with self-similar behavior of solutions*

Lasers in Eng. **24**, (2012) 95

[3] I.F. Barna "*Self-similar solutions of the three dimensional Navier-Stokes equation*", Communication in Theoretical Physics **56**, (2011) 745

[4] I.F. Barna and R. Kersner *Heat conduction: hyperbolic self-similar shock-waves in solids*

http://arxiv.org/abs/1204.4386 and under publication

[5] I.F.Barna and L Mátyás *Analytic solutions for the one-dimensional compressible Euler equation with heat conduction closed with different kind of equation of states* http://arxiv.org/abs/1209.0607 and under publication

CALCULATION OF BEYOND DESIGN BASIS ACCIDENTS WITH THE FRAPTRAN CODE

Attila Molnár, Attila Guba, István Panka, Zoltán Hózer

Objective

Fuel behaviour simulation was carried out in order to check if the fuel rods failed or not in the selected beyond design basis accidents.

Methods

The FRAPTRAN code was used to simulate the behaviour of VVER-440 fuel rods under transient conditions for two scenarios:

- break of a 50 mm diameter pipe in the cold leg of the primary circuit with total loss of high pressure emergency core cooling system,
- break of a 492 mm diameter cold leg followed by the temporary loss of low pressure emergency core cooling system at 600 s after the break and restart of the system at 1200 s.

The initial and boundary conditions were provided by RELAP and ATHLET code calculations. The FRAPTRAN calculations included five different burnup values.

Results

The results showed that cladding burst did not take place and the integrity of the fuel cladding was not lost in the two calculated cases in spite of the high (550–800 °C) maximum cladding temperatures.

The tangential strain of cladding in both cases remained below 1%. Furthermore, this strain was originated mainly from the thermal expansion process.

The degree of Zr cladding oxidation was very low and the quenching of high temperature bundles could not result in the brittle fragmentation of fuel rods.

The pellet temperatures remained well below the melting point of UO_2.

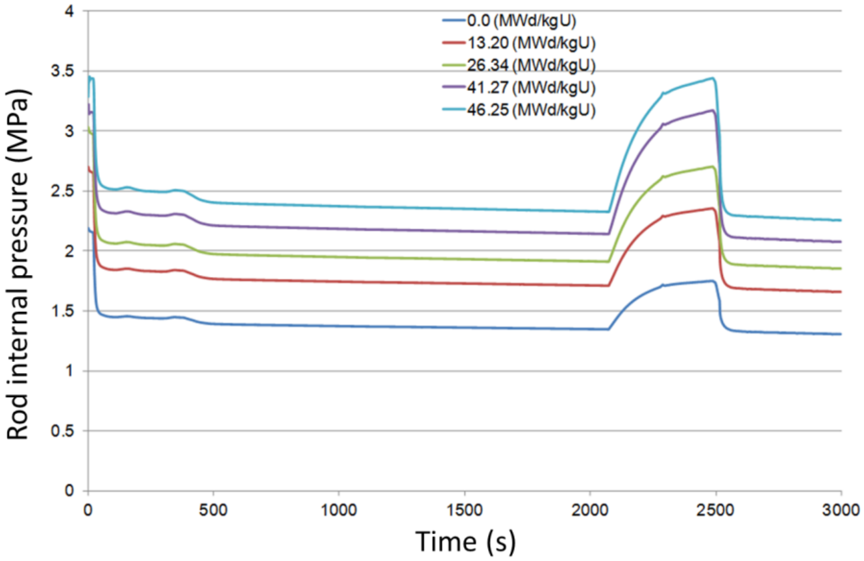

Figure 1: Calculated fuel rod internal pressure for the 50 mm pipe break case with different burnups

Remaining work

The planned calculations were completed. The introduction of new models into the FRAPTRAN code to describe the E110G alloy is foreseen in the future.

Related publication

[1] A. Molnár, A. Guba, I. Panka, Z. Hózer: Calculation of Beyond Design Basis Accidents with the FRAPTRAN code, EK-FRL-2012-758-01/01-M1 (in Hungarian)

CHARACTERISATION OF SPENT VVER-440 FUEL TO BE USED IN THE FIRST-NUCLIDES PROJECT

Zoltán Hózer, Emese Slonszki

Objective

The main objective of the work was the systematic collection of the main characteristics of damaged and leaking VVER-440 fuel, the dissolution rates of which will be analysed in the next phase of the FIRST-Nuclides project.

Methods

There were no special examination of the fresh fuel assemblies before loading them into the reactor core, for this reason factory data were used to characterise the fuel. The operational parameters were derived using power histories provided by the NPP. The calculations were carried out with fuel behaviour codes FUROM and TRANSURANUS.

The isotope inventories were determined taking into account the real power histories of each fuel assembly for almost one thousand isotopes. For future evaluation only the long lived isotopes will be used. The inventory contains important data for the determination of fractional releases.

Results

In case of damaged fuel 30 fuel, assembly were stored in the same pool. The activity release was common result from all assemblies, so the calculation of dissolution rates should take into account some average values. The following basic data for these 30 fuel assemblies have been collected:

- design characteristics of VVER-440
- operational data of damaged fuel assemblies
- total isotope inventory of 30 damaged assemblies.

In case of leaking fuel one out of 126 fuel rods was in contact with water, but the leaking rod was not identified. The assembly average values can be used for the characterisation of source rod for the evaluation of activity data from this assembly. The design characteristics of this fuel assembly were the same as of the other 30 assemblies. The additional information included the followings:

- operational data of leaking fuel assembly,
- isotope inventory of leaking assembly.

Remaining work

Dissolution rates of different isotopes from VVER fuel will be determined in the next phase of the FIRST-Nuclides project based on activity measurements at the Paks NPP.

Related publication

[1] Z. Hózer, E. Slonszki: *Characterisation of spent VVER-440 fuel to be used in the FIRST-Nuclides project*, EK-FRL-2012-421-01/01

CONSTRUCTION OF A HIGH TEMPERATURE FACILITY TO INVESTIGATE SECONDARY HYDRIDING PHENOMENA

Imre Nagy, András Vimi, Mihály Kunstár, Gergely Kracz, Zoltán Hózer

Objective

In order to investigate secondary hydriding phenomena in VVER claddings, a new facility had to be built, which is capable to reproduce the burst of cladding at high temperature and the oxidation of the open cladding tube in steam.

Methods

The facility was built in our laboratory using the outfitting available in the mechanical workshop. Several equipment were connected to each other and a detailed data acquisition system was created.

Results

The facility was successfully put into operation and the commissioning test was completed.

The facility includes the following units (Fig. 1):

1. High purity argon (carrier gas in the furnace)
2. Steam generator unit
3. Precision pump
4. Water tank for quench
5. High purity argon balloon (inner pressurization of the fuel sample)
6. Stepwise regulation valve
7. Control unit for valve
8. Buffer volume for the pressurization system
9. Hydrogen measurement device
10. Vertical tube furnace

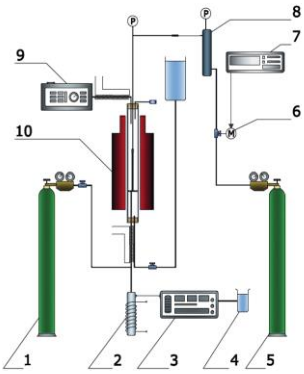

Figure 1: Scheme of the facility for the investigation of secondary hydriding phenomena

The technology for sample production was developed. VVER type cladding is used with alumina pellets. One end of the sample has connection to the pressurization system, while the other end is closed by welding (Fig. 2).

Figure 2: View of the cladding sample for secondary hydriding test

Remaining work

Experimental series will be carried out with E110 and E110G type cladding samples in the facility. The test matrix will include different oxidation times, oxidation temperatures and the samples will be cooled down with or without water quench. Mechanical testing will be performed with the oxidized tubes and detailed analyses of cladding microstructure will be carried out. The hydrogen content of the samples will be determined.

Related publication

[1] I. Nagy, A. András, M. Mihály, G. Kracz, Z. Hózer: *Construction of New Facility for the Investigation of Secondary Hydriding Phenomena in Cladding Tubes at High Temperature*, EK-FRL-2012-759-01/02 (in Hungarian)

CONTRIBUTION OF PELLET FRAGMENTATION TO FISSION GAS RELEASE DURING DBA LOCA

Katalin Kulacsy, Attila Molnár

Objective

The strong economic pressure for increasing the discharge burn-up of nuclear fuels is well known. This increase, however, has brought about new findings as to the structure of fuel pellets: at a rod burn-up of about 40 MWd/kgU, the rim region of the pellets with the highest burn-up starts to re-crystallise, the fission gases accumulate into high-pressure pores, and the high-burnup structure (HBS) starts to form.

Several experiments have shown that the HBS of very high burn-up fuel pellets can undergo fine fragmentation in the course of a LOCA sequence, releasing significant amounts of fission gases, and annealing tests have specified the conditions under which this fragmentation may occur. Since the extra fission gas release (FGR) may be a safety issue with increasing burn-up, its contribution to the total FGR for a VVER-440 reactor is estimated.

Methods

The cause of the release is thought to be the over-pressurisation of the gas-filled pores resulting in micro-fragmentation of the HBS, during which the gas content of the pores broken open is released. Based on annealing tests, a model has been established to determine the onset of HBS fragmentation leading to the extra FGR. The results of the tests were processed in a conservative manner, i.e. the lowest burn-up and temperature values where micro-fragmentation occurred were adopted, each with the highest measured FGR. Also, as the dependence of the fragmentation on heating rate was not evident, no heating rate threshold was set. The model is the following:

- below a local burn-up of 66 MWd/kgU and a local temperature of 873 K, no micro-fragmentation occurs,
- above a local burn-up of 66 MWd/kgU and at a local temperature between 873 K and 1,323 K, a local FGR of 20% is assumed,
- above a local burn-up of 66 MWd/kgU and above a local temperature of 1,323 K, a local FGR of 90% is assumed.

The whole core of a VVER-440 reactor was simulated in the best estimate (BE) and the design basis accident (DBA) approaches during normal operation, using the steady-state FUROM code up to the start of the LOCA event, to establish the state of the fuel rods and the amount of fission gas stored in the HBS pores.

The thermal-hydraulic boundary conditions for a 200% large-break LOCA were available, calculated also both with the BE and with the conservative DBA methodologies. Fuel assemblies were divided into groups according to their linear heat generation rates, and axial and radial temperature profiles were simulated for each group with the FRAPTRAN code during the LOCA sequence.

Depending on the local peak temperatures, the release due to fragmentation was predicted according to the above model, in the BE and conservative DBA approaches.

Results

The calculations predicted the following fractional FGR from the HBS fragmentation (with respect to the total core inventory):

- BE case (maximum rod burn-up: 52 MWd/kgU): 0.00%,
- conservative DBA case (maximum rod burn-up: 60 MWd/kgU): 0.09%,
- higher burn-up fuel planned for the near future, DBA case (maximum rod burn-up: 67 MWd/kgU): 0.17%.

Even the last value is an order of magnitude smaller than the core average fission gas fraction stored in the rod free volumes at the end of a cycle, i.e. HBS fragmentation during LOCA is not a safety issue for VVER-440 type reactors under present-day and near-future operational conditions. The above contributions due to fragmentation are also lower than the values currently applied in the activity release calculations of safety analyses.

Related publication

[1] K. Kulacsy, A. Molnár: *Contribution of Pellet Fragmentation to Fission Gas Release During DBA LOCA*, EK-FRL-2012-765-03/01 (in Hungarian)

Corrosion of Zirconium Based Cladding Materials in Pressurized Steam at High Temperature

Zsolt Kerner, Ákos Horváth

Objective

Reaction of zirconium and water above normal operation temperature (> 900 °C) can result in an accelerated degradation of cladding of nuclear heating elements. Reaction rate was determined earlier by many authors on different zirconium based alloys at 1 bar. However, during an ATWS (Anticipated transient without scram) type accident the pressure can be much higher (e.g. 150 bar for half an hour). The aim of this work was to determine the pressure dependence of the oxidation rate on different zirconium based cladding materials up to 1000 °C and 150 bar.

Methods

A special autoclave was created wherein the cladding samples can be heated up to 1000 °C and 150 bar water pressure can be produced. A cylindrical heating unit is installed in the centre of the autoclave vessel. Ring shaped samples can be pulled to it. Temperature of the sample is approached by measuring the temperature of a stainless steel ring placed to the heating unit, just above the sample. The pressure is adjusted by the control of autoclaves' outer heating. Temperature is measured continuously at four axial positions in the autoclave. All measured parameters are recorded. Stability of the temperature and pressure is better than 1%, due to the built in control unit.

Before experiments all samples were washed by alcohol. The air was removed from the autoclave by argon flow.

After a certain reaction time the oxidation ratio of the samples was determined using gravimetry.

Results

Some tests have been done already on Zircaloy-4 and Zr-1%Nb (E110) samples.

Preliminary results show exponential pressure dependence in the average oxidation rate during 30 minutes reaction time on both of the materials.

Results on E110 give very high scattering in the oxidation ratio in parallel experiments. Presumably the oxidation process has an incubation period the length of which follows a probability distribution.

The pressure dependence of the oxidation rate of Zircaloy-4 cladding material is presented in Figure 1.

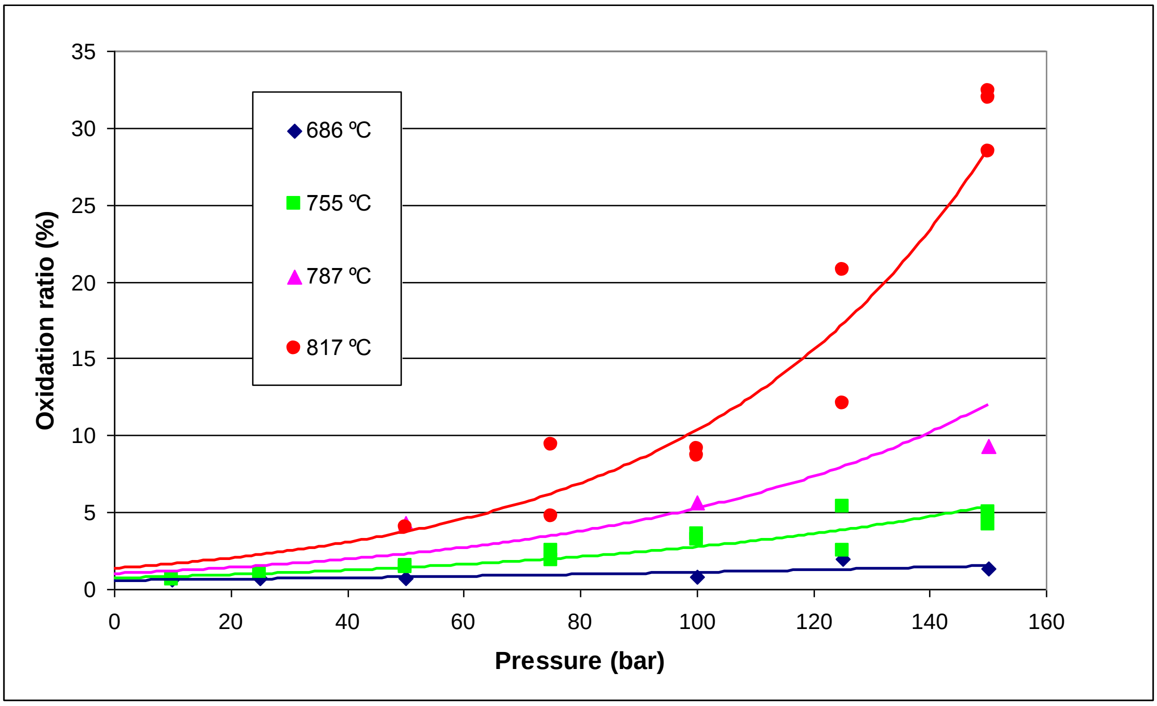

Figure 1: Pressure dependence of the oxidation ratio of Zircaloy-4 after 30 minutes treatment

Remaining work

Further measurements are planned up to 1000 °C temperature. On E110 numerous parallel measurements (with some different oxidation times) are needed to characterize the incubation period.

Development of VERETINA, a New VVER-440 Reactor Core Analyzer System

Gábor Házi, Csaba Horváth, Zoltán Kálya[1], József Páles, István Pós[1], János Végh

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Objective

The basic aim of the R&D project – initiated by Paks NPP – is to develop, test and install a coupled neutronics – thermal hydraulics code system for the analysis of the Paks VVER-440/V213 type reactors. In the coupled system the primary circuit and reactor core thermal-hydraulics calculations are performed by the RETINA two-phase flow calculation code, developed by Centre for Energy Research. Core neutron physics model is taken from the VERONA core monitoring system, currently in operation at all units of Paks NPP. The final target is to perform an accurate, time-dependent reactor physics analysis of operational transients for the Paks reactor units. The system architecture is rather unique, because the coupled neutron physics / thermal-hydraulics models were connected to a reactor core monitoring system, therefore the utilization of real operational data for model development and model tuning is a built-in feature of the system.

Methods

The neutron physics module of the system is constituted by the kinetics option of C-PORCA programme, which is a nodal neutron physics code regularly applied for off-line and on-line core analysis at Paks NPP. The C-PORCA and the RETINA two-phase thermal-hydraulics code are integrated under a new platform (runtime environment) called PCA. The PCA is also coupled to the VERONA core surveillance system of Paks NPP and a new 3D core visualization system, Core3DView (see Fig. 1). This approach makes it possible that plant operational data (including in-core measurements) – recorded at two seconds frequency – can be easily utilized during the development, tuning and validation of the various system models. The first version of the VERETINA system was validated by using a number of operational transients and dynamic benchmarks. The validation exercises were as follows: steady states, operational transients (control rod drop, main circulating pump trip, turbine trip) and benchmarks (AER-DYN-005 = double-ended break of main steam header, AER-DYN-006 = double-ended break of main steam line).

Results

Validation exercises demonstrated that the VERETINA system was able to reproduce the results of classical benchmark problems like AER-DYN-005 and AER-DYN-006 with reasonable accuracy. Calculation results obtained for steady states and operational transients (using archived operational data as initial and boundary conditions) were in good agreement with the plant measurements. Simulation results produced by the coupled reactor analyzer code illustrated the correctness of the selected approach and this fact was quite encouraging to continue the R&D project into the last work phase.

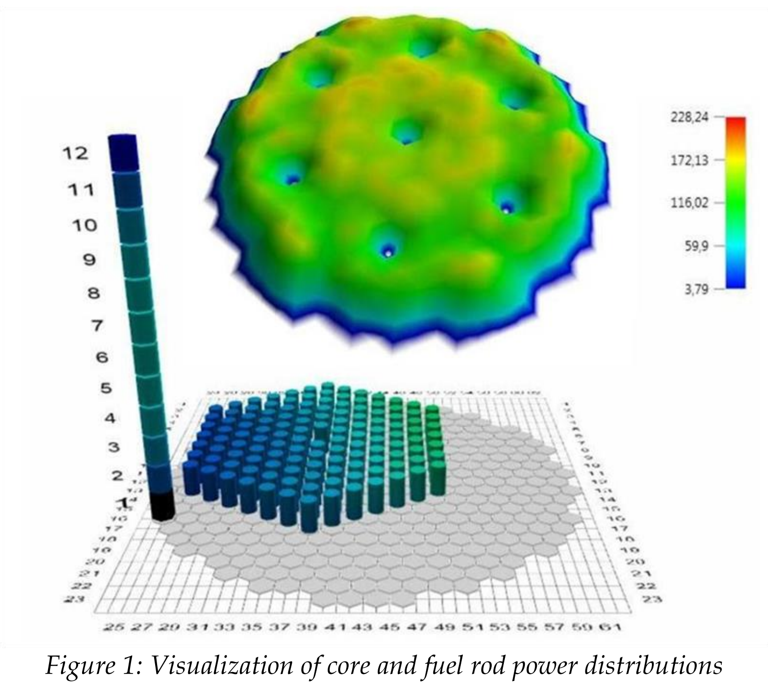


Figure 1: Visualization of core and fuel rod power distributions

The time dependent neutron diffusion equations are solved by the QS method, where the time and space dependence of neutron flux are separated. The time dependency of the amplitude function governed by dynamic reactivity is determined by a Runge-Kutta method. Effects caused by fuel and moderator temperature, as well as density changes are taken into account by two group nodal cross section data recalculated in each iteration cycle. Nodal calculation of delayed power (due to the decay heat) is carried out according to the method proposed by the US NRC regulatory guide of NUREG/CR-6999.

The neutronics model contains a module for the prediction of ex-core detector signals, in order to facilitate comparison of calculated signals with real measured ones.

RETINA uses a five-equation approach: two mass and two energy conservation equations are solved for the individual phases (water and steam). The momentum conservation equation is solved for the mixture and it is supplemented by a drift-flux model (to simulate mechanical non-equilibrium between phases). These equations are supplemented by closure relations, which calculate the interfacial mass and energy transfers in order to close the equation system. The equation system is supplemented with additional models, taking into account heat and momentum transfer between the individual phases and heat structures. RETINA uses a fully implicit time discretization, calculating the Jacobian problem by automatic derivative functions. Spatial discretization is based on the control volume approach and pressure-velocity decoupling is solved by using staggered grid for the momentum equation.

Detailed examination of core distributions is possible by using an advanced 3D visualization tool called Core3Dview. It can be used for displaying various core distributions at node or at fuel rod level, e.g. linear heat rate, fuel burnup, xenon concentration, coolant temperature. Nodal core distributions are displayed in 349 radial positions, each position has 50 axial data points. Data corresponding to fuel rod level are displayed in 126 radial and 50 axial points. Subchannel data are displayed in 258 radial positions and 50 axial points. Data to display are directly taken from the reactor physics database, no special file interface is needed for the visualization.

Remaining work

The first two development phases of the R&D project were finished in the middle of 2012. The next development phase will start in 2013 and will be continued in 2014. This third – and last – work phase will produce a VERETINA version capable of performing core analysis at fuel rod and fuel assembly subchannel level with a high axial resolution.

Related publications

[1] VERETINA V1.0 User’s Manual, MTA EK , June 2012 (in Hungarian)

[2] VERETINA V1.0 Description of programmes and algorithms, Volume I. – Description of the RETINA code, MTA EK, June 2012 (in Hungarian)

[3] VERETINA V1.0 Description of programmes and algorithms, Volume II. – Description of the reactor physics modules and the runtime environment, MTA EK, June 2012 (in Hungarian)

[4] VERETINA V1.0 Summary of V&V test results for the VERETINA algorithms, MTA EK, June 2012 (in Hungarian)

[5] J. Páles, G. Házi, Cs. Horváth, J. Végh, I. Pós, Z. Kálya: *Validation of VERETINA, a new nuclear reactor analyzer system for VVER-440,* Atomic Energy Research (AER) Symposium 2012, Pruhonice, Czech Republic, October 1-5, 2012

EK PARTICIPATION IN THE MATTER PROJECT

Levente Tatár

Objective

Construction materials for generation IV reactors have to operate under more severe environmental conditions than the currently used materials. Higher operating temperatures and irradiation doses, as well as possible interaction with liquid metal represent serious challenge for these materials. To be able to build the ASTRID and MYRRHA reactors, the designers need material standards and design rules which are currently unavailable for the operating conditions of these reactors. As a prerequisite for standardization, the MATTER project focuses on the research for candidate materials for these types of reactors. Special attention is paid to P91 and 316SS type steels. Their properties are studied under air, sodium and lead/LBE (Lead-Bismuth Eutectic) environment.

ASTRID (**A**dvanced **S**odium **T**echnological **R**eactor for **I**ndustrial **D**emonstration) is a sodium-cooled fast reactor. For this type of reactor, standardized material properties for 316 type steels are missing for temperatures above 500 °C.

MYRRHA (**M**ulti-Purpose H**y**brid **R**esearch **R**eactor for **H**igh-tech **A**pplications) is a lead-bismuth cooled prototype reactor. For this type of reactor it is needed to fill in the gaps which exist for corrosion properties of 316 type steels in LBE environment.

Methods

During the preparatory work of the project, the whole workpackage we were in was cancelled together with our original experimental plan. However, the amount of money reserved for our institute in the framework of the project remained unchanged, so we faced the inconvenient situation that the amount of money set apart for bibliographic studies and work with databases became too high. This caused the project leaders to reconsider again our participation, so, with common accord with them it has been decided that EK will make high temperature irradiations for P91 material. We proposed the following irradiation conditions:

- controlled temperatures of 550±10 °C (max. 600°C)
- doses of approximate 0.5 dpa (half year)
- fracture toughness and tensile test specimens

The Bagira3 irradiation rig is constructed in such a way that it can withstand much higher temperatures than the previous Bagira1 and Bagira2 rigs. This could be accomplished by changing the material of load carrying structures situated in the active zone from aluminum to titanium.

Post irradiation examination would be:

- fracture toughness tests for Master Curve
- tensile tests at different temperatures (i.e. 550°C, 300°C, room temp.)
- metallography
- SANS

Results

Some data available in the literature have been collected for the 316SS type steel and uploaded to the MatDB database. This work has been stopped due to the aforementioned changes in our contribution to the MATTER project. Testing of the irradiation rig Bagira3 is in progress, the results of a test irradiation indicate that most probably there will be no problems in reaching the required doses and temperatures.

Remaining work

CEA (Commisariat d'Énergie Atomique) sent a piece of approximate 1 kg of P91 material to our institute. The size and number of the samples and the irradiation conditions are still under discussion. High temperature irradiation of the P91 material will certainly fill in gaps.

Related publications

[1] MYRRHA homepage: http://myrrha.sckcen.be/, retrieved 08.03.2013

[2] J. Rouault, J.P. Serpantié, D. Verwaerde: *French R&D Programme on the SFR and the ASTRID Prototype*, Conference on Fast Reactors and Related Fuel Cycles: Challenges and Opportunities FR09. Proceedings. Kyoto, Japan, 7–11 December 2009

[3] MATTER homepage: http://www.matterfp7.it/Layout/matter/index.asp, retrieved 08.03.2013

ENHANCEMENT OF THE PHYSICAL MODEL OF THE SITONG4 FUEL CYCLE SIMULATION CODE

Áron Brolly

Objective

In the previous years the nuclear fuel cycle simulation code called SITONG4 was developed in our research centre. Fuel cycle simulation codes are used to study transient behaviour of the fuel cycle. For example, introduction of a new reactor type or starting fissile material recycling causes dynamic mass flows between the facilities and time-varying inventories like accumulation of waste or separated fissile material. A fuel cycle simulation code tracks these processes and helps to answer questions like whether equilibrium can be achieved after a transition in the reactor park.

The SITONG4 code models the operation of six fuel cycle facilities and the transfer of materials (fresh and irradiated fuel, raw and waste materials) between them taking into account 39 nuclides and radioactive decay. First version of the code is an object program, the main limitations of its physical model are: recycling of fissile material is restricted (connections between facilities are fixed); simulation events are restricted to the present conditions (current needs and demands are taken into account); enrichment, fuel fabrication and spent fuel reprocessing is handled by one plant; history of facilities is stored only for the spent fuel interim storage (using a limited solution); fuel parameters are attached to reactors.

Recycling of plutonium is effected by the decay of the short half-life ^{241}Pu. Therefore lag times in the fuel cycle (cooling time before reprocessing, operation time of reprocessing and fuel fabrication) has to be taken into account in order to determine precisely the required amount of plutonium needed to start a Pu-burner reactor. Therefore objectives of the work were: (i) separating the physical models of the three plants, (ii) introducing operation time for the plants, (iii) establishing flexible connections between the facilities and (iv) implementation of the new physical model in the code. These objectives will result in a more realistic description of the fuel cycle and enlarge the scope of fuel cycle studies the code is capable to model.

Results

The representation of the three fuel cycle plants modelled by the code is now well separated. Each plant has its own, independent physical model not influenced by the operation of the other plants.

To take into account lag times in the fuel cycle's front-end, the simulation of the fuel cycle is divided into a so-called planning phase and the actual simulation. In the planning phase fuel loadings of the reactors are determined starting from electric energy demand of each reactor. These loadings are called schedules in the model. The schedule in general describes the time-dependent fuel or material needs (demands) or loadings of a reactor or plant. Using schedules of the reactors, schedules for the fuel fabrication and enrichment plants are derived. While creating these derived schedules, operation time and losses of each plant are taken into account. The concept of event card was introduced to describe schedules of facilities. With this concept demands spanning multiple facilities and several time points can be handled very flexibly.

To be able to create facilities' schedule, information-like connections between facilities were introduced (previous model had only material-like connections). It was necessary to incorporate into the model the representation of the front-end and also the back-end of the fuel cycle. Not only the representation of the information-like connections but also the exchange of information between the facilities was elaborated. Thanks to the event card concept and the representation of the front-end and back-end, the facilities can be linked in a very flexible manner. Facilities contain only their fixed connections not changing during the simulations (e.g. the stock losses go to).

Both the old and the new physical model track each material transfer individually. In the new model the concept of package (material or fuel) was introduced storing all information needed to carry out the transfer either for the front-end or for the back-end facilities. To have a simple handling of material transfer between facilities, the simulation algorithm handles both types of packages and all types of facilities in a unified way using a predefined protocol for transfer of packages and information between the facilities.

The concepts, needs of the new physical model reached beyond the frames of FORTRAN 77, coding language of the previous version of the code. It was found that object-oriented languages fit well to the new concepts of the physical model. To maintain the compatibility in some sense, the Fortran 95 standard which is an object-based language was chosen. Introducing derived types and modules, using polymorphic variables and methods for the generalized package and generalized facility concepts helped much in the implementation of the new concepts of the physical model.

Remaining work

The new approach and concepts used in the enhanced physical model induced several changes in the code, therefore the implementation of the new physical model is accomplished only partially. Finishing the implementation and testing of the new model have to be fulfilled as a future task.

Related publication

Á. Brolly: *Physical model and system design of the SITONG4 code's v2.0 version*, EK-RAL-2012-122-01/01, 2012 (in Hungarian)

Evaluation and Display of Redundant Temperature Measurements in the VERONA Core Monitoring System

Csaba Horváth, Csaba Major, Zoltán Kálya[1], István Pós[1], János Végh

1 – Paks Nuclear Power Plant Ltd, H-7031 Paks, P.O.Box 71

Objective

Long time operation experience with the Paks NPP VERONA core monitoring system has indicated that it would be beneficial to develop a software module for monitoring the deviations between redundant temperature measurements and to issue an early warning when the deviations exceed corresponding limits. The operators' comprehension could also be enhanced by the provision of some new pictures and new alarms. The Paks NPP in-core instrumentation system provides redundant measurements for the following temperature indications: each cold leg and hot leg resistance thermometer has two redundant thermocouples and thermocouple cold junction temperatures are metered by a pair of redundant resistance thermometers (this is true not only for the 24 loop thermocouples but also for the 210 in-core thermocouples, measuring the coolant temperature at the fuel assembly outlets). In order to accomplish the design, coding, testing and implementation of the "redundant temperature monitoring"module, in early 2012 Paks NPP contracted with MTA EK to carry out the related software development tasks.

Methods

First the system design document was prepared for the software modification and it was discussed with plant experts (control room operators, reactor physics engineers, VERONA operation and maintenance personnel, safety authority). After a mutually acceptable system design was obtained, the coding and editing of new pictures started. Two new pictures were defined: one for showing deviations of the redundant loop temperature measurements (see Fig. 1) and another one to show deviations of cold junction temperature measurements belonging to the 210 in-core thermocouples.

Results

The new software version first was tested off-line in the framework of the so called VERONA expert system. After the completion of these off-line tests the new system was installed at the VERONA test system and it was tested with on-line data for several weeks. When sufficient and satisfactory test data were collected, the new system was installed at the VERONA configuration serving the full-scope training simulator. Site installations at the units were started only after the successful simulator tests and afterwards the new system was gradually put into operation at all Paks units.

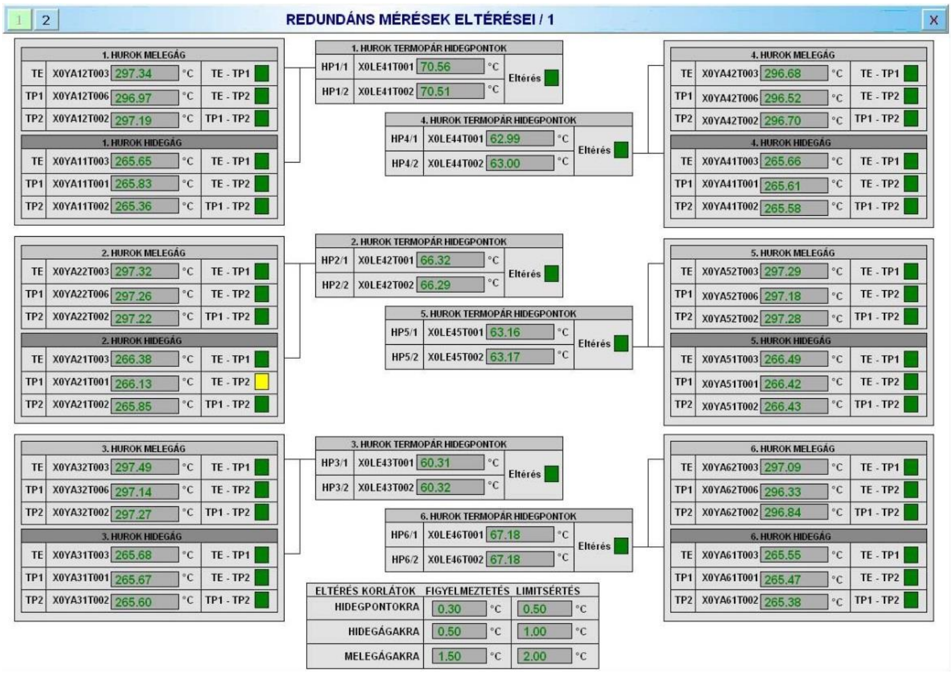


Figure 1: A new VERONA picture showing temperature measurement deviations for the cold and hot legs

Remaining work

The project was concluded, the new VERONA version was installed at all units of Paks NPP and at the simulator.

Related publication

[1] Paks NPP VERONA Core Monitoring System, System Design Document, V3.7, Volume I., Handling of redundant measurements, MTA EK , May 2012 (in Hungarian)

EVALUATION OF HRP EXPERIMENTS: PROCESSES OF THE FISSION GAS RELEASE

Ágnes Griger and Anna Pintér-Csordás

Objective

The Halden Reactor Project (HRP) provides measured data concerning the integral fuel performance under different irradiation conditions, as well as results on the individual properties of fuel components during and/or after irradiation. Our Research Centre as a member of HRP can get information and data on special measurements, which are otherwise not available in Hungary.

Our objective was to evaluate systematically the data originated from different integral experiments concerning the fission gas release (FGR) processes, as well as to compare the evaluated results to other ones from the open international literature. The work was sponsored by MVM Paks NPP.

Methods

The proper HRP integral tests and similar results from other sources have been simultaneously studied and evaluated.

Results

On the basis of the measured data obtained from HRP tests and further numerous data from literature, an integrated picture has been formed concerning the fission gas release mechanisms. The factors influencing the FGR (pellet geometry, UO_2 structure, temperature, burn-up etc.) and their direct and cross effects on the fission gas release have been interpreted in a complex manner.

A very important factor influencing the FGR process is the nano-, micro- and macro-structure of the fuel pellet including the grain and pore sizes, the chemical composition, as well as their local distribution inside the pellet. During irradiation noble gases and other fission products are formed in the crystal lattice of UO_2. The gases build in the lattice, form clusters, and appear as intra- and/or inter-granular bubbles of different sizes.

From the point of view of the UO_2 structure the irradiation associated with heat production is a strong degradation process caused by fast neutrons and by the noble gases and other fission products, at the same time it is a heat treatment too, healing the structural defects. The process causing degradation of structure and the heat treatment are competing processes.

In the FGR process one part of the released fission gas is thermally activated, while the other one is (practically) independent of the temperature. The ratio of the two release types depends on the history of the pellet material, as well as its actual states and other circumstances.

- At low burn-up the FGR takes place as single-atomic gas diffusion from the central part of the pellet, due to the high temperature enhancing the re-crystallisation and also to the slight degradation.
- At high burn-up the (athermal) FGR is controlled by the high burn up structure (HBS) i.e. the presence of a large amount of nano- and micro- gas-bubbles, and the formation of the sub-grain structure.
- At medium burn-up the FGR is particularly controlled by the radial variation of the different components of the micro structure (size of grains and bubbles, fission products) as well as by the radial distribution of the temperature.

The fission gas release of the medium and high burn-up pellets can be very large in the case of power ramps. Based on the evaluated measured data this statement can be easily explained by the combined effect of the local restructuring and the radial distribution of the temperature formed:

- The restructuring involves always FGR.
- The restructuring can occur as
  - a high temperature re-crystallisation
  - a thermal regeneration of the accumulated structural defects above a threshold temperature
  - an athermal recovery of the structure-degradation controlled by the fission energy and as
  - a low temperature re-crystallisation.
- The above mentioned temperature and burn-up dependent local processes together result in the formation of a radial maximum of the fission gas remained (generated-released) in the pellet material. The place of the maximum fission gas content along the pellet radius is about the half radius, and its extent depends on the burn-up.
- In the case of power ramps the fission gas remained in the pellet is activated by the elevated temperature which can lead to extra release.

This integrated picture helps in the better understanding and prediction of fuel behaviour under irradiation.

Remaining work

It is planned for the next year to specify and to create a simple additional FGR model based on experimental data, which properly simulates the extra gas release under power ramp conditions for fuel elements with middle and high burn-up.

Related publications

[1] Ágnes Griger, Anna Pintér Csordás: *Fission gas release*, EK-RAL-2012-729-01/01, 2012 October (in Hungarian)

EVALUATION OF HRP EXPERIMENTS: CENTRELINE TEMPERATURES

Ágnes Griger

Objective

The integral tests of the Halden Reactor Project (HRP) provide an essential basis for the validation of the thermo-mechanical models used in fuel performance codes. As the integral test data for medium and high burn-up fuel rods, especially for those applied in the VVER reactorS, are hardly available, these experiments have a major importance.

The verification of the FUROM fuel performance code against the Halden tests IFA-503.1-2 with medium burn-up VVER fuel was the objective of this work. The work was sponsored by MVM Paks NPP.

Methods

FUROM simulations have been carried out on the bases of the given irradiation histories and the calculated and measured values were compared.

Results

In the framework of the Halden Reactor Project (HRP) the tests of the IFA-503 rig were performed as the first irradiation experiments in the Halden Boiling Water Reactor (HBWR) to study and to compare the thermal and mechanical performance of medium burn up standard VVER and PWR UO_2 fuels. In the experiments the variation of the fuel temperature and the fission gas release as well as the fuel stack elongation were measured under power ramps.

The recent simulation of IFA-503.1-2 was an analysis of integral VVER fuel rod performance under slow ramp conditions. The computation was carried out at best-estimate initial and boundary conditions derived from the experimental database.

The analyses proved that both the centre line temperature and the fission gas release of the VVER fuel can be predicted by the FUROM simulations reasonably well. The calculated values of the centre line temperatures (Fig. 1) and the fission gas release (Fig. 2) have matched the experimental data with adequate accuracy. On the figures the compared parameters are shown as a function of the local heat rate.

The results of comparisons have proved again, that the FUROM code can be very well used for adequate simulation of the most important processes of the fuel behaviour under slow power ramp conditions.

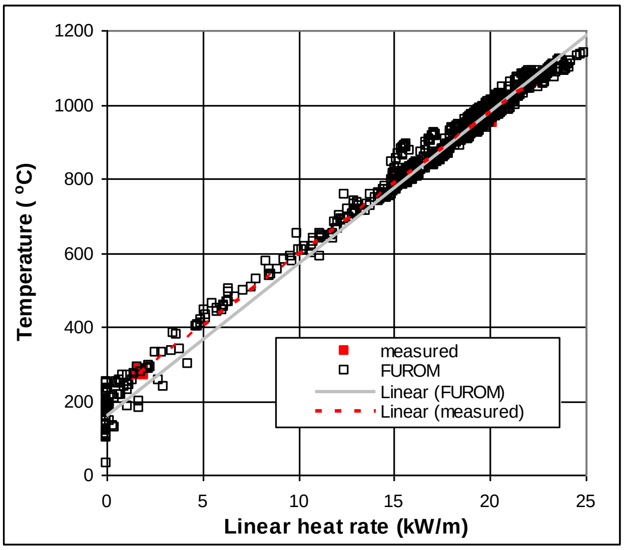


Figure 1: Calculated and measured values of centreline temperature in the ramp test

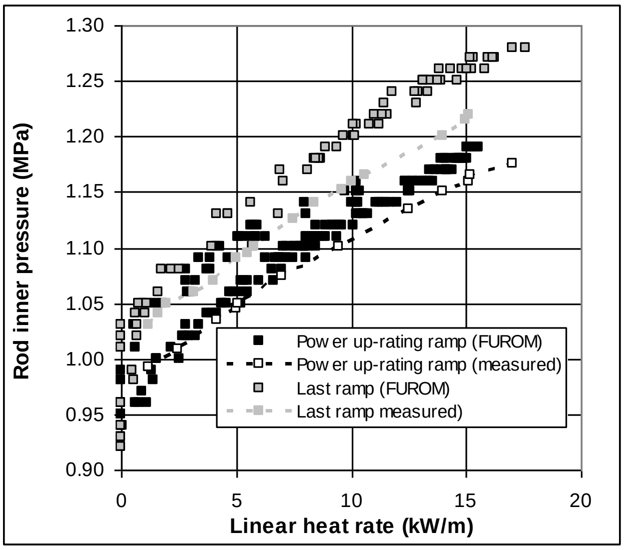


Figure 2: Calculated and measured values of rod pressure in the ramp test

Remaining work

The assessment of HRP integral tests will be continued. Results of selected experiments will be analysed by FUROM simulations for the validation of the fuel behaviour code.

Related publications

[1] Ágnes Griger: *HRP integral tests and FUROM simulations*, EK-RAL-2012-729-02/01, 2012 November (in Hungarian)

EXAMINATION OF THE PHYSICAL MODELS OF HERMET AND COMPARISON OF THEM WITH CONTAIN

Attila Nagy

Objective

The objective is to understand, test, modify (if needed) the physical models of the HERMET programme. The purpose is to make this programme validated.

Methods

Case studies were made that use one physical model at a time and so it is easier to compare the results. There were four models:

- air-water-steam calculation,
- wall heat conduction,
- mass transport,
- condensation.

First the air-water-steam model was examined. The starting point for our study was a 50000 m^3 volume filled with 1 bar, 50 °C air. Four mass transport time series into this volume were created. The first was just air with changing temperature, the other 3 were water injection defined by mass transport rate and enthalpy was costant. The results were compared to CONTAIN calculations that were made exactly for the same setup.

Results

Examining the results at a first case (air) it was found that the volume-work from the HERMET model was missing. After this model was built into the HERMET the results of the two codes were very close (Fig. 1). For the other three cases a new water-steam state calculation algorithm was created because of the working of the old function was not very clear and it has some iteration problems, it was easier to create a new one. The result with the new water-steam calculations are very close to the CONTAIN results (Fig. 2).

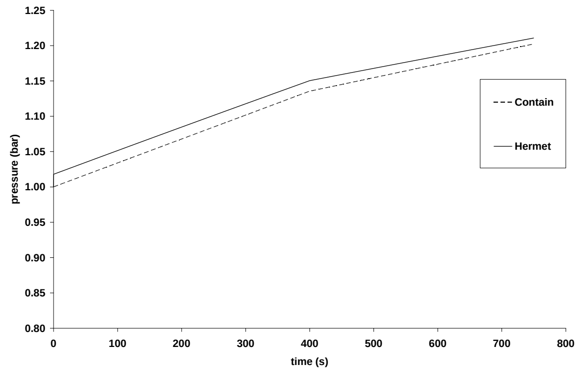


Figure 1: Comparison of HERMET/CONTAIN calculations for air alone

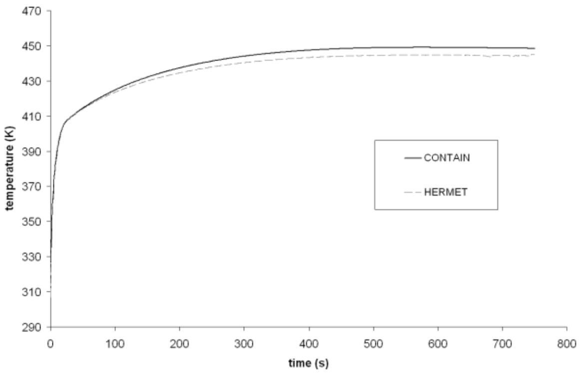


Figure 2: Comparison of HERMET/CONTAIN calculations (temperature of water, steam, air mixture)

A new wall heat conduction model was created for HERMET. The old one uses not-equidistant wall nodes because this method is less time consuming, which was an important issue at the time (1994) of creation of the HERMET but it makes the wall heat conduction model very complicated.

Remaining work

The comparison with the CONTAIN results will be continued, all the main physical models will be compared, modified (if needed) and validated.

Related publication

Attila Nagy, Zoltán Hózer, János Sebestyén Jánosy: *Modeling of VVER-440/213 hermetic rooms in training simulator*, Annals of Nuclear Energy (2013, Accepted)

FLUENT CODE VALIDATION USING ROCOM MIXING EXPERIMENTS

István Farkas, Tatiana Farkas

Objective

Recently, a 3D numerical computational fluid dynamic (CFD) model of the German ROCOM test facility, which is the 1:5 scale model of the KONVOI type PWR (Pressurized water reactors) vessel, was created. The numerical model was used for simulation of a main steam line break with the aim to validate calculation results by the experimental data. This accident scenario was studied in the PKL G3.1 test within the OECD PKL-2 project as it plays a key role in core nuclear behaviour via the coolant temperature and boron concentration distribution at core inlet. The primary loop data of the PKL test served to define the boundary conditions for the corresponding ROCOM test. The ROCOM test facility is instrumented to measure the detailed density distribution of coolant in the cold legs and in the downcomer by special grid sensors. The spatial and temporal resolution of obtained results is suitable for validation of CFD calculations. The ROCOM Test 1.2, where the mixing process following high pressure injection to two of the four cold legs was investigated, was simulated using the Fluent CFD code (FLUENT).

Methods

In order to simulate the test in FLUENT, the already existing ROCOM model had to be completed by the high pressure injection lines and by longer cold legs. The analysis was performed by running a time-dependent calculation.

Results

Analytical and test results were compared both for time averaged values and for distributions at different moments of the test. Mixing in the cold legs with high pressure injection was overestimated by the code that can be explained by imperfect knowledge of the boundary conditions. In the downcomer, however, the test displayed higher mixing: it is supposed that this was caused by the dense measurement grid that obviously was not modelled. The temperature distribution in the core inlet plane was fairly homogeneous and agreed in that respect with the measurement results: the maximum temperature difference was 2ºC. Figure 1 presents the CFD vessel model with visualized flow streamlines coming from ECC (Emergency Core Cooling) injection pipes.

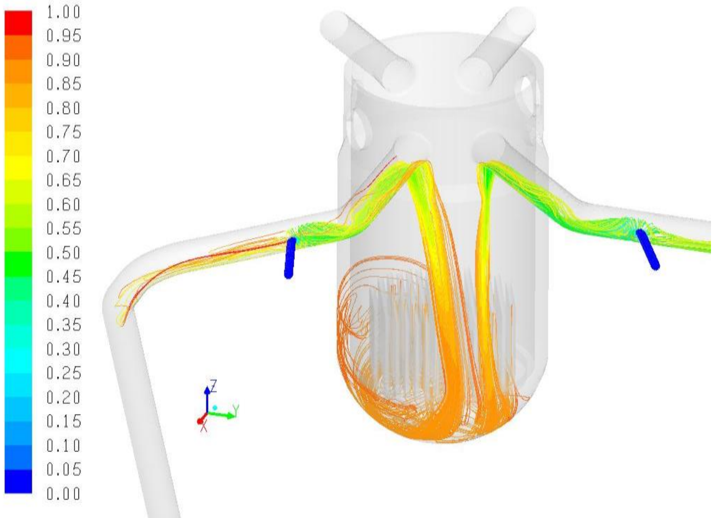


Figure 1: Calculated flow streamlines coloured by temperature

Remaining work

Although results at core inlet are promising, it'd be important to find the root cause of enhanced mixing in the cold legs, since this phenomenon plays a key role in evaluation of PTS (Pressurized Thermal Shock) issues. It is proposed to continue with the validation effort based on available experimental data. More detailed analysis of the cold leg/upper downcomer region could be performed, comparing different numerical methods (application e.g. of Large Eddy Simulation or of higher order numerical schemes).

Related publications

[1] T. Farkas and I. Farkas: *Validation of ANSYS FLUENT by the ROCOM test 1.2 performed within the OECD-PKL project* (in Hungarian), MTA EK report OAH/NBI-ABA-19/12-M (2012)

[2] T. Farkas and I. Farkas: *Fluent analysis of ROCOM 1.1 and 1.2 mixing experiments*, Joint PKL2-ROSA2 Workshop, Paris, France, 15-19 October 2012

HIGH TEMPERATURE OXIDATION OF HYDROGENATED E110G CLADDING

Erzsébet Perez Feró, Tamás Novotny, Márta Horváth

Objective

The purpose of the work was to determine the effect of the fuel cladding's hydrogen uptake under normal operating conditions on the behaviour of the cladding under LOCA (loss of coolant accident) conditions. In order to achieve this target, high temperature oxidation experiments were carried out on E110G (produced by new technology) and E110 (produced by electrolytic method) alloys hydrogenated in 2011.

Methods

High temperature oxidation of the specimens was performed in steam under isothermal conditions. Ring compression test of the oxidized samples was carried out by Instron 1195 universal test machine. The load-displacement curves were recorded and evaluated.

The main steps of the experiment were the following:

- 16 high temperature oxidation tests at 1000 °C and 1200 °C on E110G samples with 300 ppm and 600 ppm hydrogen content,
- 8 high temperature oxidation tests, under the same conditions as above, on E110 cladding (currently used at Paks Nuclear Power Plant),
- ring compression tests of all 24 samples and microstructural analysis of some selected samples.

Results

The new results were compared to the results of previous samples which did not contain hydrogen. No significant difference was observed in the oxidation kinetics of the same claddings with different hydrogen content. It was confirmed by the oxide layer thicknesses measured on metallographic images.

The original claddings showed more ductile behaviour than the samples with hydrogen content. The higher hydrogen content resulted in a more brittle behaviour (Fig. 1).

The experiments showed that hydrogen from the normal burnup process would have a negative effect on the mechanical properties of the fuel cladding in case of LOCA event. It is important to note that the fuel cladding in the reactor contains much lower amounts of hydrogen (below 100 ppm) than the hydrogen in our samples.

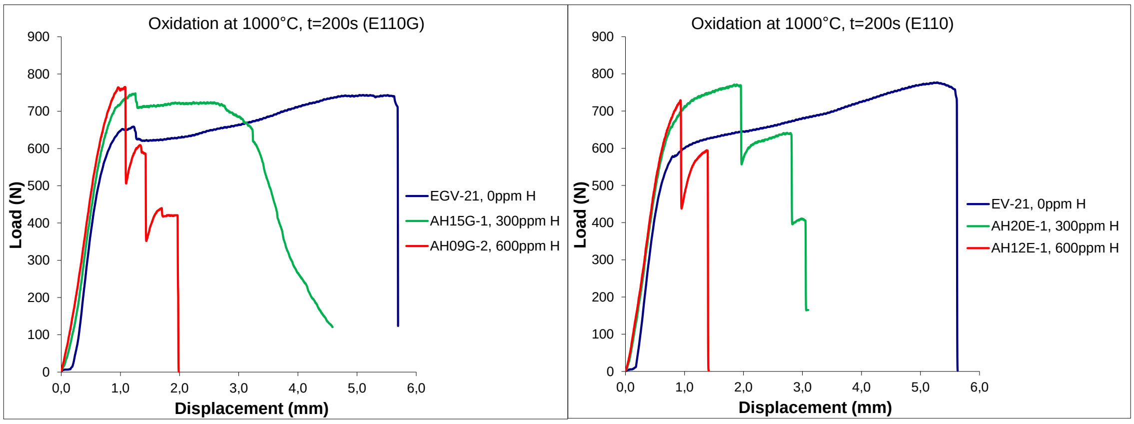


Figure 1: Load – displacement curves of oxidized E110G and E110 samples with different hydrogen content

Remaining work

The work has been completed.

Related publications

[1] E. Perez Feró, T. Novotny and M. Horváth: *High temperature oxidation of E110G cladding hydrogenated at low temperature*, EK-FRL-2012-255-01/01 (in Hungarian)

[2] T. Novotny, E. Perez Feró and M. Horváth: *High temperature oxidation of hydrogenated E110G cladding*, 18th QUENCH Workshop, Karlsruhe, 20 - 22 November 2012

LONGLIFE (NPP LIFE EXTENSION)

Ferenc Gillemot, Lászlóné Horváth, Attila Kovács, István Nagy

Objective

The purpose of the project is to study the microstructural effects on radiation embrittlement which occurs during long operational time (beyond 60 years), and to prepare guides and recommendations for ageing management, monitoring, and lifetime evaluation.

Methods

LONGLIFE is an EURATOM FP7 project. The consortium includes 18 EU institutes, the leading institute is the HZDR (Germany). Hungarian Academy of Sciences Centre for Energy Research is the leader of work-package 2, and prepared and provided the AEK-1 samples, machined from highly irradiated 15H2MFA type steel.

Collecting and evaluation of existing information has served as basis, and 21 different irradiated steel and weldment have been tested. The testing methods: mechanical testing, micro-structural testing (metallography, TEM (transition electron microscope), SANS (small angle neutron scattering), APT (atom-probe testing).

Results

On the bases of the micro-structural studies performed together with HZDR, CIEMAT and CNRS the following results were obtained:

- no saturation was found in the mechanical properties, SANS and APT results
- Cu precipitations occurred first, and Mn, Si, Ni, joined in clusters later. It is in good agreement in SANS, APT and mechanical results. (It may verify the existence of late blooming, but had no effect on mechanical properties).
- V carbides are typical in the as received steel (see Figure 1).

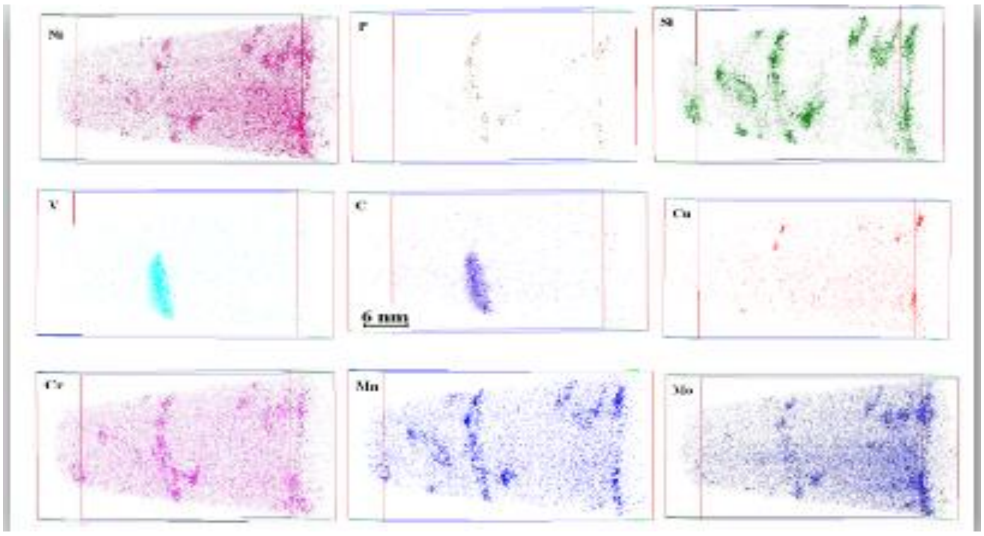


Figure 1: Atom-probe field microscope results obtained on highly irradiated AEK-1 samples.

Conclusions

- The surveillance results include thermal ageing if there are any effects.
- Long term operation can be safely managed from the viewpoint of thermal ageing using the existing surveillance results especially in the case of steels with low copper content.
- In operating conditions of the European reactor pressure vessels no significant changes caused by thermal ageing alone can be found.

Remaining work

The project will be finished in January 2014. Until then further microstuctural study has to be performed, common evaluation of the obtained results has to be made. A workshop to disseminate the results is planned, and several guides on long term operation of reactor pressure vessels have to be elaborated. Also has to finish some ongoing study on irradiation effect of RPV materials and the comparison of the „Master Curve" method to determine fracture toughness with the Russian Uniform curve method.

MODERN TOOLS FOR NUCLEAR POWER PLANT SIMULATION

József Páles, Gábor Házi, János S. Jánosy, János Végh

Objective

Full scope simulators play a key role in the training of operating personnel and thus largely contribute to the safe operation of nuclear power plants. These tools have significantly developed during the last two decades both in respect to hardware and software technology. Beside these improvements, the functionality of modern training simulators have to also been extended to support several new application areas, such as simulation assisted engineering, human-machine interface development, operating procedure validation and validation of plant equipment modifications prior to the real application.

One of the main R&D activities at the Reactor Monitoring and Simulator Department is to continuously support the development of the full scope simulator of Paks NPP. To efficiently fulfill this task it is important to preserve our competence in the field and to follow the latest improvements in power plant simulation technology. This acquired experience can also be essential in a possible simulator upgrading project at Paks NPP.

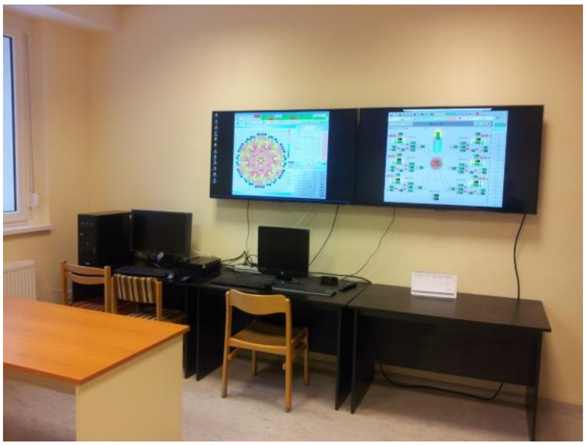


Figure 1: Simulator room

Methods

- We have studied the latest software technologies and solutions used in modern nuclear power plant simulators and compared them with the techniques used in the current training simulator of Paks NPP.

- A virtual control room communication subsystem has been developed which can be used to connect an arbitrary virtual control room application to the full scope simulator. The new communication system uses the same communication mechanism as the original VME (VERSAmodule Eurocard) based interface and provides a set of communication subroutines for the control room application.

Results

The Department has a replica simulator configuration of the Paks NPP full scope simulator. This configuration has been extended this year with the plant computer system and a new simulator room was built to support the use of the simulator (Fig. 1). The new configuration is almost complete but we need to supplement it with a virtual control room interface to fully exploit the system capabilities.

A study has been conducted to survey the latest developments in power plant simulation software technology and the results and experiences were summarized in a report [1].

A virtual control room communication system has been developed to the replica configuration of the full scope simulator. Using the new communication system, a virtual control room application or other types of graphical user interfaces can be connected to the simulator.

In the last few years a lot of modernization has been made on the physical models of the full scope simulator and the overall model documentation (the so-called "red book") has not followed these changes. A work has been started to refresh this documentation and it is still in progress.

Remaining work

In the next year we are going to develop a virtual control room application and connect it to the full scope simulator using the new communication subsystem. To simulate the real control room we build up a 3-dimensional interactive model of the room and develop advanced methods to navigate within the model and interact with the actuators.

Related publication

[1] J. Páles, G. Házi: *The architecture of nuclear power plant simulators*, Report, (2012), in Hungarian

NUKENERG PROJECT: SUPERCRITICAL WATER REACTOR CORE DESIGN - FINE MESH ANALYSIS OF EQUILIBRIUM CYCLES

Csaba Maráczy, Emese Temesvári, György Hegyi, Gábor Hordósy, Attila Molnár

Objective

The European version of Supercritical Water Reactors (SCWR), the High Performance Light Water Reactor (HPLWR) operates in the thermodynamically supercritical region of water. The basic objective of the work is to design the core of this selected reactor using an existing square fuel assembly proposal. On the basis of core design studies, the reevaluation of the equilibrium cycle was planned applying the DIF3D fine mesh code for detailed pinwise calculations.

Methods

- Monte Carlo neutron transport calculations
- 3-D coupled neutronic-thermohydraulic nodal and fine mesh calculations

Results

The interface of DIF3D with the supercritical coupled KARATE nodal code was elaborated and the code system was applied for the equilibrium cycle. With the thermohydraulic data and axial bucklings of the KARATE code 2 dimensional full core fine mesh calculations were applied to derive power peakings inside the assemblies. Conservative fuel rod level calculations were applied taking into account the uncertainty of power distributions and the non perfect mixing in mixing chambers. For the calculation of the enthalpy rise peaking factor within the assembly, the Heinecke correlation developed in the HPLWR project was used. The best estimate fuel rod linear power distribution in the most loaded irradiation time and axial level can be seen in Figure 1.

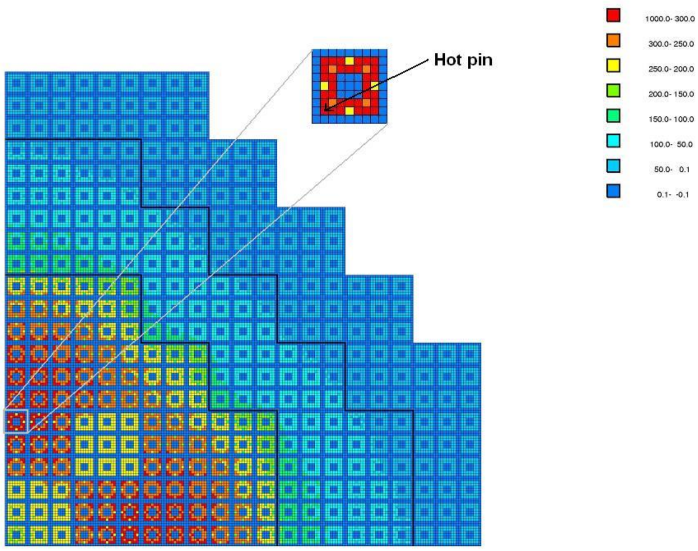


Figure 1: Fuel rod linear power distribution on the 105th day of the equilibrium cycle in the most loaded 8th level [W/cm]

The maximum of linear power multiplied by the engineering factors was achieved at 105 effective day of the equilibrium cycle. The 390 W/cm limit can just be kept. The conservative maximum of the centerline fuel temperature shows similar behaviour, it is below the melting point of uranium-dioxide. The maximum of the conservative clad surface temperature always exceeds the goal temperature of 630 °C during the equilibrium cycle. The maximum can always be found in an assembly which is next to the evaporator. As in the evaporator region the maximum linear power is close to the limit, the further direction of optimization is the partial rebalance of power from superheater 1 to superheater 2 where none of the limits are jeopardized. An obstacle of the optimization by shuffle scheme is the 3x3 cluster structure of the assemblies and the cluster-wise orifices. The possibility of assembly wise shuffling and orifices would ease the situation.

Remaining work

- The project finished in 2012.

Related publications

[1] E. Temesvári, Gy. Hegyi, G. Hordósy, Cs. Maráczy: *HPLWR Fine Mesh Core Analysis of Equilibrium Cycle*(in Hungarian), 11th Symposium on Nuclear Technology, Hungarian Nuclear Energy Society, Paks, 29-30 Nov. 2012

[2] T. Schulenberg, J. Starflinger (editors): *High Performance Light Water Reactor, Design and Analyses*, KIT Scientific Publishing 2012, ISBN 978-3-86644-817-9

PRELIMINARY SPECIFICATION OF THE STATISTICAL VERSION OF THE KARATE CODE SYSTEM

András Keresztúri, István Panka, Csaba Maráczy, Gábor Hordósy

Objective

The safe and at the same time economically competitive utilization of the present and future nuclear installations can only be based on well established reserves, "margins", responsible for the correctly evaluated uncertainties, which must be applied both for the normal operation and the accidental conditions. That is the reason of the increasing demand from nuclear research, industry and regulation for best estimate predictions provided with their confidence bounds.

According to the core design calculations, the foreseen 15 cycle lengths at Paks NPP will result in higher burnup values of the assemblies and the fuel pins, consequently smaller but well validated burnup margins could lead to significant economic advantages. However, the uncertainty of the burnup calculations are influenced by the feedback effects between the power and the burnup distributions, moreover, the impact of the reloading of the fuel assemblies before each cycle must also be regarded when the correlations of the power distributions belonging to different time intervals are accounted. These were the reasons of the decision to elaborate the "statistical version" of the KARATE code system which will also be useful for the uncertainty evaluation of other, directly not measured parameters.

Method

Study writing.

Results

KARATE involves all the libraries and computer programmes which are needed to perform fuel cycle calculations and fuel cycle design. The calculation is grouped into 3 levels. The levels involved in KARATE include cell level to provide a cell library, assembly level to provide homogenized assembly library and to calculate pin powers in selected assemblies, global level to determine criticality parameters and power distributions. A level is connected to the higher one through parameterized data libraries, these libraries provide a part of the input data for the higher level. A level is connected to the lower one also, usually boundary condition is provided for a "Lupe"-like calculation. Because the libraries play essential role providing the connections between the levels, they – together with the input and output of each calculation step - must be multiplied according to the statistical treatment in the frame of the Monte Carlo sampling of cross sections, technical data and modelling errors. The details of handling the large amount of data files, the applied file name conventions and the calculation routes controlled by the Monte Carlo sampling of selected input data are outlined in the specification document [1].

Remaining work

There is no remaining work scheduled for 2012.

Related publication

[1] G. Hordósy, Cs. Maráczy, A. Keresztúri, L. Korpás , I. Panka: *Decreasing of the engineering safety factor of the burnup*, MTA-EK RAL-2012-725/01/M0

PREPARATION OF A CONCEPTUAL PLAN FOR THE EXTENSION OF THE PAKS NPP FULL-SCOPE SIMULATOR WITH SEVERE ACCIDENT MODELLING CAPABILITIES

NUBIKI Ltd.[1], Gábor Házi, Zoltán Hózer, J. Sebestyén Jánosy,József Páles, János Végh

1 – NUBIKI Nuclear Safety Research Institute Ltd., H-1121 Budapest, Konkoly-Thege Miklós út 29-33.

Objective

In order to provide an appropriate training tool for the personnel handling potential severe accidents, in 2012 the Paks NPP decided that it was going to initiate the extension of its full-scope training simulator. The extension is motivated by the planned safety enhancement measures resulting from the Paks NPP Post-Fukushima Stress Test report and the following Action Plan, as well as by new training needs (e.g. training of the emergency operating procedures corresponding to shut-down reactor states). In the first phase MTA EK – with NUBIKI Ltd. acting as severe accident analysis expert subcontractor – was contracted by the plant to prepare a Conceptual Plan for the severe accident simulation extension. The basic aim of the Conceptual Plan was formulated in the technical specification appendix of the contract as follows:

- review and evaluation of international experience with the application of severe accident simulators for training;
- assessment of the modelling limits of the present Paks simulator and compiling proposals to improve the models;
- compilation of a proposal to realize the severe accident extension of the simulator;
- evaluation of potential partners able to contribute to the project, including international simulator vendors.

Methods

The work was split into well-defined and distinct parts between the two organizations. MTA EK was responsible for the following topics: assessment of the modelling limitations of the present simulator; review and evaluation of international trends in severe accident modelling tools applicable for NPP personnel training; assessment of the possibility to model the measurements of the plant's severe accident monitoring system; simulation of electric power supplies to measurement transducers, as well as to control room instrumentation during partial or total blackout situations; simulation of the open reactor and the spent fuel pool; analysis of miscellaneous topics (e.g. simulation architecture, hardware configuration and software tools, coupling between the present simulator and its future extension). NUBIKI Ltd. was mainly dealing with hydrogen production models, severe accident calculations for the open reactor, the spent fuel pool and the containment, as well as with the simulation of the external cooling of the reactor pressure vessel. When NUBIKI Ltd. subchapters were compiled and passed the internal review procedure, they were sent to MTA EK for integration and consistency checking. Meetings were also held with plant technology experts and with the personnel of the present Paks full-scope simulator.

Results

The first – preliminary – version of the Conceptual Plan was ready by mid-December, 2012, then it was delivered to the plant for a detailed review. During the review process simulation experts asked for some modifications and additions, but no major text revision or significant reformulation of our proposals was requested. The most important findings and proposals described in the Conceptual Plan were as follows:

- the extension of the simulator can be realized and it has meaningful training functions;
- the simulation of the severe accident monitoring system can be realized and it has meaningful training functions;
- correct modelling of the power supplies to the transducers and control room instrumentation can be accomplished;
- the inclusion of beyond design basis accidents and reactor refuelling states into the simulation scope is possible;
- the present simulator containment model must be enhanced considerably;
- it is proposed to simulate the behaviour of the reactor hall atmosphere, as well as to include activity transport and radiation dose calculation models into the extended system;
- the accomplishment of the real-time severe accident simulation extension by using the MAAP5 code is proposed.

Remaining work

The final version of the Conceptual Plan was issued in February, 2013. It is expected that the Conceptual Plan will be internally discussed in the plant, with the active participation of the interested NPP departments. Based on the result of this discussion process, the NPP management is expected to make a decision on the further work before the end of 2013.

Related publication

[1] *Extension Possibilities of the Paks NPP Full-Scope Simulator to Model Severe Accident States, Conceptual Plan*, MTA EK and NUBIKI Ltd., EK-RMSzL-2012-741-00/01, December 2012 (in Hungarian)

PREPARATION OF A CONCEPTUAL PLAN FOR THE MODERNIZATION OF THE PAKS NPP PROCESS COMPUTER

Scadanet Ltd.[1]*, Csaba Horváth, József Páles, János Végh*

1 – Scadanet Computer Engineering Ltd., H-1112 Budapest, Cirmos u. 8.

Objective

The present process computer system (abbreviated as PCS) of Paks NPP was put into operation between 1998 and 2003. In the past 10-15 years this system served the safe operation of the power plant units and the simulator training of the personnel satisfactorily, but during the 15 years passed the PCS hardware components and its Windows NT operating system became obsolete. The obsolete hardware posed an ever increasing maintenance problem and the plant had to make a decision what to do to keep the system running until the end of the extended service time of the Paks units (Unit 1 received a 20 years service time extension just recently, so it can be utilized for power production until 2032). In early 2012 the plant decided to prepare a Conceptual Plan for the modernization of the process computer system, and after the usual bidding procedure Scadanet Ltd. was selected as main contractor. In addition, Scadanet Ltd. contracted with MTA EK to prepare certain parts of the Conceptual Plan (it has to be noted that the experts of both organizations were involved in the design and implementation of the present PCS, therefore they are very familiar with the present PCS architecture and software). The basic aim of the Conceptual Plan was formulated in the bid invitation document as follows:

- assessment of the merits and problems of the present PCS (i.e. collection of the experience and opinion of operators and other regular users, as well as PCS operation and maintenance personnel),
- review and assessment of functions to be implemented in the modernized process computer,
- determination of the engineering (hardware and software) solutions to be applied for the modernization,
- identification of tasks to complete the modernization and suggestions for their schedule,
- provision of a well-grounded cost estimation for the whole modernization project.

Methods

The work was split into well-defined and distinct parts between the two organizations. MTA EK was responsible for the following topics: assessment of the present PCS from the users' perspective; review and evaluation of international experience related to recent PCS modernization projects; licensing issues (legal background, requirements of the Hungarian Safety Authority, international standards, ”data diode”and other cybersecurity issues); calculation modules (Critical Safety Function Monitoring, monitoring of operation limit violations, evaluation of alarm annunciator states etc.); PCS configuration serving the full-scope training simulator, PCS test configuration. When MTA EK subchapters were compiled and passed the internal review procedure, they were sent to Scadanet for integration and consistency checks. Several meetings were held with the plant experts and the users'feedback was collected with the help of the NPP by using special questionnaires.

Results

The full Conceptual Plan and its appendices were ready by the end of November 2012, then they were delivered to the plant for a detailed review. During the review process plant experts formulated several new proposals, recommended further PCS functions and corrected certain parts of the preliminary plan. The final version of the plan was compiled by taking into account these proposals and it was delivered to the plant in February 2013. The most important proposals formulated in the Conceptual Plan were as follows:

- general application of the ”virtual machine”concept to facilitate hardware independence of the new system;
- compulsory use of “data diodes”and “mirror servers”to separate internal and external computer networks safely;
- provision of an identical human-machine interface for the operative and external users;
- provision of a central (plant-level) data archive and a central storage facility to accommodate stored archives;
- continuation using of the MS Windows operating system and the iFIX Scada application software in the new PCS.

Remaining work

It is expected that after the finalization of the Conceptual Plan the detailed design of the modernized process computer system can be started in 2013. The actual modernization project is planned to take place during 2014 and 2015.

Related publication

[1] Conceptual Plan for the Modernization of the Paks NPP Process Computer System, Scadanet Ltd. and MTA EK , 000000J00176 SCA, November 2012 (in Hungarian)

REACTOR NOISE DIAGNOSTICS MEASUREMENTS AT PAKS NPP

Sándor Kiss, Tamás Czibók, Zoltán Dezső, Károly Krinizs, József Láz, Sándor Lipcsei

Objective

Regular reactor noise diagnostics measurements were continued at Paks NPP in 2012. Measurements were carried out by means of the PAZAR system. PAZAR systems at each unit are fed with the analogous signal sets of the VERONA systems. Basic part of this activity is monitoring of the coolant velocity along the fuel bundles equipped with SPND chains, and monitoring of vibration of the core internals. MTC values were also calculated from long term (24/72 hour) measurements of in-core and primary loop thermocouples [1].

Methods

In the given year regular measurements were performed every month. Long term (1 to 5 days) measurements were also carried out, usually two times a month. All measurements were taken to MTA EK for further processing. The evaluation of recorded data was performed off-line by means of the evaluation software PAZAR-K.

Results

According to the evaluated measurements, the average core coolant velocity was quite stable during the year, only usual small fluctuations could be observed at all four reactor units. A typical coolant velocity trend is shown in Fig. 1.

Possible vibrations of core internals were also looked for, but no such anomalies were observed in 2012. Detailed reports were compiled for the plant from each regular measurement.

During 2012 a new coupling-scheme of the loop thermocouple signals was introduced by Paks NPP (The scheme is identical at all four reactor units). This new scheme provided a more favourable temperature signal set also for diagnostics purposes and we made use of this opportunity to enhance the quality of our analysis.

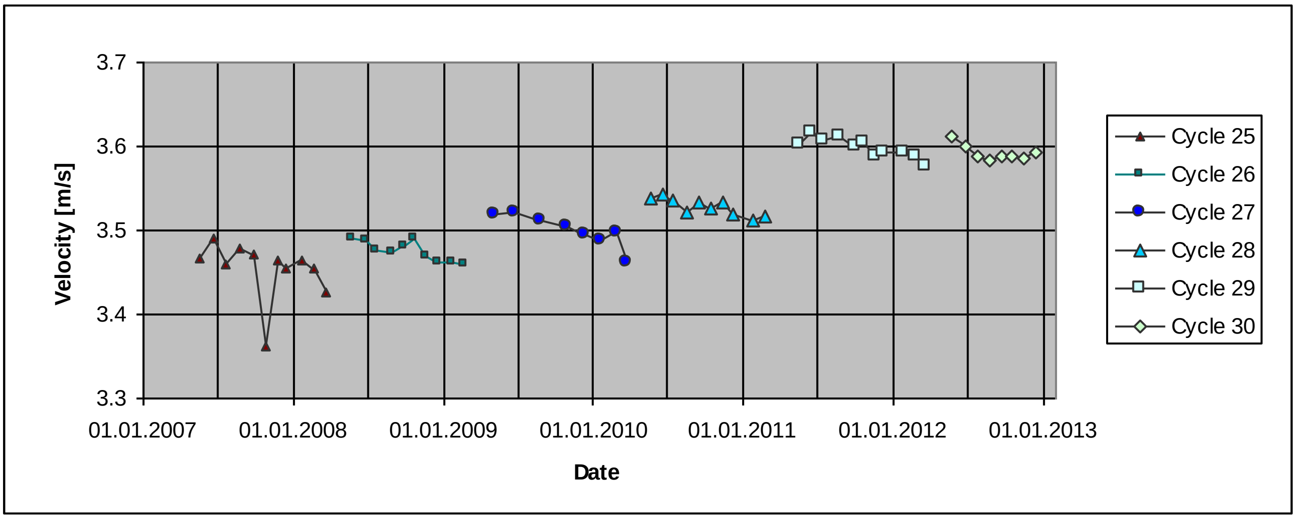


Figure 1: Six-year long trend of average coolant velocities of Unit 1 at Paks NPP

Remaining work

Regular noise diagnostics measurements will be continued in 2013.

Related publication

[1] S. Kiss, S. Lipcsei, J. Végh: *Reactor Noise Diagnostics Activities at the Paks NPP*, 21st International Conference on Nuclear Energy for New Europe, 2012, Ljubljana

ROUND ROBIN ON ZIRCONIUM OXIDATION

Erzsébet Perez-Feró, Tamás Novotny, Márta Horváth, Zoltán Hózer

Objective

The main objective of the experimental work was to carry out parallel high temperature tests in several laboratories with the same Zr cladding alloy and produce data to support the development of a standard procedure.

Methods

Round robin on zirconium oxidation programme has been started under the co-ordination of EPRI and with the participation of French, Korean, US and Hungarian institutions in 2011. All participants received the Zircaloy-4 cladding tubes from the same factory. The main technical conditions and the test matrix were specified at the beginning of the programme. The AEKI, i.e. the MTA EK after 2012, carried out the following experiments in the framework of zirconium oxidation round robin programme:

- pre-oxidation of 9 samples up to 10 and 20 µm oxide scale at 800 °C,
- high temperature oxidation of 12 samples at 1200 °C according to the strict requirements of the programme,
- ring compression tests of 21 oxidised samples at 135 °C (3 rings were cut from each oxidised tube sample),
- investigation of breakaway oxidation with on-line hydrogen measurement at 800 and 1000 °C,
- metallography of 10 selected samples.

Results

The main results of the tests could be summarised as follows:

- the oxidation kinetics of Zircaloy-4 alloys could be well described by Cathcart-Pawell correlation for both as-received and hydrogen charged samples,
- the embrittlement of hydrogen charged samples took place earlier than that of as-received samples: the ductile-to-brittle transition of as-received samples was observed between 16–18% ECR, while the samples with 600 ppm hydrogen content reached this transition at 3–4%,
- breakaway oxidation did not take place in the performed tests even for oxidation times longer than two hours.

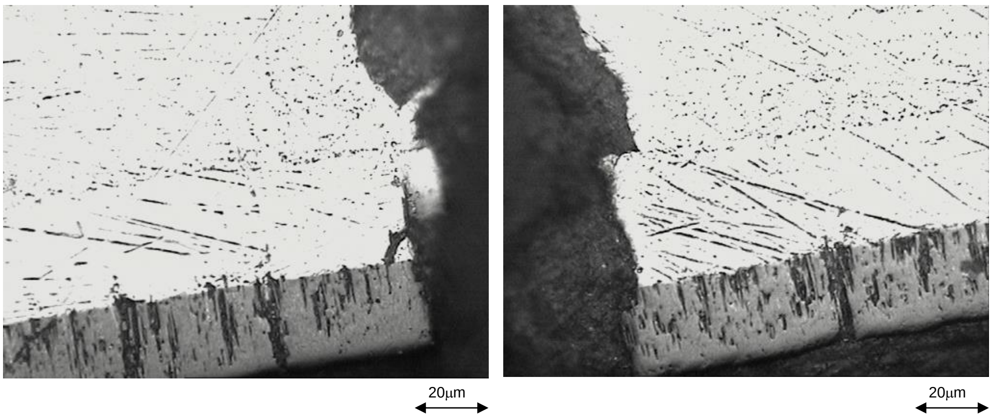


Figure 1: View of fracture surfaces after ring compression test

Remaining work

The measured data were sent to EPRI and the evaluation of the results of round robin programme has been started. Significant differences could be identified between similar tests performed in different laboratories. For this reason some additional testing was agreed. The finalization of the common procedure could be done after the execution of these specific tests.

Related publications

[1] T. Novotny, E. Perez-Feró, Z. Hózer, M. Horváth: *The Ductility of Zircaloy-4 Alloy and Breakaway of Oxide Scale,* EK-FRL-2012-263-01/01 (in Hungarian)

RUTHENIUM SEPARATE EFFECT TESTS IN THE SARNET2 PROJECT

Nóra Vér, Imre Nagy, Zoltán Hózer

Objective

In the framework of the SARNET2 project, the main results of RUSET (Ruthenium Separate Effect Test) series were summarized in order to draw common conclusion with experiments executed in other laboratories on ruthenium oxidation and transport.

Methods

The database of earlier RUSET tests covering sixty experiments was analyzed.

Results

The results showed that Ru evaporates in form of RuO_3 and RuO_4; both reached saturation concentration in the high temperature area at the given experimental conditions. In the decreasing temperature section of the experimental device between about 1100 and 600 °C the RuO_3 and most of the RuO_4 (≈95%) decomposed on the quartz surface and formed RuO2 crystals; while the partial pressure of RuO_4 in the escaping air was in the range of 10^{-6} bar, far above the value that would be expected from equilibrium. The decomposition of RuO_3 and RuO_4 to RuO_2 is a heterogeneous phase chemical reaction catalyzed efficiently by the quartz surface, its inhomogeneity and the formed RuO_2 particles. On the other hand, under the given test conditions, the surface catalyzed decomposition process of RuO_4 to RuO_2 was not fast enough to follow entirely the equilibrium with the temperature. In the later phase of tests Ru releases originated from the deposited RuO_2 by re-evaporation resulting in about 10^{-6} bar partial pressure in the outlet gas as well.

The results of the RUSET tests with different tube materials in the decreasing temperature section (1100-100 °C) demonstrated that the heterogeneous phase decomposition of RuO_3 and RuO_4 to RuO_2 was catalyzed more efficiently by the quartz surface than by the SS (stainless steel) or alumina surfaces. On the other hand, the extent of re-evaporation of RuO_2 from the SS surface was higher than from the quartz or alumina surfaces.

The presence of MoO_3 layers decreased the RuOx precipitation extent on all investigated surfaces. Based on the results of experiments performed at quartz surfaces, molybdenum oxides which are simultaneously present in the vapour phase decrease the surface catalyzed decomposition of ruthenium oxides efficiently and result in nearly one order of magnitude greater RuO_4 partial pressures in the ambient temperature escaping air compared to pure Ru oxidation.

The trapping effect of caesium deposits on ruthenium in the temperature gradient zone was proved in the case of SS surface.

High temperature reaction with caesium changed the form of the released ruthenium and caused a time delay in appearance of its maximum concentration in the ambient temperature escaping gas. If Cs was present in the charge, ruthenium escaped from the high temperature region partly in form of caesium compounds and deposited at relative low temperatures (on quartz surface between 900 and 400 °C) compared to the pure RuO_2 precipitations.

When zirconium (E110) cladding material was placed in the temperature gradient zone, no Ru transmittance occurred until the high temperature end of the zirconium tube was completely oxidized. After the intense oxidation of E110, Ru release occurred only in the presence of other fission product species in the time frame of the experiments (360 min).

Pre-oxidation of SS surfaces in steam had no significant effect on the ruthenium passage under the given test conditions. In the case of pure Ru oxidation, pre-oxidation of SS in steam slightly increased the decomposition of RuOx to RuO2 compared to the effect of pure metal surface. If other fission products were present in the high temperature area, the presence of oxide scale in the decreasing temperature region slightly enhanced the Ru release. As regards E110, pre-oxidation in steam had an effect only when it was performed outside of the breakaway regime (at 1100 °C). Otherwise the formed oxide scale (at 800 °C) was not protective against the intense air oxidation and the pre-oxidation had no effect on the Ru release.

Measurements demonstrated the importance of surface quality in the decreasing temperature zone on the heterogeneous phase decomposition of ruthenium oxides to RuO2. In this way, oxidized stainless steel surfaces, molybdenum and caesium deposits in the reactor coolant system can play an important role in the ruthenium source term in a hypothetical air ingress accident.

Remaining work

The planned activities have been completed.

Related publications

[1] N. Vér, L. Matus, A. Pintér, J. Osán, Z. Hózer, *Effects of different surfaces on the transport and deposition of ruthenium oxides in high temperature air*, J. Nucl. Mater. **420** (2012) 297-306.

[2] N. Vér, L. Matus, A. Pintér, J. Osán, Z. Hózer, *Effects of different surfaces on the transport and deposition of ruthenium oxides in high temperature air*, EK-FRL-2012-401-01/01 (2012)

SIMULATION OF LEAKING FUEL IN THE LEAFE FACILITY

Barbara Somfai, Zoltán Hózer, Gergely Kracz, Imre Nagy, András Vimi

Objective

Fuel failure during normal reactor operation is a very rare event today. The identified leaking fuel assembly normally is removed from the core and stored in the spent fuel storage pool. For the period of storage the inhermetic fuel leaks to the pool. The amount of released activity depends on the size and position of the damage, on the burnup and linear heat rate of the fuel and also on the time spent in the reactor between failure and removal.

In order to simulate the leakage process under well-defined conditions, a new experimental facility has been built with inactive components. The Leaking Fuel Experiment (LEAFE) test facility is capable to model the activity release from the leaking fuel rods under steady state and transient conditions in the spent fuel storage pool.

Methods

First a small-scale loop was built to gain experience on the operation of the equipment, then the final rig was installed.

The experimental rig is a full scale mock-up for one single fuel pin. The surrounding cooling system simulates the spent fuel storage pool. The geometry of the rod is similar to the VVER-440 rod, but its cladding is made of stainless steel. The cladding material has no influence on the results of the tests.

The inner diameter of the cladding is 7.85 mm and the outer diameter is 9.15 mm. The length of the cladding is 2554.5 mm. The pellets are made of Al_2O_3, this ceramic behaves similarly to UO_2. The diameter of the pellets is 7.52 mm and the diameter of the central hole is 3 mm. Decay heat was simulated by a heating wire installed in the central hole of the pellets.

The temperature was measured at three different positions. One K-type thermocouple was installed inside the fuel rod, one Pt-100 temperature sensor was placed at the top of the loop. The conductivity measuring instrument has also a temperature output which is in the middle along the cooling system.

The cooling flow was measured with a differential pressure transmitter; the flow was around 3.5 dm^3/h and its volume was 2.15 and 2.5 dm^3 depending on the experiment. The pressure was measured in the loop with pressure transducer.

At the beginning of the test, the fuel rod was filled up with KCl-containing water and the specified gas volume was established at the top of the fuel. The conductivity of the coolant was measured on-line and the concentration change could be recorded. It was important to do the measurement without taking samples from the loop because it would have influenced the results. We decided for conductivity measurement because it is sensitive and shows any small concentration change.

The opening of the leak was carried out with a manual mechanical device after the initial conditions were reached both inside of the fuel rod and in the cooling system.

Results

A test facility was installed for simulating leaking fuel in the spent fuel storage pool. Both steady state and transient sequences could be simulated. 19 tests were done with different hole sizes and positions, power and pressure histories.

The experiments indicated that the leakage rate for steady state conditions depends not only on the size of the hole, but also on the position of the hole and on the power of the fuel rod. Specific release rates were determined for the given VVER-440 type fuel rod.

The steady state tests showed that the failure is small enough, the release can be therefore compared to the concentration-balancing, so the release is constant. In the case of larger defects the release rate increases with the size of the failure at the beginning, but there are no major differences in the release after some time because the concentration-balancing is very slow in the rod.

The transient tests showed that the release from the rod correlates well with the expansion of the gas volume inside the fuel rod and does not depend on the hole size.

The produced data can be used for predicting the activity release from leaking fuel under storage conditions and for the interpretation of fuel examination procedures.

Remaining work

For a detailed numerical model and validation more data and parallel measurements are needed. We repeat the tests and some additional ones will be carried out at different linear heat rates (between 5-20 kW/m).

Related publications

[1] B. Somfai, Z. Hózer, G. Kracz, I. Nagy, A. Vimi: *Simulation of leaking fuel in the LEAFE facility*, AEKI-FRL-2012-732-01/01 (2012)

[2] B. Somfai, Z. Hózer, G. Kracz, I. Nagy, A. Vimi: *Simulation of leaking fuel in the LEAFE facility*, TopFuel – Reactor Fuel Performance Transactions 2012, 2-6 September 2012, Manchester, UK

SIMULATION OF NSRR RIA EXPERIMENTS WITH THE FRAPTRAN CODE

István Panka, Attila Molnár, Zoltán Hózer

Objective

The main objective of the performed calculations was the testing of FRAPTRAN fuel behaviour code against reactivity initiated accident (RIA) data from the Japanese NSRR experimental reactor.

Methods

The work was carried out in the framework of benchmark calculations organised by the OECD NEA Working Group on Fuel Safety (WGFS). The organisers provided detailed information on the experiments and on the initial state of the tested fuel rod segments.

The irradiation history was simulated with the FUROM code on the basis of NPP data. The corrosion model of the code was extended with a new correlation to simulate the oxide layer development on the surface of Zirlo type cladding in Pressurized water reactors operational conditions. The fuel state at the end of Nuclear Power Plant operation was considered as initial state for the fuel segments in the RIA experiments.

The FRAPTRAN calculations were carried out for two experiments:

- VA-1: RIA experiment in the NSRR reactor at room temperature and with atmospheric pressure,
- VA-3: RIA experiment in the NSRR reactor at 280 °C temperature and with 70 bar pressure.

Additional sensitivity calculations were performed with artificial conditions limiting boiling simulation during the tests.

In order to improve the heat transfer simulation, the FRAPTRAN code was connected to the TRABCO code, and the calculations were carried out with the coupled FRAPTRAN/TBACO system.

Results

The calculated results showed generally good agreement with the measurements, since the fuel failure observed in the tests was reproduced by the calculations.

The initial hydrogen content of the high burnup (75 MWd/kgU) fuel's cladding was an important factor to determine if fuel failure can take place or not in the calculated scenario.

The calculation confirmed that clad failure due to pellet-cladding mechanical interaction can take place before the DNB (departure from nucleate boiling) condition is reached.

The radial temperature distribution indicated that the maximum temperature was not in the centre of the pellet.

The comparison with the calculated results of other participants of the benchmark showed that our data were typically in the middle of the calculated parameters, while the calculated data of all participants were characterised by large scatter.

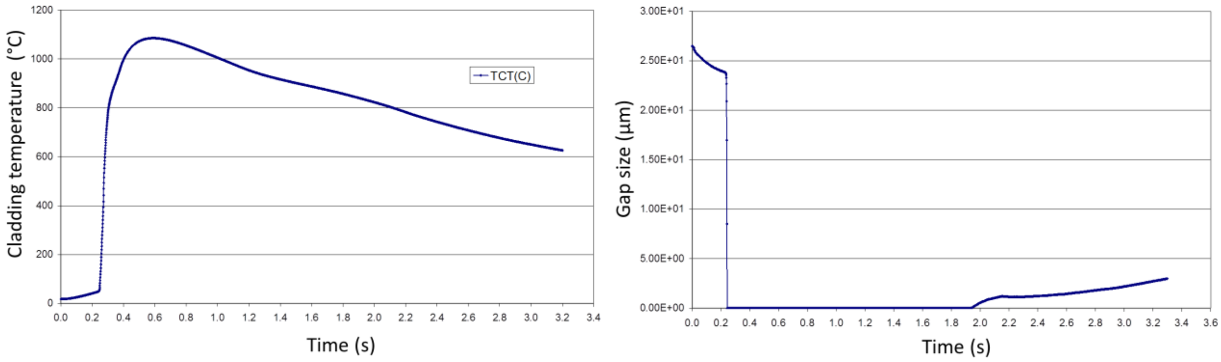


Figure 1: Calculated cladding temperature and gap size for VA-1 experiment

Remaining work

The OECD NEA WGFS intends to launch another series of benchmark calculations including uncertainty analyses with the participation of several institutions. MTA EK plans to participate in this new benchmark.

Related publication

[1] I. Panka, A. Molnár, Z. Hózer: *Simulation of NSRR RIA Experiments with the FRAPTRAN code*, EK-FRL-2012-758-01/03 (in Hungarian)

THE ROLE OF GEOMETRIC IMPERFECTIONS AND FRICTION COEFFICIENT IN TENSILE TESTS

Dániel Antók, Tamás Fekete

Objective

Within the frames of the surveillance program of the four VVER-440/213 type reactors in Paks NPP_1 uniaxial tensile tests were carried out on the 15H2MFA base material, the weld material and the heat affected zone from 1984 to 1993. In order to get reliable material properties utilizing the force – displacement diagram recorded at the crosshead one should consider the fact that the displacement of the crosshead contains not only elongation of gauge length, but displacement stemming from interactions of specimen and the testing machine. The slope of the linear elastic region of each diagram differed from expected values and had significant systematic deviation. Several axial symmetric and 3D finite element simulations were carried out to analyze the role of the friction coefficient and geometric imperfections of the grips and the specimen. Using the results we are able to construct a correction method for the force – displacement diagrams and apply it to the measured data.

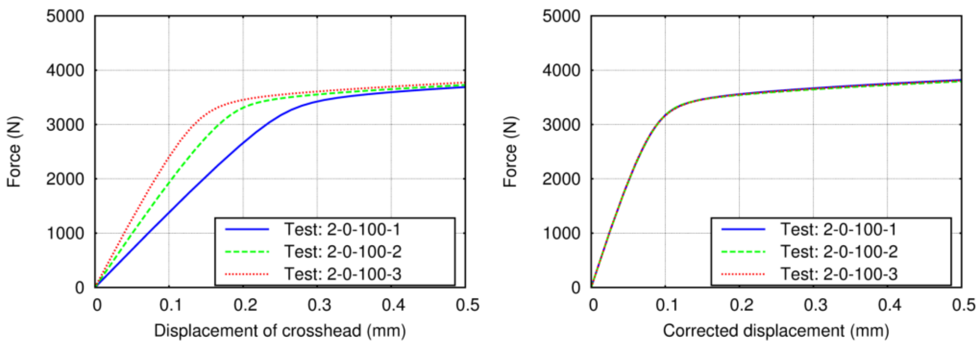
Methods

The first step of the method is to determine the slope of a given measured force – displacement diagram [1]. This slope is noted as s_{data} [N/mm]. Then an axial symmetric model with no geometric imperfections and with rigid fixture should be made to evaluate the value of the slope of the simulated data (s_{rigid}). The measured diagram consists of a set of force and displacement values. For a given pair the force is noted as F and the displacement as δ_{old}. The corrected displacement values (δ_{new}) can be calculated as follows:

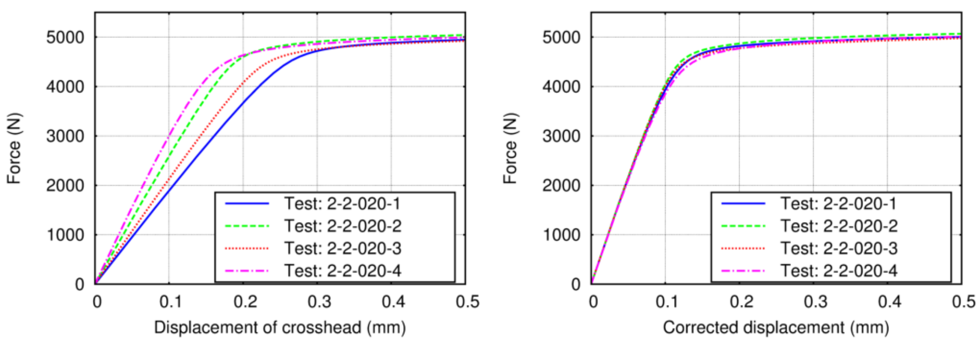
$$\delta_{new} = \delta_{old} - \left(\frac{F(\delta_{old})}{s_{data}} - \frac{F(\delta_{old})}{s_{rigid}} \right)$$

Results

The specimens noted as 2-0-100-1, 2-0-100-2 and 2-0-100-3 were tested at same conditions (irradiation, testing temperature) but their diagrams had significantly different slopes in the linear elastic stage. After using the correction method the adjustment of the curves is almost perfect.



However, there are tests (for example test series 2-2-020) on which the correction produces slightly worse results. This can be explained by significant amount of local plastic deformation at the contact of the grips and the specimen.



Related publication

[1] D. Antók, Gy. Krállics: *Fixture problems of irradiated tensile test specimens in Hungarian*. Anyagvizsgálók lapja (accepted)

UNCERTAINLY ANALYSIS OF A MAIN STEAM LINE ISOLATION VALVE CLOSURE IN THE PAKS PLANT

Attila Guba, Gábor Orbán, Iván Tóth, István Trosztel

Objective

There is a world-wide trend to perform best-estimate calculations including uncertainty analysis for licensing. In 2008-9 AEKI carried out the analysis of the limiting transient, the large break LOCA, for the Paks plant, using the BEPU (best estimate plus uncertainty) methodology and since 2010 the same procedure was used to assess the consequences of the closure of one of the main steam isolation valves (MSIV) that was shown to produce high secondary side pressure after power increase of the plant.

Methods

The RELAP5mod3.3 code was used for the analysis of the transient, while the uncertainty analysis was performed by the GRS method that is based on the probabilistic approach with propagation of input parameter uncertainties.

Results

In 2010 the calculation of the best estimate "base case" was performed. It was assumed that the main circulating pump in the affected loop is not switched off due to a single failure. As a result, heat transfer to the isolated steam generator is continuing, leading to fast pressure increase on the secondary side that finally opens both safety valves.

For the uncertainty analysis 15 uncertain parameters have been defined. These were selected by reviewing the major phenomena affecting the secondary pressure, viz. core power, primary/secondary heat transfer and mass and heat balance of the secondary side of the affected steam generator. The probability distributions of the uncertain parameters were specified based on earlier experience gained in the OECD BEMUSE project and the large break LOCA BEPU analysis.

130 calculations were run that allowed to discard the two highest values according to the Wilks formula, when defining the maximum steam generator pressure at 95 % probability and 95 % confidence level. This value only slightly exceeds 6 MPa that shows a margin of almost 2 bar to the acceptance criterion. Sensitivity analysis was performed to define the parameters of highest impact: the results indicated that practically only the parameters of the steam generator safety valves play a role [1].

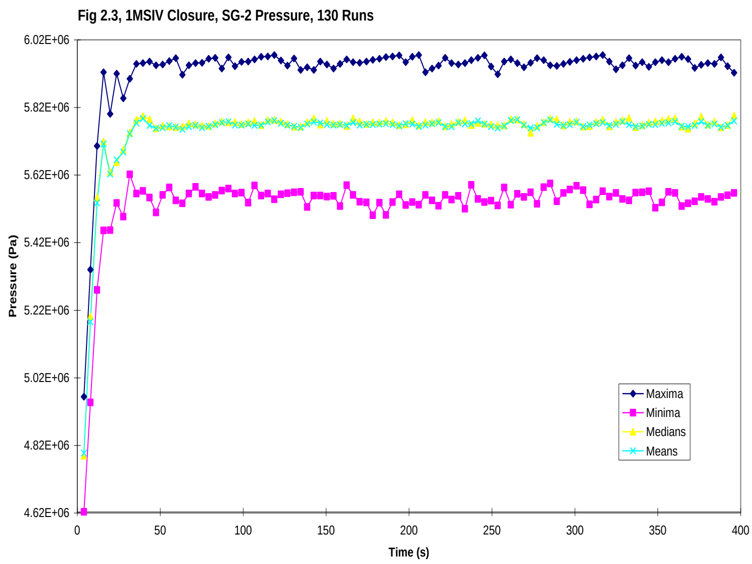


Figure 1: Maximum, minimum, median and mean steam generator pressures from the uncertainty analysis

Remaining work

The project was finished.

Related publications

[1] A. Guba and G. Orbán: *Uncertainty Analysis of a Main Steam Line Isolation Valve Closure*, AEKI report, AEKI-THL-2012-708/01/M0 (2012) (in Hungarian)

VALIDATION OF THE KARATE CODE SYSTEM AGAINST THE LATEST OPERATIONAL DATA AND STARTUP MEASUREMENTS

András Keresztúri, György Hegyi, Lajos Korpás, Emese Temesvári

Objective

In the last decades, KARATE-440 was elaborated and developed continuously to calculate VVER-440 rector cores by coupled neutron physical - thermal hydraulics models. The main goal of the calculations is the core reload design, however, certain safety analyses amenable to a static code can also be studied by KARATE-440. The programme serves economic core reload design so that the limitations demanded by the safety analysis should be observed. The latter function is utilized for the periodic independent check of the Paks NPP core design. On the other hand, in the last years several modifications of the VVER fuel construction and the corresponding core design aiming at more economic fuel utilization - like for example Gd doped fuel - were introduced by Paks NPP which made further development of the models necessary. Having regard to the above situation, continuous validation from year to year against the latest operational and start-up measurements is indispensable for the establishment of the uncertainties and the margins for the calculated safety related frame parameters.

Methods

Model validation, comparison of the calculated and measured data.

Results

In 2012, the following parameters were used for the validation

- core burnup dependent radial peaking factors based on the assembly-wise in-core temperature rises,
- core burnup dependent operational critical boron concentrations,
- critical boron concentrations measured at the Minimum Controllable Power,
- moderator temperature reactivity coefficients measured at the start-up procedure,
- integral and differential efficiencies of the control rod groups.

According to the validation results, there are no significant changes of the deviations from the measurements as compared to the earlier cycles except Unit 1 where the deviations of the calculated and measured critical boron concentrations are larger than usually. The clarification of the possible reasons has been started. It turned out that the measured and the calculated moderator temperature reactivity coefficients, which are sensitive to the boron concentration, are in good agreement at the calculated boron concentration, additionally there are no such differences between Unit 1 and the other ones which could explain a different behaviour.

Reactor state	Coolant temperature [°C]	Working control rod group position [cm]	Measured critical boron concentration [g/kg]	Calculated critical boron concentration [g/kg
Unit 1, Cycle 29 State 1 at BOC	168.0	168.0	10.60	10.15
State 2 at BOC	223.0	223.0	10.60	10.3
Unit 2, Cycle 27 State 1 at BOC	225.8	190.0	10.7	10.6
State 2 at BOC	263.1	240.0	10.7	10.65
Unit 3, Cycle 27 State 1 at BOC	220.0	186.0	10.54	10.37
State 2 at BOC	263.0	229.0	10.60	10.45
Unit 4, Cycle 25 State 1 at BOC	172.0	172.0	10.25	10.1
State 2 at BOC	241.0	241.0	9.97	10.0

Remaining work

There is no remaining work.

Related publications

[1] Gy. Hegyi, L. Korpáss, A. Keresztúri: *Comparison of the KARATE results with the measurements and C-PORCA calculations for the latest realized cycles of Paks NPP*, AEKI-RAL-2011-706/01/M0 (in Hungarian)

VALIDATION OF THE RELAP5 CODE FOR THE PRESENCE OF NON-CONDENSABLE GASES IN THE PRIMARY CIRCUIT WITH PMK 2 EXPERIMENTS

Attila Guba, Gábor Orbán

Objective

The Fukushima events revealed the importance of the analysis of the beyond design basis accidents. Recently these very unlikely events are examined for the Paks NPP. One of the scenarios analyzed is the loss of coolant accident in shutdown conditions. During the cooldown and heatup process of the Paks NPP when the primary circuit pressure is below 2.5 MPa, the pressurizer steam atmosphere is replaced by nitrogen. In these situations hydroaccumulators and high-pressure emergency core cooling system are disconnected from the primary system and the automatic start-up of the low-pressure emergency core cooling system is disabled. Therefore the long term cooling of the primary circuit relies on operator action of manual initiation low-pressure injection.

In a loss of coolant case the water from the pressurizer is surged to the primary circuit affecting the steam generator heat transfer and the behaviour of the break flow. The lack of experience of the low pressure behaviour of the nitrogen in the primary circuit necessitated a previous validation work. Three experiments were performed on the PMK-2 facility and were analyzed by the RELAP5 code.

Methods

The objective of the PMK-2 tests performed within the OECD PKL2 project was the investigation of small break loss of coolant accidents during the cool-down of the plant to cold shut-down conditions. N_2 from the pressurizer is injected to the primary system, most of it being collected in the steam generators, later on reaching the break location. Since emergency injection is not available, there is a competing process between cladding temperature rise and pressure reduction to the pump head of low-pressure injection that strongly depends on the heat transfer effectiveness in the steam generators, this latter being impacted by the presence of N_2. Obviously, secondary bleed is an important action for reaching low-pressure injection in time.

In order to investigate the processes described above, three test runs were defined with the same break size of 1%:

- T2.1: Steam atmosphere in the pressurizer, secondary bleed by one relief valve.
- T2.2: Air atmosphere in the pressurizer, secondary bleed by one relief valve.
- T2.3: Air atmosphere in the pressurizer, secondary bleed by two relief valves.

Test T2.1 constitutes the base case without non-condensables in the primary circuit, while T2.2 addresses the effects of the presence of the nitrogen with the same conditions. T2.3 investigates the effect of secondary bleed in presence of non-condensables.

A post test calculation was made with the standard RELAP5 model for the test T2.1 with steam, the results showed good agreement with the measured data. Then the same input was used for the cases T2.2 and T2.3, which gave – of course – relatively poor results. To overcome the issues, modifications in the input deck were investigated until reaching reliable predictions. The input improvements for the PMK-2 model were recommended for the plant calculations.

Results

The main findings of the validation work are the following:

- The steam generator, the pressurizer surge line, the core and downcomer nodalization is refined for better modelling the nitrogen propagation in the primary circuit. The break area nodalization was upgraded to avoid unphysical oscillations in the break flow when nitrogen is depleted.
- The pressurizer surge line heat loss plays an important role, after the first large air injection from the pressurizer the local condensation leads to water appearance in the pressurizer surge line trapping the remaining nitrogen in the pressurizer. The modification corrected the pressurizer behaviour.
- Test calculations have shown that using the Ransom-Trapp critical flow model gives slightly better agreement with the measured results than the default Henry-Fauske model.

Remaining work

The PMK-2 tests supplied important data for code validation; the findings were incorporated to the plant calculation. The work has been finished.

SUSTAINABLE NUCLEAR ENERGY TECHNOLOGY PLATFORM

István Vidovszky

The Hungarian Sustainable Nuclear Energy Technology Platform was launched summer 2010. The main goal of the Platform is to influence the agenda of nuclear energy research and development activities in Hungary and to participate in its coordination. The agenda should take into account the needs related to:

- the lifetime extension of Paks nuclear power plant (four VVER-440 units);
- the realization of new nuclear units;
- the closing of the fuel cycle and the development of Generation IV reactors.

Launching the platform is due to the needs and necessities in Hungary, influenced by the European development as well. The above three goals answer the requirements of the nuclear industry and serve as basis for the future development. The lifetime extension of the existing units requires the maintaining of the high safety level reached up to now and also leads to some important further modifications, such as the refurbishment of the process control system. Though no final decision has been made concerning new units, it is expected in the near future, and licensing and tendering may already start. Later the platform should facilitate the transfer of new technology to Hungary.

Closing the fuel cycle would mitigate the risks related to the radioactive waste management and would promote the better utilization of the Uranium resources. The use of fast reactors may solve both problems. The majority of the candidate reactors for Generation IV are fast reactors; therefore, an important long term task of the platform is to promote the research and development related to fast reactor technology in Hungary. At the moment the joint effort of Czech, Hungarian and Slovak research institutes for hosting the ALLEGRO gas cooled fast reactor demonstrator is in the focus of the programme.

All the important stakeholders in nuclear energy in Hungary are represented in the platform. Development of research infrastructures is one of the main goals of the Platform's activity.

In 2010 – 2012 the Platform elaborated its Strategic Research Agenda, which determines the research priorities for the coming decade. There is good hope, that the new R&D financing strategy of Hungary will allow the Platform to reach the goals.

The platform is represented by the Hungarian Academy of Sciences Centre for Energy Research.

III. HEALTH PHYSICS, SPACE DOSIMETRY

POSSIBLE CONSEQUENCES OF INHOMOGENEOUS DOSE DISTRIBUTION AND THE LNT-MODEL

Balázs G. Madas, Imre Balásházy

Objective

The aim of this work is to introduce an alternative method of calculation of effective dose, which offers the opportunity for the consideration of suborgan inhomogeneity of exposure and to investigate, how microscopic nonlinearities may manifest at macroscopic level when lung epithelium is inhomogeneously exposed to inhaled radon progeny.

Methods

To take account of suborgan distribution of absorbed dose, the investigated organ must be divided into small parts (tissue units – TUs), where absorbed doses and equivalent doses are computed. To determine effective dose, equivalent doses of TUs are summed up. To avoid inconsistency, the sum of the weighting factors of TUs ($w_{TU,i}$) must be equal to the tissue weighting factor (w_T). Since there is no information about differences in radiation sensitivity of the different parts of the epithelium, the weighting factors of the TUs are proportional to the mass of the TUs ($m_{TU,i}$). With the definition of TU weighting factors, alternative effective dose can be determined by the following expression: $E = \sum_i w_{TU,i} \cdot \sum_j w_{R,j} \cdot D_{i,j}$, where m_T is the mass of the tissue, $w_{R,j}$ is the radiation weighting factor, $D_{i,j}$ is the dose absorbed by TU i from radiation type j, and so $\sum_j w_{R,j} \cdot D_{i,j}$ is the equivalent dose (H_E) in TU i. Because of the observed, non-linear microscopic effects of radiation, four basically different functions are investigated besides the linear one. These functions are summarized in Table 1.

Table 1: The non-linear functions applied for alternative equivalent dose

Type	Alternative equivalent dose
supralinear	$H_E(D) = w_R \cdot D \cdot (1 + \exp(-36 \cdot D))$
sublinear	$H_E(D) = w_R \cdot D \cdot (1 - \exp(-36 \cdot D))$
biopositive	$H_E(D) = w_R \cdot D \cdot (1 - 10 \cdot \exp(-72 \cdot D))$
threshold	$H_E(D) = \begin{cases} 0, & \text{if } D \leq 96 \text{ mGy} \\ w_R \cdot D \cdot (1 - 10 \cdot \exp(-24 \cdot D)), & \text{if } D > 96 \text{ mGy} \end{cases}$

Results

Figure 1 shows alternative effective doses as the function of mean tissue dose. Exposure in WLM (Working Level Month) and alternative excess nominal risk are also presented. The left panel shows the case, when hit probability distribution over TUs is supposed to be uniform. The right panel shows the realistic case, when the hit distribution is strongly inhomogeneous over the TUs. Comparing the black curves, one can see that inhomogeneity cannot be considered if the relationship between absorbed dose, effective dose and nominal risk are linear. In addition, it is suggested that nonlinearity in low dose effects is less significant in case of inhaled radon progeny than in case of radiation sources producing homogeneous exposures.

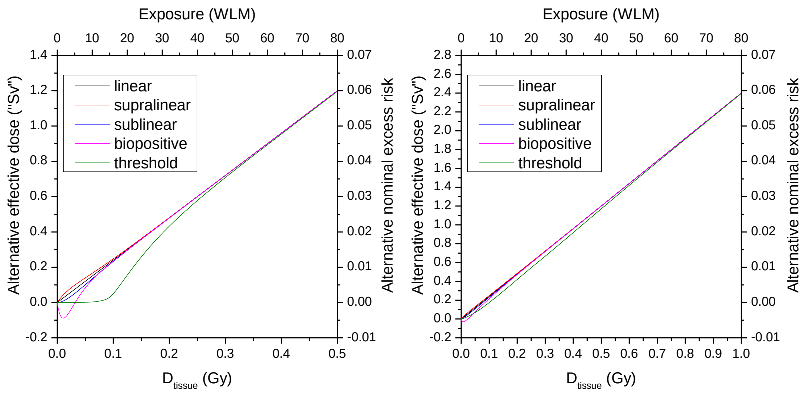


Figure 1: Alternative effective dose as the function of mean tissue dose considering the dose distribution in TUs supposing homogeneous exposure (left panel), and considering the realistic, inhomogeneous dose distribution in TUs (right panel)

Related publications

[1] B. G. Madas and I. Balásházy: *Possible consequences of inhomogeneous suborgan distribution of dose and the linear no-threshold dose-effect relationship*, 13th International Congress of the International Radiation Protection Association, Paper TS1a.6. (2012)

[2] B. G. Madas: *Numerical modelling of the biological effects of ionizing radiation at the tissue level*, PhD dissertation, Eötvös Loránd University, 95 (2012)

DEVELOPMENT OF DOSIMETRY EXPERIMENTS FOR BEXUS STRAROSPHERIC BALLOONS

Balázs Zábori, Ágnes Gyovai, Dorottya Habos*, Tamás Hurtony*, Marianna Korsós*, Orsolya Ludmány*, Dávid Mesterházy, József Pálfalvi*, István Apáthy, Antal Csőke, Sándor Deme, Attila Hirn, Tamás Pázmándi, Péter Szántó*

Objective

Due to significant spatial and temporal changes in the cosmic radiation field, radiation measurements with advanced dosimetric instruments on board spacecrafts, aircrafts and balloons are very important. The Hungarian CoCoRAD (Combined TriTel/Pille Cosmic RADiation and dosimetric measurements) and TECHDOSE (Development of a Complex Balloon Technology Platform for Advanced Cosmic Radiation and Dosimetric Measurements) teams were selected to participate in the BEXUS (Balloon Experiment for University Students) 12&14 projects with the support of the Centre for Energy Research, Hungarian Academy of Sciences. In the frame of the BEXUS programme Hungarian students from the Budapest University of Technology and Economics carried out a radiation and dosimetric experiment on a research balloon, which was launched from Northern Sweden in September of 2011 and 2012.

The central part of the experiment was the TRITEL 3-dimensional silicon detector telescope which had been originally developed for cosmic radiation and dosimetric measurements for use on board the International Space Station. In the frame of the experiment the TRITEL instrument was modified and extended with additional mechanical, thermal and electrical parts to meet the requirements of the BEXUS stratospheric balloon system.

Methods

During the development phase the relatively harsh environmental conditions, like the very high accelerations during the flight profile of the balloon, the very low (-60°C – -90°C) external temperatures in the stratosphere, as well as the electrical interface requirements between the experiment and the BEXUS balloon's own communication system were taken into account (Fig. 1). Moreover, the experiment box had to withstand the 8 m/s landing velocity and the design loads +/-10 g in the vertical direction and +/-5 g in the horizontal direction. Therefore a thermal and a mechanical model of the experiment hardware were developed.

Tests in thermo-vacuum chamber and in vibration facility were performed on the flight hardware to demonstrate conformance to specification and to detect possible manufacturing defects, workmanship errors.

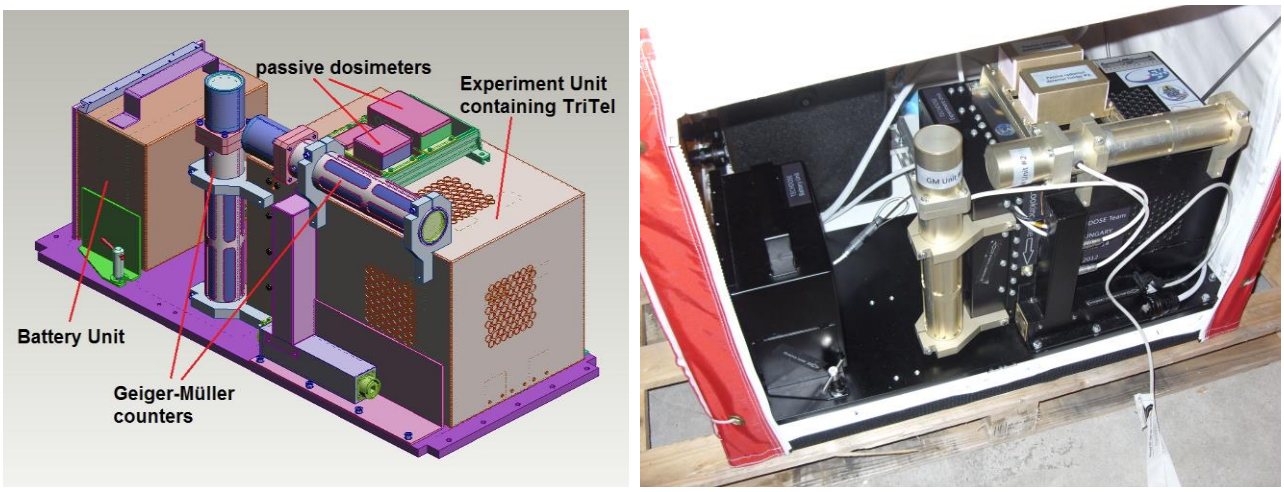


Figure 1: The experiment hardware (left: the mechanical design, right: the experiment in the gondola of the balloon)

Results

A mechanical protection was developed for the BEXUS flight to protect the instrumentation inside against the high accelerations during the flight. After the end of the mission all instruments were received without any damage, which was considered to be the final verification of the mechanical design.

The power consumption of the experiment during the flight was about 3.5 W (3 W for TRITEL and about 0.5 W for the remaining electronic units). The temperatures measured inside and outside the experiment box (ΔT = 38 °C) during the flight were in good agreement with the values calculated from the thermal model.

Remaining work

As an extension of the balloon measurements we are developing a measurement system containing two mutually orthogonal Geiger-Müller counters for the STRATOS II rocket flight. The instrument will perform radiation measurements up to an altitude of 60 km. The launch is due at the end of 2013.

Acknowledgements

The REXUS/BEXUS programme is realised under a bilateral Agency Agreement between the German Aerospace Center (DLR) and the Swedish National Space Board (SNSB). The Swedish share of the payload has been made available to students from other European countries through a collaboration with the European Space Agency (ESA). EuroLaunch, a cooperation between the Esrange Space Center of the Swedish Space Corporation (SSC) and the Mobile Rocket Base (MORABA) of DLR, is responsible for the campaign management and operations of the launch of vehicles. Experts from ESA, SSC and DLR provide technical support to the student teams throughout the project.

The BEXUS CoCoRAD and the BEXUS TECHDOSE experiments were co-funded in the frame of the PECS contracts No. 4000103810/11/NL/KML and No. 4000107210/12/NL/KML, respectively.

Related publication

[1] B. Zábori, A. Hirn, T. Pázmándi: *The Hungarian CoCoRAD experiment in the BEXUS program of the ESA*, 63rd International Astronautical Congress, paper, 2012

JOINT DOSE MAPPING INSIDE THE COLUMBUS MODULE ON ISS

József K. Pálfalvi, Julianna Szabó

Objective

In the frame of the European Space Agency (ESA) the project called DOSIS (Dose Distribution inside the Columbus module) experiment, lead by the German Aerospace Center (DLR), with the participation of nine countries, aimed at the determination of the radiation field parameters inside the European Columbus Laboratory of the International Space Station (ISS). The first measurements started in the mid of 2009 during the lowest Sun activity, at the end of the 23rd Sun cycle. The second phase ended in the mid of 2010, when still very low Sun activity was observed. Then, the experimental technique was revised and a new measuring regime, the DOSIS-3D was started. Altogether six phases have been planned to study the change of the space climate. The first 125-day long exposure was carried out between May and September, 2012 during the 24th Sun cycle. The second experimental phase started in October, 2012.

Methods

Thermoluminescent dosimeters (TLD) and solid state nuclear track detectors (SSNTD) were applied by the EK Space Dosimertry Group to investigate the dose contribution of the low and high Linear Energy Transfer (LET) cosmic radiation. In our case, two SSNTDs and six TLDs formed one stack, altogether fourteen of them were constructed for each phase. After exposure the stacks were transferred to the Earth for data evaluation. The calibration was made at high-energy particle accelerators simulating the cosmic radiation. The TLDs have already been evaluated by a computerized device, type Harshaw-2000. The SSNTDs will be evaluated by a semi automated image analyzer and the LET spectra, the absorbed dose, the dose equivalent, as well as the mean quality factor will be obtained.

Results

In Fig. 1 the absorbed dose rates of the low LET part (< 10 keV/μm) of the cosmic radiation are presented. As expected from previous experiments, the absorbed dose nearby the end-cone (location 2) of the module was the highest comparing with the connection tunnel (location 10), which was better shielded against the cosmic ray particles by other sections of the ISS. It was also observed that during the 2nd year of 24th Sun cycle the daily dose rates of the low LET radiation were 20-26% higher than 2 years earlier.

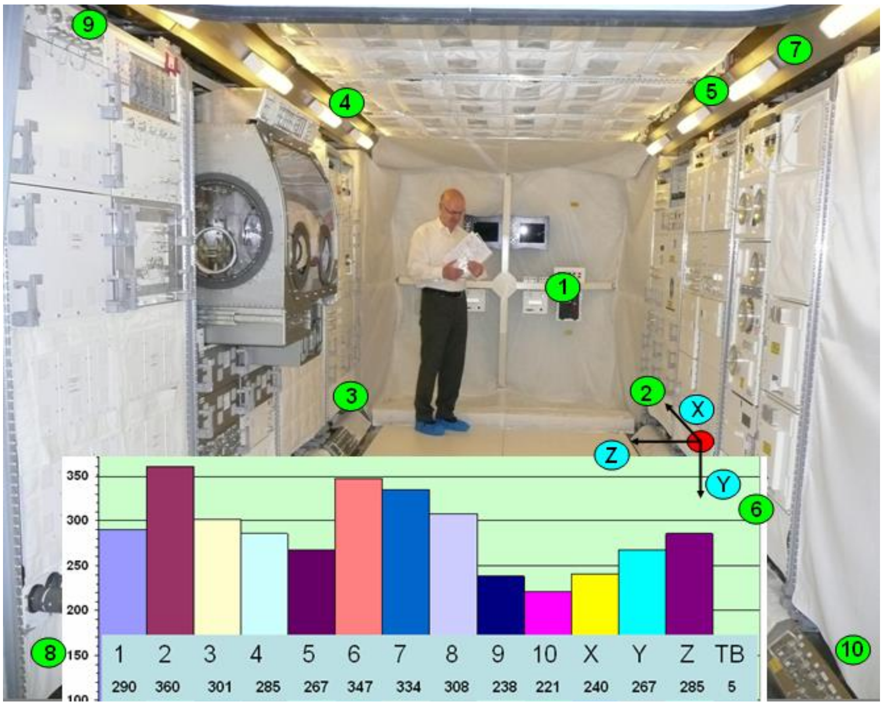


Figure 1: Interior of the Columbus module on ISS with dose rate distributions by locations numbered from 1 to 10 and the directional dose rates (X, Y, Z) at the middle of the module, all in μGy/day. TB=travelling background. Z=velocity vector of the ISS, Y=direction to the Earth, X=the axis of the module.

Remaining work

The evaluation of the remaining DOSIS-3D detectors is still in progress and planned to be completed in early 2013.

Related publication

[1] J. Szabo, J. K. Palfalvi: *Calibration of solid state nuclear track detectors at high energy ion beams for cosmic radiation measurements: HAMLET results.* Nuclear Inst. and Methods in Physics Research, A, **694**,193-198 (2012)

PILLE, A PORTABLE TLD SYSTEM ON THE ISS

István Apáthy, Antal Csőke, Sándor Deme, István Fehér, Attila Hirn, Péter Szántó

Objective

Measurement of dose due to ionizing radiation of cosmic rays during space flights as well as at environmental monitoring on the Earth is mainly based on thermoluminescent dosimetry (TLD). This method offers considerable advantages because of its high precision, wide range, rigidity etc. At the same time, its application generally involves the disadvantage that the readout of most types of dosimeters can be done only in laboratories equipped with relatively large and heavy TLD readers. This means that it is not possible to read out such dosimeters e.g. during a space mission on board, and at terrestrial environmental measurements an uncertainty occurs caused by the extra dose collected during the transport of the dosimeter from and to the laboratory. Our small, portable and space qualified TLD reader Pille, in its first version developed at the end of the 1970's, capable of evaluating the thermoluminescent (TL) dosimeters at the place of exposure (in-situ TLD reader), eliminates the above mentioned disadvantages. A new implementation of the dosimetry system helps researchers understand the space radiation environment on board the International Space Station (ISS) and can also be used for personal dosimetry.

Methods

TLDs record the total absorbed dose from ionizing radiation. As a form of passive detector, they accumulate a "signal" over the course of the exposure. At readout, the TLD is heated while giving off visible light proportional to the dose, which is converted to an electrical quantity, amplified, measured and evaluated by a reader.

The Centre for Energy Resesarch (the former Atomic Energy Research Institute) has developed and manufactured a series of TLD systems named "Pille" specifically for spacecrafts. All of them consist of a set of TL bulb dosimeters containing $CaSO_4$:Dy TL material and a compact TLD reader suitable for on-board evaluation of the dosimeters. The newest implementation of the system, Pille-MKS (a TLD reader and 10 dosimeters) was placed and installed as part of the service installation in the Russian Zvezda module of the ISS in 2003. Four new dosimeters were transported later to the ISS and installed there while two old, degraded dosimeters were transported back to the Earth for further analysis in 2009. Eleven dosimeters are located at different places of the ISS and read out monthly by the cosmonauts. Two of them are dedicated to ExtraVehicular Activities (EVAs) as well and the twelfth dosimeter is permanently inserted in the Pille reader and read out automatically every 90 minutes, providing high resolution dosimetry data. During coronal mass ejections of the Sun impacting also the Earth, certain dosimeters serve for individual monitoring of the astronauts with read-outs once or twice every day.

Results

In 2012, during the flight of ISS Expeditions 29/30 and 31/32, more than 3500 measurements were performed, among others the extra doses of astronauts during their four EVAs have been detected. The data obtained were evaluated, analysed, interpreted and published.

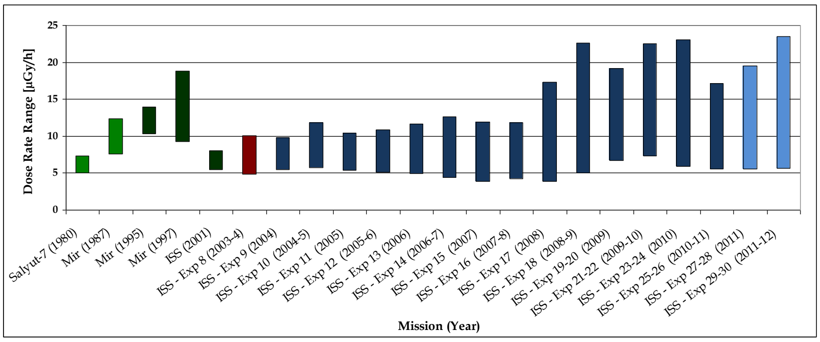


Figure 1: Dose rate ranges measured by Pille in space

Between September 2010 and December 2011 an on-board experiment has been performed for investigating the shielding effect of a protective curtain by using among others four Pille dosimeters. Hygienic wipes and towels containing water were stored in the protective curtain located at the wall of the crew cabin providing an additional shielding thickness of about 8 g/cm^2 water-equivalent matter. The measurement data were evaluated and a publication was submitted in 2012. [1]

The development of a new type of dosimeter with reduced shielding for EVAs continued in 2012.

Remaining work

Evaluating and interpreting on-board data, maintaining the on-board system; continuing terrestrial calibrations by high energy heavy particles; continuing the development of the EVA dosimeters.

Related publication

[1] P. Szanto, I. Apathy, S. Deme, A. Hirn, I. V. Nikolaev, T. Pazmandi, V. A. Shurshakov, R. V. Tolochek and E. N. Yarmanova: *Onboard Cross-calibration of the Pille-ISS Detector System and Measurement of Radiation Shielding Effect of the Water Filled Protective Curtain in the ISS Crew Cabin*, Radiation Protection Dosimetry (submitted)

STUDY OF THE BIOPHYSICAL EFFECTS OF ENVIRONMENTAL RADIOACTIVITY

Árpád Farkas, Imre Balásházy

Objective

The main objective of the work was to characterize the radiation burden of central airways due to inhaled radioactive particles as a result of combined effects of deposition and clearance. Applying the results and a biological model, a specific objective was to analyze the validity of the linear-nonthreshold (LNT) hypothesis in the case of inhaled radon progenies.

Methods

Three dimensional digital airway and mucus models have been created based on morphometrical data derived from the published literature. Flow fields of the inhaled air and the mucus escalator have been computed by computational fluid and particle dynamics (CFPD) techniques. Trajectories of particles were computed in the air and in the mucus lining the surface of the selected central airway bifurcation. In addition, activity of the particles cleared up from the deeper airway regions was computed in this geometry and compared to the activity of the particles deposited in the target airway segment. The inhomogeneity of deposition was characterized by deposition enhancement factors (DEF) defined as local per average deposition densities. The inhomogeneity of particle distribution yielded by the simultaneous action of deposition and clearance was described by particle enhancement factors (PEF).

Results

Simulation results revealed the existence of a slow clearance zone around the peak of the bifurcation causing delayed clearance of the radioactive particles located in this region. Particles clearing up from the deeper airways and passing through the studied bifurcation do not accumulate in this zone, because they avoid it. Furthermore, clearance pattern of these particles does not depend on particle size. However, clearance pattern of particles deposited in the target bifurcation is strongly particle size dependent, because deposition is considerably particle size specific. Although activity density of particles deposited in the slow clearance area is one-two orders of magnitude higher than the average activity density, these values are reduced by clearance with a factor of 3-7 (see Figure 1). The contributions of directly deposited and upcleared particles to the total activity within the studied bifurcation (airway generations 4-5) are roughly similar. Left panel of Figure 1 presents the velocity field of mucus, while the right panel demonstrates DEF and PEF values computed at different elementary surface sizes.

The unit track length biological model was applied to compute the biological endpoints corresponding to the burdens received above in case of inhaled radon progenies. As a result, cell inactivation and cell transformation probabilities show nearly linear-nonthreshold relationship with the exposure time. In this approach the cell to cell communication is neglected.

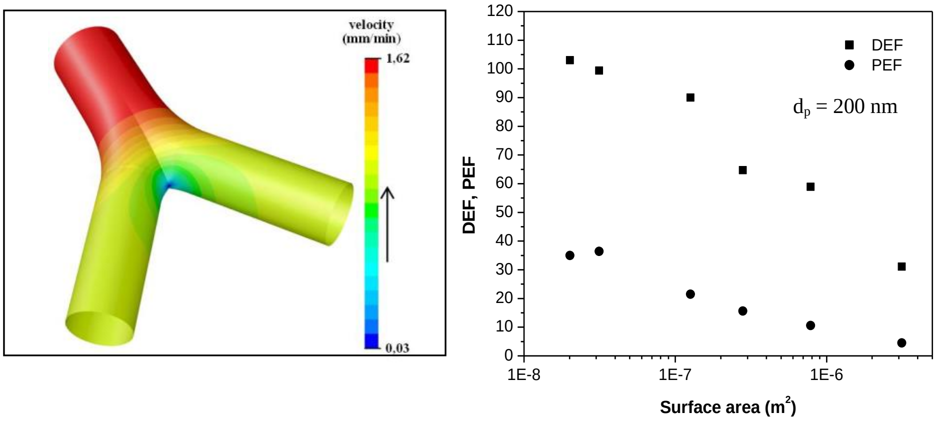


Figure 1: Simulated velocity field of mucus (left panel). Deposition enhancement factors (DEF) and deposition plus clearance, that is, particle enhancement factors (PEF) (right panel).

Related publications

[1] I. Szőke, Á. Farkas, I. Balásházy and W. Hofmann: *3D-modeling of radon-induced cellular radiobiological effects in bronchial airway bifurcations: direct versus bystander effects.* International Journal of Radiation Biology. Vol. 88, No. 6, 477-492 (2012)

[2] Á. Farkas, I. Balásházy and I. Szőke: *Simulation of Bronchial Mucociliary Clearance of Insoluble Particles by Computational Fluid and Particle Dynamics Methods,* Journal of Aerosol Science (submitted)

[3] A. Belchior, I. Balásházy, O. Monteiro Gil, P. Almeida and P. Vaz: *Does the number of irradiated cells influence the spatial distribution of bystander effects?* Carcinogenesis (submitted)

THE TRITEL 3D SILICON DETECTOR TELESCOPE

Attila Hirn, István Apáthy,Atal Csőke, Sándor Deme, Tamás Pázmándi, Péter Szántó, Balázs Zábori

Objective

One of the many risks of long-duration space flights (e.g. International Space Station expeditions, future lunar or Mars-missions, etc.) is the excessive exposure to cosmic radiation. The dose equivalent on board the International Space Station (ISS, at an altitude of ~400 km) in orbit might be two orders of magnitude higher than that under the shield of Earth's atmosphere. Due to significant spatial and temporal changes in the cosmic radiation field, radiation measurements with advanced dosimetry instruments on board space vehicles are extremely important. In cooperation with BL-Electronics Ltd., a three-dimensional silicon detector telescope (TRITEL) was developed at MTA Centre for Energy Research (MTA EK, the former MTA KFKI AEKI) in the past years. The main objective of the instrument was to measure not only the absorbed dose in the cosmic radiation field, but also the linear energy transfer (LET) spectrum of the charged particles and their average quality factor in three mutually orthogonal directions in order to give an estimation of the equivalent dose, too.

In 2012 the main objectives were

- to provide on-ground support for the installation and operation of the TRITEL-SURE experiment and to start analyzing the first measurement data received from the European Columbus Laboratory of the ISS;
- to finish the acceptance tests of the TRITEL-RS instrument to be delivered to the Russian Segment of the ISS in 2013;
- to manufacture the engineering and qualification model of a specific version of the instrument (TRITEL-JMS) for the Japanese microsatellite RISESAT in cooperation with the Space Robotics Laboratory (SRL), Tohoku University, Sendai, Japan.

Methods

TRITEL's measurement data are received from the ISS in the following way: firstly data are automatically downloaded to a USB (Universal Serial Bus) pendrive by inserting it to any of the two USB slots of the TRITEL Electronic Unit. Once all data have been copied to the pendrive, they are transferred to one of the Orbiter Communications Adapter (OCA) laptops and then transmitted to a ground server via the communication system of the ISS. The pendrive is also transported to ground at the end of each measurement period. The data received are displayed and evaluated using TRITEL's ground software.

Concerning the qualification and acceptance tests of the TRITEL instrument, the Engineering Qualification Model (EQM)/Flight Model (FM) philosophy is followed, i.e. qualification tests are performed on the EQM, that is, principally, identical to the FM and the model to be flown (FM) is subjected to acceptance testing. While the objective of qualification testing is the formal demonstration that the design implementation and manufacturing methods have resulted in hardware and software conforming to the specification requirements, the purpose of acceptance testing is to demonstrate conformance to specification and to detect manufacturing defects, workmanship errors, the start of failures and other performance anomalies, which are not readily detectable by normal inspection techniques.

The noise level of TRITEL's analogue electronic units was measured with a pulse generator and a Po-210 and an Am-241 alpha-source.

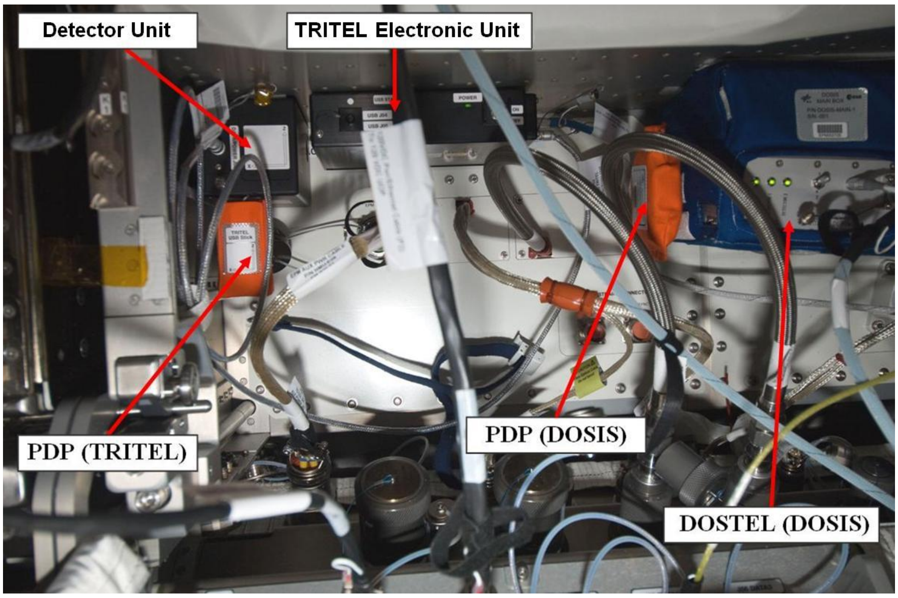


Figure 1: The TRITEL-SURE experiment in the Utility Panel Area of the European Physiology Module in the Columbus Laboratory of the International Space Station. The experiment hardware is located close to the DOSIS experiment containing two one-dimensional telescopes and a passive detector package

Results

The off-gassing tests performed on the flight hardware of the TRITEL-SURE experiment at Bremen Umweltinstitut, Germany, confirmed that the acceptance level of the toxicity value for TRITEL is maintained. The flight model was then delivered to the European Space Research and Technology Centre (ESTEC), where it passed the Flight Acceptance Review and the Bench Review needed for getting the green light for the flight.

The active part of the TRITEL system was delivered to the European Columbus Laboratory of the International Space Station on October 31, 2012 with the Russian cargo spacecraft Progress M-17M. Since November 6, 2012 the TRITEL instrument (Fig.1) has been collecting measurement data. A preliminary data download was performed three days after installation and switch-on for check-out purposes. According to the housekeeping parameters and the scientific measurement data received by the instrument, the active hardware is in good shape and functioning properly. The time spectra for the first three days are shown in Fig.2. The passive detector package (PDP) of the experiment, containing solid state nuclear track detectors and thermoluminescent detectors, was delivered to ISS on December 19, 2012 with Russian spacecraft Soyuz TMA-07M.

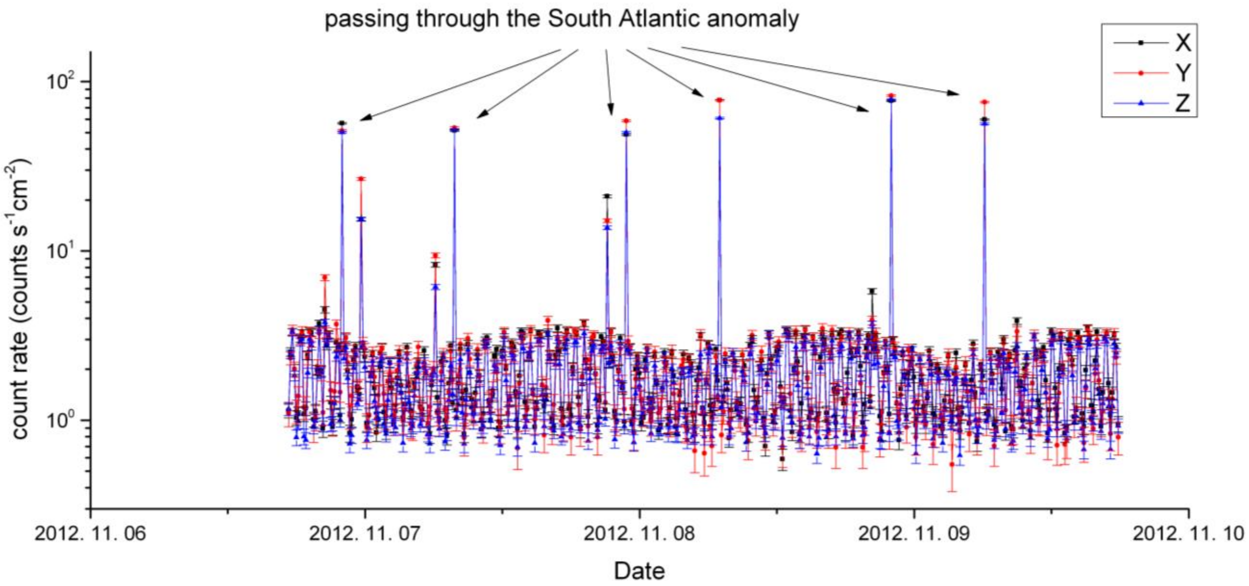


Figure 2: Count rates measured with TRITEL on board the Columbus Laboratory of the ISS, November 6-9, 2012. The connecting lines in the figure are only for better visibility.

The TRITEL-RS flight instrument was handed over to Rocket Space Corporation (RSC) Energia in autumn 2012. The hardware passed the EMC tests at Energia's ISS mock-up facility and got ready for the flight. The delivery of the TRITEL-RS experiment to the Russian segment of the ISS is expected in March 2013 with Soyuz TMA-08M. TRITEL-RS is an advanced version of the TRITEL system provided with menu-driven graphical interface (TRITEL-RS) and preliminary on-board data evaluation.

The engineering and qualification model of the TriTel-JMS instrument was manufactured and its functional tests have already got underway.

Remaining work

The end of the TRITEL-SURE experiment is due in May 2013 when all the data downloaded from the TRITEL Electronic Unit will be received and the passive detector package will be retrieved. This will be followed by an extensive data evaluation and interpretation as well as the intercomparison of data with those obtained parallel with other dosimetry systems in the Columbus Laboratory.

After delivery of the TRITEL-RS experiment to the ISS in March 2013, our task will be to provide technical and scientific on-ground support for the Russian partners (IMBP and RSC Energia). According to the plans, after the end of the TRITEL-SURE experiment, the detector unit located in the Columbus Laboratory will be transferred to the Russian segment of the ISS and connected to the Central Unit of the TRITEL-RS experiment. An advantage of measuring with two detector units in parallel is that the time- and the location-dependent variations might be separated. One of the detector units, then, will be located at a fix point and it will be used as a radiation monitor while the other one will be relocated after each measurement period in order to study the differences in effective shielding at different points of the module. Results of the measurements performed with the TRITEL space dosimetry system will be published in peer-reviewed scientific journals.

After finishing the qualification tests of the engineering model of TRITEL-JMS, manufacturing and acceptance testing of the flight model of the instrument will be started.

Acknowledgements

The TRITEL-SURE experiment is co-funded by the EC project SURE, contract number RITA-CT-2006-026069 and the PECS contract No. 98057. TRITEL-RS will be uploaded to the ISS in cooperation with the Institute of Biomedical Problems, Moscow and with the former financial support of the Hungarian Space Office.

CONTRIBUTION OF BIOMASS COMBUSTION AND TRAFFIC TO URBAN AEROSOL DURING HIGH PARTICULATE POLLUTION EVENTS

János Osán, Endre Börcsök, Felicián Gergely

Objective

An increase of the frequency and the length of high pressure meteorological conditions was encountered in Hungary due to the climate change. These events may result in prolonged periods of elevated atmospheric pollution with high PM_{10} concentration (particulate matter with aerodynamic diameter less than 10 μm). Such periods were experienced in Budapest at wintertime e.g. in November 2011 and in January 2012. Traffic is known as a major source of PM_{10} in urban atmosphere. Due to the increase of natural gas prices, the usage of solid fuel such as firewood has been extended for heating purposes, using boilers and stoves with limited emission control. For this reason, the contribution of biomass combustion and traffic as sources of PM_{10} in urban atmosphere is an important issue. The aim of the present study was to determine the contribution of the two sources based on sampling campaigns in different cities (Budapest, Paks, Szeged). Since both major sources are variable in time, markers characteristic to biomass (wood) combustion were selected for this purpose, allowing a time resolution of less than an hour.

Methods

The black carbon (BC) concentration and the wavelength dependence of the optical absorption of aerosols was monitored using a 7-λ portable aethalometer, with an ultimate time resolution of 2 min. For a single source of light-absorbing particles, the aerosol optical absorption coefficient (A) is an exponential function of the wavelength (λ): $A = k\lambda^{-\alpha}$, where α is the so called absorption Ångström exponent and k is a constant. α is close to unity for traffic-related aerosols (diesel soot) while it is close to 2 for wood combustion aerosols (brown carbon). In parallel, PM_{10} samples were collected on Teflon filters for elemental analysis using X-ray fluorescence (XRF). The size distribution of the elemental concentrations was investigated using a modified May-type cascade impactor allowing the collection of aerosol particles down to 70 nm, using Si wafers as impactor plates. The aerosol-loaded Si wafers were measured using total-reflection XRF (TXRF), calibrated with standards containing Cr pads imitating deposited microparticles, prepared using photolithography [1]. The size distribution of K concentrations is also characteristic for the sources, for biomass combustion the maximum of the distribution is below 1 μm.

Results

Taking advantage of the portability of the aethalometer, the instrument was mounted to a bicycle and the BC concentration and α were monitored along a path crossing central Budapest during a day with high PM_{10} concentrations (18 Nov. 2011, Figure 1). An increase of the BC concentration (> 10 μg/m^3) was observed in the city and crossing the main roads, with a minimum of 2.5 μg/m^3 in a green area (Városliget). The α exponent was close to unity along the whole path indicating that traffic was the major source of aerosols. Comparing the data with PM_{10} mass concentrations at Széna tér and Erzsébet tér, BC (mostly diesel soot) accounts for 20–30% of PM_{10} in the inner city.

Assuming a constant ratio of organic material in the aerosol and using the α exponents characteristic for traffic and wood burning, the contribution of the two sources could be calculated for winter campaigns in Budapest, Szeged and Paks. In contrary to Budapest, the BC concentrations were found to account for 8% of $PM_{2.5}$ in Paks and Szeged. During the day, traffic-originated particles dominate, while particles of wood burning origin contribute more to $PM_{2.5}$ during evening and night time. However, for days with low minimum temperatures (<–10 °C), wood burning originated particles dominated during the whole day. The maximum contribution of wood burning source to $PM_{2.5}$ was as high as 43%, under anticyclonal circumstances. In Szeged, the K/Ca concentration ratio (K as marker of wood combustion, Ca as marker of resuspension caused by traffic) was found to be correlated with the wavelength dependence of the optical absorption of aerosols [2].

The size distribution of elemental concentrations was studied at Paks and in Budapest. The extension of the impactor allowing to collect particles below 250 nm was found to be important, since the maximum concentration of elements related to high-temperature processes (e.g. K – biomass combustion, Zn – smelters) was observed in the 130–250 nm fraction.

Remaining work

Since the consumption of solid fuel other than wood (e.g. brown coal, lignite) is also increasing, air sampling and aethalometer monitoring is being performed close to the chimney of a house with a stove where the fuel type and the combustion is controlled. It is expected to derive characteristic parameters for distinguishing the heating-related pollution caused by different fuels combusted. The standardization of direct TXRF analysis of aerosol particles is planned to be verified using ICP-MS (Inductively coupled plasma mass spectrometry).

Related publications

[1] F. Reinhardt, J. Osán, S. Török, A.E. Pap, M. Kolbe and B. Beckhoff: *Reference-free quantification of particle-like surface contaminations by grazing incidence X-ray fluorescence analysis*, J. Anal. At. Spectrom., **27**, 248-255 (2012)

[2] Á. Filep, T. Ajtai, N. Utry, M. Pintér, Z. Török, E. Börcsök, J. Osán, Z. Bozóki and G. Szabó: *A proposal for a new source indicator for light absorbing aerosol measured by a multi-wavelength photoacoustic instrument*, J. Aerosol Sci., submitted (2012)

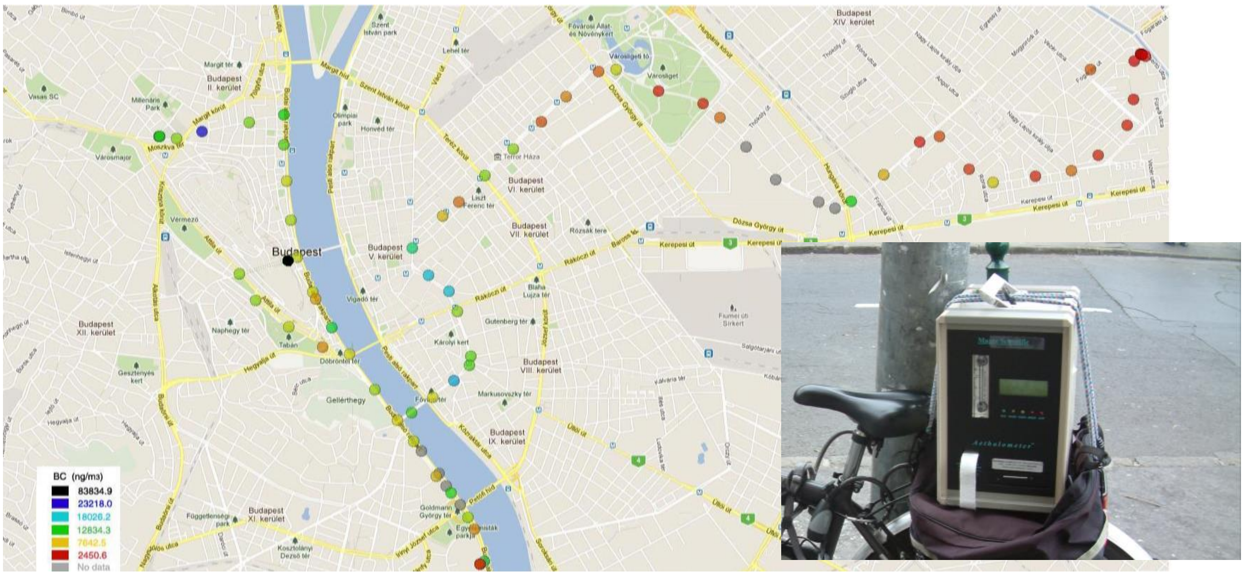


Figure 1: Survey of the BC concentrations in Budapest during a day with elevated PM_{10} concentrations (18 Nov. 2011) using a 7-λ portable aethalometer mounted to a bycicle. High BC concentrations were observed in the inner city

DUST IMPACT MONITOR, SIMPLE PLASMA MONITOR

István Apáthy, Attila Hirn, Attila Péter

Objective

The *Rosetta* spacecraft of the European Space Agency is the first mission designed to both orbit around and land on a comet. During its trek to Comet 67P/Churyumov-Gerasimenko, *Rosetta* made two excursions into the main asteroid belt and flew by two asteroids, Steins and Lutetia. After entering its orbit around the comet, in 2014, *Rosetta* will release a small Lander named *Philae* onto the icy nucleus.

The objective of the mission is to study the origin of comets and the relationship between cometary and interstellar material and implications their to the origin of the Solar System.

The Centre for Energy Research, Hungarian Academy of Sciences (MTA EK) is participating in two of the nine scientific experiments the Lander carries. The first one, *DIM (Dust Impact Monitor*) is a part of the SIP (Small Instrument Package) SESAME (Surface Electrical, Seismic and Acoustic Monitoring Experiments) for determining the mechanical and electrical properties of the comet's surface; the second one, *SPM (Simple Plasma Monitor)* is a part of another SIP known as ROMAP (Rosetta Lander Magnetometer and Plasma Monitor) which complements the plasma packages on board the *Rosetta Orbiter*. The *DIM* acoustic dust detector will investigate the material that impacts and falls on the nucleus of the comet; the *SPM* sensor is capable of measuring the major solar wind parameters as a function of the distance from the Sun.

Methods

The piezoelectric sensors of *DIM*, located outside the Lander, with active surfaces looking into three orthogonal directions, will detect the impacts of particles having energies in the range of 10^{-11} J ... 10^{-7} J. The sensor's electric output signals of broad dynamic range are amplified by wide-band logarithmic amplifiers. The characteristics of the impact signals (peak amplitudes, half-contact time, average) are measured by an appropriate electronic circuit, connected to the common Data Processing Unit of SESAME by a digital bus-system.

The *SPM* sensor is a type of electrostatic, hemispherical analyzer having 2 ion channels and 1 electron channel. It contains a Faraday cap as well. The energy range of the instrument is 0-12.6 keV for ions with a resolution of 3%, and 0-4.5 keV for electrons with a resolution of 10%; the field of view of the sensor is 140°x150° for ions and 8°x15° for electrons. The sensors of ROMAP are mounted on the end of a short boom and are coupled to a small DPU (Digital Processing Unit) to store data and control the power consumption in modes with reduced data rates.

Results

Since its launch in 2004, Rosetta has been flying on its orbit to comet 67P/Churyumov-Gerasimenko, which lasts approximately 10 years. During this time, systematic in-flight test campaigns for checking the service and scientific instrumentation of the Orbiter and the Lander are fulfilled. All operations on the flying Lander are first tested on the identical Ground Reference Model (GRM). Keeping in operation of the Ground Reference Model (GRM) of *ROMAP* (integrated with the GRM of the Lander) was continued at DLR, in Cologne, Germany.

In 2012, *Rosetta* was put in a deep hibernation phase so there were no on-board payload checking campaigns but the *FSS (First Surface Science) Campaign 2012-01* was executed on the Philae-ROMAP GRM to imitate the operation of ROMAP just after landing. ROMAP is one of the only two experiments which will be switched on at that time. The evaluation of the data of ROMAP achieved during the FSS Campaign proved the proper operation of the instrument.

During September-October Attila Hirn spent 6 weeks at the Max Planck Institut für Sonnensystemforschung (MPS) in Katlenburg-Lindau, Germany, where he performed tests with 1 mm ruby, low-density polyethylene and steel balls by *DIM's* mechanical ground support equipment for investigating the impact angle dependence of the piezo sensor. The results were summarized in a comprehensive report.

Experts of MTA EK participated in the activity of the Lander Operation Working Group (LOWG) as well as the Lander Science Working Team (LSWT). On the LSWT meeting in Seggau, Austria (October, 2012) a report was given about *SPM*'s and *DIM*'s activity during the previous period and the plans/goals in the post-hibernation phase of Philae's flight. The preparation for on-ground operations, the landing site selection strategy and different organization tasks have been discussed in detail.

MTA EK experts were taking part in data archiving and planning the operation during descent and the first scientific measurements.

Remaining work

To participate in the on-board test after hibernation during the last cruise phase payload checkout; to participate in on-ground calibrations of the sensors and tests of the Ground Reference Model; to take part in data archiving and planning the operation during descent and the first scientific sequence on the cometary surface.

MEDIUM- AND LONG-TERM STRATEGY FOR RADIATION PROTECTION RESEARCH

Tamás Pázmándi, Attila Hirn

Objective

According to the task defined in article 3 of Agreement ÁNI-ABA-13/12-M made between the Hungarian Atomic Energy Authority (OAH) and MTA Centre for Energy Research (MTA EK), a proposal for the strategy of the national radiation protection research was prepared taking into account the international trends as well as the national needs [1].

From several points of view the formulation of the strategy for national radiation protection, especially radiation protection research was a must:

- Most experts of the field in Hungary have either been retired or passed away and the generation following them is missing.
- Financial resources for national radiation protection research fell considerably in the last 10-15 years.
- Particular attention has been given to the need for radiation protection due to the events of the previous year, such as the accident at Fukushima NPP.
- There have been political decisions in Hungary on starting preparative work for building new nuclear reactor unit(s).
- The documentation of the international as well as the national regulatory systems is currently being revised.
- Since January 1, 2012, the Hungarian Academy of Sciences Isotope Research Institute has been embedded into the Hungarian Academy of Sciences KFKI Atomic Energy Research Institute which continued its activity under the name Centre for Energy Research, Hungarian Academy of Sciences. The Radiation Protection Department was also established by merging research groups previously belonging to different departments.

Methods

When formulating the strategy, the recognized specialists of the Hungarian radiation protection as well as the representatives of the potential end-users and customers were asked about their opinion; their recommendations have been taken into account.

The main research areas in radiation protection both at national and international level, their applications in Hungary and the potential needs expected in the coming years have been reviewed, and based on is information a strategy was elaborated for the next 5-10 years taking also into account the possibilities and capabilities at national level. The strategy focused on the interdisciplinary (physics-chemistry- engineering) fields of radiation protection and their practical aspects.

Research related to the non-ionising radiations and the biological and health effects of radiation was not considered in the frame of the project. The strategy related to radioactive waste management was not part of the work either, since its middle- and long-term plan is regularly issued by the Public Limited Company for Radioactive Waste Management (RHK Kft.).

Results

Among the strategic fields identified in the frame of the project, the priority of the following ones have been highlighted based on the capabilities and the potential needs:

- environmental dispersion calculations,
- environmental measurements,
- dosimetry (personal, environmental and space dosimetry),
- internal dosimetry (measurements and modelling).

Resources need to be focused on these fields in the near future. Later on the spectrum might be widened as necessary.

Remaining work

The project has been finished, there is no remaining work.

Related publication

[1] A. Hirn, T. Pázmándi: *Medium- and Long-term Strategy for Radiation Protection Research (in Hungarian)*, EK-SVL-2012-253-01-01-01 (2012)

ENVIRONMENTAL CONSEQUENCES OF SEVERE ACCIDENTS FOLLOWING THE INTRODUCTION OF THE SEVERE ACCIDENT MANAGEMENT GUIDANCE

János Gadó, Tamás Pázmándi, Emese Homolya

Objective

Chapter 15.4 of the safety analysis report (SAR) of the Paks NPP was written on the basis of the results of the PSA-2 project, finished in 2003. Actualisation became reasonable due to several causes, since during the last decade significant development and analyses were made, e.g. the severe accident management guidance has been introduced, causing relevant changes in the results of the probabilistic safety analysis (PSA) level 2.

Revision of the release categories has become necessary in accordance with the requirements of EUR (European Utility Requirements) documents and the new national regulations (Nuclear Safety Regulations – NBSz). Release categories in EUR documents and national regulations were analysed and recommendations for practical applications were made.

Methods

In order to estimate release occurring in case of design extension conditions (DEC), regulations and propositions used in the national and international practice were examined.

The methodologies and criteria used for assessing the environmental impact shall be based on the assessment of the releases to the environment. In case of DEC four criteria are identified:

- no emergency protection action beyond 800 m from the reactor,
- no delayed action at any time beyond about 3 km from the reactor,
- no long term action at any distance beyond 800 m from the reactor,
- limited economic impact out of the plant.

During calculations the following aspects shall be taken into consideration:

- Nine reference isotopes have to be considered in the analyses, coefficients for them contain the contributions of other isotopes.
- Characteristics of emissions should be provided by NUBIKI (Nuclear Safety Research Institute) as the results of calculations carried out using the MAAP code.
- In case of the first criterion of EUR documents the released activity for the first 24 hours, in case of the second criterion the released activity for the first 4 days and in case of the third and fourth criterion the released activity during the whole process has to be taken into account.
- Radioactive decay can be neglected until release to the environment.
- Coefficients for elevated releases have been determined with reference to releases occurring from a stack of about 100-m height. The coefficients for ground level releases shall be applied to releases from a height less than 100 m.
- In case of an operating nuclear unit for all initial operation conditions and effects – excluding sabotage and earthquake – the collective frequency of severe accident event sequences resulting in extensive releases shall not exceed 10^{-5}/year, and with every reasonable modification and intervention of 10^{-6}/year shall be targeted.

Analyses for operation at nominal capacity were performed, 13 emission categories were defined in PSA level 2.

Results

According to the results, the summed frequency of the scenarios for which any of the four criteria were exceeded is $1.012 \cdot 10^{-6}$ 1/year. This value does not exceed the value of 10^{-5}/year presented in the point 3.2.4.09000 of the NBSz. When comparing the results with previous results it can be seen that the summed frequency has been reduced significantly.

Remaining work

This project has been finished.

Related publications

[1] J. Gadó, T. Pázmándi: *Revision of the release categories the in case of severe accidents*, EK-SVL-2012-734-01-01-01 (August 2012)

[2] T. Pázmándi: *Assessment of the consequences of severe accidents*, EK-SVL-2012-734-01-02-02 (January 2013)

IV. MISCELLANEOUS

PRELIMINARY INVESTIGATION OF THE FUEL OPTIMIZATION METHODS TO BE APPLIED IN THE BUDAPEST RESEARCH REACTOR

Gábor Patriskov, Emese Temesvári

Objective

By refuelling at the Budapest Research Reactor (BRR) the main deal is to maximize the neutron flux of the irradiation channels whilst the fuel power peaking factors stay under their limit. In the near future, within the framework of a PhD study, new software will be developed for selecting the possible core configurations which satisfy these requirements. For this year, studying the possible optimization algorithms and a preliminary statistical investigation was planned.

Methods

To determine what kind of load patterns are preferable for the above discussed requirements, preliminary calculations have been made for random configurations of load pattern. Large number of random configurations overlaps the search space therefore the desired parameters as function of load pattern are examined. The data processing of the preliminary calculations based on statistical tools like correlation which is a good method for earning information about a large database with a large number of variables.

Results

For reloading it is essential to know the behaviour of the parameters, as a function of the in-core positions and the fuel element burn up, which determine that the reactor satisfies the operational assumptions. Therefore a large number of calculations were made to discover and analyze the properties of the reactor core.

The KIKO3D program for BRR was used to perform the calculations. The responses of 5000 random load patterns gives estimate about the "strength" of the fuel element positions. The response means the following parameters: epithermal and thermal neutron flux, burn up and fuel element power peaking factor (kq).

The main parameters (kq, burn up increase) which determine the behaviour of the actual core configuration could be estimated with a second degree polynomial function:

$x(i) = \sum_{j=0}^{2} a(i)_x^j LP(i)^j + \varepsilon\left(LP_{\delta(i)}\right)$, where

i: the number of fuel element position

x(i): amount k_q or burn up increase for the "i"th position

LP(i): burn up in per cent for "i"th position

$a_x(i)_j$: "j"th polynomial coefficient of the "x" amount (k_q or burn up increase) for the "i"th position

$\varepsilon(LP_{\delta(i)})$ means the effect of the neighbouring fuel elements which can modify the parameters by 10-20%.

Unfortunately, there are high variances of the fitting what may make the designing more difficult. The kq and burn up increase are described by 3x190 polynomials. The three polynomials for each position match the three rod positions which model the different states of the cycle (beginning, half-time and end), therefore we are able to estimate these parameters in several steps of the rods pulling.

The results of the calculation could be usable to give estimations for burn up and kq for a possible load pattern. We can give forecast which positions exceed their kq limits and schemes of possible core design. The further exercises are finding the possible schemes by this procedure. We may utilize the fitted polynomial to determine the burn up in the end of cycle.

Remaining work

In the following years the work will continue with further analyzing to select one or two optimization algorithm(s) which can be coupled with the KIKO3D program to create a loading pattern optimization code system using the special features of the Budapest Research Reactor.

Related publications

[1] G. Patriskov: *Preliminary Calculations for Optimization Algorithms of Nuclear Fuel Reloading at the Budapest Research Reactor*, Proceeding of the 22nd AER Symposium, Průhonice, Czech Republic, October 1-5, 2012, Vol.I: pp. 391-412, ISBN 978-963-508-625-2

[2] G. Patriskov and Á. Horváth: *Neutron Irradiation Testing of Copper Alloy in the Budapest Research Reactor*, Progress in Nuclear Energy, submitted

[3] G. Patriskov: *Optimization Algorithms of the Fuel Reloading and Irradiation Channels in the Budapest Research Reactor*, Literature Summary as an introduction section of the PhD paper, MTA-EK-RAL-2012-113/3-M0, in Hungarian, 2012

REGIONAL WORKSHOP ON THE ESTABLISHMENT AND USE OF AN UNCERTAINTY BUDGET FOR DOSE IN PRODUCT

Kovács András

The International Atomic Energy Agency (IAEA) in collaboration with the Government of Hungary organized the workshop at the Centre for Energy Research of the Hungarian Academy of Sciences in the period of 5 – 7 November, 2012. This workshop was part of the Regional Technical Co-operation Programme, „ RER 1011 – Introducing and Harmonizing Standardized Quality Control Procedures for Radiation Technologies, 2012-2013”, of the International Atomic Energy Agency.

Objective

The purpose of the training course was to enhance the professional capabilities of the participants of RER 8017 in the field of the establishment and use of an uncertainty budget for dose in radiation processed products for countries being already in an advanced level or in the introductory phase of radiation processing technology. The workshop was a platform for getting acquainted with the role of estimating uncertainties in the dosimetry procedures in radiation processing technologies.

Background

Radiation processing exists in many European countries mainly for the sterilization of medical products and for the production of advanced polymer materials. The expansion of the European Union results in increased trade, requiring strictly controlled radiation technologies through standardized quality control methods and procedures. The RER 1011 technical cooperation project was initiated in the scope of 2012-2013 TC Regional Programme in order to enhance European Member States' abilities in the application of standardized quality control methods and procedures for radiation processing of human health products and advanced materials, and to promote the contributions of nuclear technology to human health and environmental protection. The successful implementation of the project will result in the standardization of radiation processing technologies in the participating countries with regard to international and national standards. Sustainability will be ensured through the use of new radiation initiated processes, the routine production of radiation processed advanced materials, the establishment of new or upgraded irradiation facilities, increased volume of health care products using harmonized quality control methods, use of standardized quality control methods, advanced international trade, increased technology transfer and establishment of national standard regulations. National and international regulations and governmental financial contributions assure the long term execution of environmental technologies. This workshop corresponds to the important activity of this RER project, which is to provide training in the field of "Establishment and use of uncertainty budget for dose in product".

Scope

Gamma, X-ray (bremsstrahlung) and electron irradiation facilities are used to irradiate various medical, food and polymer products on routine basis. The measurement of absorbed dose is of basic importance for process control. The procedure of estimating uncertainties is a significant part in the dosimetry procedures since the absorbed dose value without its uncertainty limits is meaningless. The workshop included the determination of sources of errors in dosimetry measurements and discussed the procedures for estimating the magnitude of uncertainties for the measured absorbed dose results. The components of uncertainty were also discussed and methods were shown and given for calculating the combined standard uncertainty and an estimate of the overall uncertainty. The course followed the corresponding ISO/ASTM standard. The programme of the workshop consisted of lectures and exercises in the following topics:

- general introduction to uncertainties, traceability;
- determination of uncertainties during calibration, facility characterization (IQ and OQ), product dose mapping and routine process control.

Outputs of the workshop

The outputs of the workshop included:

- increased knowledge on the uncertainties in the dosimetry procedures,
- increased ability to establish and use uncertainty budget in radiation processing technologies for dose in product.

Participation

The following countries were represented at the workshop with 16 participants: Azerbaijan, Bulgaria, Croatia, Hungary, Kazakhstan, Moldova, Poland, Portugal, Romania, Russian Federation, Serbia, Slovakia, Turkey, Ukraine.

Two lecturers, Prof. A. Miller (Denmark, Ris∅, High Dose Reference Laboratory) and Dr. Mark Bailey (UK, National Physical Laboratory) gave the lectures and the practical exercises.

PROMPT GAMMA MEASUREMENTS WITHIN THE NMI3 EU FP7 FACILITY ACCESS PROGRAMME

László Szentmiklósi, Zoltán Kis, Tamás Belgya

Objective

NMI3 (Integrated Infrastructure Initiative for Neutron Scattering and Muon Spectroscopy) is a European initiative funded by the 7th Framework Programme. Through its Facility Access Programme ('Research Infrastructures' action of the 'Capacities' Programme, NMI3-II Grant number 283883), NMI3 provides access to all major national neutron and muon sources and experimental infrastructures in Europe, including the Budapest Neutron Centre. Funding through the NMI3 Access Programme is open to researchers affiliated to Institutions from EU member and associated states.

Methods

Application of the prompt gamma activation analysis methodology as described in the “Standard Operating Procedure of the Budapest PGAA-NIPS/NORMA-DÖME facility” (NAL-PGAA-01) for the analysis of material science samples. For the in-beam catalysis measurements a special temporary setup has been constructed.

Results

We completed the following experiments in 2012:

Project Number	Project Title	Principal proposer	Instrument	Experiment duration (days)
BRR_284	Non-destructive characterization of ^{10}B targets	P. Schillebeeckx, EC JRC IRMM, Geel	NIPS NORMA	10
BRR_287	New generation of Deacon catalysts: in-situ Prompt Gamma Activation Analysis	D. Teschner, Fritz Haber Institute, Berlin	PGAA	10
BRR_303	Measurement of the content and segregation of B at grain boundaries in experimental Co-Re polycrystalline alloys	Technische Universität Braunschweig	PGAA	4

The data analysis and the publication of the results are not supported by this grant; therefore they were completed and reported within the “Application of PGAA” project of the Nuclear Analysis and Radiography Department.

Remaining work

We are open to offer our analytical potential to various scientific collaborations and adapt our methodology to the requests.

Related publication

The scientific publications made from the present experiments are listed at the “Application of PGAA” project. Technical reports of the experiments will be published in the Progress Report of the Budapest Neutron Centre.

INVESTIGATING OF THE VISCOSITY CHANGE OF HIGH VISCOSITY MATERIALS DUE TO RADIATION

János Balog, Zsolt Kerner, Tamás Pázmándi, Róbert Schiller

Objective

One of the most important mechanical properties of the viscous medium applied in a pulse dampener is shearing viscosity. The change of the viscosity of four materials potentially applied in pulse dampeners used in high radiation fields – such as in nuclear power plants (NPP) – were investigated.

Methods

A simple, fast and reliable method of viscosity measurement was determined. The modified Koppers vacuum viscosimeter was found to be the most appropriate. The instrument does not contain any moving components, only measurement of the flow time is necessary. It is applicable to materials with viscosity range of 42 to 200 000 poise according to the ASTM D2171 standard. The instrument is calibrated considering the regulations of the ISO 9001:2000 standard. Vacuum of 300 mm Hg was applied during the measurements. They were performed at 25 °C.

The dose rate in the possible location of the pulse dampener device was estimated. The expected annual and life time gamma dose of the instrument was also calculated on the possible place of application. The calculations were performed using conservative assumptions, in view of the exact location of the instrument, correction of the calculations or in-situ measurements are possible. Dose calculations were made with the MicroShield software.

The irradiations were performed in the high activity Co-60 irradiation chamber at the KFKI Campus. They were performed without shielding and with 10 mm of steel shielding as well. The parameters of the radiation field were determined by chemical dosimeters during all irradiations.

Results

Based on the calculations, the dose load of the device is around 1.5 kGy/year. For a new NPP, presuming 60 years of operation, the expected dose load is 90 kGy for the period of service.

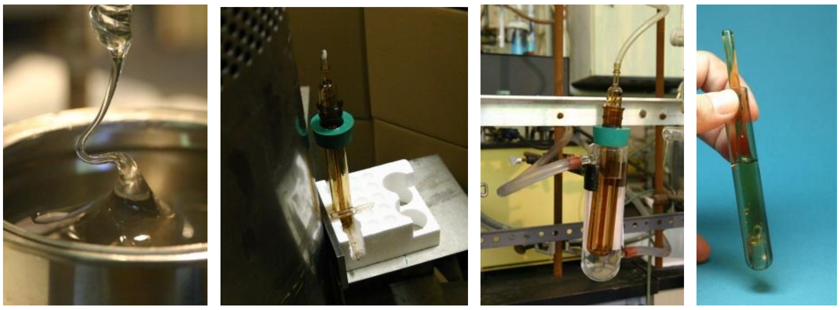


Fig 1: Pictures of the investigated materials, the irradiations and the measurement

Based on the measurements performed, it can be stated, that the viscosity of the investigated materials has significantly changed due to the irradiations, thus the increase of viscosity has to be considered in case of long term application of the product, if it is used in high radiation environment.

Table 1: Relative viscosity change measured without shielding during the irradiation.

Sample	**Dose [kGy]**							
	0	**3**	**6**	**9**	**18**	**30**	**60**	**90**
1	1.0	1.7	-	6.0	-	n/a	n/a	n/a
2	1.0	1.2	-	2.3	19.1	n/a	n/a	n/a
3	1.0	1.3	1.6	1.9	6.6	n/a	n/a	n/a
4	1.0	1.2	-	1.8	4.3	29.5	n/a	n/a

n/a: After irradiation the viscosity was not measurable. The material became rubber-like, elastic, which has suffered elastic deformation instead of plastic deformation due to the 300 mm Hg of pressure. Formally the viscosity of the sample was higher than some MPoise

Remaining work

The project is finished.

Related publication

[1] J. Balog, Zs. Kerner, T. Pázmándi, R. Schiller: *Investigating of the viscosity change of high viscosity materials due to radiation*, AEKI-AT-2011-309-01/05 (2012)

RADIATION INDUCED MODIFICATION AND RADIATION RESISTANCE OF POLYMERS

Erzsébet Takács, László Wojnárovits,
Tamás Fekete

Objective

New polymeric materials can be produced with tailored properties by applying energy saving irradiation technologies. At the same time, these studies give important contribution to our understanding of the radiation resistance of polymers which is of essential importance for application of polymers in high-energy irradiation fields. The aim of this project was the high--energy radiation induced synthesis of natural polymer based hydrogels with good absorption properties.

Methods

Glycidyl methacrylate (GMA) was grafted onto cotton-cellulose. Two grafting techniques were applied. In pre-irradiation grafting (PIG), cellulose was irradiated in air and then immersed in the GMA monomer solution, whereas in simultaneous grafting (SG) cellulose was irradiated in an inert atmosphere in the presence of the monomer. The degree of grafting (DG) was determined by measuring the masses of dry samples before (w0) and after (wg) grafting: DG (%) = 100 (wg-w0)/w0. The samples were characterized by FTIR spectroscopy. SEM pictures were taken on gold-coated samples.

Results

Cotton-cellulose was functionalized using gamma-irradiation-induced grafting of glycidyl methacrylate (GMA) to obtain a hydrophobic cellulose derivative with epoxy groups suitable for further chemical modification. PIG led to a more homogeneous fiber surface, while SG resulted in higher DG but showed clear indications of some GMA-homopolymerization. Effects of the reaction parameters (grafting method, absorbed dose, monomer concentration, solvent composition) were evaluated by SEM, gravimetry (DG) and FTIR spectroscopy. Water uptake of the cellulose decreased, while adsorption of a pesticide molecule increased upon grafting. The adsorption was further enhanced by β-cyclodextrin immobilization during SG. This method can be applied to produce adsorbents from cellulose based agricultural wastes.

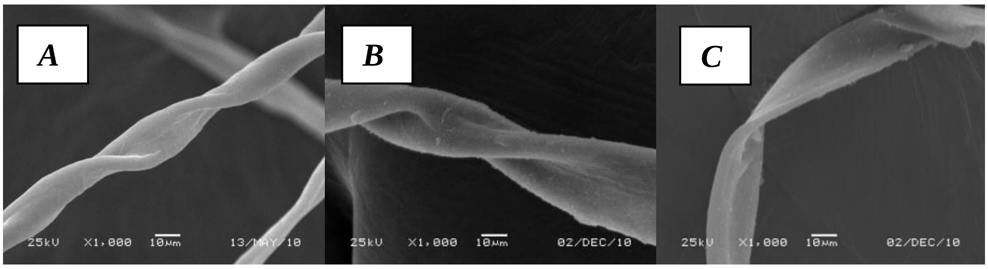


Figure 1: SEM photos of untreated cellulose fibres (A), and fibres SG grafted by GMA ~30% (B) and 72% (C)

Remaining work

As a continuation of the work, we intend to clarify the practical applicability of the synthesized polymers. The production of hydrogels with superabsorbent properties and their application for the removal of impurities in water are also planned.

Related publications

[1] E. Takács, L. Wojnárovits, É. Koczog Horváth, T. Fekete, J. Borsa: *Improvement of pesticide adsorption capacity of cellulose fibre by high-energy irradiation-initiated grafting of glycidyl methacrylate,* Radiation Physics and Chemistry **81,** 1389 (2012)

[2] T. Fekete, E. Takács, J. Borsa: *Szelektív adszorbens előállítása cellulózból nagy energiájú sugárzással iniciált ojtással,* Magyar Textiltechnika **LXV/4** 115 (2012)

[3] E. Takács, J. Borsa, T. Fekete, É. Koczog Horváth, L. Wojnárovits: *Radiation-induced grafting of cellulose for synthesis of absorbents and superabsorbents*, invited lecture, 10th Meeting of the Ionizing Radiation and Polymers Symposium IRaP'2012, 14-19 October, 2012, Krakow, Poland

[4] E. Takács, J. Borsa, T. Fekete: *Radiation-induced grafting of cellulose for synthesis of absorbents and superabsorbents*, International Joint Conference on Environmental and Light Industry Technologies, 21 – 22 November 2012, Óbuda University, Budapest, Hungary

DIGITAL GEOMETRY

Attila R. Imre

Objective

Analysis of size and shape of various patches embedded into two-dimensions is a common scientific problem. The patches can be islands, lakes, forest fragments, soil pores, corrosion patches, etc. The common way to analyze them is the application of some computer-assisted image analysis and the common results of these kinds of analysis are some size-distribution functions, very often a fractal dimension. Various fractal dimensions have been used to describe size- and shape-related properties of individual patches, as well as for sets of patches since the pioneering work of Mandelbrot. Although for a set of statistically similar patches one can use perimeter–area analysis for fractal analysis, this method requires the accurate knowledge of the areas and perimeters of the patches composing the landscape mosaic. It has been known for some time, that experimentally obtained perimeter values are problematic; for example they can be measured with much bigger errors than the corresponding area values. This can be explained quite well with the recently described violation of translational and rotational invariances in digital geometry. Due to the error propagations, all descriptors calculated from the perimeters – like for example the fractal dimension calculated by the perimeter–area relation – would have errors at least as big as the perimeter-measurement error. For this reason, one should find a method, which requires only the knowledge of the areas of the studied patches.

Results

In this project we introduced a proper method for Korcak analysis to obtain the correct Korcak-exponent. The Korcak-method is based on the number-distribution of objects, bigger than a variable limiting size. With improper analysis, one can easily obtain utterly artificial Korcak-exponents (see Fig. 1). A novel method was developed to choose bias-free limiting area set. It was also shown that the Korcak-exponent is not related to the Hausdorff fractal dimension of the individual patches – which is still a very popular spatial descriptor in ecology [2]. Therefore this exponent should not be handled as $D_f/2$ (D_f - fractal dimension), it should be handled as a non-fractal descriptor. The method's applicability for samples of ecological origin (lakes, forest fragments, etc.) has been already tested, showing promising results.

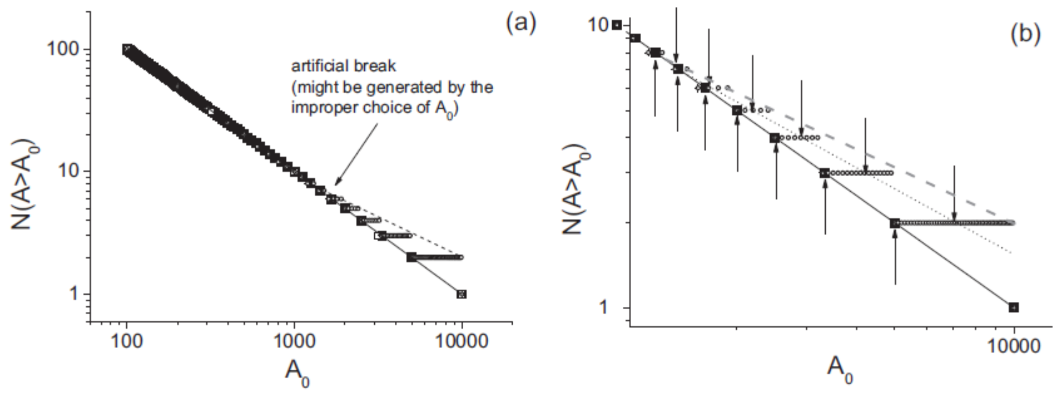


Figure 1: (a) Korcak-plots of an artificial data-set with different choices of limiting areas (A_0). (b) Magnification of the high-A_0 part. It can be seen that the choice of A_0-set influences the value of the exponent (slope).

Remaining work

A quantitative description for the translational and rotational invariance should be developed in the near future. Applicability of the Korcak-method on some relevant areas (corrosion patches, granular materials, etc.) should be tested. Also, some mathematical problems related to the Korcak-method should be solved.

Related publications

[1] Attila R. Imre, Josef Novotný and Duccio Rocchini: *The Korcak-exponent: a non-fractal descriptor for landscape patchiness*, Ecological Complexity, **12**(2012)70-74

[2] Duccio Rocchini, Niko Balkhenol, Luca Delucchi, Anne Ghisla, Heidi C. Hauffe, Attila R. Imre, Ferenc Jordán, Harini Nagendra, David Neale, Carlo Ricotta, Claudio Varotto, Cristiano Vernesi, Martin Wegmann, Thomas Wohlgemuth, Markus Neteler: *Spatial algorithms applied to landscape diversity estimate from remote sensing data,* Models of the Ecological Hierarchy: From Molecules to the Ecosphere (Eds.: Sven Erik Jorgensen and Ferenc Jordán), Elsevier, pp391-413 (2012)

PHASE EQUILIBRIA AND PHASE TRANSITIONS IN VARIOUS FLUIDS

Attila R. Imre, Imre F. Barna

Objective

The aim of this project was twofold: (i) to study the flow- and heat-transfer-related properties of supercritical water under circumstances relevant for Generation IV Supercritical Water-Cooler Reactors (SCWRs) [1,2] and (ii) to study the process of energy release during relaxation to stable phases from metastable, superheated water [3].

Results

Supercritical water is a promising working/cooling fluid for Generation IV nuclear power plant. Flow- and heat transport-related properties of supercritical water have to be known for the safe operation. Recent results suggest that the supercritical region is not homogeneous, a „liquid-like" and a „vapour-like" sub-region can be found. These regions are separated by the Widom-lines. At the Widom-line, a thermodynamic function should have inflection or extremum. In the immediate vicinity of the critical point, one can define one Widom-line, but at higher pressure, Widom-line(s) are diverging (see Fig. 1). Above 50 MPa, the extrema and inflections are so weak, that Widom lines cannot be defined any more. The exact location of the Widom-lines for water is important for thermal and hydraulic calculations, therefore – by using the IAPWS equation of state – several kinds of Widom-lines were determined [1].

Along the Widom-lines, properties can change drastically in a relatively narrow temperature or pressure range. For numerical calculations (i.e. for various thermohydraulic codes) the accuracy can be severely affected by these fast changes. To avoid artificial results, new methods (data tabulation, extrapolation, etc.) are needed; some methods were developed for this purpose [2].

In the sub-critical region, Widom-lines extended as stability lines, showing the limit of overheating. One can overheat water to an extreme extent; at ambient pressure, pure and undisturbed water can remain in metastable liquid phase up to 300 °Celsius! During the metastable-to-stable relaxation, extreme amount of energy can be released by an explosion-like boiling. Some conservative estimate has been done for the energy release [3], showing that during explosive boiling the energy release can be comparable to the energy release of the explosion of similar amount of TNT, although the relaxation process can be slower.

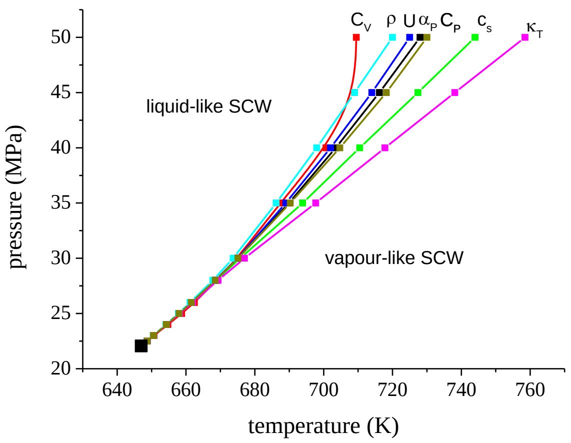


Figure 1: Various Widom lines (from 22.5 MPa to 50 MPa) and the critical points (black squares). C_V, ρ, U, α_P, C_P, c_S and κ_T are isochoric heat capacity, density, internal energy, isobaric thermal expansion, isobaric heat capacity, speed of sound and isothermal compressibility, respectively.

Remaining work

More realistic calculations are necessary for the energy release during explosive boiling. Concerning supercriticality, the model should be extended into an other relevant fluid, carbon-dioxide.

Related publications

[1] A. R. Imre and I. Tiselj: *Reduction of fluid property errors of various thermohydraulic codes for supercritical water systems*, Kerntechnik, (2012)18-24

[2] A. R. Imre, U.K. Deiters, T. Kraska and I. Tiselj: *The pseudocritical regions for supercritical water*, Nuclear Engineering & Design, 252(2012)179-183

[3] A. Imre and I.F. Barna: *Energy release during phase transition of superheated water*, OAH Report, OAH/NBI-ABA-18/12-M, 2012 (in Hungarian)

Developments on the Measurements of the Mobile Laboratory

Károly Bodor

Objective

The task of the Environmental Protection Service (EPS) is the continuous monitoring of radioactivity levels at the KFKI Campus and in the neighbouring areas. To satisfy this obligation, primarily in-situ gamma-spectrometry is applied. To improve the proficiency of this measurement type an intercomparison experiment was done between our in-situ gamma-spectrometry system and the laboratory of the Institute of Isotopes Ltd..

Another plan was in 2012 to prepare the compilation of the Cs-137 map of the KFKI Campus.

Methods

The in-situ gamma-spectrometry system was installed in the laboratory of the Institute of Isotopes Ltd. The two HPGe detectors were placed above each other, the in-situ detector was faced down and the other detector was faced up (Fig. 1)

Figure 1: Direction of the detectors

The background of the laboratory was measured with both detectors. The measuring time was 60 000 sec. After then a certified reference point source was placed on the horizontal half-line between the two detectors. The detector-source distance was equal from both detectors: 100 and 400 cm distances were applied. The relative efficiency of the in-situ and the fixed detectors are 22.2% and 10% respectively at 1333 keV energy.

To compile the Cs-137 map of the campus, soil samples were collected. To map the activity-distributions, the area of the campus were divided into equal sections. From this subdivisions, soil samples were taken by random sampling method (IAEA TECDOC 1415 Soil sampling for environmental contaminants). The samples were measured by the main gamma-spectrometry system of the EPS.

Results

The measured spectra were evaluated for both detectors. The average spectrum peak area ratio between the two detectors was about 2.04 as it was expected (Fig. 2) from the active volumes of the detectors. From the results it can be seen that the efficiency ratio is varying with the energy.

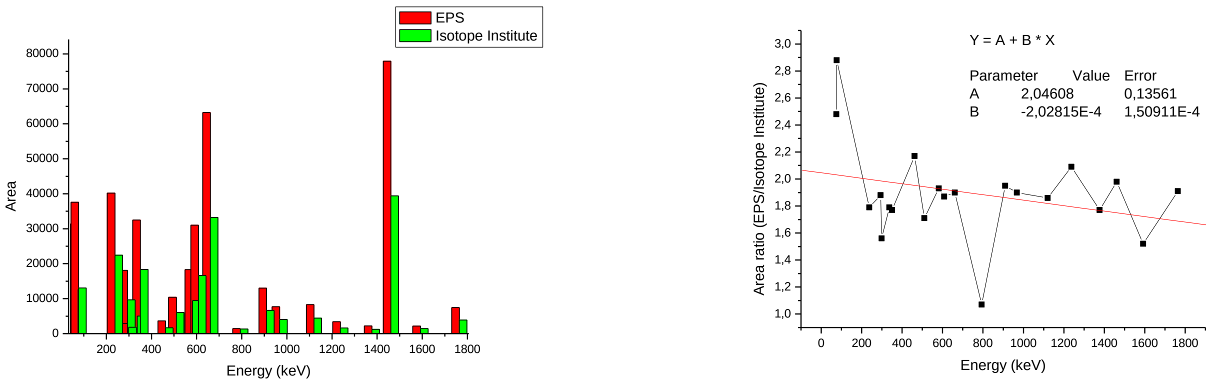


Figure 2: Spectrum peak area ratio of the detectors in function of the energy

Remaining work

To get further information about the detectors other comparison measurements are needed.

The spectra of the measured soil samples need evaluations. After the process the Cs-137 map will be created by the Surfer software.

IMPROVEMENT OF GAMMA-SPECTROMETRY AND ESTABLISHING OF A COMPREHENSIVE DATABASE AT THE EPS

András Kocsonya

Objective

Annually 500 gamma-spectroscopy analyses are performed at the Environmental Protection Service (EPS). The majority of these measurements are performed as a part of the regular environmental monitoring system of the KFKI campus. Beyond these routine measurements, great variety of occasional analytical problems are solved. The quality of environmental monitoring of the campus depends significantly on these analyses.

Methods

The EPS operates 4 fixed and shielded gamma-spectrometers in the laboratory. Additional devices related to gamma-spectrometry are the in-situ gamma-spectrometer, the detectors of the whole-body counter and the thyroid monitor. The operation, maintenance and calibration of these devices are tasks of the EPS.

The spectrum evaluation procedures are renewed for the routine types of analyses. The detection limits are determined for the regular analysis types. The analysis procedure is optimized for the measurement of aerosol filters of the "Reference"-station to obtain best detection limits. Soil, grass, fungus and moss sampling and measurement became regular parts of the environmental monitoring programme. Appropriate calibration and spectrum evaluation procedures were developed for these measurement types.

The comprehensive database of the gamma-spectrometry measurements done at the Environmental Protection Service is established which contains all spectra, their evaluations, the background and calibration spectra, calibrations etc. This database is stored on a new server computer. The installed and partly home-made computer codes provide the searching and multi-aspect filtering in analysis results.

The development and assembling of a new, portable aerosol sampler has been started. Due to technical difficulties this equipment is not ready yet. It is intended to be use for radiation monitoring of workplaces. This device will complement the aerosol sampler of the mobile laboratory, since indoor sites will be accessible with the new device.

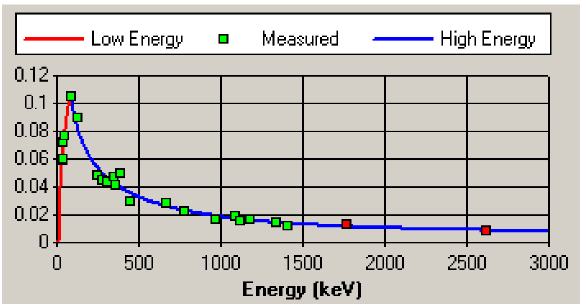
The accreditation procedure of the gamma-spectrometry laboratory is completed by the Hungarian Accreditation Board according to the MSZ EN ISO/IEC 17025:2005 criteria.

The EPS initiated a country-wide gamma-spectrometry intercomparison with the participation of 9 laboratories in order to improve the analytical skills and to exchange professional experiences.

Results

The energy and efficiency calibration of "B" and "D" detectors are extended down - to 30 keV energy. This opportunity allows of the correct determination of ^{125}I isotope, which is one of the key nuclides of the environmental monitoring of the KFKI campus. The necessary self-absorption correction procedure is also developed.

The calibration is extended toward higher energies as well. Using environmental samples containing ^{208}Tl and ^{214}Bi terrestrial radioisotopes, the energy and efficiency calibration of B detector is extended to 2614 keV. Since properly chosen environmental samples were used instead of certified radioactive sources, this extension was rather cost efficient.



Extended efficiency calibration of the B detector covering the 30 – 2614 keV energy range

In case of sophisticated spectra or ambiguous nuclide identification multiple or repeated measurements are performed on samples in question. The reasons of some erroneous nuclide identification (^{109}Cd, ^{85}Sr) of the applied gamma-analysis computer-codes are cleared. Spectrum analysis method was developed to improve the deconvolution of ^{226}Ra and ^{235}U gamma-emission lines.

Remaining work

The installation of mobile aerosol sampler should be finished soon. The on-line uploading of spectra should be improved. The implementation of new functions depends on the planned moving of the Service.

Research article should be written about the improvements of nuclide identification, and line deconvolution.

Related publications

[1] A. Kocsonya: *Gamma-spectrometry on samples prepared for trace element analysis proficiency tests*, poster at the 13th International Symposium on Biological and Environmental Reference Materials (BERM-13)

[2] A. Kocsonya: *Application of methods and experiences of X-ray emission spectrometry on the evaluation of low-energy range of gamma spectra,* poster at the European Conference of X-ray Spectrometry (EXRS)

Redox and Sorption Processes Influencing Long Time Migration of Radionuclides in Boda Claystone Samples

Károly Lázár, János Megyeri

Objective

The work performed was the finishing part of the participation in the EUFP7 EURATOM ReCosy (Redox Controlled System) Collaborative Project in a consortium with 32 partners. Support was also obtained from a twin Hungarian project (BONUS-HU_08 – ReCosy II) which had provided co-funding directly for participation in the basic project. The principal target of the EU project was to reveal the role of redox processes which may influence the migration processes of long half life radionuclides in various rocks. The results obtained in the project are intended to be utilized primarily in construction of deposition sites for high level nuclear wastes.

The contribution of the of the IKI-team to the project was the evaluation and characterization of redox processes in Boda Claystone samples related to migration of long life time anionic ($^{99}TcO_4^-$) and cationic (UO_2^{2+}) waste components. In particular, the aim of the participation in the last year was to reveal whether the $UO_2^{2+}{}_{solution} \Leftrightarrow UO_2{}_{solid\ precipitaion}$ reduction process in the solution could be coupled with a simultaneous $Fe^{2+} \Leftrightarrow Fe^{3+}$ oxidation taking place in the clay minerals of the rock.

Methods

Three methods were principally applied. For determination of the migration rate the so called break-through cells were applied. In this simple arrangement two compartments are separated by a 8 mm thick borecore disc made of claystone sample, the break-through of the radionuclide was detected from dilute solution from one side of the sample to the opposite one where the concentration increase of the radionuclide can be monitored by regular sampling. The time span of the whole experiment was long – ca. 5 years [1]. The distribution of the uranium in the borecore samples was determined by laser ablation ICP-MS (Inductively coupled plasma mass spectrometry) technique at the end of the experiments. The Fe^{2+}/Fe^{3+} ratio in the clay minerals was determined by Mössbauer spectroscopy in both sides of the rock sample before and after the experiments [1].

Results

No break-through of UO_2^{2+} cations was detected in the probe cells during considerably long (~ 5 years) time span of measurements. (In contrast, it can be mentioned for comparison that detectable break-through can be observed for anionic $^{99}TcO_4^-$ component already in the first 20 – 30 days [2]). Distribution of 235 and 238 uranium isotopes in direction of the expected migration path are shown in Figure 1. The decrease of the concetration is exponential (linear as shown in the logarithmic scale in Figure 1), and the longest migration path reached is ca. 4 mm.

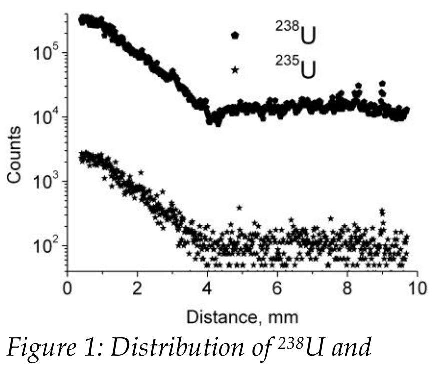


Figure 1: Distribution of ^{238}U and ^{235}U in the bore core sample after ca. 5 years of exposure to uranyl acetate solution

From these data a rough estimation can be done for the effecive diffusion coefficient, which provides $D_{eff} \approx 10^{-13}\ m^2s^{-1}$ value [2]. The shapes of all the Mössbauer spectra were similar, regardless whether the samples were collected before or after the experiments from the surface layers either from the side exposed to uranium solution or from the non-exposed side of the bore core disc. Thus, it means that $Fe^{2+} \rightarrow Fe^{3+}$ oxidation was not involved in the strong sorption of uranium, it can be explained only with chemisorption processes.

It can also be mentioned that a summarizing chapter in a related book was also prepared in which basic aspects of utilization of claystones as storage media for high level nuclear wastes are discussed by comparing the properties of Callovo-Oxfordian (in France) the Opalinus (in Switzerland) and Boda (in Hungary) claystones, and a compilation of detailed geological description with experimental results collected in various EU projects on Boda claystone are also included [2].

Related publications

[1] K. Lázár, Z. Máthé, J. Megyeri, É. Széles, Z. Mácsik, J. Suksi: *Redox properties of clay minerals and sorption of uranyl species on Boda Claystone,* in: 4th Annual Workshop Proceedings of the Collaborative Project "Redox Phenomena Controlling Systems" (FP7 RECOSY), ed. M. Altmayer, B. Kienzler et al., KIT Scientific Reports **7626**, 231-239 (2012)

[2] K. Lázár, Z. Máthé: *Claystone as a potential host rock for nuclear waste storage*, Chapter 4, in: Clay Minerals in Nature - Their Characterization, Modification and Application, ed. M. Valaskova, Intech, 55-80 (2012), (open access on the www.intechopen.com/books/clay-minerals-in-nature-their-characterization-modification-and-application page).

SOLVATED ELECTRONS IN NORMAL AND SUPERCRITICAL FLUIDS

Robert Schiller and Ákos Horváth

Objective

The aim of the present theoretical work was to offer a quantitative understanding of the solvated electron yields observed in normal and supercritical water and ammonia. Beyond basic interest, the results might have some relevance to the future technology of supercritical nuclear reactors.

Methods

An ion-electron pair model was constructed: the pairs of charge carriers, embedded in the completely relaxed fluid, were considered as Rydberg atoms. Electron escape was thought to be effected by energy fluctuations of the medium. The probability of electron escape was evaluated and compared with experimental data.

Results

The escape probability P_{esc}, was expressed on the basis of the above model by the function $P_{esc} = (1/2)\left[1 - erf\left(\sqrt{2}a \Big/ T\varepsilon_s^2 \sqrt{C_v^m}\right)\right]$ and was compared with the experimental survival probability as $\Omega = AP_{esc} + (1 - A)$. Here A is a fitting parameter, a is related to the Rydberg energy, T, ε_s and C_v^m denote absolute temperature, static dielectric constant and constant volume molar heat capacity, respectively [1],[2]. The results are given in Figs.1. and 2.

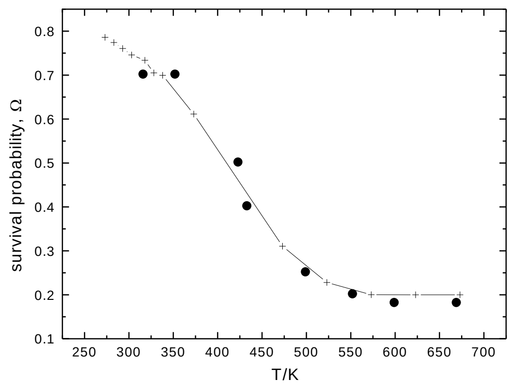


Figure 1: Survival probability of solvated electrons in water as a function of temperature ● Experimental points (Kratz et al., 2010)

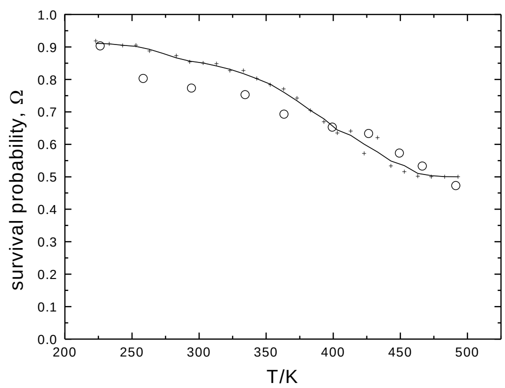


Figure 2: Survival probability of solvated electrons in ammonia as a function of temperature O Experimental points (Urbanek et al., 2012)

Remaining work

A crucial point of the model is the role of the molar heat capacity in the escape process, a parameter not featuring in any of similar theories. This problem must be investigated in more detail together with a thermodynamic description of the chemical details of recombination.

Related publications

[1] R. Schiller and Á. Horváth: *Hydrated electron yields in liquid and supercritical water – a theory*, Radiat. Phys. Chem. **81**, 1291-1293 (2012)

[2] R. Schiller and Á. Horváth: *Solvated electron yields in liquid and supercritical ammonia – a statistical mechanical treatment*, J. Chem. Phys. 137, 214501-1-3 (2012)

TIME-DEPENDENT SELF-SIMILAR SOLUTIONS OF THE NON-LINEAR MAXWELL EQUATIONS

Barna Imre Ferenc

Objective

In our recent study we investigate the non-linear Maxwell equation obtained with the help of the non-linear field-dependent constitutive equations and look for shock-wave like solutions with compact supports.

Methods

Wave propagation in non-linear media is a fascinating field in physics. To study such effects, various non-linear partial differential equations(PDEs) have to be investigated with various methods. One of the most powerful analytical tool is to apply the self-similar Ansatz which may describe dispersive solutions with reasonable physical interpretation. The validity of such solutions is very wide in continuum mechanics and mostly used to study shock-waves and other fluid dynamical problems. We used this Ansatz formerly for heat conduction and for viscous fluid flow problems [1,2].

Results

It is well-known that from the four Maxwell field equations combined with the two constitutive relations a linear second-order hyperbolical wave equation can be derived for the field variables. In such cases the constitutive equations contain only linear relations for the electrical permittivity and for the magnetic permeability.

In our study we consider nonlinear, power-law field-dependent constitutive relations like $\varepsilon = E^r$ and μ= const.,

where ε is the electrical permittivity and E is the electrical field.

Inserting this two relations into the last two time-dependent Maxwell equations we arrive to a coupled non-linear hyperbolic partial differential equation PDE system. Such systems conserve non-continuous initial conditions describing electromagnetic shock-waves. Inserting the self-similar Ansatz into this PDE system a nonlinear first order ordinary differential equation can be derived which can be analyzed with different methods. We found that for $r > -1/2$ there are continuous solutions available, however for for $r \le 1/2$ there are solutions which have a compact support and a finite jump at the end points. We hope that such kind of waves will exist in dense plasmas which will be available to excite with the ELI laser facility in Szeged in a decade. Our results were presented in various conferences [3,4].

Remaining work

The most general case has still to be investigated and the results have to be published.

Related publications

[1] I.F. Barna and R. Kersner: *Heat conduction: a telegraph-type model with self-similar behavior of solutions*, J. Phys. A: Math. Theor. 43, (2010) 375210

[2] I.F. Barna: *Self-similar solutions of the three dimensional Navier-Stokes equation*, Communication in Theoretical Physics 56, (2011) 745

[3] HPLA International High-Power Laser Ablation Conference, USA, Santa-Fe, 30 of April – 3 May 2012, 15 Section: High Power Lasers, Applications and Diagnostics, http://www.usasymposium.com/hpla/documents/2012%20HPLA%20Speaker%20Instructions.pdf

[4] 15th Conference on Laser Optics, Russia St Petersburg June 25 – 29 2012, Section: Super-intense light fields and ultra-fast processes, Nr.of the Talk: 0171

RETENTION MECHANISMS OF U(VI) IN BODA CLAYSTONE FORMATION AS THE CANDIDATE HOST ROCK OF HIGH ACTIVITY AND LONG-LIVED NUCLEAR WASTE REPOSITORY IN HUNGARY

Dániel Breitner, János Osán, Szabina Török

Objective

The argillaceous rock formations due to their high clay content and low permeability have significant radionuclide retention/retardation capacity, therefore, these rock types are in the focus of high level and long-lived nuclear waste (HLW) repository management in several countries. Such formations are Opalinus clay in Switzerland, Boom and Ypresian clays in Belgium, Callovo-Oxfordian and Toarcian clays in France. In Hungary the Boda Claystone Formation (BCF) has been defined as the potentially suitable host rock of HLW. One of the major aspects in evaluating the long-term safety of a potential radioactive waste repository in a deep geological formation is to understand the geochemical and physical processes that influence the mobility of the radionuclides in the deep geoenvironment imposed by the host rock and to quantify these processes. Among several important radionuclides, which can be accidently released from the wastes and technical barriers toward the natural barrier, uranium nuclides are some of the most important materials due to their long half-life and abundance in HLW. The present study deals with the identification of U(VI) uptake mechanism on the micrometer scale in two samples from the mineralogically different blocks (i.e. Gorica and W-Mecsek Anticline (WMA) Blocks) of BCF as a potential host rock of HLW repository, and the major objective is to understand such geochemical processes, which affect the retardation capacity of BCF and provide additional information for the site selection.

Methods

From two core samples (Ib-4 and D-11, representative for the Gorica and WMA Blocks, respectively) pure Si wafer-mounted thin sections (ca. 50 µm and 1 cm^2) were prepared. The thin sections were exposed for 72-hour to a U(VI) containing solution (2×10^{-6} M) at pH 6.8 having an ionic strength similar to that of the pore water of the host rock (0.1 M NaCl solution). The spatial distribution of U on the treated thin sections was measured using micro-XRF (X-ray fluorescence) at the FLUO beamline at the ANKA storage ring (Karlsruhe, Germany). Micro-XRF maps were recorded from pre-selected areas of the samples such as clayey matrix and fracture- and vug-fillings, using a step size of 5 µm and 4 to 10 s counting time per pixel. Elemental distribution maps were formed for the U and for the major and minor elements of the rock (e.g. K, Ca, Fe) using the resulting net characteristic X-ray intensities. The mineralogy and structural characterization of the areas selected was studied using Nikon Eclipse E600 Pol polarization microscope and FEI Quanta 3D scanning electron microscope (SEM) at Eötvös University Budapest, Hungary. In order to preserve the vacuum-sensitive clay fraction for further analyses, the SEM was operated at 110 Pa H_2O atmosphere at low vacuum mode. Energy-dispersive X-ray (EDX) microanalysis was performed using a 20 kV accelerating voltage in order to excite the L3 edge of uranium.

Results

Based on the micro-XRF mapping performed on the selected areas, the spatial distribution of U in sample D-11, derived from WMA Block, is different from that of Ib-4 sample collected from Gorica Block (Figure 1). On the sample Ib-4, where a calcite, dolomite and analcime filled fracture and clayey matrix were studied, U distribution shows strong relation with K and Fe. In contrast, on the sample D-11 where a K-feldspar, albite, calcite and ankerite rimmed dolomite filled fracture and the adjacent argillaceous matrix was selected for the mapping, the U(VI) uptake onto the Fe and K rich clayey matrix is less significant, however, around the dolomite rhombohedra with ankerite rim U- and Fe-rich rings formed.

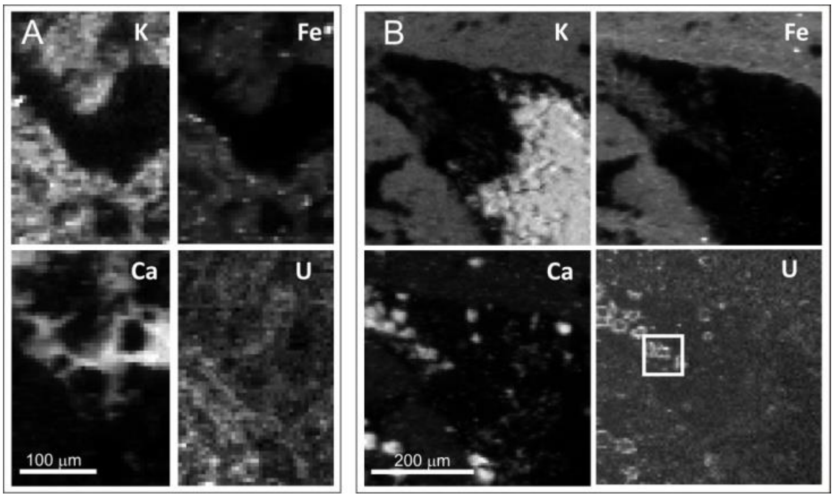


Figure 1: SR micro-XRF maps of K., Fe, Ca and U in the areas marked by black rectangle on Fig. 3 in sample Ib-4 from Gorfica Block (A) and D-11 from WMA Block (B). The white rectangle shows the area where scanning electron microscopy was performed.

In the sample D-11 (WMA Block) where U- and Fe-rich rims were formed replacing ankerite rims, the polarization microscopic study revealed that these newly formed phases are 2-10 microns thick and have reddish colour under reflected light (Figure 2c). On the scanning electron microscopic images it can be seen that the newly formed rim has spongy structure, which indicates formation of acicular or lens-shaped precipitation (Figure 2d). The reddish colour, the local maximum of Fe intensity, furthermore the acicular shape of the newly formed phase indicate secondary FeOOH formation.

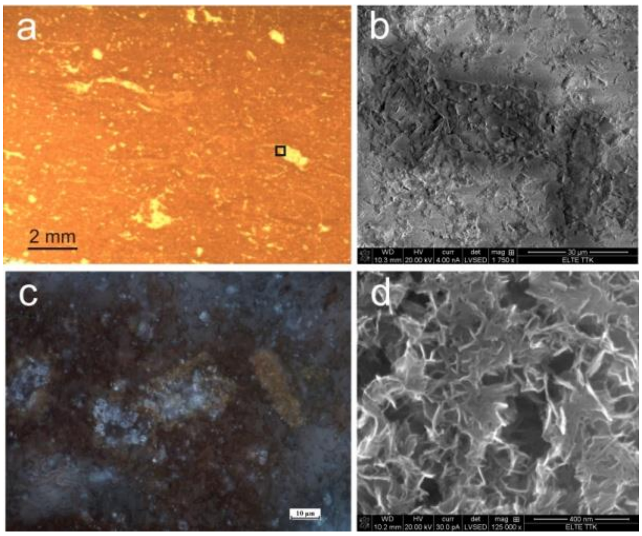


Figure 2: Microscopic image (reflected light) of BCF sample D-11 from WMA Block (a) the area studied marked by black rectangle. The secondary electron images (b and d) show spongy structured mineralization formed around and on ankerite octahedra. The reddish colour of the newly formed rim on microscopic image (c) (reflected light) indicate newly formed FeOOH minerals

Although, in the sample Ib-4 (Gorica Block) the vug and veinlet infilling calcite and Fe-bearing dolomite (Figure 3a and b) are affected by leaching as it is indicated by the corroded surface (Figure 3c), no spongy structured rims were formed in contrast to the sample D-11.

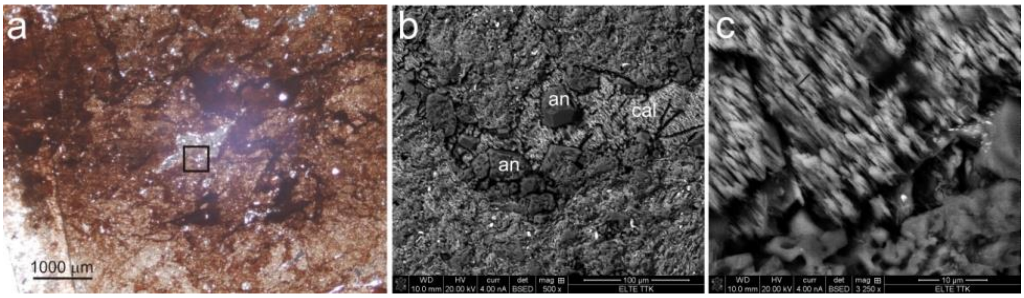


Figure 3: Microscopic (a) and back scattered electron images (b and c) of analcime (an) and calcite (cal) filled veinlet in BCF sample Ib-4 from Gorica Block

The proportion of the newly formed phase in U(VI) uptake was calculated based on the distribution of the U-Lα X-ray intensities (*I*) over the area selected on sample D-11 (Figure 1B). The measured distribution was plotted in equidistant intervals in log *I*, since lognormal distribution of X-ray intensities was assumed for the U(VI) uptake by both the clayey matrix and the U-rich rings. The fit of the measured distribution using two lognormal distributions represents the uptake by the clayey matrix (peaking at $\log I = 0.475$) and by the U-rich rings (peaking at $\log I = 1.089$). The contribution of the U-rich rings in the total U content of the selected area was calculated using the integral of the fitted distributions. Based on the calculations, these newly formed phases are responsible for 25 % of the total U(VI) uptake.

Remaining work

The uptake of Cs(I), Nd(III) and Th(IV) representing fission products and actinides in HLW is also planned to be studied on polished sections of BCF.

Acknowledgement

The research leading to these results has received funding from the Swiss-Hungarian Cooperation Programme through Project n° SH/7/2/11. We acknowledge the Synchrotron Light Source ANKA for provision of instruments at beamline FLUO. The courtesy of the Public Limited Company for Radioactive Waste Management (PURAM, Hungary) for providing the samples for analysis is also appreciated.

Related publication

[1] D. Breitner, J. Osán, M. Fábián, Cs. Szabó, R. Dähn, M. Marques, I. Sajó, Z. Máthé, and Sz. Török, *Applied Geochemistry*, submitted (2013)

V. INTERNATIONAL ACTIVITIES

AER (ATOMIC ENERGY RESEARCH)

István Vidovszky

AER is a loose organization of 22 institutions (utilities and research institutes) from eight countries. AER provides the only regular scientific-technical co-operation for the VVER user countries. The main activities of AER are the yearly organized symposia, where usually 70 - 80 experts meet. In 2012 the Symposium was organized in Průhonice, Czech Republic, 1 – 5 October. The participants presented 63 papers, published in the proceedings. Recently, selected symposium presentations have been sent to the journal Kerntechnik for presentation. Kerntechnik offers a special issue annually for AER papers.

Important part of the work is conducted in seven working groups. The working groups deal with the following topics: a. Improvement, extension and validation of parametrized few-group diffusion libraries for VVER-440 and VVER-1000, b. Core design (advanced fuel cycles, code validation), c. Core monitoring (flux reconstruction, in-core measurements), d. VVER reactor safety analysis, e. Physical problems on spent fuel, radioactive waste and decommissioning of nuclear power plants, f. Spent fuel transmutations, g. Thermal hydraulics. Working groups usually organize yearly meetings for the participating experts, where the details of work are discussed.

The organization of AER is performed by a secretariat, based in the Hungarian Academy of Sciences Centre for Energy Research. The secretariat organizes a yearly meeting for making organizational and financial decisions. In these meetings every participating organization is authorized to be represented.

BUDAPEST NEUTRON CENTRE

Rózsa Baranyai, Mihály Makai

The role of the Budapest Neutron Centre (BNC) is to coordinate the reactor utilization and to provide scientific infrastructure for the international user community. BNC maintains its access programme; instruments are offered through the international user programme. BNC participates in several EU supported programmes like NMI3 (Integrated Infrastructure Initiative for Neutron Scattering and Muon Spectroscopy), CHARISMA (Cultural Heritage Advanced Research Infrastructures: Synergy for a Multidisciplinary Approach to Conservation/Restoration) and ERINDA (European Research Infrastructures for Nuclear Data Applications). Scientists who want to get access to BNC's instrumentations are requested to submit proposals. Information on the application procedure can be found on the BNC web page. Beam time applications are evaluated and ranked by the International Selection Panel. In special cases "urgent beam time application" is also possible.

The NMI3-I project was completed in 2012. During the 4 years projects, BNC had delivered 205 beam days to the EU eligible users, which is two times more than the NMI3 funded days. These numbers reflect the high demand of neutron beam access in Europe. The 11 projects were carried out by 11 scientists. All were supported by the NMI3 travel and subsistence (T&S) fund. Our NMI3 budget allows supporting only one user per experiment. 82% of users came from the CE region (CZ, SK, RO, BG) which again confirms BNC's regional role. The majority of the projects covered the field of material sciences.

An international board called International Scientific Advisory Committee (ISAC) assists BNC's work mainly in strategic issues. ISAC had an annual meeting on the 16th-17th November, 2012. On the meeting the members were informed about the reorganization of the Hungarian research institute network, the progress of the BNC instrument developments (In-beam Mössbauer spectrometer, FSANS and GINA instruments), and the research reactor fuel issues.

As a satellite event of ISAC meeting the 4th User Meeting was organized. Among the 13 presentations there were 6 user presentations, the others were given by the local scientist.

We would like to publicize the neutron research among the young scientists and university students. The 80th anniversary of the neutron discovery gave a good opportunity for this purpose. A so called "Neutron80" day was organized at the Eötvös Lóránd University, where the neutron methods and research were introduced to the university and Ph.D. students.

NULIFE NETWORK OF EXCELLENCE

Ferenc Gillemot

Objective

NULIFE was a Network of Excellence and not a research project. The purpose of NULIFE was to enhance the integration and to initiate a stand alone network (financially not supported by the EU) and to coordinate the European research on the field of the lifetime of nuclear power plant, material ageing.

Methods

NULIFE was active in three fields:

Elaboration of a virtual European institute dealing with the ageing and lifetime of the existing and GEN3 (3[d] generation) nuclear power plants. The members of this institute are EU research organisations, NPP-s, regulatory bodies, universities. The integration plan is shown in Figure 1.

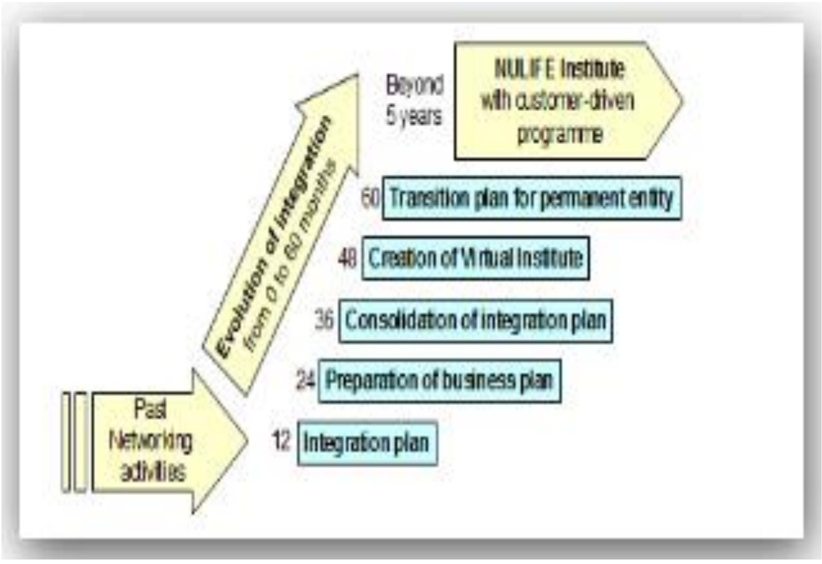


Figure 1: Preparation plan of the NULIFE institute

Co-ordinating and harmonisation of the research on the relevant fields, collecting proposals, evaluation and developping them, forming consortium to perform the research and organisation of dissemination of the results.

Elaboration of studies on the relevant topics, initiate and conduct so called pilot projects on ageing of NPP structures.

Results

The virtual institute has been founded and named NUGENIA. NUGENIA included the members of the NULIFE network,

the AMES, NESC, SARNET networks and the GEN2, GEN3 working groups. NUGENIA started the life at the 2012 March meeting in Budapest, when the NULIFE project and network was finished. The second NUGENIA meeting was also held in Budapest in March 2013.

AEKI (later MTA EK) participated in several working groups, elaboration of pilot projects and studies on ageing.

NULIFE organised FP7 projects where AEKI (MTA EK) became member of the consortium and performed ageing and structural integrity research. The two main ongoing project where the institute has been participating were the LONGLIFE and the STYLE projects.

AEKI initiated 3 project proposals (Harmony, STAR and VALUE) and participated in the elaboration of others (POLYLIFE etc:) in the pilot studies, and prepared a study on RPV cladding,

Remaining work

The NULIFE project finished in March 2012.

Related publication

[1] Ferenc Gillemot: *Overview of Reactor Pressure Vessel Cladding*, Int. J. Nuclear Knowledge Management 2010

VI. NUCLEAR SECURITY, NON PROLIFERATION

APPLICABILITY OF THE INFRARED RADIOPHOTOLUMINESCENT SIGNAL OF THE SUNNA DOSIMETER FOR RADIATION PROCESSING DOSE CONTROL

A. Kovács, A. Kelemen, D. Mesterházy, I. Slezsák, S. Miller, M. Murphy**

Objective

Imperfections are produced by ionizing radiation within the ionic lattice of alkali-halide compounds (e.g. LiF). These defects are known as colour centres to absorb and re-release energy in the form of light photons of characteristic wavelengths. The measurement of radiophotoluminescent light (RPL) for dosimetry purposes in radiation processing applications is a promising technique for validation and process control. In the case of the Sunna photofluorescent dosimeter the M center fluorescence can be measured and this dosimeter has already been proven suitable for dose control in the range of 1 - 200 kGy by measuring the green fluorescent signal. There is, however, an increasing need for the use of routine dosimeters capable of measuring doses below 1 kGy. The aim of the present work was to study the use of the Sunna film below 1 kGy by measuring the infrared (IR) luminescent signal and its dosimetry characteristics including post irradiation stability.

Methods

The Sunna film is a composite dosimeter consisting of polyethylene and LiF fine powder manufactured by injection molding. The analysis of the irradiated dosimeter films was carried out by measuring the infrared radiophotoluminescent light using a simple programmable table-top fluorimeter (FR-2141, Sensolab, Göd, Hungary) specifically designed for this type of Sunna film and for IR evaluation. The excitation of the irradiated films was performed at 450 nm using a blue LED, while the measurement of the resulting infrared emission was measured at 1040 nm with a solid-state Ga-As detector. The net RPL value was then related to absorbed dose by means of a calibration function stored in the memory of the reader. Gamma irradiations of the Sunna dosimeters were performed with the pilot-scale ^{60}Co gamma irradiation facility (nominal activity: 3 PBq) of the Institute of Isotopes Co. Ltd in the dose range of 50 Gy – 20 kGy (dose-rate range: 0.1 – 10 kGy/h). Post irradiation stability of the films was studied in short and longer term in the same dose range.

Results

The results indicate that the infrared signal of the gamma irradiated Sunna dosimeters, measured with the new IR fluorimeter, provides a broad dose response (50 Gy – 20 kGy). The calibration curve in the dose range of 50 – 1000 Gy is shown in Fig. 1. Suitable reproducibility (+/- 3% at 1 σ), in the whole dose range studied, was observed. The effect of dose rate on the response of the dosimeter films showed no significant difference in the 0.1 – 6.3 kGy/h range. The post irradiation stability of the dosimeter films was investigated from measurements carried out immediately after irradiation up to one month, and an approximately 10 % increase in the response was observed in the first 2 days after irradiation. A post irradiation heat treatment (70 °C, 10 minutes) stabilized the response due to the stabilization of the shallow charge carrier traps. Based on the results achieved the Sunna dosimeter, using the IR evaluation, looks suitable for dose control especially in blood and food irradiation, and in environmental technologies.

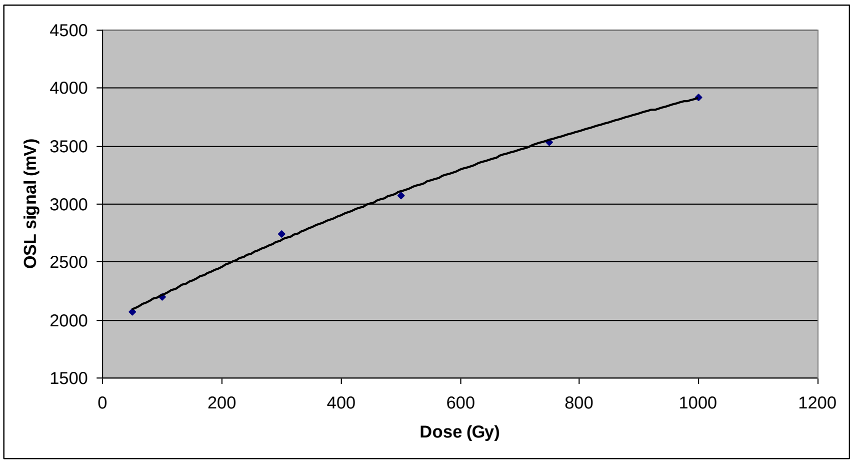


Figure 1: Calibration curve of the Sunna dosimeter using IR evaluation

Remaining work

Some more tests to establish the lowest measurable doses (below 50 Gy), need to be finished followed by the completion of a manuscript to be sent for publication.

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DEVELOPMENT OF NEW MATERIALS AND MEASURING METHODS IN LUMINESCENCE DOSIMETRY

András Kelemen, Dávid Mesterházy, András Kovács

Objective

Luminescent materials are widely used in the field of dosimetry. Special tasks need special measuring methods and at the same time special detector materials that are suited for them. Tissue equivalency of the detector material is required in the personal and clinical dosimety. Differently doped lithium teraborates (LTB) are promising candidates. Having synthesized the materials (LTB:Cu, LTB:Mn, LTB:Ag), the first step was the determination of their basic luminescent and dosimetric properties.

New $CaSO_4$ materials doped with Tm or Dy and codoped with Cu in both cases show favorable wide dose range properties. Application of Cu results in a larger linear dose-response range, a better glow curve structure, but at the same time a reduced sensitivity.

Finding common objects containing materials that make possible a post-event dose estimation after an accident or a terror attack, using special evaluation method is the most important challenge of retrospective dosimetry. Surface mounted (SM) resistors that are components of the modern electronic devices have a ceramic base consisting mainly of Al_2O_3. This material shows proper luminescent properties giving this way possibility for the dose estimation.

Methods

Having synthesized the materials (LTB:Cu, LTB:Mn, LTB:Ag), the first step was the determination of their basic luminescent and dosimetric properties. Photoluminescence, radioluminescence, optical absorption measurements were applied. Thermoluminescence (TL) and (with the help of an Italian research group) spectrally resolved TL measurements were also carried out.

Using consecutive RL/TL measuring techniques developed in the Institute we measured the trapping efficiency of the $CaSO_4$:Tm,Cu samples as the function of the amount of the dopants.

Both TL and optically stimulated luminescence (OSL) seemed to be suitable for measuring the luminescence response to irradiation.

Results

Spectrally resolved TL of non-doped and Ag, Cu and Mn-doped LTB single crystals revealed that TL emission bands for differently doped samples proved to be at different wavelengths: 272, 370 and 608 nm, respectively. These bands perfectly agree with the photoluminescence (PL) emission bands of Ag^+, Cu^+ and Mn^{2+} ions. This supports our suggestion that these dopants are directly involved as recombination centres in the TL process.

Cu addition, depending on its amount, reduced the trapping efficiency of $CaSO_4$:Tm,Cu samples. This may play the main role in the sensitivity loss and form one of the factors in the explanation of the linear dose range widening.

Both TL and OSL measurements verified, that SM resistors of different types show definite dose dependence in a large range (100 mGy – 30 Gy) with nearly linear response at low doses. The TL glow curves may differ a little bit depending on the special type of the resistors but all of them contain the so called dosimetry peak.

Remaining work

LTB materials: dependence of the properties on the concentrations of dopants.

$CaSO_4$ materials: sample preparation with new method using solid state reactions, characterization of the new samples.

SM resistors: detailed investigations of the fading properties in order to work out the dose estimation calculation procedure.

Related publications

[1] M. Ignatovych, M. Fasoli and A. Kelemen: *Thermoluminescence study of Cu, Ag and Mn doped lithium tetraborate single crystals and glasses*, Radiat. Phys. Chem. **81**(9), 1528 (2012)

[2] A. Kelemen, D. Mesterházy, M. Ignatovych and V. Holovey: *Thermoluminescence characterization of newly developed Cu-doped lithium tetraborate materials,* Radiat. Phys. Chem. **81**(9), 1533 (2012)

[3] D. Mesterházy, M. Osvay, A. Kovács and A. Kelemen: *Accidental and retrospective dosimetry using TL method,* Radiat. Phys. Chem. **81**(9), 1525 (2012)

[4] A. Kelemen, I. Kása, P. Mell and D. Mesterházy: *Effect of the Cu co-activator on the charge-carrier trapping efficiency in $CaSO_4$:Tm,Cu,* submitted for publication to Radiat. Meas. (2013)

ANALYSIS OF SAFEGUARDS SWIPE SAMPLES COLLECTED DURING VERIFICATIONS BY ICP-MS TECHNIQUE

Éva Kovács-Széles, Kornél Fél

Objective

The main objective of the study was to analyze safeguards swipe samples collected during official verification by inspectors of Hungarian Atomic Energy Authority.

Methods

International safeguards have been applied for about 30 years to verify that nuclear materials declared by the Member States to the International Atomic Energy Agency (IAEA) are used for peaceful purposes only. States in 1995 adopted measures for a strengthened safeguards system that authorize and equip inspectors to assure that any undeclared nuclear activities would not be overlooked. One of the principal strengthening measures studied under this programme was the use of environmental sampling and analysis to detect nuclear signatures which might reveal undeclared activities. The most effective sampling type is swipe samples. A large amount of information can be obtained from the small amount of material collected in one sample that inspectors swipe on a 10 x 10 cm piece of cotton cloth. Bulk analysis of swipe samples gives information about the average concentration and isotopic composition of uranium and plutonium in the whole sample.

A rapid, robust and simple sample preparation method was applied for the determination of plutonium and uranium isotope ratios in safeguards swipe samples by ICP-MS (Inductively coupled plasma mass spectrometry). The sample preparation procedure based on low power microwave digestion, easy and fast extraction chromatographic technique for separation of uranium and plutonium from the sample matrix and each other, and preconcentration of the fractions before the instrumental analysis. The schematic diagram of the sample preparation is shown in Figure 1.

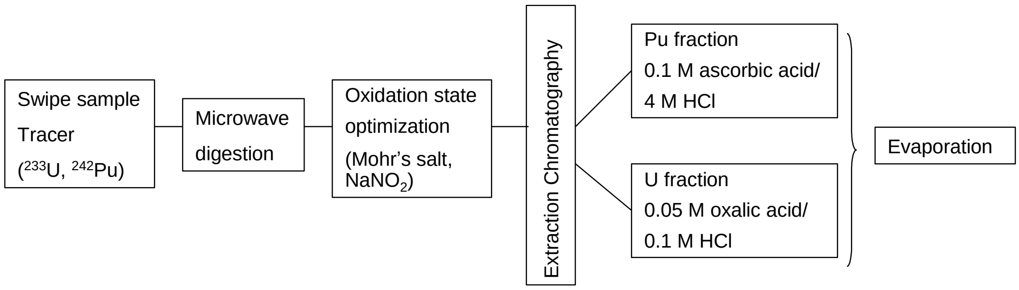


Figure 1: Schematics of sample preparation

For ICP-MS analysis, bracketing method was used for real and correct blank and mass bias correction. More certified reference materials (IRMM-187, IRMM-184 isotopic standards) were used for checking of the measurements. Samples were analyzed in tree repetition.

Results

During the official verification six different facilities were inspected in Hungary. 30 different swipe samples were collected, analyzed and evaluated.

As the analytical results, natural uranium composition was found in the samples in most of the cases without any plutonium traces. Different from natural uranium was found in the case of 3 facilities. Uranium was presented in low enriched, highly enriched and depleted composition on the swipe samples. Plutonium results showed similarities: samples which contained uranium in not natural form also contained plutonium in higher concentration.

Remaining work

Further sampling and analysis is required for re-verification of facilities.

CALORIMETRY, NEUTRON COUNTING, RADIOGRAPHY AND MCNP SIMULATION FOR CHARACTERIZATION OF PUBE NEUTRON SOURCES

János Bagi , László Lakosi, Cong Tam Nguyen

Objective

In order to support and refine in-field NDA (non-destructive assay) methods developed for the assay of PuBe (Plutonium-Beryllium) sources, a complex measurement campaign consisting of calorimetry, neutron counting, gamma spectrometry and radiography was carried out. The objective of this work was to determine the individual (α,n) conversion factors for all Pu isotopes and ^{241}Am present in PuBe sources, to clear the role of secondary reactions occurring in such sources, to determine their contribution to the neutron output and to reveal the inner structure of such sources.

Methods

The plutonium isotopes and ^{241}Am emit α-particles with different energy and intensity, which are slowing down in the material losing their energy by elastic scattering and producing neutrons in parallel. The cross section of (α,n) reaction is a sensitive function of alpha energy and the number of neutrons produced by alpha particles depends on their initial alpha energy and the stopping power of the material. Therefore the (α,n) conversion factor, i. e. , the number of neutrons per alpha particles needed for the calculation of Pu mass of the source, is different for each Pu isotope and ^{241}Am. These conversion factors have been both calculated theoretically and determined empirically.

A series of PuBe sources were characterized by NDA methods. Neutron measurements were carried out with a JCC-13 neutron coincidence counter and the neutron output was determined. The isotopic composition of Pu and the abundance of ^{241}Am were determined by gamma spectrometry and their heat power was measured by calorimetry. Using the results of these measurements the PuBe sources were completely characterized and the (α,n) conversion factors were determined.

For the determination of these factors, we used the fact, that ^{241}Pu and ^{242}Pu don't play a role in neutron production. The average alpha energies for ^{238} Pu and ^{241}Am are 5.49 and 5.48 MeV, for ^{239}Pu and ^{240}Pu is 5.15 MeV. This implies that the conversion factors for ^{238}Pu, $k_{Pu\text{-}238}$, and for ^{241}Am, $k_{Am\text{-}241}$, can be assumed to be equal to each other, $k_{238\text{-}241}=k_{Pu\text{-}238}=k_{Am\text{-}241}$. The same is true for the conversion factors of ^{239}Pu and ^{240}Pu, $k_{Pu\text{-}239}$ and $k_{Pu\text{-}240}$, i.e., $k_{239\text{-}240}=k_{Pu\text{-}239}=k_{Pu\text{-}240}$. Therefore only two unknown parameters, $k_{238\text{-}241}$ and $k_{239\text{-}240}$ are to be determined. The ratio of $k_{238\text{-}241}$ and $k_{239\text{-}240}$ was taken to 1.27, assuming to be equal to the ratio of the conversion factors for thick target of Be at 5.5 MeV and 5.15 MeV.

The theoretical calculation was based on the following equation:

$$Y_{PuBe} = \frac{n'_{Be}}{N} \int_{E_\alpha}^{0} \frac{\sigma(E)_{Be}}{\varepsilon(E)_{PuBe}} dE$$

where Y_{PuBe} is the probability of neutron production, N is the total atom density of the material, n_{Be} is the atom density of Be in the alloy, $\varepsilon(E)_{PuBe}$ is the stopping cross section of the material for alpha particles, $\sigma(E)_{Be}$ is the total cross section of (α,n) reaction.

The role of secondary reaction in neutron production was investigated by MCNP (Monte Carlo N-Particle code) simulation. In contrast to alpha particles, neutrons have a long free path in the source. Thus, the size of the source, the place of origin and the initial direction of alpha particles may matter. These effects were examined by MCNP simulation.

We have also determined the material density and the size of the active segment of a series of PuBe sources by radiography.

Results

The measurement campaign and the calculations resulted in a set of well characterized PuBe sources. The (α,n) conversion factor was determined for each alpha-emitting isotope present in a PuBe source, and the experimentally and theoretically determined values are in good accordance. It became obvious, that the primary neutron production does not depend on the density of the material, but on the atomic ratio of Pu and Be.

Both double and triple neutron coincidences were measured on all PuBe sources, whereas for AmBe sources only the doubles, count rate was significant. This fact alone proves the presence of both (n,f) and (n,2n) reactions in PuBe sources.

MCNP simulation shows that the rate of secondary reactions depends most on the mass of the source but this is not the only factor. The shape and density of the source, and the isotopic composition of Pu influence their contribution to the neutron yield.

Using radiography the inner structure of the sources has been revealed, that enhances the precision of the NDA methods developed for the assay of the Pu content of PuBe sources.

Related publication

[1] János Bagi , László Lakosi, Cong Tam Nguyen, Hamid Tagziria, Bent Pedersen: *Characterization of PuBe neutron sources by calorimetry and neutron assay* in Nuclear Instruments and Methods b.

DETERMINATION OF LONG-LIVED ACTINIDES IN BIOLOGICAL SAMPLES USING LASER ABLATION ICP-MS METHOD

Éva Kovács-Széles, Kornél Fél

Objective

The main objective of the study was to develop a relatively simple and fast method to analyze long-live actinides (e.g. U) in biological samples using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) technique.

Methods

Nowadays, due to the increasing of risk of terrorism worldwide, the potential occurrence of terrorist attacks using also weapon of mass destruction containing radioactive or nuclear materials as dirty bombs, is a real threat. The use of dirty bombs, i.e. which also contaminate the environment with radioactive isotopes, represents a particularly dangerous form of attacks. Other potential risk of the contamination of environment and people by radioactive and nuclear materials is a possible nuclear accident. Consequently, it is of high importance to develop analytical methods which can provide early means of detection of the exposure of people. Fast detection of the contamination for the sake of further medical treatment of victims after a terrorist attack or nuclear accident is essential.

The method developed in this work is capable to determine actinides in low level directly in solid samples, e.g. from one droplet dried blood or urine. Calibration method to determine exact concentrations using laser ablation ICP-MS technique is a real challenge, due to the hard matrix effects of the sample and different ablation properties of the element of interest in the different sample matrices and standard materials. Matrix matching by standard materials is a possibility to carry out precise quantitative LA-ICP-MS analysis.

In this study, matrix matching calibration method was developed for analysis of biological samples (blood and urine) and for determination of uranium in these sample types. As a sample preparation procedure, blood and urine samples (0.2 µl) were dropped to microscopic glass surface, 0.2 µl uranium standard solutions (with known concentration: 0.000001 – 10 ng) were added, homogenized and dried at room temperature. More repetitions were used to study the reproducibility. During the method development, optimization of laser ablation ICP-MS measurement parameters was performed. The optimized parameters are shown in Table 1.

Table 1: Optimized parameters of LA-ICP-MS measurement

	Diameter of laser beam (µm)	Laser energy (mJ)	Repetition (Hz)	Scanning speed (µm/sec)	Measurement time (min)
Laser parameters	95	0.059 (70%)	10	70	2

For ablation of the sample 'raster scan' mode was used for laser. LA-ICP-MS signals were corrected by gas background.

Results

Using the method developed the following calibration curves were obtained for uranium in blood and urine: Figure 1, a) and b). The detection limits obtained: 4.2 pg uranium in the case of blood and 8.5 pg uranium in the case of urine.

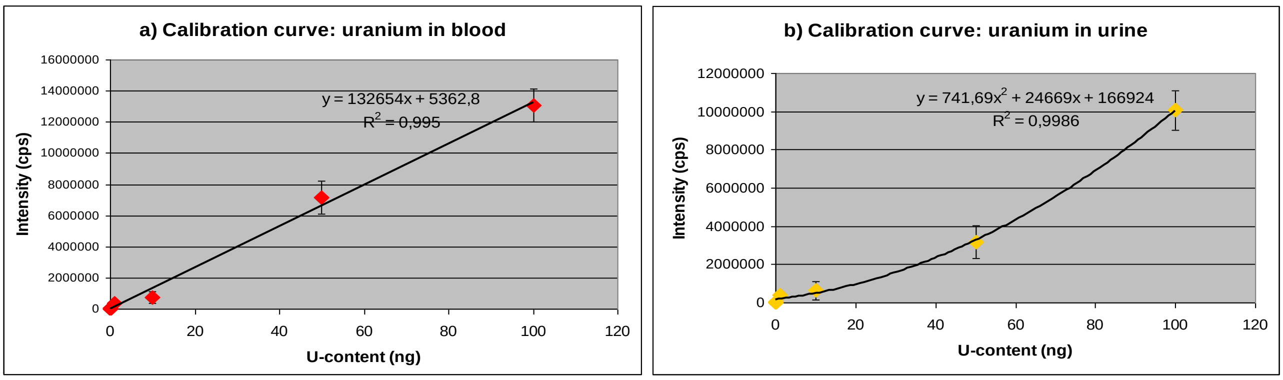


Figure 1: Calibration curves for uranium in blood a) and urine b) samples

The LA-ICP-MS method developed is capable to determine uranium in low level the biological samples and considering the low amount of sample needed, the method has several advantages compared to other methods (e.g. solution based techniques with time consuming sample preparation or other methods with lower sensitivity).

Remaining work

The results obtained and the developed method is under publication. In the following, we would like to extend the work to other important radionuclides which can be interesting for our purposes due to their importance in terrorist activity and using dirty bombs (e.g. cesium, americium).

IDENTIFYING REPROCESSED URANIUM BY GAMMA SPECTOMETRY

Tam Cong Nguyen, László Lakosi

Objective

For establishing the origin of illicit nuclear samples and safeguarding reactor fuel it is important to know, whether or not they were manufactured from irradiated material or U ore. A non-destructive method (High Resolution Gamma Spectrometry, HRGS) was therefore developed for identification of reprocessed U content in seized and unknown U samples as well as in fresh reactor fuel.

Methods

High resolution gamma spectrometry (HRGS) can reveal whether or not uranium has been reprocessed, based on the detection of ^{232}U by mass spectrometry that indicates the presence of ^{236}U. The ^{232}U activity was quantified by gamma spectrometry, irrespective of the ^{235}U enrichment, from the activity of its descendants, ^{212}Bi and ^{208}Tl. Their activities were determined relative to ^{238}U, using a relative efficiency curve for each sample. The activity ratio ^{232}U/^{238}U was measured in a low-background iron chamber using a 150 cm^3 coaxial high purity Ge detector. For the study a set of certified reference materials (CRM) and several other samples were used, with U-235 enrichment in the range of 0.23 – 90 %.

Results

The ^{232}U content in the samples plotted in Fig. 1 as a function of the enrichment indicate that seized reactor fuel pellets and ITWG (International Technical Working Group on Nuclear Smuggling) Round Robin (RR) samples incorporate reprocessed material. This is supported by some Np-237 content found by HRGS in the RR samples and declared or measured (by mass spectrometry) ^{236}U content of the samples. As can be seen, however, ^{232}U can be found in all the enriched and even depleted CRM samples. The ^{232}U content in the not reprocessed (“virgin”) materials (a dotted curve is fitted to their values in Fig. 1) may be due to the ^{232}U contamination in the enrichment facilities.

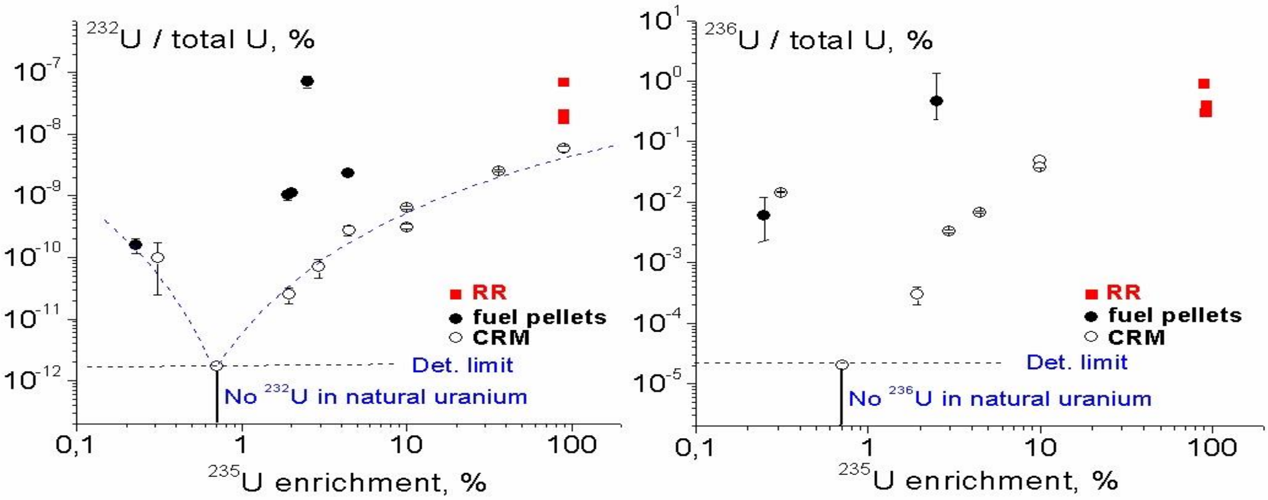


Figure 1: ^{232}U and ^{236}U content of several reference and various other materials as a function of ^{235}U enrichment

For certified reference material samples, results of mass spectrometric U isotope ratio measurements were also available. The mass spectrometric results showed that in the samples in which a higher amount of ^{232}U was found, there is also much more ^{236}U than in the other ones, confirming that these samples, indeed, contain reprocessed uranium. For comparison, ^{236}U content of these materials is plotted in Figure 1 as well. It was provided for the CRM samples in the certificates, while fuel pellets and RR samples were analysed for ^{236}U content by ICP-MS (Inductively Coupled Plasma Mass Spectrometry); a similar pattern of isotope distributions is revealed. It would appear that ^{236}U content in virgin material is also due to the contamination in the enrichment facilities. Preliminary results show strong correlation between the two minor isotopes, indicating a 236-to-232 ratio of about 10^7, in accordance with values in the literature. More data are clearly needed.

The 0.6% ^{236}U content in a seized reactor fuel pellet (Fig. 1) is an evidence of the presence of reprocessed material in the fuel, which may have consequences in depletion calculations. Corresponding ^{232}U content bears the same witness in the Figure.

Remaining work

More seized samples are to be measured, also by mass spectrometry for ^{236}U content. Measurements of fresh fuel assemblies at Paks Nuclear Power Plant have been done, evaluations are to be finished. Conference talk and publication are in preparation.

METHOD DEVELOPMENT FOR DETERMINATION OF ACTINIDES IN BIOLOGICAL SAMPLES USING ICP-MS TECHNIQUE

István Almási, Éva Kovács-Széles

Objective

The main objective of the study was to develop an analytical method for determination of long-lived actinides in biological samples using inductively coupled plasma mass spectrometry (ICP-MS).

Methods

Expansion of terrorism has been causing an incresingly intensive illicit trafficking of radioactive and nuclear materials during the last few decades. It also gives possibility for using of dirty bombs during terror attacks. Other potential danger in connection with radioactive and nuclear materials is the possibility of nuclear accidents (e.g. Fukushima). During these events lots of people are affected in most cases and therefore detection of the contamination and selection of the victims is necessary after the incident or accident as soon as possible for decision of further treatment. For fast selection and categorization of people, taken biological samples can be informative and using rapid measurement methods with small sample necessity for the analysis is essential. Mass spectrometry is sensitive enough to detect long-lived radionuclides (uranium, plutonium, thorium, americium, etc.) in ultra-low level (fg-pg range) in biological samples like blood or urine. Utilizing this advantage the technique is capable to determine low dose absorbed in the body by analysis of body fluids.

The aim of this work was to develop a sample preparation method which is relatively simple and rapid for fast analysis of biological samples. The main goal was to decrease the sample preparation time and to make the method applicable for biological matrices.

Sample preparation method bases on acidic digestion of the samples and some chemical treatment after the digestion to provide the optimal oxidation states of the sought materials (actinides) for chromatographic separation. Second step is the separation of the radionuclides from each other and the matrix components. Results are obtained using special measurement type (isotope dilution) and mathematical calculations.

Methods were tested and validated using human body samples. For work using biological samples the institute has been using valid ethical licences.

Results

The method is well-applicable for determination of uranium, plutonium and americium of ultra trace level in blood and urine matrices. During the extraction, chromatographic step of the chemical sample preparation nuclides could be fully separated from the sample matrix and each other. The analytical performance parameters obtained are shown in Table 1 and Table 2.

Table 1 The obtained detection limits for isotopes in the case of blood

Isotope	Detection limit
^{239}Pu	15 fg
^{240}Pu	4.5 fg
^{241}Pu	3 fg
^{238}U	5 ng
^{235}U	35 pg
^{234}U	0.65 pg
^{236}U	0.12 pg

Table 2 The obtained detection limits for isotopes in the case of urine

Isotope	Detection limit
239Pu	300 fg
240Pu	85 fg
241Pu	65 fg
238U	100 ng
235U	750 pg
234U	10.5 pg
236U	2.55 pg

Using the developed analytical method it is possible to estimate the dose absorbed in the body after the exposure. The methods with low detection limits are rapid and simple enough for short sample analysis and absorbed dose estimation after the in-field triage.

NUCLEAR FORENSIC APPLICATION OF XPS AND AES

Zoltán Schay, Zoltán Hlavathy, Tamás Biró

Objective

The objective of the study was to explore the feasibility of using specific surface sensitive electron spectrometry (X-ray photoelectron spectroscopy (XPS, ESCA) and Auger electron spectroscopy (AES) methods), for nuclear forensic investigations of nuclear materials of unknown origin.

Methods

The conception of the study was based on two observations obtained from literature survey. First, most of the techniques usually applied provide bulk analytical information, little is known on the chemical composition and state of the surface layer of a material sample. Secondly, no nuclear forensic application of the surface sensitive electron spectrometry techniques, such as XPS or AES has been published up to now. It was expected, that the chemical composition and state could contribute essential additional information to nuclear forensic investigations, if they prove to be characteristic to material type and/or fabrication procedure and/or to the environment the sample has been exposed to.

XPS and Auger spectrometry have been used for many years in the Institute; therefore the techniques (instruments) and expertise were available. The first question to be answered was whether these instruments could provide meaningful analytical results for nuclear materials, such as uranium and uranium oxides. The next question was that the measured analytical features, such as chemical composition and chemical state, could be attributed to a specific product and/or a production procedure, helping to reveal the origin (provenance) of the material.

Preliminary measurements, to test the available techniques, have been made on samples of uranium oxide pellets confiscated from smugglers, and powders from other sources.

Results

The ESCA and AES spectra showed clearly distinguishable uranium, oxygen and carbon peaks and also the chemical shift caused by different oxidation states of different chemical compositions of the oxides. An example is shown in Fig. 1.

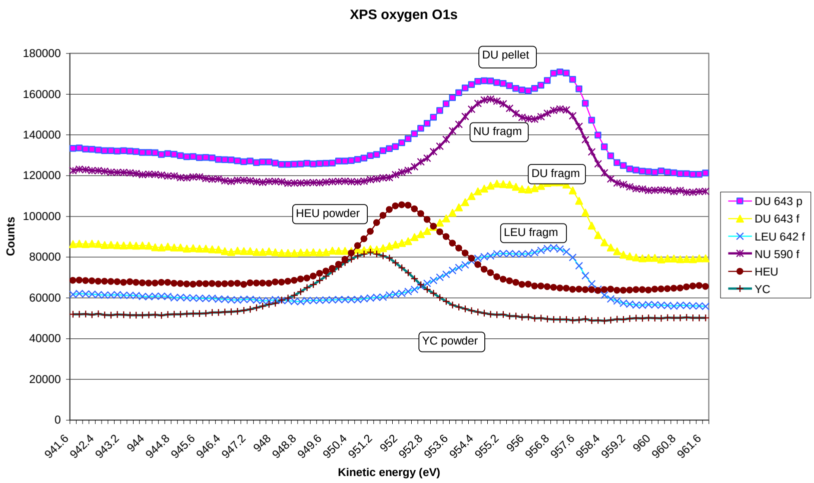


Figure 1: XPS spectra – O1s peak (oxygen)

An additional feature of the chemical composition of the surface layer is the depth profile. Ar ion bombardment was used to remove the upmost oxide layer and a consecutive ESCA measurement was carried out. It was found that the sample was covered by a mixed oxide layer containing carbon and masking the uranium peaks, while the next layer was free of carbon and the uranium could be identified.

Remaining work

More samples have to be analyzed to investigate the analytical value of the methods used and to further assess their capabilities in nuclear forensics. Sample types should be extended for the inclusion of metals and reference material compounds. Any conclusion should be based on more experimental data.

Related publication

[1] T. Biro, Z. Schay, Z. Hlavathy: *Nuclear Forensic Application of XPS and AES,* ITWG for Nuclear Forensics Annual meeting, Den Haag, Netherlands, 2012 June 26-28

PROVISION OF SCIENTIFIC AND TECHNICAL BACKGROUND FOR MANAGING LOST, FOUND, SEIZED NUCLEAR AND OTHER RADIOCTIVE MATERIALS

László Lakosi, Éva Kovács-Széles, István Almási

Objective

The goal was to give an account on the work performed in the frame of the contract No. OAH-220/2012 concluded between the Hungarian Atomic Energy Authority and the Centre for Energy Research

Tasks performed

According to the contract, the main tasks of the project were performed as follows:

- *Nondestructive measurement techniques:*
- Gamma spectrometry: an HPGe (cooled down) and a CdZnTe (CZT) detector with suitable multichannel analysers were kept on the alert continuously for assaying and characterizing lost, found, seized nuclear materials, when necessary. Such gamma spectrometers were applied several times both in laboratory use and at the Paks Nuclear Power Plant.
- A neutron coincidence measuring device with the digital multiplicity spectrometer and software, developed at the institute, was kept on the alert continuously and applied for assaying neutron emitting nuclear materials and for laboratory testing new developments.
- Safeguards verification of the depleted uranium content of irradiators' containers in hospitals (6 sites) and of irradiators' heads dismounted by the Institute of Isotopes Ltd. and stored at the campus (32 items). Identification of U-, Pu-, and Th-containing materials to be transported for disposal at Püspökszilágy in the Faculty of Colloid Chemistry, Debrecen University (45 items).
- *Destructive measurement techniques:*
- Clear laboratory conditions were maintained continuously at the ICP-MS mass spectrometer, first of all air conditioning. Sample preparatory laboratory proved to be Class 10 000, whereas instruments laboratory proved to be Class 100 000. Systematic maintenance work was carried out. HEPA filters were changed. The pressure control and the electric steering of the air blowing system were repaired. Some components of the mass spectrometer were regularly cleaned and occasionally changed. A yearly accrediting supervision was performed and the accredited status was prolonged, at a price of about 1 MFt.
- The operating parameters (sensitivity, resolution, detection limit) were systematically checked and the necessary improvements in case of deviation were carried out. The accuracy and reliability of the analytical methods developed for safeguards purposes was controlled by certified samples and reference materials. Determination of the accuracy of the U isotopic ratio in swipe samples was compared by independent methods, by using various reference materials added to sample taking material.
- Participation took place in international analytical exercises, organized by the laboratory network (called CETAMA) of the French Atomic Energy Commission (CEA) and by the Joint Research Centre IRMM of the European Commission, for determining trace element contamination in U-containing acidic solution and U and Pu isotopes and isotopic ratios in nitric acid solution, respectively.

International scientific results and ongoing research projects related to nuclear measurement techniques

The following list relies on the information gathered from the literature and conferences, first of all in the fields of safeguards and security of nuclear materials:

- Superconducting microcalorimeters for alpha- and gamma-spectrometry. A ten times higher energy-resolution can be achieved than by HPGe gamma spectrometry (e.g. 53 eV at 97 keV for determining Pu isotopic composition).
- Algorithms and software were developed for improving energy resolution also in traditional fields like scintillation detectors, resulting in a 2-3 times improvement for NaI and the existence of photopeak even for plastic crystals (the british firm Symetrica, partaker in the EU FP-7 project SCINTILLA).
- Boron coated "straw" detectors were developed for neutron detection purposes, to be used in bundles.
- Use of semiconductor detectors is getting more and more widespread in nuclear security, medicine, nuclear physics and high-energy physics, e. g. SiC fast and thermal neutron detectors for measuring spent reactor fuel, pixellated CZT detectors for medical or industrial imaging (CZT camera).
- Development works are going on for revealing in-field alpha contamination, by detecting characteristic UV photons created during ionization of N (air) atoms. The 60 keV peak of Am-241, even in very low amount, is detectable through the coincidence signal of UV photons, in a high gamma background.
- A resolution as high as 10 pm can already be achieved by a desktop Laser Induced Breakdown Spectrometr (LIBS), where the peaks of U-235 and U-238, 25 pm distant from each other, are split, this a direct enrichment measurement can be made by them.

REVIEW OF SOFTWARE FOR NEUTRON COINCIDENCE DATA ACQUISITION SYSTEM

József Huszti

Objective

In the recent years a list mode neutron data acquisition system was developed for safeguards purposes. The system is called Pulse Train Recorder or PTR-32 and consists of a software package and a hardware unit. The original programme had been developed for internal use but the system got meanwhile acceptance at international research sites, which made a refresh necessary. Main goal of the software package review was to give it a uniform, user-friendly look, implementing high voltage control. Several new data handling features were implemented in accordance with IAEA needs including export capability to the widely used INCC neutron coincidence evaluation programme.

Methods

The software package is written in Delphi and runs under Windows. The package consists of four executables which can be started from within the main control programme, too. The main programme controls data acquisition and detector high voltage via USB line and displays the follow-up distribution of impulses. Other programme parts show multiplicity, Rossi-alpha and impulse rate distributions. Each programme part is responsible for data manipulation features connected to the displayed distribution.

Results

The software package consists of four separate programmes with a similar look as that of the main control programme in the Figure below. Several new features extended the main programme. The high voltage unit in the hardware part is fully software controlled.

The new hardware gives not only follow-up time information but also on channel number of the incoming pulses. This feature made several channel related functions available. Data of a noisy or defect channel can be removed without disturbing the remaining part. The saved impulse train can be unfolded into single channel files for evaluating them separately.

Bulk evaluation of measuring data residing in a directory was implemented. Repeated measurement data can be converted into export files for the widely used INCC program.

The new Chopper program can tailor the length of data files by functions like chopping, cutting and merging.

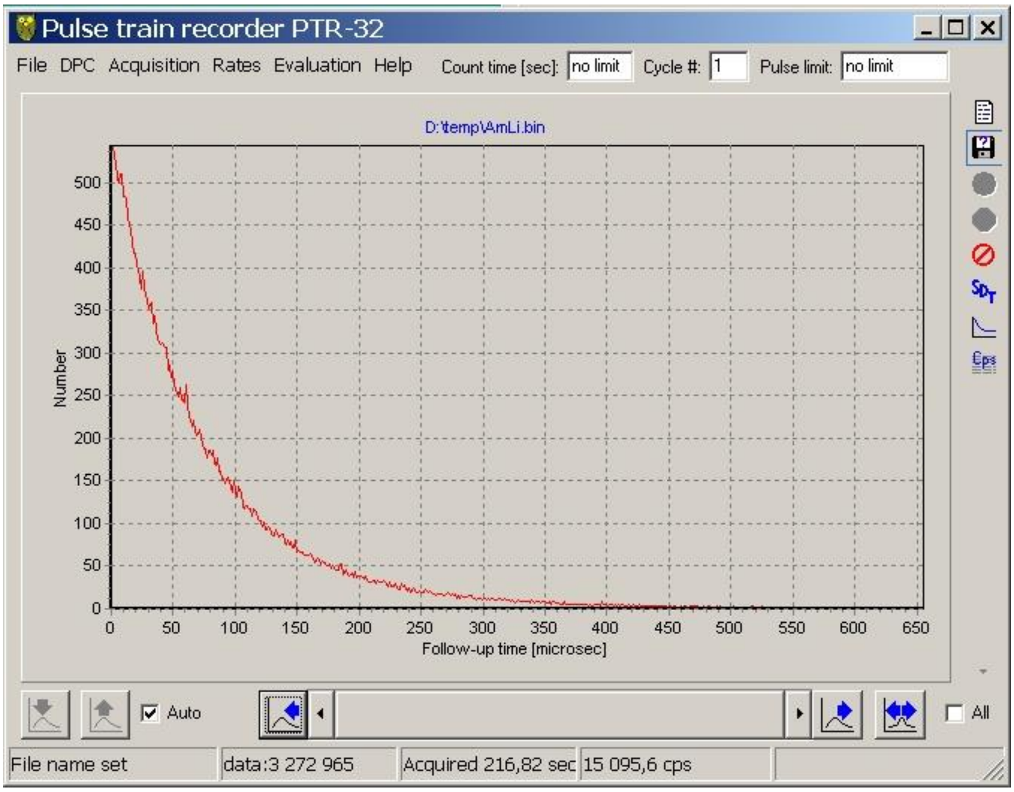


Figure 1: User interface

Remaining work

For browsing list mode files a small data base is planned.

SPECIALIZED ICP-MS TRAINING FOR NUCLEAR FORENSICS PURPOSES

Éva Kovács-Széles

Objective

The aim of the special course was to give a comprehensive and detailed training on inductively coupled plasma mass spectrometry (ICP-MS) in the field of nuclear forensics.

Introduction

Investigation and analysis of nuclear materials (radioactive materials with uranium, plutonium and/or thorium content) has become of high importance in the last few years due to an increase in the occurrence of terrorist activities and the related illicit trafficking. Nuclear forensics is the analysis of nuclear materials recovered from e.g. the capture of unused nuclear materials or radioactive material to provide evidence for determining the history of the sample material. It contributes significantly to the identification of the sources of the materials and the industrial processes used to obtain them. Nowadays, nuclear forensics has high importance, therefore training of personnel in the field is essential. Identification and characterization of these materials is generally based on mass spectrometric measurements, hence training using ICP-MS instrument is obvious and can be helpful for future experts in the field.

Description of the training

The training course included both the theoretical background as well as a practical hands-on training with nuclear materials: practical work at the laboratory (sample preparation and radiochemistry) and analysis by inductively coupled plasma mass spectrometry.

The programme of the training (presentations and exercises) involved the following topics:

A. Introduction

- - About Nuclear Forensics in general
- - Mass spectrometry in general (Basics of mass spectrometry, types of mass spectrometers, advantages and disadvantages of ICP-MS technique relative to other mass spectrometric techniques, role of ICP-MS in elemental and isotope analyses, comparison to the radioanalytical techniques with emphasis on nuclear forensics, applicability, capabilities of ICP-MS technique: sample types, typical detection limits and precisions)
- - ICP-MS instrumentation: instrumentation and hardware, software overview
- - Needful environment and equipment to a mass spectrometry lab
- - Other special applications: e.g. analysis of safeguards swipe samples

B. Sample preparation

- - General methods for sample preparation (liquid and solid samples)
- - Dissolution and preconcentration methods
- - Sample preparation of nuclear materials
- - Sample preparation for laser ablation ICP-MS measurement

C. Sample introduction techniques (nebulizers, spray chambers, laser ablation)

D. Evaluation, data processing and software operation

- - Calibration techniques (external calibration, standard addition, isotope dilution, laser ablation analysis)
- - Special requirements for isotope analysis (mass discrimination, detector dead time)

E. Quality control

F. Measurements

- - Precise uranium isotope ratio analysis of dissolved uranium materials. Measurement capabilities of minor isotopes, improvement possibilities (e.g. desolvation)
- - Trace-level impurities, or multielemental analysis in uranium bearing materials; calibration approaches
- - Precise isotope analysis of different samples containing uranium, plutonium and americium
- - Analysis by laser ablation technique

Summary

Specialized ICP-MS training on nuclear forensics was given to participants interested in the topic. Presentations and practical exercises were carried out successfully.

Participants could see and practice the instrument maintenance and reparation, change of some important tools like torch, cones, O-rings and solving a few technical problems.

We are planning more specialized trainings in the future in the topic of nuclear forensics and nuclear safeguards.

DEVELOPMENT AND EVALUATION OF A MULTIPLICITY SPECTROMETER PROTOTYPE

József Huszti

Objective

A multiplicity spectrometer is an assay instrument for gathering neutron impulse trains from which the fission material content in nuclear samples can be determined. The IAEA (International Atomic Energy Authority) accepted this project as part of the Hungarian support programme in 2007. Since beginning of work the prototype became a neutron coincidence data acquisition and evaluation system. The first version was a single channel instrument which was presented to the IAEA and ESARDA NDA working group (European Safeguards Research and Development Association, Non-Destructive Assay). It found a good acceptance and answering diverse suggestions it was extended to a sixteen channel device. It extended the achievable measuring range considerably by loss-free merging of sixteen inputs which rose measurable impulse rate from some hundred thousand into the million counts per second range.

A further improvement was saving of input channel numbers for each incoming impulse as proposed in the ESARDA NDA working group. Besides this, the channel number was increased to 32 for a test measurement in Los Alamos. The device was compared with the LANL (Los Alamos National Laboratory) developed multichannel device and the commercial JSR-15 of Canberra. Measurement results were well within acceptable range.

Methods

The system consists of an external hardware part and a PC program package. The hardware part of the system is based on an FPGA (Field Programmable Gate Array) developing board. It is extended by some special circuitry for accepting incoming impulses and generating high voltage. Logical functions are implemented by a high level programming environment.

The software package consists currently of four stand-alone programmes each of which presents a different view of acquired data. Follow-up, multiplicity, Rossi-alpha and impulse rate distributions can be viewed and evaluated.

Results

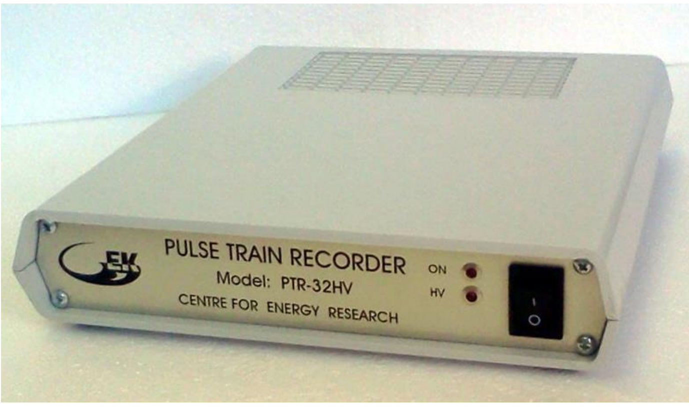


Figure 1: Data acquisition device

A fully software controlled high voltage supply, an input adapter and detector power supply were added. The firmware of the hardware part was updated accordingly. Software package was extended by cps-view, high voltage commands and diverse export functions. A link to the widely used INCC (IAEA Neutron Coincidence Counting) software was implemented.

During developing work a gauge for replaying saved impulse trains was also developed. It is called Virtual Source and can be applied also as a training and educational tool.

Remaining work

There is a range of possible further developments for the Pulse Train Recorder system. Some of them are on the anvil as part of the continuing Support Programme.

- Adding new analysis techniques such as Feynman-alpha and Feynman with overlapping gates to the already implemented standard evaluation techniques
- Diverse small software modifications for regular safeguards use
- Data base for browsing data files
- International collaboration for gathering data files for comparing detectors and training purposes

VII. NON NUCLEAR ENERGY RELATED STUDIES

IDENTIFYING RESEARCH NEEDS OF ALTERNATIVE ENERGY CYCLES

Árpád Farkas, Szabina Török, Endre Börcsök

Objective

The main objectives of the work were to justify the research and development activities of the newly established energy and environmental security research institute, and to elaborate a comprehensive research strategy for the coming years. New scientific partnerships were established, seeking for research opportunities compatible with the expertise and infrastructure of the research center.

Methods

A comprehensive documentation of the published literature in the area of alternative energies in conjunction with the study of the relevant European and Hungarian legislation and energy policy has been performed. Research activities of other Hungarian academic institutes were surveyed, and industry representatives consulted to identify the gaps in alternative energy research. Networking with stakeholders (organizing seminars and workshops) meetings resulted in objective view on the relevance of suggested research ideas. Competences and research infrastructure of the research centre were evaluated by consulting with the heads of different laboratories and the researchers. Potentially accessible research funds were identified by studying different national and European funding schemes. Scientific cooperation partnerships were established as a result of multiple discussion and negotiation rounds held both in our research centre and at the partners.

Results

One of the most important results of our activity was the elaboration of a research strategy in the field of renewable energies. It has been submitted to the Hungarian Academy of Sciences. According to this strategy, research opportunities for the next five years are related to sequestration of carbon dioxide (CCS), steam/gas energy conversion systems, development and qualification of biomass boilers/furnaces, wind turbine blade optimization, thermo-hydraulics of molten salt coolant, emerging energy storage systems, hydrogen storage and smart grids. For the accomplishment of the above tasks, partnerships with the Physikalisch-Technische Bundesanstalt (Berlin, large research infrastructure), Budapest University of Technology and Economics (electricity grid simulation), Fritz Haber Institute (Berlin, energy storage), ELTE University (solar energy), Hungarian Geological and Geophysical Institute (CCS) have been established.

The strategic research agenda is based on the existing expertise and research experience in the field of power generation. Accordingly, the planned research activities are thought to be integrated into a broader frame of fossil fuel-renewable-nuclear energy research (Figure 1), with several connections among the different types of energies.

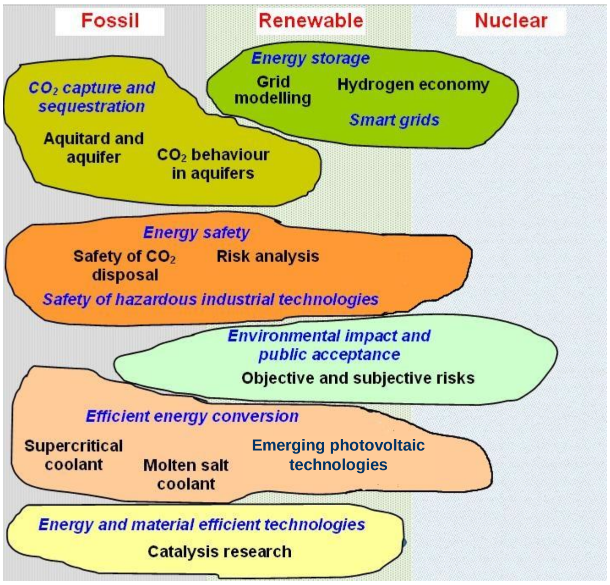


Figure 1: Identified research fields related to fossil, renewable and nuclear energy

Another result of the research efforts was the completion of an extended study concerning the use of computational fluid dynamics (CFD) methods in alternative power generation research. Modelling of heat transport in furnaces, optimization of biomass combustion boilers, simulation of the fate of carbon dioxide injected into saline aquifers and modelling of the load of wind turbine blades to optimize their shapes were identified as potential future applied research fields.

Related publication

[1] Sz. Török, E. Börcsök, Á. Farkas, D. Breitner, M. Fábián, J. Osán, Á. Horváth, E. Takács and A. Tungler: *Research strategy of the Centre for Energy Research, Hungarian Academy of Sciences in the field of environmental and energy safety,* (In Hungarian) (2012)

DEGRADATION OF PHARMACEUTICAL RESIDUES IN AQUEOUS SOLUTIONS BY IONIZING RADIATION INDUCED HYDROXYL RADICALS

Erzsébet Takács, László Wojnárovits, Renáta Homlok, Tamás Csay

Objective

Radiation treatment of wastewater is a process already working on industrial level. However, the radiolysis of water is regarded as the cleanest source of hydroxyl radicals and this is the only method where the amount of hydroxyl radicals injected into the solution is exactly known. Therefore, the radiolysis experiments give excellent possibilities to study the mechanism of radical induced reactions. The aim of this work is to help understanding the mechanism of the advanced oxidation processes.

Methods

Pulse radiolysis and gamma radiolysis experiments were executed to characterize the intermediates and final products of ibuprofen formed during the degradation in 0.1 mmol dm^{-3} solution. For end-product experiments, a ^{60}Co γ-irradiation facility was used and the irradiated samples were evaluated either by taking UV-Vis spectra or by HPLC with UV or MS detection. The ecotoxicity of the solution was monitored by Daphnia magna standard microbiotest and Vibrio fischeri luminescent bacteria.

Results

The reactions of •OH lead to hydroxycyclohexadienyl type radical intermediates, in their further reactions hydroxylated derivatives of ibuprofen form as final products (Fig. 1). The hydrated electron attacks the carboxyl group and induces degradation with low efficiency Ibuprofen degradation is more efficient under oxidative conditions than under reductive ones. The toxic effect of the treated aerated ibuprofen solution first increased then decreased with the absorbed dose, indicating higher toxicity of the degradation products. With prolonged irradiation complete mineralization of organics was achieved, the organic molecules were transformed to water and carbon dioxide.

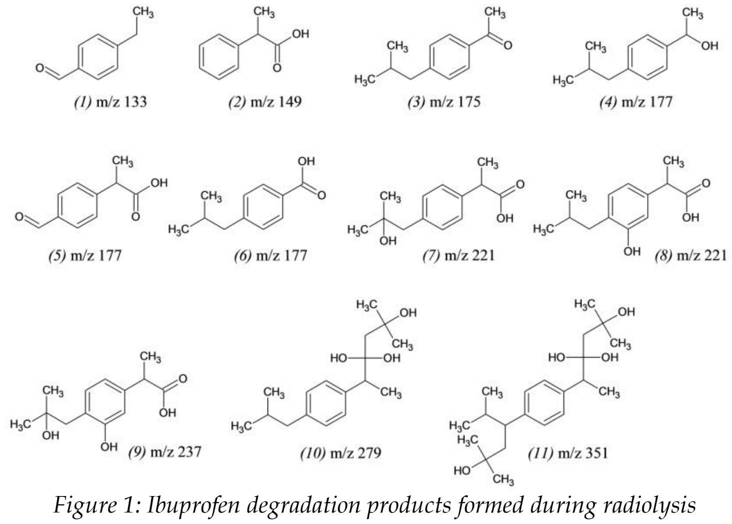


Figure 1: Ibuprofen degradation products formed during radiolysis

Remaining work

We plan to continue the work with investigating the radiation induced decomposition of antibiotics. We also plan to combine the ionizing radiation and biological treatments.

Related publications

[1] E. Illés, E. Takács, A. Dombi, K. Gajda-Schrantz, G. Rácz, K. Gonter, L. Wojnárovits: *Hydroxyl radical induced degradation of ibuprofen*, Science of the Total Environment **447**, 286 (2013)

DEVELOPMENT AND APPLICATION OF CATALYTS BASED ON C_1 CHEMISTRY: FORMATION OF CO AND CLEAN H_2 FROM METHANE

Anita Horváth, László Borkó, Zoltán Schay, Andrea Vargáné Beck, Krisztina Frey, Nóra Győrffy, Norina Nagy, Zoltán Paál, László Guczi

Objective

Three related catalytic processes for H_2 production were to be studied and the corresponding highly active nanostructured catalysts were to be developed. These topics were: i) dry reforming of methane with CO_2 to yield CO and H_2 mixture on gold modified Ni/$MgAl_2O_4$ catalysts (modelling the future utilization of biogas), ii) conversion of methane with N_2O on multifunctional M/Ga/H-ZSM-5 catalysts (M: noble or transition metal) in the presence or absence of CO traces and iii) removal of small amount of CO from the H_2 feed (PROX studies) for example for fuel cell applications on unsupported PtSn samples, on gold based CuO-CeO_2 systems and on Co- and Mn-oxides.

Methods

For the preparation of catalyst samples, different traditional (impregnation) or newly developed liquid phase reduction or precipitation methods were applied. For the structural and surface characterization of the catalysts, temperature programmed oxidation or reduction, nitrogen adsorption, X-ray diffraction, X-ray photoelectron spectroscopy and normal or high resolution transmission electron microscopy were carried out. Catalytic reactions (dry reforming, $CO_2+CH_4=CO+H_2$, selective oxidation of CO to CO_2 in the presence of large amount of hydrogen, viz. PROX reaction, and N_2O conversion with methane, $N_2O+CH_4+(CO)=N_2+CO_2$ reaction) were carried out under different conditions (see the related publications for details), usually in flow systems with Gas chromatography and mass spectrometry analysis. Circulation system with isotope tracing ability was calibrated and tested for the mechanistic studies in dry reforming to follow the critical carbon deposition steps.

Results

The interaction of the catalyst components (support and metals) and the effect of composition and structure on catalytic activity were studied in order to yield efficient catalysts and to better understand the elementary reaction steps. Dry reforming studies revealed that the catalytic properties of monometallic Ni/$MgAl_2O_4$ samples are independent of the preparation method if Ni content and particle size are the same, and that NiAu phase produced with sol preparation method undergoes structural changes during the high temperature pretreatments and the catalytic reactions. The addition of Au has a negative effect in terms of catalyst stability and the easiness of carbon removal.

PROX on PtSn sample after O_2 and H_2 treatment resulted in better CO oxidation activity than after only H_2 treatment, moreover, in situ XPS detected more Pt in the near surface region (Pt_3Sn) and some Sn-oxides. The Au/CuO/SiO_2 catalysts investigated next turned to be more effective than the Au/SiO_2 and CuO/SiO_2 systems, while the presence of Au weakened the performance of the highly active CuO/CeO_2 system. The third type of samples in PROX studies were the Mn- and Co-oxides without any noble metal. The non-stoichiometric MnOx with Mn oxidation state of ~3.4 prepared by Mn-oxalate precipitation resulted extremely high CO oxidation activity, however, the delicate high surface area structure was changed during reaction. PROX parameters of the mixed Mn-Co oxide prepared also by co-precipitation exhibited the best activity compared to the reference samples due to the presence of Mn built in the Co-oxide framework thus changing the strength of framework oxygen bonds.

Investigations on N_2O decomposition and N_2O reduction by methane carried out with different M/Ga/H-ZSM-5 (M: Fe, Co, Ni, Mo, Ru, Pd, Ag, Ir, Pt, Au) catalysts arranged the samples into 2 groups: the presence of CH_4 increased N_2O conversion in the case of Pt and Pd, while there was no effect observed in the case of all other metals. The synergetic effect of Ga observed in some systems is explained by the increased reducibility of transition metals induced by Ga. The N_2O+CH_4+CO reaction was also investigated on the above samples and it was observed that 0.5% CO causes a reversible deactivation only for Pt sample while it is detrimental for Fe. This can be explained by the differences of active centres of catalytic turnover for the competitive N_2O+CH_4 and $CO+CH_4$ reactions on Pt.

Related publications

[1] K. Frey, A. Beck, I. Sajó, J. Osán, G. Sáfrán, M. Veres, N Kruse and Z. Schay: *Manganese-promoted cobalt oxide with high catalytic activity in different reactions*, 15th International Congress on Catalysis 2012, Munich, 2012. 07. 1-6, Abstract #7573 (2012)

[2] K. Frey, V. Iablokov, G. Sáfrán, J. Osán, I. Sajó, R. Szukiewicz, S. Chenakin and N. Kruse: *Nanostructured MnOx as highly active catalyst for CO oxidation,* J. Catalysis **287,** 30 (2012)

[3] D. Teschner, A. Wootsch and Z. Paál: *Preferential CO oxidation in hydrogen (PROX) on unsupported PtSn catalyst*, Appl. Cat. A: Gen **411-412,** 31 (2012)

[4] A. Horváth, Gy. Stefler, V. La Parola, L. F. Liotta, G. Pantaleo, A. M. Venezia and L. Guczi: *Comparative study on Au-modified Ni/MgAl2O4 catalysts for dry reforming of methane*, 15th International Congress on Catalysis 2012, 01.07.2012 - 06.07.2012, Munich, Germany, Abstract #1605 (2012)

[5] A. Horváth, L. Guczi, N. Nagy, G. Sáfrán, V. La Parola, L. F. Liotta, G. Pantaleo and A. M. Venezia: *The effect of preparation on the structure of Au-modified Ni/MgAl2O4 catalysts and its methane dry reforming activity,* accepted for the 10th Natural Gas Conversion Symposium, Doha, 2-7 March (2013)

[6] L. Borkó, N. V. Vlasenko, Zs. Koppány, Z. Schay, P.E. Strizhak and L. Guczi: *Oxidation of CH_4 with N_2O on M/Ga/H-ZSM-5 (M-transition metal) catalysts: combined redox and acid-base effect,* 15th International Congress on Catalysis, 01.07.2012 - 06.07.2012, Munich, Germany, Extended Abstracts, PS. 44 3.01_1926, oral presentation (2012)

[7] L. Borkó, N. V. Vlasenko, Zs. Koppány, Z. Schay, P.E. Strizhaka and L. Guczi: *Oxidation of CH_4 with N_2O on M/Ga/H-ZSM-5 (M-transition metal) catalysts: the role of gallium*, NanoCatalysis 2012, 24-28 September, Uzhgorod/Ukraine, Extended Abstracts, p. 47-48, oral presentation (2012)

DEVELOPMENT, CHARACTERIZATION AND MODELLING OF SELF-POWERED NANOGENERATORS ON FLEXIBLE FIBROUS ASSEMBLIES

Erzsébet Takács

Objective

The overall objective of this collaborative work is to develop and model the piezoelectric characteristics of fibrous assemblies consisting of Zinc oxide (ZnO) nanowires assembled in the form of nonwoven structures. These nanowires will be grown on the surface of textile fibres (viscose) which would be orientated in various alignments ranging from purely random to highly preferentially orientated structures. The optimization of fibre orientation coupled with geometrical characteristics of nanowires can maximize the output power and voltage of their piezoelectric effect. Furthermore, theoretical models for predicting the output power and voltage would be developed by combining the proven theories of fibre contacts; Hertzian contact among the nanowires and piezoelectric induced potential distribution. This year our task in the project was the modification of the nonwoven cellulose based material (viscose) by radiation iniciated grafting of acrylic acid to its surface in order to form nucleation points. The characterization of the samples was also our task by using our SEM and element analysis instrument.

Methods

Samples of 1x12 cm dimensions were treated as follows:

- Soxhlet extracted in ethanol for 5 hours,
- washed in distilled water,
- extracted in 1% NaOH solution for 3 hours,
- washing in 1% acetic acid solution several times,
- drying at room temperature.

Preirradiation grafting method was used with the following steps: after measuring the mass of samples, they were irradiated by 20 kGy in a ^{60}Co gamma source. 0.5 mol dm^{-3} acrylic acid solutions were deareated by nitrogen bubbling and just after irradiation the samples were placed in the solution heated previously to 40 °C. After 0.5 or 1 hour grafting (with continuous nitrogen bubbling) the remaining monomer was extracted in distilled water at 70 °C. After extraction the samples were washed several times in water and dried at room temperature. The degree of grafting (DG (w%) = 100 (wg-w0)/w0) was determined by weighting the dried samples before (w0) and after (wg) grafting.

Results

ZnO nanorods were formed by hydrothermal method on the surface of the previously grafted samples (this was the task of the collaborating partner). The nucleation of the nanorod is expected on the grafted points. As Fig. 1 shows, the nanorod formation started on the surface of the grafted samples. No nanorods were formed on samples which were not grafted previously.

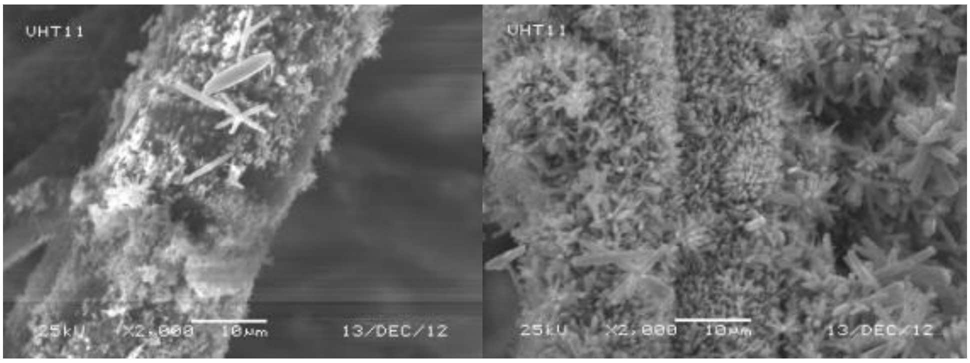


Figure 1: Viscose fibres with ZnO nanorods formed on the grafted surface

Remaining work

The samples produced are not homogenous enough; therefore we should continue the experiments to produce nanorodes of similar dimensions. Both the grafting parameters and the method for nanorod formation should be changed.

ENVIRONMENTAL TECHNOLOGIES: WET OXIDATION, DESULFURIZATION, METALOXIDE CATALYSTS IN OXIDATIONS FOR ENVIRONMENTAL PROTECTION

Antal Tungler, Erzsébet Takács, Tamás Ollár, Krisztina Frey, Nóra Győrffy, Zoltán Schay

Objective

The disposal of liquid and gas-phase effluents with catalytic methods has been investigated. The subtopics were: wet oxidation of high organic content liquid wastes with catalytic and high energy radiation assisted methods, investigation of hydrodesulfurization catalysts with compounds labelled with radioactive isotopes, investigation of metal and oxide catalysts in oxidation of gas pollutants (CO, NO).

Methods

In wet oxidation the degree of conversion was followed by COD (chemical oxygen demand) and TOC (total organic carbon) measurement and the final reaction characterized by BOD measurement. The high energy radiation assisted oxidations were carried out with LINAC and Co60 gamma source in autoclaves, the radiation doses were determined with chemical dosimetry. The mechanism of hydrodesulfurization was tested with ^{35}S labeled compounds, measuring methods were gas-chromatography and radiation determination. The metal and oxide catalysts were characterized with different methods (TEM (transmission electron microscopy), XRD (X-ray diffraction), TPR-TPO (temperature programed reduction-temperature programed oxidation), XPS (X-ray photoelectron spectroscopy)) and their activity determined in gas phase reactors in CO oxidation and in NO reduction with CO.

Results

The necessary degree of wet oxidation was determined, which ensures the biodegradability of the treated wastewater without totally eliminating the organic carbon content of it. Oxidation of water solution of model compounds could be carried out **in room temperature** with irradiation, instead of 180 ^{o}C. Monolith catalysts were characterized in wet oxidation of real wastewaters. (Two papers were published in journals, 1, 2).

Over alumina supported Ni, Mo and NiMo catalysts with thiophene HDS process simultaneously thiophene recyclization is taking place too (one paper. 4, and one presentation in conference, 5 were published). Interaction of butadiene with catalyst sulfur results in formation of thiophene via heterocyclization and that of hydrocarbons different from butadiene. The sequence of heterocyclization activities is similar to that of thiophene hydrodesulfurization observed (one paper, 5, and one presentation in conference, 6, were published).

Investigations of the effect of Au on the CO oxidation activity of different oxide overlayers (FeO_x, TiO_2 and CeO_2) in MO_x/Au/SiO_2/Si(100) type model systems were summarized in paper 7. Promoting effect of gold on the catalytic activity of the FeO_x overlayer and an inhibiting effect of gold on the TiO_2 and CeO_x overlayers was found. They were discussed in terms of electronic interactions at the Au/metal-oxide interface.

High surface area Mn promoted Co-oxide ($Mn_mCo_{3-m}O_4$ as evidenced by XRD), MnO_x and Co_3O_4 was prepared by oxalate deposition followed by controlled temperature programmed oxidation. The high CO oxidation activity of monometallic oxides was exceeded by that of mixed oxide, while Mn substitution into Co_3O_4 decreased the activity in NO+CO reaction.

Remaining work

The wet oxidation of wastewaters and the hydrodesulfurization are planned to be continued in 2013 under No. 108.

Related publications

[1] M. Chamam, C.M. Földváry, A.M. Hosseini, A. Tungler, E. Takács, L. Wojnárovits, L.,: *Mineralization of aqueous phenolate solutions: a combination of irradiation treatment and wet oxidation,* Radiation Physics and Chemistry Volume 81, Issue 9, September 2012, Pages 1484-1488, IF 1,159

[2] A.M. Hosseini, A. Tungler, Z. Schay, S. Szabó, J. Kristóf, É. Széles, L. Szentmiklósi,: *Comparison of precious metal oxide/titanium monolith catalysts in wet oxidation of wastewaters*, Applied Catalysis B: Environmental, Volume 127, (30 October 2012), Pages 99-104, IF 5,625

[3] T. Ollár, P. Tétényi, T. Szarvas: *The Conversion of Butadiene on Thiophene Hydrodesulfurization Catalysts*, Topics in Catalysis 55 (2012) 792-799

[4] P. Tétényi, T. Ollár, T. Szarvas: *Sulfur exchange capacity and thiophene hydrodesulfurization activity of sulfided molybdena-alumina catalysts promoted by nickel*, Catalysis Today 181 (2012) 148– 155

[5] T. Ollár, T. Szarvas, P. Tétényi: *Mechanism of Butadiene heterocyclization over sulfideded HDS catalyst*,
IX International Conference Mechanisms of Catalytic Reactions, October 22-25, 2012 St. Petersburg, Russia

[6] T. Ollár, T. Szarvas, P. Tétényi: *Consequence of the reverse reaction in HDS*, 15th International Congress on Catalysis, July 1– 6, 2012, München, Germany

[7] K. Frey, G. Pető, K. V. Josepovits, L. Guczi: Gold *catalysts for the abatement of environmentally harmful materials: Modeling the structur depenedency*, Vacuum, 86 (2012) 745-749

NEW ADVANCED OXIDATION PROCESSES IN WATER TREATMENT

László Wojnárovits, Erzsébet Takács, Renáta Homlok

Objective

This research is aimed at contributing to develope ionizing radiation based simple, energy saving and economically advantageous technologies for wastewater treatment. In the Advanced Oxidation Technologies (AOt) the transformation of organic molecules is initiated by aggressive short-lived radicals, principally by hydroxyl radicals. The rate of degradation of organic molecules is highly structure dependent. Here this structure dependency is investigated.

Methods

Municipal wastewaters, containing large number of organic impurities of various chemical structures are usually characterized by the chemical oxygen demand (COD). COD is the total concentration of substances that can be chemically oxidized to inorganic products. It is expressed in mg O_2 needed for oxidation in 1 dm^3 solution. In COD measurement the oxidation is carried out by the very strong oxidant dichromate. COD here was measured according to the ISO Standard 6060:1989 by a Behrotest TRS 200 system. The technique involves boiling 10 cm^3 sample at 148±3 ^{O}C for 2 h in an 8 mol dm^{-3} H_2SO_4 solution with introduction of $K_2Cr_2O_7$ as oxidizing agent, Ag_2SO_4 as catalyst and $HgSO_4$ for removing chlorides. The non-reacted $Cr_2O_7^{2-}$ is removed by titration with Mohr salt ($Fe(NH_4)_2(SO_4)_2(6H_2O)$) using ferroin indicator.

Hydroxyl radicals were generated by water radiolysis. Up to ~50% decrease of COD the dose dependence was linear. The slope of the dose dependence was used to characterize the degradability of organic molecules.

Results

In laboratory experiments the oxidation of many organic compounds was studied, however, very few works reported on comparison of degradability of different compounds. Here the radiation induced degradation of 22 carefully selected molecules was studied, investigating the efficiency – structure relationship. The selected molecules include simple aromatic molecules (phenol, cresols, chloropenols, aminophenols, pharmaceutical molecules (aspirin, ketoprofen, acetaminofen, diclofenac, 2,6-dichloroaniline, acetovanillone, gallic acid), a pesticide (2,4-Dichlorophenoxy-acetic acid), a dye molecule (Acid Red 1) and the non-aromatic maleic and fumaric acids.

The slopes of the COD - absorbed dose linear relations were found in the 3 - 10 mg dm^{-3} kGy^{-1} range. The values showed strong structural variations. By the ratio of the decrease of COD and the amount of reactive radiolysis intermediates introduced into the solution, the oxidation efficiencies were calculated. Efficiencies around 0.5–1 (O_2 molecule built in products/$^{\bullet}OH$) found for most of compounds show that the one-electron-oxidant $^{\bullet}OH$ induces two–four electron oxidations. The high oxidation rates were explained by $^{\bullet}OH$ addition to unsaturated bonds (in aromatic molecules forming hydroxy-cyclohexadienyl radicals) and subsequent reactions of dissolved O_2 with organic radicals. When amino, acetamide or hydrazo groups are attached to the ring of phenol, the rate is lower, one $^{\bullet}OH$ induces one–two electron oxidations. The low rate is probably due to intermediate radicals (phenoxy, anilino, semi-iminoquinone, hydrazyl) with low reactivity with oxygen.

The experiments also revealed that in aerated solutions the reductive water radiolysis intermediates, e_{aq}^- and $H^{\bullet}$ also contribute to oxidative degradation.

Remaining work

With the work outlined here, the structure - degradation relation was clarified for a large number of organic molecules. However, it is generally observed that at the beginning of oxidative treatment the toxicity of the solution increases. The first degradation products are more toxic than the starting molecules. With prolonged oxidation, however, there is a strong decrease in the toxicity, and with most methods complete mineralization of the organic contaminants can be achieved. We intend to investigate the relation between the structure and the changes in the toxicity during AOP treatment.

Related publications

[1] R. Homlok, E. Takács, L. Wojnárovits: *Degradation of organic molecules in advanced oxidation processes: relation between chemical structure and degradability*, Chemosphere http://dx.doi.org/10.1016/j.chemosphere.2012.11.073

[2] R. Homlok, E. Takács, L. Wojnárovits: *Szerves molekulák oxidatív lebontása nagyhatékonyságú oxidációs eljárásokkal, összefüggés a kémiai szerkezet és a lebonthatóság között*, Őszi Radiokémiai Napok 2012, Magyar Kémikusok Egyesülete

NEW ENERGY SAVING TECHNOLOGIES FOR WASTEWATER TREATMENT

László Wojnárovits, Erzsébet Takács,
Renáta Homlok, Tamás Csay, Erzsébet Illés

Objective

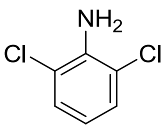
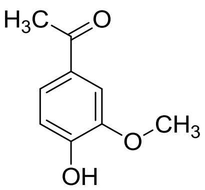
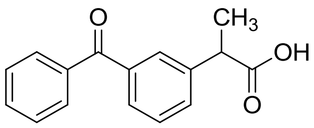
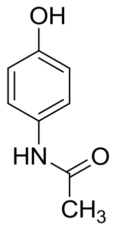
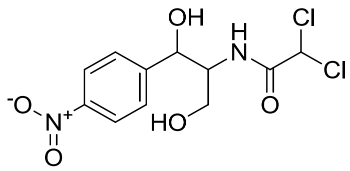
This research is aimed to contribute to developing ionizing radiation based technologies for wastewater treatment. Through the investigation of the mechanism of high-energy radiation induced degradation of highly toxic pharmaceuticals with high-risk for the environment, a theoretical basis can be established for the industrial application.

Methods

Dilute aqueous solutions with concentrations in the range of 0.1–1 mmol dm^{-3} were prepared. They were irradiated either by a Linac type 4 MeV electron accelerator for investigating the intermediates or by a ^{60}Co gamma source for end-product measurements.

The chemical changes were followed either by an UV-Vis spectrophotometer without separation of the products or after separation by HPLC using diode array or MS-MS detection. The change in chemical oxygen demand (COD), total organic carbon content (TOC) and toxicity were also followed by using the standard methods.

Results

2,6-dichloroaniline *acetovanillone* *ketoprofen* *paracetamol* *chloramphenicol*

The investigations were made with five compounds used as pharmaceuticals or intermediates: 2,6-dichloroaniline, acetovanillone, ketoprofen, paracetamol and chloramphenicol.

Mono- and dichloroanilines are considered to be highly hazardous pollutants in wastewaters. These compounds are important chemical intermediates of dye production and agricultural agents. They may form also during degradation of some medicines. In pulse radiolysis investigations the hydroxyl radical formed in water radiolysis reacts with 2,6-dichloroaniline in radical addition to the ring forming hydroxy-cyclohexadienyl radical and also in hydrogen atom abstraction from the amino group resulting in anilino radical. The hydroxy-cyclohexadienyl radical in the absence of dissolved O_2 partly transforms to anilino radical, when dissolved oxygen is present the radical transforms to peroxy radical. According to chemical oxygen demand measurements, the reaction of one OH radical induces the incorporation of 0.6 O_2, into the products.

Acetovanillone (AV, Apocynin) is a derivative of vanillin. AV is known for its anti-inflammatory capabilities which are attributed to its ability to selectively prevent the formation of free radicals, oxygen ions and peroxides in the body. Hydroxyl radical, hydrated electron and hydrogen atom intermediates of water radiolysis react with acetovanillone with rate coefficients of $(1.05\pm0.1) \times 10^{10}$, $(3.5\pm0.5) \times 10^{9}$, and $(1.7\pm0.2) \times 10^{10}$ mol^{-1} dm^{3} s^{-1}, respectively. Hydroxyl radical and hydrogen atom attach to the ring forming cyclohexadienyl type radicals. The hydroxyl-cyclohexadienyl radical formed in hydroxyl radical reaction in dissolved oxygen free solution partly transforms to phenoxyl radical. In the presence of O_2 phenoxyl radical formation and ring destruction is observed. Hydrated electron in O_2 free solution attaches to the carbonyl oxygen and undergoes protonation yielding benzyl type radical. In air saturated 0.5 mmol dm^{-3} solution using 15 kGy dose most part of acetovanillone is degraded, for complete mineralization five times higher dose is required.

Ketoprofen (2-(3-benzoylphenyl)propionic acid) belongs to the class of non-steroidal anti-inflammatory drugs, the compound is frequently used as a photosenzitizer for biological substances both *in vivo* and *in vitro*. The reactions of •OH lead to hydroxylated derivatives of ketoprofen as final products. The hydrated electron is scavenged by the carbonyl oxygen and the electron adduct protonates to ketyl radical. •OH is more effective in decomposing ketoprofen than hydrated electron. Chemical oxygen demand and total organic carbon content measurements on irradiated aerated solutions showed that using irradiation technology ketoprofen can be mineralized. The initial toxicity of the solution monitored by the *Daphnia magna* test steadily decreases with irradiation. Using 5 kGy dose no toxicity of the solution was detected with at test.

Paracetamol is heavily used as analgesic and antipyretic drug. Paracetamol is regularly detected in the surface waters in micromol dm^{-3} concentration. Here, similarly to the previously discussed compounds, •OH adds to the aromatic ring producing hydroxycyclohexadienyl type radicals (see Figure 1). However, the reaction mechanism differs from that of the above mentioned compounds; there is a difference in the further reaction steps. These radicals either transform to hydroxy-paracetamol stable products in several reaction steps, or after water elimination transform to semi-iminoquinone radical. In the reactions of •OH hydroxylated paracetamol derivatives, quinone type molecules and acetamide form.

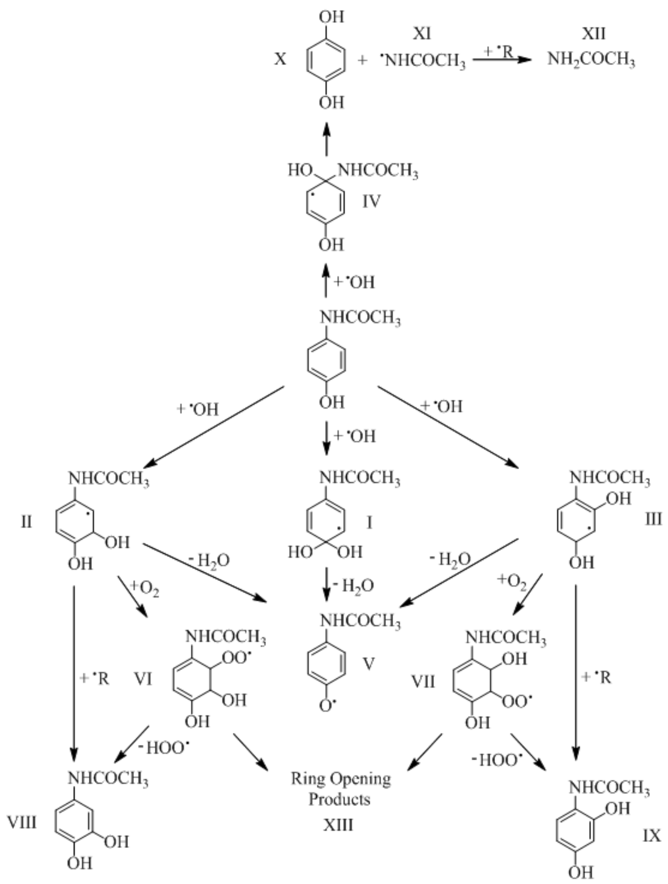


Figure 1: Suggested mechanism of paracetamol degradation

Chloramphenicol (CPL) is a highly toxic broad spectrum antibiotic. Its radiolytic degradation was studied both under oxidative and reductive conditions. Results indicate that •OH can add onto the CPL aromatic ring or can abstract H-atom from the side chain. The reductive dechlorination of CPL was also studied based on the reaction of e_{aq}^- with CPL. The toxicity increased as a function of dose to 1.0 kGy. At doses higher than 1.0 kGy the toxicity decreased continuously due to further degradation.

Remaining work

Investigations of the previously discussed compounds show that by using irradiation technology these harmful organic contaminants can be easily degraded. However, it is necessary to compare the degradability of different compounds and characterize the relation between the molecular structure and the degradability.

Related publications

[1] K. Gonter, E. Takács, L. and Wojnárovits: *High-energy ionizing radiation initiated decomposition of acetovanillone*, Radiation Physics and Chemistry 81, 1495 (2012)

[2] T. Csay, G. Rácz, E. Takács, and L. Wojnárovits: *Radiation degradation of pharmaceutical residues in water: chloramphenicol*, Radiation Physics and Chemistry 81, 1489 (2012)

[3] E. Illés, E. Takács, A. Dombi, K. Gajda-Schrantz, K. Gonter and L. Wojnárovits: *Radiation induced degradation of ketoprofen in dilute aqueous solution*, Radiation Physics and Chemistry 81, 1479 (2012)

[4] M. Chamam, C.M. Földváry, A.M. Hosseini, A. Tungler, E. Takács and L. Wojnárovits: *Mineralization of aqueous phenolate solutions: a combination of irradiation treatment and wet oxidation*, Radiation Physics and Chemistry 81, 1484 (2012)

[5] L. Szabó, T. Tóth, R. Homlok, E. Takács and L. Wojnárovits: *Radiolysis of paracetamol in dilute aqueous solution*, Radiation Physics and Chemistry 81, 1503 (2012)

[6] R. Homlok, E. Takács and L. Wojnárovits: *Ionizing radiation induced reactions of 2,6-dichloroaniline in dilute aqueous solution*, Radiation Physics and Chemistry 81, 1499 (2012)

PREFERENTIAL OXIDATION OF CARBON MONOXIDE IN PRESENCE OF HYDROGEN (PROX REACTION)

Zoltán Schay, Krisztina Frey, Anita Horváth, Zoltán Paál, László Borkó, Andrea Beck, Attila Wootsch

Objective

One possibility for the development of the so-called zero-emission vehicles is the application of the Proton Exchange Membrane Fuel Cells (PEMFC). The CO content in the hydrogen feed to the anode of the PEMFC must be, however, below 10 ppm, because it poisons the noble metal anode catalyst. Catalytic PROX reaction can be the most economic way to remove H_2 traces of CO from originated from natural gas, biogas, hydrocarbons - including (bio)diesel - and (bio)alcohols. In the frame of OTKA project #NF-73241, between 2008 and 2013 our research was focused on investigation of different type promising catalyst systems (oxide promoted Au based, PtSn, multi oxide containing) in order to reveal the relation between the catalyst composition and structure and catalytic properties for supporting the development of highly efficient PROX catalysts.

Methods

SiO_2, CeO_2 and CeO_2/ZrO_2 supported Au-CuO and SiO_2 supported Au-TiO_2 catalysts were fabricated by adsorption of different size Au colloids on the support and by impregnation with Cu-nitrate or Ti-lactate complex in different sequences followed by calcination for removal of organic residues and forming CuO or TiO_2. Co-, Mn- and mixed MnCo oxides were prepared via oxalate and carbonate deposition followed by temperature programmed oxidation for oxide formation. Unsupported PtSn catalysts were produced by direct reduction of a solution containing both H_2PtCl_4 and $SnCl_4$ using hydrazine as reducing agent. For structural characterization of the catalysts, temperature programmed oxidation and reduction (TPO and TPR), X-ray photoelectron spectroscopy (XPS), in cooperation elemental analysis, N_2 adsorption, transmission electron microscopy (TEM) and high resolution TEM (HRTEM), X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS) and synchrotron based in situ XPS techniques were applied. For catalytic characterization a test flow system based on continuous mass spectrometric and periodic gas chromatographic analysis was developed and built, by that the PROX properties (CO and O_2 conversion, selectivity of O_2 conversion into CO_2) were determined typically in temperature programmed reactions (TP-PROX). The different catalysts were compared between standardized conditions.

Results

The Au-CeO_2, CuO-CeO_2 and the three active component containing Au-CuO-CeO_2 systems and the cobalt oxide (Co_3O_4) and first of all the mixed Mn-Co oxides ($Mn_mCo_{3-m}O_4$) presented the best PROX performance among the catalysts studied. In cases of Au-CuO/CeO_2 samples no synergetic effect could be observed between Au and CuO in any of the variously prepared systems; furthermore, weakened properties appeared in some of the three-component ones. In the Mn substituted Co_3O_4, however, the synergism was clear as demonstrated in Fig. 1. The experienced catalytic effect of different catalysts was correlated with the structural properties.

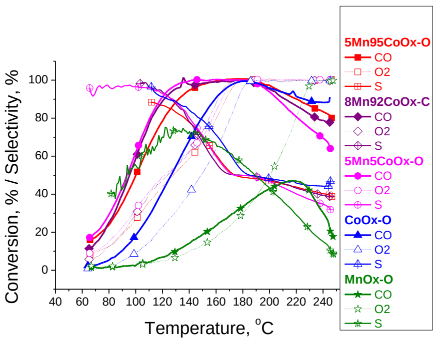


Figure 1: TP-PROX reaction on the oxalate (-O) and carbonate (-C) derived MnCo mixed oxides, CoOx and MnOx

Related publications

[1] K. Frey, A. Beck, I. Sajó, J. Osán, G. Sáfrán, M. Veres, N. Kruse and Z. Schay: *Manganese-promoted cobalt oxide with high catalytic activity in different reactions*, 15th International Congress on Catalysis 2012, Munich, 2012. 07. 1-6, Abstract #7573 (2012)

[2] K. Frey, V. Iablokov, G. Sáfrán, J. Osán, I. Sajó, R. Szukiewicz, S. Chenakin and N. Kruse: *Nanostructured MnOx as highly active catalyst for CO oxidation*, J. Catalysis **287,** 30 (2012)

[3] D. Teschner, A. Wootsch and Z. Paál: *Preferential CO oxidation in hydrogen (PROX) on unsupported PtSn catalyst*, Appl. Cat. A: Gen **411-412,** 31 (2012)

[4] OTKA #NN-73241 final report

PRODUCT DEVELOPMENT FOR CONTROLLED HOUSEHOLD RIPENING OF FRUITS

Erzsébet Takács

Objective

The project's aim is the development of a product line that makes possible the controlled ripening of fruits at household level. Production technology and prototypes are also outcomes of the project. Ethylene gas accelerates ripening and a salt is used for gas evolution which releases ethylene when dissolved in alkaline water. It is a project with five participants and our task has been to produce hydrogels with controlled water swelling, water releasing properties in order to control the rate of gas production.

Methods

Monomer solutions of 5, 10, 20% were prepared from hydroxyethyl methacrylate (HEMA) and N-vinylpirrolidone (NVP). Hydrogels were synthesized by irradiating the solutions in PE bags using a Co-60 gamma source with a dose rate of 5,7 kGy/h and 5, 10, 15, 20, and 25 kGy absorbed doses. The masses of the samples were measured after preparation (m_n) and after freeze drying (m_{sz}). The swelling in water (D%) was calculated as follows:

$$D\% = \frac{m_n - m_{sz}}{m_{sz}} \times 100$$

Results

The equilibrium swelling of poly-HEMA hydrogels was about 200% and it was not changing significantly with the crosslinking dose. Equilibrium swelling was reached in one hour. NVP hydrogels with the highest equilibrium swelling (about 5000%) were obtained by irradiation with 10 kGy. The swelling of this sample was continuously increasing for 72 hours. With increasing the crosslinking dose the equilibrium swelling somewhat decreased but the time to reach equilibrium also decreased. Based on these results we found that the poly-NVP gels prepared from 10% monomer solution with 15 kGy absorbed dose have swelling properties most convenient for ethylene gas evolution.

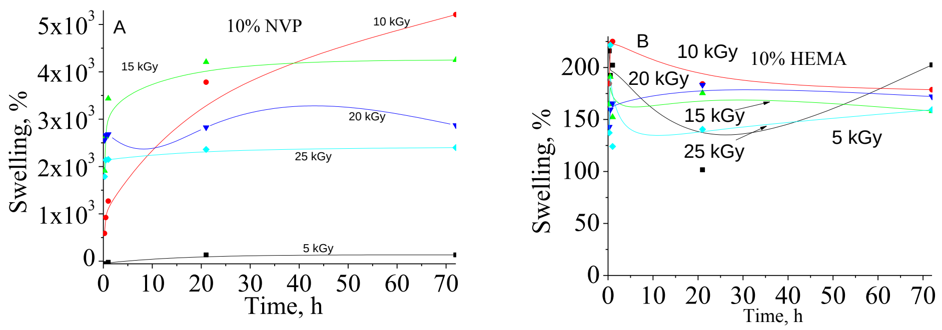


Figure 1: Swelling kinetics of samples prepared from 10% monomer solution with various absorbed doses. A: – poly-NVP, B: – poly-HEMA

Remaining work

As a continuation of the work we will characterize the ethylene gas permeability of the polymer samples, processed by our partner. The gas concentration in the ripening boxes will be controlled either by the rate of gas evolution from the salt or by the rate of gas permeation through a polymer foil.

RESULTS OF THE HUNGARIAN-MOROCCAN BILATERAL INTER-GOVERNMENTAL COLLABORATION (TÉT-10-1-2011-0492)

László Szentmiklósi, Tamás Belgya

Objective

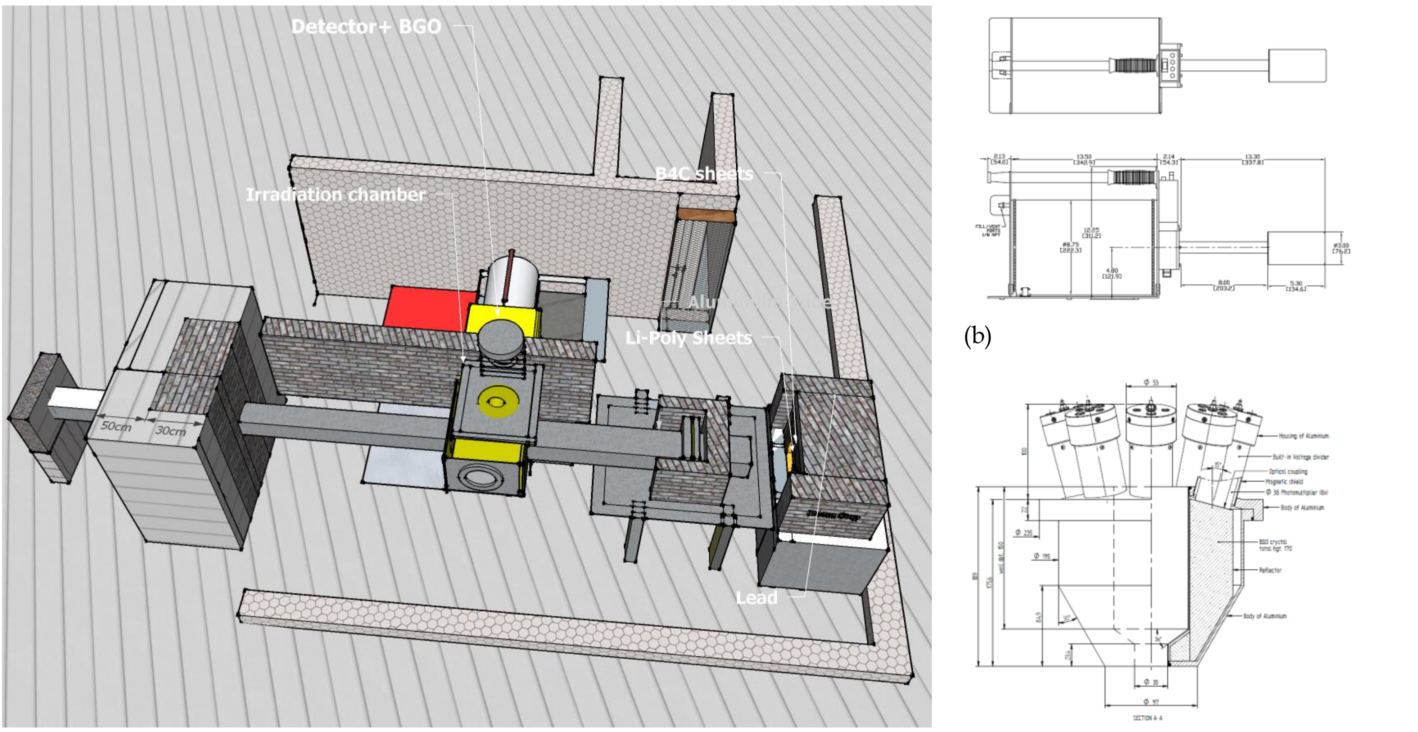
A Hungarian-Moroccan bilateral inter-governmental collaboration (TÉT-10-1-2011-0492) has been established to promote the development of prompt gamma neutron activation technique (PGAA) at CNESTEN, Rabat, and its applications in environmental science and archaeology. The project started in March 2012 and will last for 24 month.

Methods

Application of the prompt gamma activation analysis methodology as described in the "Standard Operating Procedure of the Budapest PGAA-NIPS/NORMA-DÖME facility" (NAL-PGAA-01), Monte Carlo simulations with the MNCP code, negotiating with IAEA officer Danas Ridikas to purchase equipment through the Agency.

Results

In fulfilment of the first year tasks, two guest scientists from CNESTEN (Mr. Hamid Amsil and Mr. Khalid Embrach) were trained for two months (16 Sep – 16 Nov) and two weeks (16 Sep – 29 Sep), respectively. They became familiar with the PGAA method to support the setup of the first Moroccan PGAA facility. Two visiting scientists from the same institution (Dr. Moussa Bounakhla, Mr. Nacir Bouzekri) were hosted as a part of an IAEA MOR 1007 TC. Two scientists of the PGAA group made a visit at CNESTEN between 21-27 Oct 2012. We visited the reactor hall to see the planned site of the facility. With two oral presentations we participated in the TANCA 2012 (Conférence sur les Techniques Analytiques Nucléaires et Conventionnelles et leurs Applications) conference. We contributed to the design of the Moroccan PGAA facility by defining the geometry of the central HPGe detector, and recommending geometry for a Compton suppressor. A layout of the beam shutter was also proposed, but it needs an adaptation to the local geometry.



(a) (b) (c)

Fig.1: a) the conceptual design of the facility, b) the geometry of the HPGe detector, c) the geometry of the Compton suppressor

Remaining work

We will continue to provide support for the engineering of the facility and we will contribute to the implementation of the facility in 2013 on site. We will host another 2 guests for training in nuclear analytical techniques.

STRUCTURE OF IRON-CARBOXYLATE MOF'S: INFLUENCE OF SYNTHESIS CONDITIONS

Károly Lázár

Objective

Study of porous Metal-Organic-Framework (MOF) materials has recently gained significant emphasis. These materials have defined, although flexible 3D structure, enabling incorporation of small simple guest molecules. Typically a central metal ion is coordinated by oxygen ions, and these octahedra are linked together with organic chains, benzene rings, etc.

It was found in a recent study performed at the Kemijski Institut, Ljubljana, that replacement of the aqueous solvent with 1:1 acetone/water mixture in a simple synthesis results in a drastic change in the structre. Namely, MIL-100(Fe) forms in the aqueos media, whereas MIL-45(Fe) is obtained in the 1:1 aceetone/water mixture. Our team contributed to the related structure studies following the stages of synthesis by Mössbauer spectroscopy in the framework of a bilateral Slovenian-Hungarian TeT project (bilateral cooperation).

Methods

For hydrothermal synthesis of MIL(Fe) aqueous solutions of $FeCl_3$. 6 H_2O and $C_9H_6O_6$, trimesic-acid (benzene-1,3,5,tricarboxylic acid) were used. In another syntthesis the aqueous solution was replaced by 1:1 mixture of acetone/water. The formed products were analysed by Scanning Electron Microscopy, powder XRD (X-ray diffraction), infrared spectroscopy as well as with synchrotron XAS (X-ray absorption spectroscopy) at the XAFS (X-ray absorption fine structure) beam line at the ELETTRA (Synchrotron Light Laboratory) and at the DESY (Deutsches Elektronen Synchrotron) beam line of HASYLAB. The coordination and oxidation states of iron were analysed by Mössbauer spectroscopy [1].

Results

The structures of the mentioned MIL-45(Fe) and MIL-100(Fe) have been determined from XRD and XAS measurements (Figure 1).

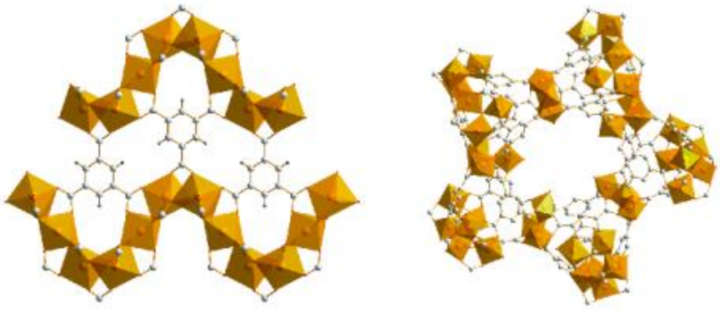


Figure 1: Structures of MIL-45(Fe), left, and MIL-100(Fe), right

As for the Mössbauer analysis, final products of syntheses were analysed first. MIL-100(Fe) and MIL-45(Fe) exhibit distinctly different patterns. Namely, in the MIL-100 structure iron is trivalent in the centre of octahedra whereas iron is in ferrous state in MIL-45. This indicates that ferric to ferrous reduction has taken place during formation of MIL-45. Thus, in the further stage the emphasis was laid on studying the steps of formation of MIL-45(Fe). First, spectra were collected on the starting $FeCl_3/H_2O$/acetone + trimesic acid brownish gel. Iron ions were found in the same trivalent state as in the starting $FeCl_3$. 6 H_2O. The gel became a greenish liquid after a few (3-4) hours of hydrothermal synthesis at 180 °C, the corresponding spectra of samples taken from this liquid show the presence of ferrous iron. Large crystals of FeMIL-45(Fe) can be collected from the synthesis autoclave only later, after 2-3 days. These measurements clearly demonstrate that ferrous iron is reduced at a very early stage in the synthesis mixture to ferrous state. Upon reduction the ligand sphere around iron is changing, and this small change may have a structure directing influence, which finally ends up in formation of the MIL-45 framework. Thus, the Mössbauer studies might provide important information on the oxidation state of iron and prove that reduction has taken place in the very beginning. The detailed description of the complete study has been published in a reputed journal [1].

Remaining work

There is no remaining work left for the study of this particular MIL-45(Fe)/MIL-100(Fe) pair of compounds. However, the cooperation was fruitful, and it is worth to sustain it for future characterisation of other promising iron containing MOF's.

Related publication

[1] T. Birsa Čelič, M. Rangus, K. Lázár, V. Kaučič, N. Zabukovec Logar: *Spectroscopic evidence for the structure directing role of the solvent in the synthesis of two iron carboxylates*, Angewandte Chemie, International Edition, **51,** 12490-12494 (2012)

STUDY OF HIGHLY SELECTIVE HETEROGENEOUS CATALYTIC PROCESSES. „GREEN CHEMISTRY"

Andrea Vargáné Beck, László Borkó, Zoltán Schay, Krisztina Frey, Anita Horváth, Antal Tungler, Nóra Győrffy, Tamás Ollár, Tibor Szarvas, Pál Tétényi, László Guczi

Objective

Investigations were performed for supporting the development of highly selective catalytic systems in three different reactions, two of them relating to fine chemical processes and the third in connection with biodiesel fuel production from vegetable oils containing triglicerids and fatty acids. The subtopics were: (i) selective oxidation of glucose and benzyl-alcohol as model substrates on AuAg and AuCu bimetallic catalysts, as a part of exploration of potential of promising Au-based bimetallic catalyst systems, (ii) asymmetric heterogeneous catalytic hydrogenation, study on molecular requirements of asymmetric induction, and (iii) oleic acid decarboxylation by hydrotreating process on sulfided alumina supported NiMo (containing P) and NiW catalysts.

Methods

For selective oxidation investigation, silica and alumina supported AuAg and AuCu and the monometallic reference catalysts were prepared by colloid methods, via formation of aqueous monometallic or bimetallic sols followed by adsorption of the metal nanoparticles with well-controlled size and structure on the support. For the structural characterization of the sols, as prepared and used catalysts UV-vis spectroscopy, transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) were applied. Glucose oxidation catalytic studies were performed with oxygen in aqueous solution applying high precision liquid chromatograpy (HPLC) analysis, for characterization of O_2 activation ability CO oxidation tests were done with quadrupole mass spectroscopy (QMS) analysis. The catalytic system for liquid phase and vapour phase selective oxidation of benzyl alcohol with gas chromatoraphy (GC) analysis is under construction. Asymmetric hydrogenations were performed in liquid phase applying Pd catalysts, the reaction mixture was analyzed by chiral gaschromatography. Oleic acid hydrotreating reaction was investigated in a special microanalytical reactor by ^{14}C- and ^{35}S-labelling of the reactant $C_{17}H_{33}$-$^{14}COOH$ and the sulfided catalysts, respectively, providing information on the mechanism of the process and sulfur leaching.

Results

Aqueous phase reduction of Ag-nitrate in presence of stabilizer, followed by the reduction of $HAuCl_4$ in the preformed Ag sol produced alloyed AgAu nanoparticles, as evidenced by UV-vis, HRTEM and XPS. This structure was retained after adsorption on the support, however, calcination applied for removal of organic residues resulted in formation of Au-Ag_2O structure based on XPS results. This form of AuAg catalysts and also the monometallic analogues provided 100% selectivity towards gluconic acid formation in glucose oxidation reaction under optimized conditions. Synergism was observed in activity of bimetallic samples of Ag/Au≤0.5. Their activity inversely correlated with the Ag/Au surface atomic ratio determined by XPS. The presence of Ag_2O on or beside the Au surface possibly enhances the O_2 adsorption ability, however, decreasing the extended Au surfaces necessary for glucose adsorption [1] lowers the activity.

In model AuAg/SiO_2/Si(100) systems prepared by molecular beam epitaxy (MBE) the electronic interaction of Au and Ag in bimetallic phase was studied by UPS showing modification of the valence bands in Ag rich layers, however, in CO oxidation no extreme could be observed in activity related to Ag/Au ratio [2].

For the study of the supported AuCu catalyst in selective oxidation bimetallic nanoparticles of different structure (alloyed, core/shell type) stabilized in sols were prepared and characterized by UV-vis spectroscopy and TEM, HRTEM. The nanoparticles were successfully adsorbed on Al_2O_3 and SiO_2 support. The catalytic tests and further characterization are in progress.

Studying the kinetic resolution of 2- és 3-methylcyclohexanone with (S)-prolin by reductive alkylation and asymmetric hydrogenation of 3,5-dimethyl 2-cyclohexenone, it was established that in case of the 2-methyl derivative significant enantioselectivity can be found. Thus this is smaller than in case of trimethyl-cyclohexanone. Hydrogenation of dimethyl cyclohexenone results in one stereoisomer (meso).

The developed radioactive microanalytical method using oleic acid-1-^{14}C is suitable for the evaluation of different catalysts in hydrotreating process of vegetable oils.

Remaining work

Investigation of the supported AuCu system in selective oxidation will be continued. Publication is under preparation.

Related publications

[1] L. Guczi, A. Beck and Z. Pászti: *Gold catalysis: Effect of particle size on reactivity towards various substrates*, Catalysis Today **181**, 26– 32 (2012)

[2] K. Frey, G. Pető, F. Tanczikó, I. Sajó and L. Guczi: *Iron oxide on gold/silver inverse model system prepared by molecular beam epitaxy*, 15th International Congress on Catalysis, München, Germany, July 1– 6, 2012

THE CORRELATION IN BETWEEN HYDRODESULFURIZATION ACTIVITY AND SULFUR EXCHANGE CAPACITY OF SOME SULFIDED CATALYSTS

Tamás Ollár, Tibor Szarvas and Pál Tétényi

Objective

To compare thiophene hydrodesulfurization (HDS) activity of sulfided $NiMoO_x$ catalysts with the extent of their sulfur exchange capacities in reaction $H_2{}^{35}S \leftrightarrow H_2{}^{32}S$ applying catalysts received in the framework of research contract with Pannon University.

Methods

The aim of this study was to state: whether there is in general a linear correlation between sulfur exchange capacity and hydrodesulfurization activity of sulfided Ni, Co, Pd and Pt promoted MoO_3, catalysts observed before [1] in this laboratory. With this aim six catalyst samples (Table 1) have been sulfided with ^{35}S labelled hydrogen sulfide ($H_2{}^*S$) in a circulation system, and the isotopic exchange capacity between catalyst sulfur and gas phase H_2S has been determined. Radioactivity determinations have been performed by *ex situ* liquid scintillation measurements. Thiophene HDS conversion data have been determined in pulse system [2].

Results

In Figure 1 thiophene HDS conversion data (m_{HDS}) are presented, determined for "Rec. Cat." *i.e.* for catalysts in Table 1 [3]. Comparison with data in the former study [1] indicates similar coefficient, characterizing the linear m_{HDS} vs. S_{TE} correlation for these two groups of catalysts. This allows to assume that the different chemical content of these groups does not influence the character of this correlation.

Table 1: Content of metal atoms in catalysts

Catalyst	$NiMet_{ratio}$	$NiMo_{0.06}$	$NiMo_{0.21}$	$NiMo_{0.31}$	$NiMo_{1.42}$	$NiW_{0.36}$	$NiW_{0.5}$
Surf. Area	10^3 mm²/mg	172	188	229	193	542	306
Mo or W	10^{17} atoms/mg_{cat}	2.39	11.00	7.49	1.50	12.4	16.6
Ni		0.06	2.30	2.30	2.13	4.48	8.36

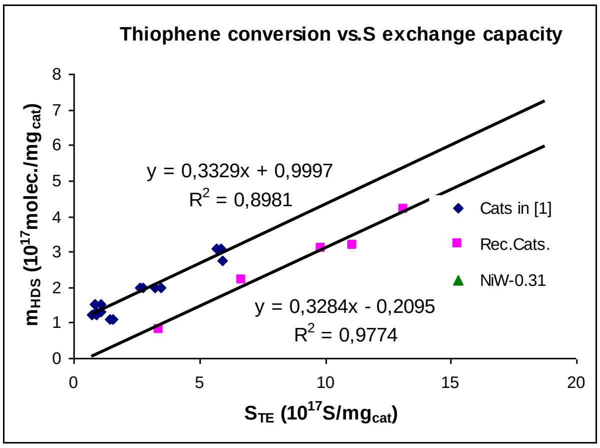


Figure 1: Thiophene HDS vs. exchangeable S

Remaining work

On several catalysts reported here, study of tiophene recyclization from C_4 hydrocarbons as the reverse process of HDS is planned for the next year.

Related publications

[1] F. E. Massoth, Tamás Koltai, Pál Tétényi: *Theoretical Analysis of Sulfur Exchange Experiments*, Journal of Catalysis, **203**, 33 (2001)

[2] Pál Tétényi, Tamás Ollár, Tibor Szarvas: *Sulfur exchange capacity and thiophene hydrodesulfurization activity of sulfided molybdena-alumina catalysts promoted by nickel*, Catalysis Today **181,** 148–155(2012)

[3] Tamás Ollár, Tibor Szarvas, Pál Tétényi: *On the Correlation in Between Sulfur Exchange Capacity and Hydrodesulfurization Activity of Mo- or W-sulfide Based Supported Catalysts,* in preparation

TOWARDS A SUSTAINABLE FINE CHEMICAL AND PHARMACEUTICAL INDUSTRY: SCREENING AND RE-UTILIZATION OF CARBON-RICH LIQUID WASTES

László Wojnárovits, Antal Tungler, Erzsébet Takács, Arezoo Hosseini, Chamam Mounir, Andrea Jobbágy, Gábor Tardy, Péter Mizsey, Tamás Benkő, Edit Cséfalvai, Magdolna Makó, Szilvia Szikora Tarjányiné, Cesar Pulgarin

Objective

The purpose of the project is (i) to elaborate a novel biological screening methodology, taking the concentration dependence of biodegradability and toxicity as well as possibilities offered by the co-treatment with domestic wastes into consideration, (ii) to work out pre-treatment procedures using physical-chemical separation processes possibly combined with chemical and/or catalytic methods in order to make originally non-biodegradable, toxic wastes utilizable and/or biodegradable.

Methods

The concentration dependence of biodegradability was tested on real wastewaters with respirometry specially designed for pharmaceutical process wastewaters. The oxidation properties of real wastewaters were determined. The finally planned characterization methods are: TOC, COD, BOI, special respirometry, special anaerobic digestion test, Zahn-Wellens test, qualitative and quantitative determination of volatile content with distillation and GC-MS, wet oxidation properties, HPLC-tandem MS for determination of non volatile , high molecular weight contaminants.

Results

The distillation parameters for real wastewaters of high volatile content and AOX, conditions of complete AOX removal from these waters have been determined. Samples were prepared for biodegradability and wet oxidation experiments, of which volatile components have been removed. Rectification column has been designed and built at EGIS company.

The necessary degree of wet oxidation was determined, which ensured the biodegradability of the treated wastewater without totally eliminating the organic carbon content of it.

An optimized photo-Fenton process, ultrasonic+AOP treatment for the nearly complete degradation of micropollutants of pharmaceutical origin has been developed.

The minority of wastewaters are toxic for activated sludge treatment also in small concentration. With activated sludge adapted to wastewaters containing industrial effluents some hardly biodegradable wastewaters could be degraded. In some cases partial wet oxidation treatment was necessary to make wastewaters biodegradable.

The tested wastewaters turned to be non degradable by anaerobic digestion. The wet oxidation pretreatment improved digestion properties.

The identified 37 micropollutants from the water of Lake Geneva could be eliminated by photo Fenton process. Both with photo-Fenton process and high energy electron irradiation the nearly complete degradation of the tested compounds could be achieved. The identification of intermediates of the irradiation processes was also carried out. So both methods seem to be appropriate for the treatment of emerging pollutants, which usually get through the activated sludge treatment in small concentration and therefore they are present in natural waters.

Duties of repair were assessed and planning for the restarting of wet oxidation reactor and that of the bioreactor working with activated sludge were carried out at Geosan. At Geosan the bioreactor has been tested and turned to work correctly in treatment of industrial wastewater. At the oxidation reactor the exchange of malfunctioning parts has begun. Preparation of the pilot scale digestion experiments at BSW has been carried out. The concentration and sort of wastewaters to be treated has been determined.

Remaining work

Pilot scale experiments of wet oxidation and anaerobic digestion. Verification and testing the design methodology by case studies. Economic and environmental evaluation, field test for the applicability of the project results under Hungarian and Swiss conditions. Cost analysis under Swiss and Hungarian conditions. Risk analysis of the main component of the pharmaceutical waste degradation.

Related publications

[1] Chamam, M., Földváry, C.M., Hosseini, A.M., Tungler, A., Takács, E., Wojnárovits, L., *Mineralization of aqueous phenolate solutions: a combination of irradiation treatment and wet oxidation.* Radiation Physics and Chemistry Volume 81, Issue 9, September 2012, Pages 1484-1488

[2] Arezoo M. Hosseini, Antal Tungler, Zoltán Schay, Sándor Szabó, János Kristóf, Éva Széles, László Szentmiklósi, *Comparison of precious metal oxide/titanium monolith catalysts in wet oxidation of wastewaters,* Applied Catalysis B: Environmental, Volume 127, (30 October 2012), Pages 99-104

RESEARCH REACTOR UTILISATION

APPLICATIONS OF PROMPT-GAMMA ACTIVATION ANALYSIS

Zsolt Kasztovszky, László Szentmiklósi, Boglárka Maróti, Katalin Gméling

Objective

To apply the prompt-gamma activation analysis method for determination of samples' elemental composition, in the fields of catalysis, material science and archaeometry, and to support the activities of the EU-funded projects NMI3-II and CHARISMA.

Methods

PGAA and NIPS facilities at a cold neutron guide of the Budapest Research Reactor, complementary methods: NORMA imaging facility, in-situ catalytical characterization (e.g. iodometric titration), solid state nuclear track detectors.

Results

Chemical catalysis

With a customized in-beam catalysis setup and oven at the PGAA station, we are able to determine slight changes in the surface and bulk elemental compositions of catalytic materials in operando. These measurements have been on-going since 2008, in collaboration with the Fritz-Haber Institute, Berlin. Based on these results, we can make highly relevant statements on the mechanism of heterogeneous catalytic processes.

In earlier years, the selective hydrogenation of alkynes in presence of alkenes was studied, that is an essential step in the large-scale polymer industry. The data analysis of the 2010-2011 experiments has now been completed, and two conclusive papers were published [1, 2]. Efforts to understand the reaction mechanism and design a proper catalyst for selective hydrogenation resulted in a low-cost, but similarly effective alternative (Al-Fe intermetallic compound) of palladium.

An eco-friendly process to replace the conventional electrolysis for producing chlorine is the so-called Deacon-reaction, based on the heterogeneous gas phase oxidation of HCl. CeO_2-based [3], and Hf, Zr, La, Y-doped CeO_2 catalysts were measured and the results were compared to the RuO_2 [4, 5], which was studied in 2011. This year much more experimental conditions (such as feed compositions, $p(O_2)$, p(HCl) and $p(Cl_2)$, and reaction temperature) could be studied. A CeO_2-based catalyst has already been further-developed for industrial application [6].

The compositions of Ti-based monolith catalysts were analyzed by conventional PGAA. They were small fragments of a Ti mesh, covered with precious metal oxides, weighting about 50-250 mg. Some of them were new, obtained with different preparation methods or from a commercial supplier, while others had already been used in wet oxidation of high organic content wastewaters. The results revealed both the performance of the preparation of the catalysts and their ageing during wet oxidation under harsh conditions. The latter could be determined by the decrease of precious metal content which occurred by leaching [7].

Material science

Co-Re based alloys are being developed at the TU Braunschweig to supplement Ni-base Superalloys at ultra-high temperature (>1200°C) applications. Grain boundaries in these polycrystalline alloys are strengthened by boron. B is known to segregate grain boundaries in Ni-alloys and improve low temperature ductility. The mechanisms to strengthen the grain boundaries are being explored for the Co-Re alloys. To have a better understanding of the effect of boron addition, a set of experimental alloy was manufactured with known added boron amounts up to 1000 ppm. However, as boron is volatile, the quantity remained in the alloy is presumably lower than added.

We quantified the B content of Co-Re-Cr(-Ta) alloys by PGAA, and a method was worked out to obtain the spatial distribution of the boron in the alloys, involving the solid state nuclear track detector (SSNTD) technique. Thanks to the high cross-section of the $^{10}B(n,\alpha\gamma)^7Li$ reaction, we could quantify boron already in a few ppm quantity, based on its 477.6 keV gamma-ray, whereas spatial mapping was based on the alpha particle. We achieved spatial resolution in the order of 10 μm, which was sufficient to map the segregation. The light-optical microscope images of the SSNTDs were compared to the texture of the metal. The comparison revealed that the boron concentrated indeed at the grain boundaries, which was the intention [8-9].

Archaeometry

Various provenance studies of chipped and polished stone tools have been continued, including obsidian, silex, porphyry and high-pressure metamorphit. The geographical region of interest has been broadened with new Polish, Romanian and Italian artefacts. We have achieved further results in classification of archaeological obsidians, which contribute to explore the prehistoric trade routes in the Central-European region (2 posters on 39th ISA, 1 talk on X. Erdélyi Régészeti konferencia, [10]).

In one particular methodological study, degradation process and possible provenance of Mycenaean (16th-13th c. B.C.) glass beads have been investigated by PGAA, PIXE and SEM-EDS. The chemical elements which changed during degradation have been determined contrary to the elements which might be used for provenance purposes (1 poster on 39th ISA).

Additionally, composition of different archaeological metal objects (Iron Age and Roman iron, Roman brass and bronze) have been measured, in order to survey their present conditions and/or to determine their origin or technology of production. The bulk PGAA has been combined with neutron radiography at the NIPS-NORMA station. The results will be published soon. Results of previous research on Inka pottery have been published in 2012 [11].

Besides scientific papers and presentations, review papers about the use of neutron methods in Cultural Heritage research have been published [12, 13].

Geochemistry

Kodolányi et al. published boron and other PGAA data measured earlier on ocean floor and fore-arc serpentinites. Serpentinites are hydrous rocks (H_2O contents up to 15-16 wt %) that form through the alteration of olivine- and orthopyroxene-dominated rocks at relatively low temperatures (below 400 degree Celsius). They can be a major component of the upper part of the oceanic lithosphere. Enrichments in Cl, B, Sr, U, Sb, Rb, Cs, and sometimes in Li, of the deep see ultramafic rocks are related to the process of serpentinization. Serpentinites show compositional variability as a function of the tectonic setting of the serpentinization. Serpentinites from mid-ocean ridge environments are characterized by high relative enrichments in Cl, B, U, Sr, Sb, Pb and Li. Passive margin serpentinites show the highest B contents. Serpentinites are the most important carriers of H, Cl and B into subduction zones when compared with other subducted components, such as sediments or altered igneous oceanic crust [14].

Remaining work

The data analysis of the completed experiments is in part still in progress. Further publications are foreseen.

Related publications

[1] M. Armbruster, M. Behrens, F. Cinquini, K. Fottinger, Y. Grin, A. Haghofer, B. Klotzer, A. Knop-Gericke, H. Lorenz, A. Ota, S. Penner, J. Prinz, C. Rameshan, Z. Revay, D. Rosenthal, N. Rupprechter, Sautet, R. Schlogl, L.D. Shao, L. Szentmiklosi, D. Teschner, D. Torres, R. Wagner, R. Widmer and G. Wowsnick: *How to Control the Selectivity of Palladium-based Catalysts in Hydrogenation Reactions: The Role of Subsurface Chemistry.,* ChemCatChem **4**, 1048 (2012)

[2] M. Armbruster, K. Kovnir, M. Friedrich, D. Teschner, G. Wowsnick, M. Hahne, Gille, L. Szentmiklosi, M. Feuerbacher, M. Heggen, F. Girgsdies, D. Rosenthal, R. Schlogl and Y. Grin: *Al13Fe4 as a low-cost alternative for palladium in heterogeneous hydrogenation.,* Nature Materials **11,** 690 (2012)

[3] R. Farra, M. Eichelbaum, R. Schlögl, L. Szentmiklósi, T. Schmidt, A.Amrute, C. Mondelli, J. Pérez-Ramírez, and D. Teschner, *Do observations on surface coverage-reactivity correlations always describe the true catalytic process? A case study on ceria.,* Journal of Catalysis **297**, 119 (2013)

[4] D. Teschner, R. Farra, L.D. Yao, R. Schlogl, H. Soerijanto, R. Schomacker, T. Schmidt, L. Szentmiklosi, A.Amrute, C. Mondelli, J. Perez-Ramirez, G. Novell-Leruth, and N. Lopez: *An integrated approach to Deacon chemistry on RuO2-based catalysts.,* Journal of Catalysis **285,** 273 (2012)

[5] D. Teschner, G. Novell-Leruth, R. Farra, A. Knop-Gericke, R. Schlogl, L. Szentmiklosi, M.G. Hevia, H. Soerijanto, R. Schomacker, J. Perez-Ramirez, and N. Lopez: *In situ surface coverage analysis of RuO2-catalysed HCl oxidation reveals the entropic origin of compensation in heterogeneous catalysis.,* Nature Chemistry **4,** 739 (2012)

[6] M. Moser, C. Mondelli, T. Schmidt, F. Girgsdies, M.E. Schuster, R. Farra, L. Szentmiklósi, D. Teschner, and J. Pérez-Ramírez, *Supported CeO2 catalysts in technical form for sustainable chlorine recycling,* Applied Catalysis B **132–133** 123 (2013)

[7] A.M. Hosseini, A. Tungler, Z. Schay, S. Szabo, J. Kristof, E. Szeles and L. Szentmiklosi: *Comparison of precious metal oxide/titanium monolith catalysts in wet oxidation of wastewaters.,* Appl. Catal. B **127**, 99 (2012)

[8] D. Mukherji, J. Rösler, M. Krueger, M. Heilmaier, M.-C. Bölitz, R. Völkl, U. Glatzel, and L. Szentmiklósi: *Effects of boron addition on microstructure and mechanical properties of Co-Re-based high temperature alloys.* Scripta Materialia **66,** 60 (2012)

[9] D. Mukherji, J. Rösler, J. Wehrs, Strunz, Beran, R. Gilles, M. Hoffmann, M. Hölzel, H. Eckerlebe, L. Szentmiklósi, and Zs. Mácsik: *Application of In-situ Neutron and X-ray Measurements at High Temperatures in the Development of Co-Re-based Alloys for Gas Turbines.* Metallurgical and Materials Transactions A, **44** 22 (2013)

[10] F. Bernardini, A. De Min, D. Lenaz, Z. Kasztovszky, Turk, A. Velušček, V. Szilágyi, C. Tuniz, and E. Montagnari Kokelj: *Mineralogical and Chemical Constraints on the Provenance of Copper Age Polished Stone Axes of 'Ljubljana Type' from Caput Adriae.* Archeometry, 2013: in press.

[11] V. Szilágyi, J. Gyarmati, M. Toth, H. Taubald, M. Balla, Z. Kasztovszky, and G. Szakmany: *Petro-mineralogy and geochemistry as tools of provenance analysis on archaeological pottery: Study of Inka Period ceramics from Paria, Bolivia.,* Journal of South American Earth Sciences **36,** 1 (2012)

[12] Zs. Kasztovszky and L. Rosta, *How can neutrons contribute to cultural heritage research?,* Neutron News **23,** 25 (2012)

[13] T. Belgya, Kasztovszky, Zs., Kis, Z. Szentmiklósi L, *Hidegneutronok alkalmazása elemanalitikai és magfizikai kutatásokban*, NUKLEON **5**: p. 121. (2012)

[14] J. Kodolanyi, T. Pettke, C. Spandler, B.S. Kamber, and K. Gmeling: *Geochemistry of Ocean Floor and Fore-arc Serpentinites: Constraints on the Ultramafic Input to Subduction Zones*, Journal of Petrology **53,** 235 (2012)

IN-BEAM MÖSSBAUER FACILITY FOR STUDYING NOBLE METAL CATALYSTS

Károly Lázár, Sándor Stichleutner, Tamás Belgya, Anita Horváth

Objective

The objective has been the construction of a facility enabling to perform low-temperature Mössbauer measurements by producing Mössbauer sources with neutron in-beam excitation. In the first stage of the work the emphasis is laid on the assembly of a closed He circuit to provide means for low temperature measurements and to perform pilot off-beam ^{197}Au and ^{193}Ir measurements with bimetallic supported catalyst samples containing gold and iridium. This first stage is supported by the four-year long OTKA 81863 project. The completion of the real in-beam activation arrangement is planned in a further stage.

Methods

The principal method applied is the Mössbauer spectroscopy which can be used for studying catalysts, too [1]. Introduction of the in-beam activation broadens widely the number of available sources, demanding, however, low measuring temperature [2]. For preparation of catalysts conventional and sol-based methods have been used [3]. For design of the protection shield against neutron generated γ-radiation the MCNP5 simulation code was used [4].

Results

Certain progress has been made related to four different sides of the original basic project. Namely, at the first stage a starting overview has been prepared [2]. Then, the method has been introduced in different intenational conferences [5]. On the practical side, pilot measurements have been carried out at 80 K temperature, ^{197}Au spectra were collected on monodisperse gold particles of different diameter (4 – 29 nm). It was proven that the strength of the signal (connected to the probability of the Mössbauer effect) depends on the particle size, as expected [2]. Typical spectrum is presented in Figure 1.

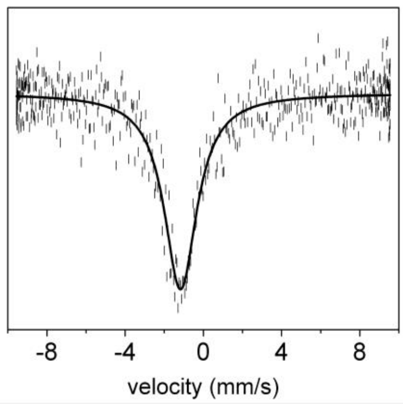


Figure 1: 80 K Mössbauer spectrum of 29 nm gold particles stabilized with dextrane [2]

Progress has also been made in synthesis and catalytic characterisation of the proposed bimetallic systems: Au modified Ni/Al_2O_3 catalysts have been prepared and characterised [3]. The mentioned three developments are connected primarily to the OTKA project.

A fourth action, with regard to the construction of the final in-beam assembly, has also been done. First the nominal temperature of neutrons in the guide was estimated [6]. Further on, design of the protection shield against neutron induced γ-radiation along the 7 m long neutron guide was performed. Assuming 5 x 10^8 neutrons cm^2 s^{-1} flux at the entrace of the guide and considering only two sources of emerging γ-radiation (reactions with boron and with the Ti/Ni layer, emitting 478 keV and 8 MeV rays, respectively). It was found in the calculations that about. 5 cm thick lead may provide an appropriate protection (100 μGy/h dose rate) [4].

Remaining work

For completion of the OTKA project the assembly of the He circuit should be completed soon in order to provide sufficient time for recording off-line ^{197}Au and ^{193}Ir spectra during the remaining approx. one year left from the OTKA project. Further on, the construction of the real in-beam assembly should also be persisted.

Related publications

[1] K. Lázár: *Study of catalysts by Mössbauer spectroscopy*, Mössbauer Effect Reference and Data Journal, **35,** 134 (2012)

[2] K. Lázár, T. Belgya, E. Csapó, I. Dékány, V. Hornok, S. Stichleutner: *In-beam Mössbauer spektroszkópia*, Nukleon **5**, 120 (2012)

[3] A. Horváth, Gy. Stefler, V. La Parola, L. F. Liotta, G. Pantaleo, A. M. Venezia and L. Guczi: *Comparative study on Au modified Ni/MgAl$_2$O$_4$ catalysts for dry reforming of methane*, 15th International Congress on Catalysis, Munich, Germany, Abstract# 1605 (2012)

[4] T. Belgya, S. Stichleutner: *Az in-beam Mössbauer berendezéshez tartozó 7 méteres neutronvezető ólomvédelmének tervezése,* Internal Report 3 pp. (2012)

[5] S. Stichleutner, T. Belgya, K. Lázár: *^{197}Au Mössbauer Experiment at the New In-Beam Mössbauer Spectroscopy Station at the Budapest Research Reactor.* 12th International Conference on the Applications of the Mössbauer Effect, Suzdal, Russia, Contribution C8-6, Conf. Proc., p. 167 (2012)

[6] T. Belgya: Prompt gamma activation analysis at the Budapest Research Reactor, Physics Procedia **31,** 99 (2012)

CHARISMA - CULTURAL HERITAGE ADVANCED RESEARCH INFRASTRUCTURES: SYNERGY FOR A MULTIDISCIPLINARY APPROACH TO CONSERVATION/ RESTORATION

Zsolt Kasztovszky, Boglárka Maróti, László Szentmiklósi, Zoltán Kis, László Rosta, György Káli*, Zoltán Szőkefalvi-Nagy*, Imre Kovács**

**Wigner Research Centre for Physics, Hungarian Academy of Sciences*

Objective

CHARISMA is an EU-funded integrating activity project carried out in the FP7 Capacities Specific Programme "Research Infrastructures". The project – which lasts from October 2009 until March 2014 – provides transnational access to most advanced scientific instrumentation and knowledge allowing scientists, conservators-restorers and curators to enhance their research at the field forefront. Transnational Access programme offer European scientists to carry out their experiments utilizing 3 different and complementary groups of facilities (ARCHLAB, MOLAB and FIXLAB) through a service embedded in a multidisciplinary environment involving material science and artwork conservation/restoration. The Budapest Neutron Centre – with the leadership of Wigner Research Centre for Physics and in cooperation with the Centre for Energy Research – offers non-destructive investigations of objects with Cultural Heritage significance (i.e. archaeological finds and other art objects), as a Transnational Access provider.

Methods

The following facilities are available for CHARISMA users, within the BNC consortium:

- Prompt Gamma Activation Analysis and Neutron Induced Prompt Gamma Spectrometer (supplemented with Prompt Gamma Activation Imaging / Neutron Tomography unit): applicable for determination of bulk elemental composition with optional tomography and elemental mapping of large objects – at the Centre for Energy Research
- Time of Flight Neutron Diffraction, Triple Axis Spectrometer and Small Angle Neutron Scattering: applicable for non-invasive micro structural- and phase analyses– at the Wigner RCP
- External milli-beam PIXE (Particle Induced X-ray Emission) and compact XRF (X-ray fluorescence): applicable to determine the near-surface elemental composition – at the Wigner RCP.

Results

In 2012, ten various projects, proposed by European scientists, have been completed. The material investigated comprises Palaeolithic stone objects, Roman copper alloy objects, iron and glass objects, Bronze Age and Medieval armour. With the help of compositional and structural results, users hope to gain information regarding the provenance or techniques applied to produce the objects, as well as information to support conservation actions needed. In most research projects, combinations of the available non-destructive methods, being complementary to one another, have been applied. The summary of the projects in 2012 can be found in Table 1.

Remaining work

The CHARISMA project will be continued until the spring of 2014. New proposals are expected in two calls of 2013, and successful experiments will be scheduled. Evaluation of the experimental data, as well as dissemination of the results is continuous.

Related publications

[1] F. Bernardini, A. De Min, D. Lenaz, Z. Kasztovszky, P. Turk, A. Velušč, V. Szilágyi, C. Tuniz, E. Montagnari Kokelj: *Mineralogical And Chemical Constraints On The Provenance Of Copper Age Polished Stone Axes Of 'Ljubljana Type' From Caput Adriae*, Archaeometry (in press)

[2] Zs Kasztovszky, K. T. Biró, V. Szilágyi, B. Maróti, T. Težak-Gregl, M. Burić, A. Hágó, C. Astalos, I. Nagy-Korodi, S. Berecki, A. Hajnal, B. Rácz: *Recent Provenance Study of Obsidian Artefacts found in Central Europe* (p), 39th International Symposium on Archaeometry, 2012.05.28-06.01., Leuven, Belgium

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[4] T. Birch, P. Crew, Zs. Kasztovszky, B. Maróti, T. Mighall: *Using PGAA to determine the composition of experimental iron smelting residues: strengths and limitations of a non-destructive analytical technique* (p), 39th International Symposium on Archaeometry, 2012.05.28-06.01., Leuven, Belgium

[5] T. Birch, P. Crew, Zs. Kasztovszky, B. Maróti and T. Mighall: *Ore, slag and inclusion: measuring variability in the direct process and assessing its implications for provenancing iron using the SI method* (o), 39th International Symposium on Archaeometry, 2012.05.28-06.01., Leuven, Belgium

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Table 1: Summary of CHARISMA projects in 2012.

BNC Proposal Nr.	*Principal Proposer*	*Principal Proposer's Affiliation*	*City, Country*	*Proposal Title*	*Experiments' Date*	*BNC Instruments*	*Main Achievements*
301	Otis Crandell	Babes-Bolyai University	Cluj-Napoca, Romania	Carpathian Regional Exchange Materials of the Eneolithic and Neolithic Eras	2012.01.24-29	PGAA	Based on the PGAA results, along with petrographic analyses and previous PGAA data, the source of the artefacts can be identified, which in turn supports the theory of long distance import.
298	Iwona Sobkowiak-Tabaka	**Inst of Archaeology and Ethnology Polish Academy of Sciences**	Poznan, Poland	Origin and distribution of obsidian in Poland	2012.02.14-18	PGAA	According to the results, all the objects show a typical composition, characteristic for the "Carpathian 1" obsidian type, a well localized geological source region on North of the Tokaj mountains (Vinicky or Cejkov locations).
282	Alan Williams	**The Wallace Collection**	London, UK	Non-destructive Prompt-Gamma Activation Analysis of Swords and Helmets	2012.04.24-26	TOF-ND, PGAA, NIPS-NORMA	Trace elements of B, P, S, Cl, Ca, Mn, Co, Ni, Cu, Ag and Au were detected. Despite the expected high level of C in Oriental steels, it was still below the detection limit of PGAA. The presence of Mn and S suggests MnSO4 inclusions which suggests modern steel.
281	David Watkinson	**Cardiff University**	Cardiff, UK	Quantitative Analysis and Distribution of Chloride in Archaeological Iron	2012.05.14-16	PGAA, NIPS-NORMA	Ten iron nails were analyzed for bulk Cl content with PGAA and 5 nails on NIPS to look for chloride distribution in 10-20 slices of 3 mm. 3D NT of a nail and TOF neutron diffraction was applied, too. The work has contributed significantly to further studies of archaoelogical iron corrosion.
297	Nicolas Thomas	**INRAP –Laboratoire de médiévistique occidentale de Paris**	Paris, France	Cuivre, laiton, dinanderie mosane : Ateliers et productions métallurgiques…	2012.06.26-29	PGAA, NIPS-NORMA	Four archaeological cauldrons and an experimental reconstruction were analyzed. The comparison of metal composition between feet and body answered definitely the question whether the different parts have been cast separately or not.
299	Marianne Mödlinger	**University of Genoa, Dept. of Chemistry and Industrial Chemistry (DCCI)**	Genoa, Italy	Analyses of Hungarian Armour of the Bronze Age: Alloy Composition and Texture	2012.06.25-29	TOF-ND, PGAA, External m-PIXE, XRF	Two complete helmets, one greave, three fragments of shields were investigated by PGAA, TOF-ND and PIXE. Limited information can be gained from TOF-ND about the texture, and bulk PGAA can reveal the alloying components even in corroded objects.
317	Bogdan Constantinescu	**National Institute of Nuclear Physics and Engineering**	Bucharest, Romania	Archaeological obsidian characterization using PGAA, External milli- PIXE and XRF	2012.08.28-09.07	PGAA, External m-PIXE, XRF	50 archaeological obsidians from Neolithic sites from Romania were analyzed by milli-PIXE and by PGAA. With PIXE, Mn/Ti ratios and Rb, Sr, Y and Zr were determined as "fingerprints" to distinguish between different geological sources. PGAA provided major elements and specific traces of B, Cl, Nd, Sm and Gd.
320	Nicholaos Zacharias	**Department of History, Archaeology and Cultural Resources Management, University of Peloponnese**	Kalamata, Greece	Provenance Oriented Interdisciplinary Glass Studies: the Hagia Sofia Metal, Glass Tesserae from the Hagia Sofia, Konstantinopolis and a Mycenaean Glass Collection from Patras, Achaia	2012.10.16-19	PGAA, External m-PIXE, XRF	PGAA provided data on historical glass samples. Results are considered as unique indicators of base glass used for the production of the material. Values were compared with earlier SEM/EDAX and EDS/XRF data. Application of PIXE on selected non-corroded samples was initiated.
300	Massimo Rogante	**Rogante Engineering Office**	Civitanova Marche, Italy	NIPS, TOF-ND and PIXE Investigation of Roman-Picenum metal archaeological objects from the academia Georgica Treiensis collection	2012.11.12-15	TOF-ND, External m-PIXE, PGAA, NIPS-NORMA	Nine Roman copper-based objects (fibulas, vessels and a lamp) with unknown composition were analyzed with PGAA, TOF-ND and PIXE. Based on the results, most of the objects turned to be tin-bronze, whereas the polilicnes lamp proved to be very high Zn brass.
319	Daniela Stan	**National Institute of Nuclear Physics and Engineering**	Bucharest, Romania	Mineral pigments studies on XVth and XVIIth centuries Iznik ceramics artifacts from Romanian Museums	2012.11.12-15	PGAA, External m-PIXE, XRF	Mineral pigments on glazed 15th-16th c. ceramics were investigated with PIXE; Independently, bulk composition of coloured glass beads from Mycenean era were measured with PGAA.

COMMERCIAL MEASUREMENTS OF THE PGAA GROUP IN 2012

László Szentmiklósi, Zsolt Kasztovszky, Boglárka Maróti

Objective

To provide analytical service to the customers on a commercial basis, using the PGAA (prompt-gamma activation analysis) technique.

Methods

Application of the prompt gamma activation analysis methodology as described in the "Standard Operating Procedure of the Budapest PGAA-NIPS/NORMA-DÖME facility" (NAL-PGAA-01).

Results

We completed the following measurements in 2012:

- Composition of 6 silicon samples
- Composition of 19 mineralogical samples
- Impurities of Al alloys (3 samples)
- Panorama analysis of 6 inactive graphite samples and 3 rock samples
- 3 archaeological samples for the HNM Centre for National Cultural Heritage

Remaining work

We continue to offer our analytical services for the customers and adapt our methodology to the requests.

Related publications

6 analysis reports (confidential)

DEVELOPMENT OF ANALYTICAL METHODS AND NUCLEAR DATA DETERMINATION

Tamás Belgya, László Szentmiklósi, Zoltán Kis and Boglárka Maróti

Objective

To develop our analytical and imaging capabilities in Prompt-Gamma Activation Analysis, PGAI (Prompt Gamma Activation Imaging) / NT (Neutron Tomography), XRF (X-ray fluorescence) and low-level counting, to determine relevant nuclear data related to nuclear reactors, transmuters and nuclear physics, to conduct teaching in PGAA.

Methods

Hardware upgrade, programming, Monte Carlo modelling, comparison of PGAA and XRF measurements, measurements on reactor related materials, evaluation of data and comparison to literature, teaching.

Results

The hardware at the PGAA-NIPS facilities has been upgraded with several new components, including the new NORMA tomograph (NT) and the Compton-suppressed NIPS detector. These are key components of our new PGAI/NT equipment. The Budapest PGAA Data Acquisition Software was developed further to serve both NT and PGAI acquisition tasks, in batch or manual acquisition modes. The development of our facility and methods were presented at several conferences or workshops at 10 workshops and published in Refs. [1-3].

We performed (n,γ) measurements on ^{237}Np and ^{242}Pu samples to extend the PGAA spectroscopic library and nuclear data [4]. Results of our earlier (n,γ) nuclear data measurements have also been published [5-7]. Measurements of hydrogen content in the corrosion of Zr fuel cladding have been performed in collaboration with the Fuel and Reactor Materials Department. The first results show good correlation between the applied methods.

Monte Carlo modelling of our PGAA detector's response function is in progress using the GEANT4 code of CERN and we have been modelling gamma strength functions in ^{114}Cd. Partial results have been presented at workshops.

We have finished the commissioning of our hand-held XRF equipment and started a comparison between the PGAA and XRF methods, in order to complement PGAA results for elements with low-sensitivities. The first results show acceptable agreement between the two methods; however, the role of the corrosion is still to be investigated.

Our low-level counting system was also utilized in various projects, including environmental studies of radon content of Hungarian slag samples in cooperation with ELTE, counting of activated ^{238}Np and ^{243}Pu samples and measuring absorptions of muons in lead and iron with a muon imaging system, in cooperation with colleagues from ELTE and Wigner Research Centre [8].

Practical and theoretical training in PGAA were provided for about 60-70 persons:

- Students from BME (laboratory practice) and ELTE, from FRM2 at Garching.
- Scientists delegated by the IAEA,
- Young scientists attending the 6th Central European Training School on Neutron Scattering (supported by the EU NMI3) and the European school on EXperiments, Theory and Evaluation of Nuclear Data (EXTEND-2012) projects, where measurement methods and data evaluation were presented,
- Scientists in our Morocco-Hungary TéT (bilateral cooperation) project.

Related publications

[1] Belgya, T., Z. Kasztovszky, Z. Kis, and L. Szentmiklósi: *Hidegneutronok alkalmazása elemanalitikai és magfizikai kutatásokban*, Nukleon, **V. évf. Art. num. 121** 1-6 (2012),

[2] Belgya, T., M. Balaskó, Z. Kis, S. Kiss, and S. Lipcsei: *Roncsolásmentes vizsgálati módszerek az Energiatudományi Kutatóközpontban*, Innotéka, **II. évf. május** 28-29 (2012)

[3] Belgya, T.: *Prompt Gamma Activation Analysis at the Budapest Research Reactor,* Physics Procedia, **31** 99-109 (2012)

[4] Genreith, C., M. Rossbach, E. Mauerhofer, T. Belgya, and G. Caspary: *Measurement of thermal neutron capture cross sections of 237Np and 242Pu using prompt gamma neutron activation*, J. Radioanal. Nucl. Chem., **294** 1-5 (2012)

[5] Schramm, G., R. Massarczyk, A.R. Junghans, T. Belgya, R. Beyer, E. Birgersson, E. Grosse, M. Kempe, Z. Kis, K. Kosev, M. Krticka, A. Matic, K.D. Schilling, R. Schwengner, L. Szentmiklosi, A. Wagner, and J.L. Weil: *Dipole strength in Se-78 below the neutron separation energy from a combined analysis of Se-77(n, gamma)and Se-78(gamma, gamma ') experiments*, Physical Review C, **85**(1) art. num. 014311 1-14 (2012)

[6] Hurst, A.M., R.B. Firestone, B.W. Sleaford, N.C. Summers, Z. Revay, L. Szentmiklosi, T. Belgya, M.S. Basunia, R. Capote, H. Choi, D. Dashdorj, J. Escher, M. Krticka, and A. Nichols, *Thermal Neutron Capture onto the Stable Tungsten Isotopes* in: Cnr*11 - Third International Workshop on Compound Nuclear Reactions and Related Topics, Prague, Czech Republic, September 19 - 23, 2011: EPJ Web of Conferences eds. M. Krticka, F. Becvar, and J. Kroll, p. 1-4 (2012)

[7] Belgya, T., L. Szentmiklósi, Z. Kis, N.M. Nagy, and J. Kónya, IAEA: Vienna. p. INDC(HUN)-0037 1-10 (2012)

[8] Kálmán, D., G.G. Barnaföldi, T. Belgya, G. Hamar, Z. Kis, H.G. Melegh, L. Oláh, G. Surányi, K. Takács, D. Varga: *Kozmikus müonok elnyelődése vas és ólom abszzorbensben*, Nukleon, **V. évf.** 122-127 (2012)

ERINDA – EUROPEAN RESEARCH INFRASTRUCTURES FOR NUCLEAR DATA APPLICATIONS

Tamás Belgya, László Szentmiklósi, Zoltán Kis

Objective

The EUROATOM FP7 ERINDA project aims at providing a convenient platform to integrate all scientific efforts needed for high-quality nuclear data measurements in support of:

- waste transmutation studies,
- design studies for Gen-IV systems that include an objective of producing less waste.

The ERINDA consortium groups 13 partners equipped with nuclear data research infrastructure. The proposal unifies facility management, research community and stakeholders. The aim of ERINDA is to integrate all infrastructure-related aspects of nuclear data measurements and to provide access for external user to the participating facilities. Particular emphasis will be given to the following objectives:

- initiate networks leading to a stronger partnership in infrastructure management and exploitation,
- promote access and coherent use of all participating infrastructures to meet the scientific and industrial nuclear data requests,
- merge the complementary nuclear data measurement capabilities and expertise.

Methods

We provide transnational access (TA) to our cold thermal neutron beam within the ERINDA project to perform Prompt-Gamma Activation Analysis, radiative neutron capture experiments with our spectrometer system and we assist in making use of custom setup to carry out more demanding experiments, provided that it is transported to our experimental site.

Results

In 2012 we hosted 2 projects supported by peer review proposal evaluation body (PAC) of ERINDA.

1./ PAC1/7 Spokesperson: A. Oberstedt (U. Oerebro, Sweden): Correlation measurements of prompt fission gamma rays and fission fragments. Facility: IKI, Budapest, Hungary, Requested beam time: 200 h.

Measurements were done in 2012 May.

2./ PAC2/5 Spokesperson: M. Rossbach (FZ Jülich, Germany): Characterisation of prompt gamma signatures of actinides Facility: IKI, Budapest, Hungary Requested beam time: 120 h.

Measurements were done in 2012 March, results have been published [1].

Remaining work

The $^{235}U(n_{th},f)$ prompt gamma spectrum is still analyzed. More work is needed on ^{237}Np and ^{242}Pu with better target preparation to decrease the uncertainties of the capture cross sections.

Related publication

[1] C. Genreith, M. Rossbach, E. Mauerhofer, T. Belgya, and G. Caspary: *Measurement of thermal neutron capture cross sections of ^{237}Np and ^{242}Pu using prompt gamma neutron activation*, J. Radioanal. Nucl. Chem., **294** 1-5 (2012)

METHODS FOR APPLICATIONS IN NUCLEAR CHEMISTRY

Károly Lázár, Sándor Stichleutner, Tamás Belgya

Objective

Studies in three correlated directions have been performed, namely, i/ assembly and tuning of an in-beam Mössbauer facility at one of the cold neutron beams at BNC (The Budapest Neutron Centre) (in connection with an OTKA project), ii/ structure determination and analysis of porous ferrisilicates and other potential catalysts by using ^{57}Fe Mössbauer spectroscopy, and iii/ application of long life-time radionuclides in isotope migration studies on rock samples and compilation of the corresponding results with respect to perspective final disposal of high level nuclear waste.

Methods

Two methods were principally applied: ^{57}Fe and ^{197}Au Mössbauer spectroscopies as well as using radiotracers (for liquid samples of $^{99}TcO_4^-$, $H^{14}CO_3^-$, HTO with liquid, and $^{235,238}U$ with NaI crystal scintillation detection, respectively). Additionally, LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry) was also used to study the distribution of U in some rock samples.

Results

In the topic of the assembly and tuning of an in-beam Mössbauer facility three stages were accomplished. First the separate parts (cryostat, compressor and the low and high pressure He collection system) have been installed and assembled, then ^{197}Au spectra were obtained from high dispersion stabilized gold particles (4.5 – 29 nm size range) at 77 K, and finally a communication was also prepared and published on the preliminary results [1]. To achieve better performance, the 4 K measuring temperature should be achieved in the future.

Mössbauer spectroscopy was applied for structure determination of porous subtances. Studies performed in the framework of a bilateral TeT (bilateral cooperation) project showed that a slight modification of the composition of the synthesis gel may result in stabilisation of iron either in ferric or in ferrous form in metal-organic frameworks [2]. Stabilisations of Fe and Co ferrites in mesoporous MCM-41 and SBA-15 substances were compared [3]. A broader review was also published on structural information obtained by applying the method for studying microporous zeolite analogues [4]. Catalysts have also been studied, e.g. double-layered hydroxides [5] or reaction components in environmentally benign processes [6]. We have also participated in studies of Sn-Ni-Fe electrodeposited alloys which may become perspective battery materials alternative to Li ion based ones [7,8]. Overviews were also published on the potentials of Mössbauer spectroscopy in catalysts studies [9,10].

Results of final stages of isotope migration studies performed in the framework of the EU FP-7 (ReCosy) project were also compiled in [11]. A more general overview on the evaluation of the Boda Clastone Formation as potential geological medium for repository site of high level nuclear waste was also published [12].

Related publications

[1] K. Lázár, T. Belgya, E. Csapó, I. Dékány, V. Hornok and S. Stichleutner: *In-beam Mössbauer spektroszkópia*, Nukleon **5,** 120 (2012)

[2] T. Birsa Čelič, M. Rangus, K. Lázár, V. Kaučič and N. Zabukovec Logar: *Spectroscopic evidence for the structure directing role of the solvent in the synthesis of two iron carboxylates,* Angewandte Chemie International Edition, **51,** 12490 (2012)

[3] M. Popova, Á. Szegedi, K. Lázár and Z. Károly: *The physico-chemical and catalytic properties of ferrite-containing MCM-41 and SBA-15 materials,* Microporous and Mesoporous Materials, **151**, 180 (2012)

[4] K. Lázár: *Transition metal ions in zeolites: case of iron*, in: Zeolites: Synthesis, Chemistry and Applications (eds: M.K. Andreyev and O.L. Zubkov), Novapublishers, pp. 251-260 (2012)

[5] T.J. Vulic, A.F.K. Reitzmann, K. Lázár: *Thermally activated iron containing layered double hydroxides as potential catalysts for N_2O abatement,* Chemical Engineering Journal, **207-208**, 913 (2012)

[6] A. Saini, L. Kótai, I.E. Sajó, I.M. Szilágyi, K. Lázár, Z. May, P. Fazekas, I. Gács, V. Sharma, K.K. Banerji: *Solid phase sulphatizing of zinc ferrite spinel with iron sulphates as an environmental friendly way of recovering zinc,* European Chemical Bulletin **1**, 7 (2012)

[7] L. Sziráki, E. Kuzmann, G.B. Lak, M. El-Sharif, C.U. Chisholm, S. Stichleutner, K. Havancsák, K. Zih-Perényi, Z. Homonnay, A. Vértes: *Study of electrodeposition of amorphous Sn-Ni-Fe ternary alloys from a gluconate based electrolyte*, Surface & Coatings Technology, **211**, 184 (2012)

[8] E. Kuzmann, L. Sziráki, G.B. Lak, S. Stichleutner, K. Havancsák, K. Süvegh, M. El-Sharif, C.U. Chisholm, Z. Homonnay, A. Vértes: *Mössbauer, X-ray diffraction and microscopy investigations of novel electrodeposited amorphous alloys*, in: Mössbauer Spectroscopy in Materials Science - 2012, AIP Conf. Proc. **1489,** 3 (2012)

[9] K. Lázár: *Study of catalysts by Mössbauer spectroscopy*, Mössbauer Effect Reference and Data Journal, **35**, 134 (2012)

[10] K. Lázár: *Environmental applications: Catalysts and removal or re-cycling of by products*, Hyperfine Interactions, **206**, 51 (2012)

[11] K. Lázár, Z. Máthé, J. Megyeri, É. Széles, Zs. Mácsik, J. Suksi: *Redox properties of clay minerals and sorption of uranyl species on Boda claystone*, in: 4th Annual Workshop Proceedings of the Collaborative Project "Redox Phenomena Controlling Systems" (7th EC FP CP ReCosy), eds: Altmaier M. et. al, KIT Scientific Reports, **7626**, 231 (2012)

[12] K. Lázár, Z. Máthé: *Claystone as a potential host rock for nuclear waste storage,* Chapter 4 in: Clay Minerals in Nature – Their Characterisation, Modification and Application (ed: M. Valaskova), Intech, pp. 55-80 (2012)

PROVENANCE STUDY OF LITHIC RAW MATERIALS OF STONE TOOLS FOUND IN THE CARPATHIAN BASIN

Zsolt Kasztovszky, György Szakmány[1], Katalin T. Biró[2], Katalin Gherdán[1], András Markó[2], Bálint Péterdi[3], Boglárka Maróti, Péter Hegedűs

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Objective

Prompt Gamma Activation Analysis (PGAA) has been successfully applied to investigate various lithic assemblages, chipped and polished stone tools made of obsidian, metarhyolite, flint, radiolarite, basalt and greenschist-metabasite varieties. Special merit of the method is its non-destructive character, imperative in the study of intact museum pieces. The present project is a continuation of a previous OTKA* research, with a focused aim to map, analyse and characterise prehistoric resources, taking into consideration contemporary geographical and social endowments in the Central European region, as well as „long distance" raw material sources known to play important role in the European prehistoric exchange network. The expected results will contribute essentially to the knowledge on the system of contacts of the prehistoric communities by fingerprinting, characterising and tracing important lithic resources like obsidian, radiolarite, flint, high-pressure metamorphites, serpentinite and nephrite. The four-year project has started in April 2012.

Methods

The research plan equally consists of geological sample collection on field work, conventional petrography (macroscopic and microscopic investigations), as well as instrumental analytical measurements. The leading analytical method applied is PGAA, mainly because of its absolutely non-destructive character. PGAA is applicable to quantify all the major components and some trace elements in the lithic material. It is unique in determination of H and B. Occasionally, we plan to perform complementary measurements using XRF (X-ray fluorescence), INAA (Instrumental Neutron Activation Analysis), EPMA (Electron Probe Micro-Analyzer) or ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy), ICP-MS (Inductively Coupled Plasma Mass Spectrometry).

Results

In the first year of the present project, we have continued the work of previous OTKA and TéT projects (bilateral cooperation) with PGAA investigations of archaeological and geological samples made of obsidian [1, 2], Szeletian felsitic porphyry (metarhyolite) , and other metamorphic [3, 4] and silex-type rocks from Hungary and – thanks to the CHARISMA Transnational Access – from Poland and Romania. Approximately 150 samples have been measured with PGAA.

On the basis of our continuously increasing obsidian database, we undoubtedly ascertained the "Carpathian 1" type (North Tokaj mts, Slovakia) of Polish artefacts, while the pieces found in Romania proved to be "Carpathian 1" and "Carpathian 2" types (Fig. 1). The Melos (Greece) origin of these objects can be excluded with high probability.

Artefacts, supposed to be Szeletian felsitic porphyry (another popular prehistoric raw material named after the Szeleta cave in Hungary), turned out to be either real Szeletian porphyry with relatively lower amount (75.3-82.4) wt% SiO_2, while for the second group, SiO_2 content was found between 95.5 and 98.5 wt%, which is characteristic for hornstone, radiolarite or for limnic quartzite (Fig. 2). Besides the silica content, concentrations of Na_2O, K_2O and TiO_2 were found to be discriminative factors. Partly on the basis of the analytical results, the intensive use of felsitic porphyry is well documented as on-site processing of Vanyarc type industry in the Cserhát mts at the distance of 100-125 km from the source area of Bükk mts.

We have started to construct a dedicated, internet accessible database of lithic objects and raw materials, which we intend to make accessible for scientists when a usable version is ready.

Remaining work

In the following three years, we will systematically continue the on-field collection of raw materials in the Central European region and beyond, as well as non-destructive investigation of the material and building our comparative database.

Related publications

[1] Zs. Kasztovszky, K. T. Biró, V. Szilágyi, B. Maróti, T. Težak-Gregl, M. Burić, A. Hágó, C. Astalos, I. Nagy-Korodi, S. Berecki, A. Hajnal, B. Rácz: *Recent Provenance Study of Obsidian Artefacts found in Central Europe* (p), 39th International Symposium on Archaeometry, 2012.05.28-06.01., Leuven, Belgium

[2] Zs. Kasztovszky, K. T. Biró, V. Szilágyi, B. Maróti, T. Težak-Gregl, M. Burić, A. Hágó, C. Astalos, I. Nagy-Korodi, S. Berecki, A. Hajnal, B. Rácz: *Közép-európai obszidián régészeti leletek roncsolás mentes eredetvizsgálata - újabb eredmények*, X. Erdélyi Magyar Régészeti Konferencia, 2012.11.09-11., Marosvásárhely, Románia

[3] Gy. Szakmány, K. T. Biró, F. Kristály, Zs. Bendő, Zs. Kasztovszky, N. Zajzon: *Long distance import of polished stone artefacts: HP metamorphites in Hungary* (p), 39th International Symposium on Archaeometry, 2012.05.28-06.01., Leuven, Belgium

[4] F. Bernardini, A. De Min, D. Lenaz, Zs. Kasztovszky, P. Turk, A. Velušček, V. Szilágyi, C. Tuniz, E. M. Kokelj: *Mineralogical and Chemical Constraints on The Provenance Of Copper Age Polished Stone Axes Of 'Ljubljana Type' From Caput Adriae*, Archaeometry (in press)

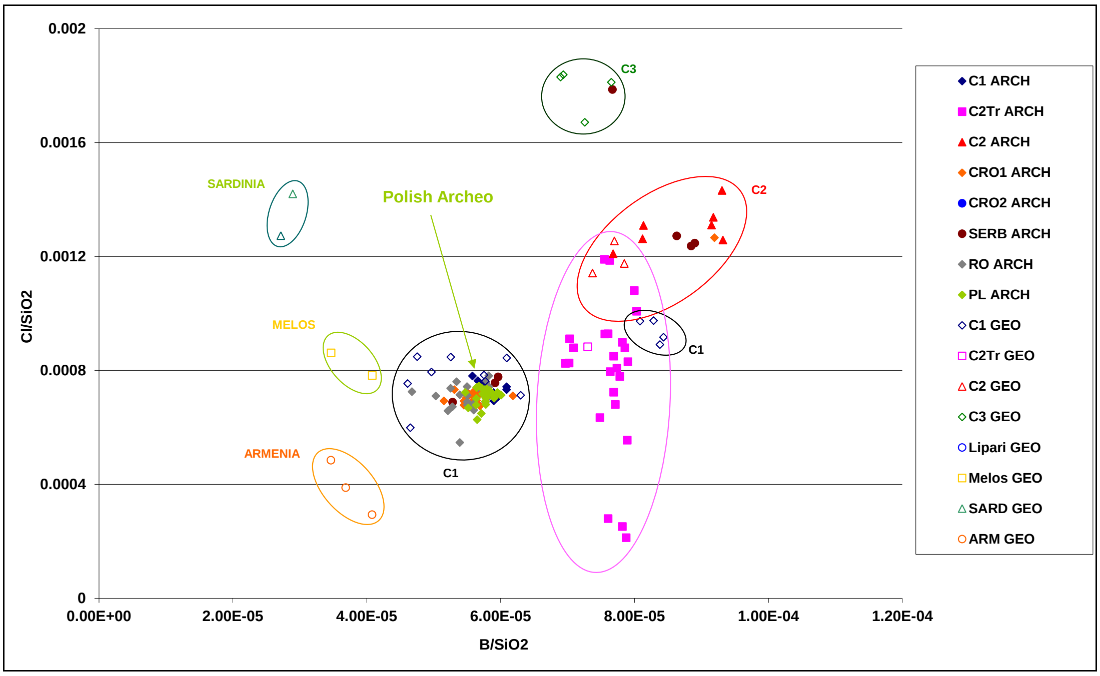


Figure 1: Characterisation of obsidian samples, based on their B- and Cl-contents

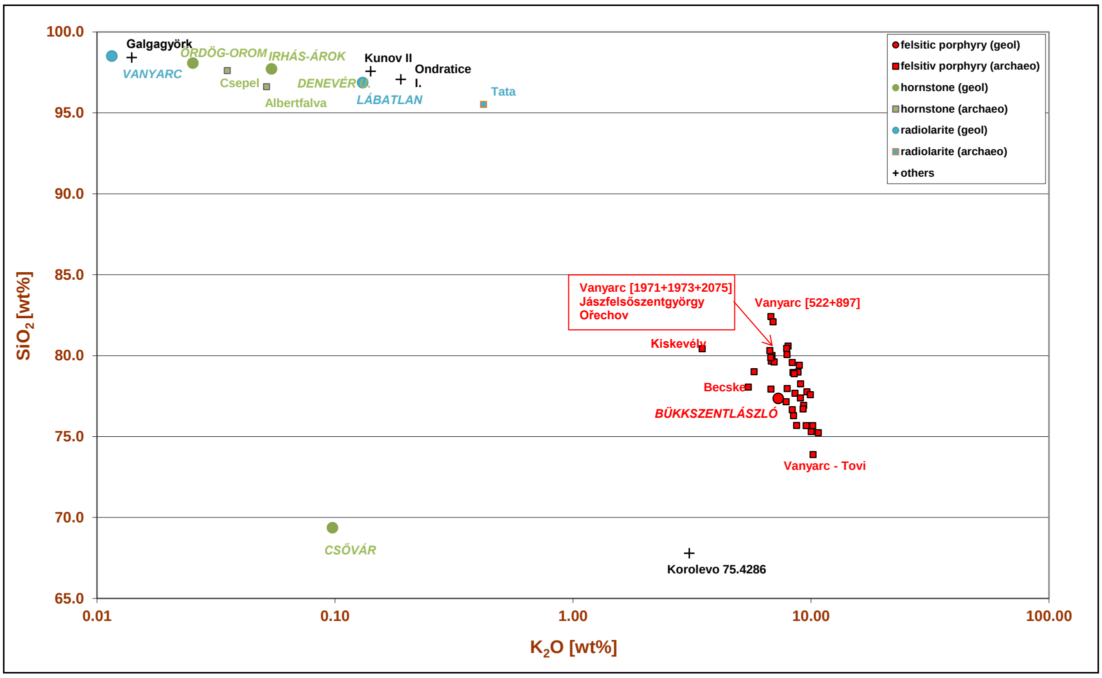


Figure 2: Differentiation between Szeletian felsitic porphyry and silex samples, based on their Si- and K-contents

RADIOGRAPHY/TOMOGRAPHY-DRIVEN PGAI AT NIPS-NORMA

Zoltán Kis, László Szentmiklósi, Tamás Belgya

Objective

Integration of the PGAA (prompt-gamma activation analysis) and the NI (neutron imaging) techniques in one instrument at the Budapest Research Reactor.

Methods

Neutron imaging is a direct method for non-destructive investigation of objects. The step towards micro- and nano-resolution can be made with the help of imaging methods in the framework of EU FP7 NMI3-II Imaging JRA. The combination of PGAA for bulk elemental analysis and PGAI (I for imaging) technique with neutron radiography and tomography (NR/NT) for mapping of materials' heterogeneity will be developed as complementary tool. NR or NT provides a 2D or 3D visual representation of the sample, and the spatial data of internal regions could be linked to the positions of a motorized sample stage [1]. This way one can localize and move selected parts of the sample into the neutron beam, where the subsequent acquisition of gamma-spectra results in characterization of these selected spots in a selective way. A setup called NORMA has been installed as a part of the The Neutron Induced Prompt gamma-ray Spectroscopy station at the Budapest Research Reactor [2].

Results

The spatial resolution of the method reached to date the range of few mm. An example of the elaborated technique is the measurement of the ^{10}B surface-density profile of a flux monitor developed at EU JRC IRMM (Geel, Belgium) institute. The sample was a stainless steel backing (∅50 mm) with a boron layer (∅38 mm), having a nominal thickness of 30 µg/cm². The projection of the 2.5 × 5 mm² collimated neutron beam was 5 × 5 mm² on the surface of the sample, as its plane was set in 30° relative to the beam.

Having known the production process it was presumed that the layer thickness changes along the radius. Therefore, a scanning along the diameter of the disk was carried out in 7 spots (see Fig. 1). To reach the statistical uncertainty of 0.25%, the acquisition time at each irradiated spot was 18000 sec. According to the results, the original assumption was proven. The thickness of the boron layer is decreasing radially from the middle point to the perimeter. The change was 1.5%. The importance of this measurement is that due to the lack of availability of ^{3}He, the future neutron detectors will apply surfaces covered with boron layers.

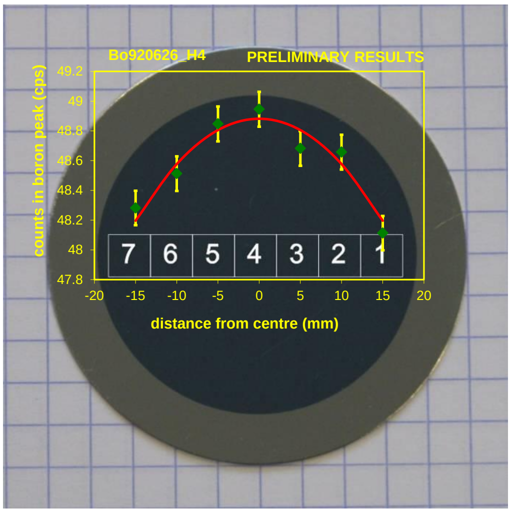


Figure 1: Scanning the ^{10}B surface-density profile for IRMM flux monitor

Remaining work

There are plans for improvement of the spatial resolution of the PGAI method.

Related publications

[1] Z. Kis, T. Belgya, L. Szentmiklósi, Z. Révay: *NORMA_10 összefoglaló záróbeszámoló*, Baross Gábor pályázat NORMA_10, OMFB-00494/2010, REG_KM_09-1-2009-0007 (2012)

[2] L. Szentmiklósi, Z. Kis, T. Belgya, Zs. Révay: *Prompt Gamma Activation Imaging at the Budapest Research Reactor*, in Report of the IAEA-F1-TM-40776 Catalogue of Products and Services of Research Reactors: Applications of Neutron Beams; IAEA, Vienna, Austria (ed. D. Ridikas), in press

TRAINING AND EDUCATION ACTIVITIES OF THE PGAA GROUP IN 2012

Zoltán Kis, László Szentmiklósi, Tamás Belgya

Objective

Providing training and education for guest researchers and students in the field of the PGAA (prompt-gamma activation analysis) and the NI (neutron imaging) techniques at the Budapest Research Reactor.

Methods

Guest researchers can spend here shorter (days) or longer periods (weeks) to get familiar with the above mentioned neutron based methods. The training is usually a part of international or national initiatives. We take actively part in organizing scientific courses.

Our department offers lab practices since 1998 for undergraduate chemist and physicist students. They can become familiar with the principles and the practical aspects of prompt-gamma activation analysis, by analyzing a standard reference material. A lab guide has been updated and made available for download [1]. For undergraduate nuclear engineer students of Budapest University of Technology and Economics, we offer another course more related to nuclear physics. The task is to determine very simple level schemes for carbon and beryllium using prompt-gamma spectra and various literature sources [2].

Results

We hosted several guest researchers:

- In the framework of Hungarian-Moroccan bilateral inter-governmental collaboration (TÉT-10-1-2011-0492) two guests from CNESTEN (Mr. Hamid Amsil and Mr. Khalid Embrach) were trained for two months (16 Sep – 16 Nov) and two weeks (16 Sep – 29 Sep), respectively. They learnt the PGAA method to help the setup of the first Moroccan facility. Two visiting scientits from the same institution (Dr. Moussa Bounakhla, Mr. Nacir Bouzekri) were hosted as a part of an IAEA TC.
- In the framework of the IAEA and the Hungarian Atomic Energy Authority two Egyptian researchers (Mr. Nader Mohamed and Ms. Asmaa Abo El-Nour) were trained for one month (10 Oct – 9 Nov). They learnt the PGAA method to help the setup of the first Egyptian facility.
- In the framework of the bilateral co-operation between the Nuclear Analysis and Radiography Department and TUM FRM-II PGAA Group (Garching, Germany) Mr. Stefan Söllradl spent 3 days (12 – 14 Nov) to learn the PGAI-NR/NT method.
- In the framework of the co-operation with the Budapest University of Technology and Economics (BME) we hosted an experiment (7 – 9 May) as a part of a Master's Thesis dealing with the idea of combining prompt-gamma neutron activation analysis and gamma detection with Compton-camera [3].

We gave lectures at international training courses:

- 6th Central European Training School on Neutron Scattering 14 May - 19 May: Nuclear Analytical Techniques
- EXTEND2012 course organized together with Budapest University of Technology and Economics: cross-section measurements

We provided undergraduate lab practices:

- For students from Budapest University of Technology and Economics (5 Nov): decay scheme determination using (n,γ) reaction (7 students)
- Summer training (3 weeks) for an M. Sc. student (Lajos Máté) from Budapest University of Technology and Economics: developing computer codes for modelling efficiency function in the wide energy range of PGAA.

Remaining work

There are plans to continue our efforts as before.

Related publications

[1] http://www.energia.mta.hu/content/pgaa-lab-practice-students-elte-university

[2] http://www.energia.mta.hu/content/lab-practice-nuclear-engineering-students-bme-university

[3] T. Hülber: *Transmission, emission and excitation gamma tomography*, Budapest University of Technology and Economics, Institute of Nuclear Techniques, Master's Thesis (2012)

VISEGRAD COOPERATION FOR DEVELOPMENT AND APPLICATION OF NEUTRON SPECTROSCOPY TECHNIQUES IN MULTIDISCIPLINARY RESEARCH

Tamás Belgya, László Szentmiklósi, Zsolt Kasztovszky, Zoltán Kis, Boglárka Maróti

Objective

To develop the neutron experimental infrastructure and experimental techniques, to perform multidisciplinary research, to extend research collaborations in the neighbouring countries and co-operation with the world leading neutron center of ILL, Grenoble, to cooperate with the members of the NAP VENEUS08 project.

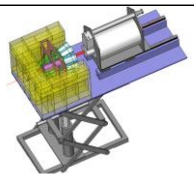
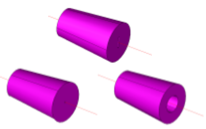
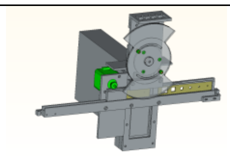
Methods

Planning and building infrastructure, developing experimental methods and instrumentation, performing experiments with the PGAA (Prompt gamma activation analysis) – NIPS (Neutron- induced prompt gamma- ray spectrometry) facilities and widening research collaborations, evaluating and publishing data.

Results

There are four work packages in the NAP VENEUS project (here we can only very briefly describe our results):

1. Development of the neutron research infrastructure at the Budapest Research Reactor
   - We modernized the data acquisition system at the PGAA facilities by purchasing CAEN N6724 module.
   - We completed the vacuum separation of our two beams and finished the shielding of the NIPS detector and a new computer-controlled collimator changer has been built.
   - Coordination of upgrade of the research infrastructure

			
NIPS detector shielding	Gamma collimators	Computer-controlled collimator changer	NORMA neutron radiograph and sample holder

2. Middle European collaboration and ILL partnership
   - We have research projects with researchers from neighbouring countries and running transnational access programmes (NMI3, ERINDA, CHARISMA) to support users coming from EU including the neighbouring countries.
   - One of us is a member of the ILL subcommittee 3 (Nuclear and Fundamental Physics).
   - We have participated in organization of the regional neutron school (CETS 2012).
3. Research and development of neutron instrumentation technology
   - We have designed and characterized the NIPS detector shielding by Monte Carlo and experimental methods.
   - We have measured the neutron flux spatial and energy distribution of our beam by TOF method.
   - We have characterized supermirror neutron guide surface absorptions and reflection, developed our neutron imaging technique, studied HPGe signal processing and performed Monte Carlo modelling of HPGe response functions.
4. Material research with neutrons and complementary methods
   - We have performed measurements and data analysis in the field of material sciences, development of catalysts for the industry, geology (with PGAA and ICP-MS (Inductively coupled plasma mass spectrometry)), nuclear materials and nuclear technology (hydrogen content of Zr cladding material, Fe, ^{237}Np, ^{241}Am, ^{242}Pu), and in cultural heritage.

Most of our works can be traced back to the support of this project via its funding for infrastructure development and personal support. In 2012, 8 peer reviewed articles appeared with acknowledgement to this project. Several talks and posters were presented at various places of the world.

Remaining work

We still need to complete some parts of the neutron infrastructure. There are still many data to be analyzed and to publish their results.

Related publication

[1] NAP VENEUS08 final report for NKTH and MAG Zrt.

WATER CHEMISTRY AT THE BUDAPEST RESEARCH REACTOR

Ibolya Sziklai László, Dénes Elter

Objective

The main objective of this study is to measure the activity concentrations of characteristic fission and corrosion products in the primary cooling water and the chemical concentrations of different impurity components in various water systems of the Budapest Research Reactor (BRR).

Methods

Instrumental Neutron Activation Analysis, high-rate gamma-ray spectrometry, the Hypermet-PC tandem spectrum deconvolution software and the INAACNC program for concentration computation.

Results

The increase of fission product activities in the primary coolant indicates the presence of fuel defects. In order to investigate the status of fuel cladding integrity and to detect any failure at the earliest stage during the fuel conversion from the highly enriched uranium (HEU) to low enriched uranium (LEU), samples from the primary cooling water were measured in every reactor cycle. Samples were taken three (1^{st}) and nine days (2^{nd}) after the reactor start and at the time of the shutdown (3^{rd}). The water purification system was put into operation after the second sampling process in every cycle. In 2012, one of the main tasks of the project was to monitor the activities of two characteristic iodine nuclides during the normal operation of the BRR. Based on a comparison of ^{131}I and ^{133}I activities in Cycles from **30/9** to **31/10** (reactor core with mixed HEU and LEU) and Cycle **27/10** (before the fuel conversion procedure began) no damage to the fuel elements was indicated. Figure 1 and 2 show the variation of activity concentrations of ^{131}I and ^{133}I nuclides in water samples, taken from the primary circuit during normal operation and reactor shutdown. The highest concentrations were generally measured for ^{131}I in the 2^{nd} samples. Comparing the maximum values of activity concentrations of measured radionuclides to the total authority limit (40 MBq/l), it can be stated that the data are well below the specified limit. The total activity concentration levels (minimum and maximum) ranged only from 1.2 to about 4.2% of the referred limit.

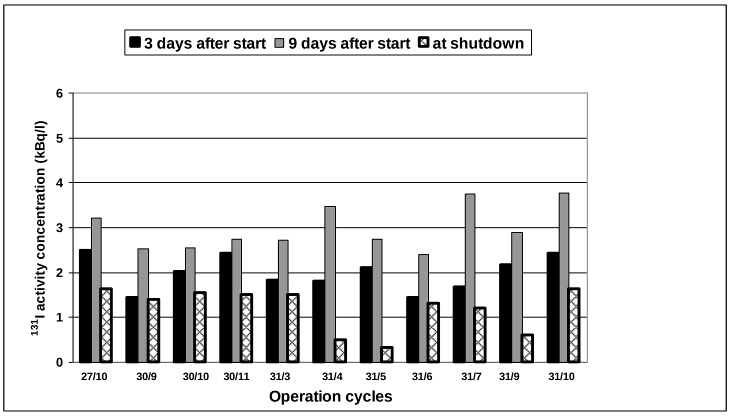


Figure 1: Variation of activity concentrations of ^{131}I nuclide in the primary water of the BRR in 2012

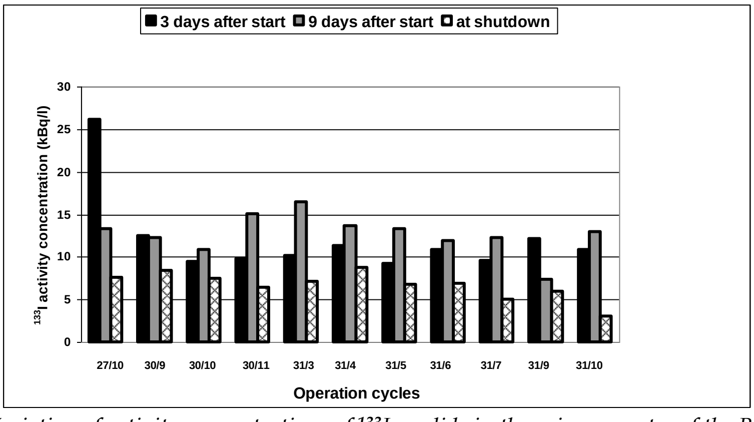


Figure 2: Variation of activity concentrations of ^{133}I nuclide in the primary water of the BRR in 2012

Remaining work

To monitor the primary coolant for fission products and impurities in order to check the variations of the activity concentrations of the radionuclides during the operation with low enriched fuel.

ABBREVIATIONS

3D	three dimensional
AER	Atomic Energy Research
AES	Auger electron spectroscopy
ATWS	Anticipated transient without scram
BEXUS	Balloon Experiment for University Students
BRR	Budapest Research Reactor
BUTE	Budapest University of Technology and Economics
BUTE INT	Institute of Nuclear Techniques of Budapest University of Technology and Economics
CoCoRAD	Combined TriTel/Pille Cosmic RADiation and dosimetric measurements
COD	Chemical Oxygen Demand
C-PORCA	neutron physics code applied at Paks NPP for core load design
DEC	Design Extension Conditions
DIM	Dust Impact Monitor
DLR	German Aerospace Center (Deutsches Zentrum für Luft- und Raumfahrt)
DPU	Digital Processing Unit
DTM	difficult-to-measure
EPS	Environmental Protection Service
EQM	Engineering Qualification Model
ESA	European Space Agency
ESARDA	European Safeguards Research and Development Association
ESCA	Electron Spectroscopy for Chemical Analysis
ESTEC	European Space Research and Technology Centre
EUR	European Utility Requirements
EVA	extravehicular activity
FM	Flight Model
FPGA	Field Programmable Gate Array
FSS	First Surface Science
GC	Gas Chromatography
GRM	Ground Reference Model
HAEA	Hungarian Atomic Energy Authority
HEU	highly enriched uranium
HLW	high level waste
HPLC	High Pperformance Liquid Chromatograpy
HPLWR	High Performance Light Water Reactor
HRTEM	High Resolition Transmission Electron Microscopy
IAEA	International Atomic Energy Agency
ILW	intermediate level waste
INCC	IAEA Neutron Coincidence Counting
INT	Institute of Nuclear Techniques
ISS	International Space Station
LANL	Los Alamos National Laboratory
LEAFE	Leaking Fuel Experiment
LET	linear energy transfer
LEU	low enriched uranium
LLW	low level waste
LOCA	Loss of coolant accident

LOWG	Lander Operation Working Group
LSWT	Lander Science Working Team
MAAP	Modular Accident Analysis Programme
MCNP	Monte Carlo N-Particle code
MORABA	Mobile Rocket Base
MPS	Max Planck Institute für Sonnensystemforschung
MTA	Hungarian Academy of Sciences
MTA EK	Centre for Energy Research, Hungarian Academy of Sciences
MTC	moderator temperature coefficients
NBSz	Hungarian Nuclear Safety Regulations
NDA	Non-destructive Assay
NPP	Nuclear Power Plant
NRC	Nuclear Regulatory Commission
NRIRR	National Research Institute for Radiobiology and Radiohygiene
NUBIKI	Nuclear Safety Research Institute Ltd.
NUREG	nuclear regulatory guide
OAH	Hungarian Atomic Energy Authority
OECD NEA	Nuclear Energy Agency (within the Organisation for Economic Co-operation and Development)
WPRS	Working Party on Scientific Issues of Reactor Systems
OCA	Orbiter Communications Adapter
PAZAR	Hungarian acronym for Noise Diagnostics Measurement System at Paks NPP
PAZAR-K	Signal evaluation software for PAZAR system
PCA	Plant and Core Analyzer
PCS	Process Computer System
PDP	Passive Detector Package
PSA	Probabilistic Safety Analysis
PuBe	Plutonium-Beryllium
QMS	Quadrupole Mass Spectroscopy
QS	quasy stationary
R&D	research and development
RETINA	Reactor Thermohydraulics INteractive Analyzer
RHK Kft.	Public Limited Company for Radioactive Waste Management
RIA	Reactivity Initiated Accident
ROMAP	Rosetta Lander Magnetometer and Plasma Monitor
RSC	Rocket Spaces Corporation
SAR	Safety Analysis Report
SCADA	Supervisory Control and Data Acquisition
SCWR	Supercritical Water Reactor
SCWR-FQT	Supercritical Water Reactor-Fuel Qualification Test
SESAME	Surface Electrical, Seismic and Acoustic Monitoring Experiments
SIP	Small Instrument Package
SNSB	Swedish National Space Board
SPM	Simple Plasma Monitor
SPND	Self Powered Neutron Detector
SSC	Swedish Space Corporation
Tecdoc	Technical Documentation
TECHDOSE	Development of a Complex Balloon Technology Platform for Advanced Cosmic Radiation and Dosimetric Measurements
TEM	Transmission Electron Microscopy

TL	thermoluminescent
TLD	Thermoluminescent Dosimetry
TOC	Total Organic Carbon (for wastewater characterization)
TPR-TPO	Temperature Programed Reduction – Temperature Programed Oxidation
TSO	Technical Support Organisations
UPS	Ultraviolet Photoelectron Spektroscopy
USB	Universal Serial Bus
VERONA	VVER ON-line Analysis
VERONA	Reactor Core Monitoring System for VVER type NPPs (VVER ON-line Analysis)
VLLW	very low level waste
VVER	Pressurized Water Reactor of Russian (formerly Soviet) design
WI/CI	waste/clearance index
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction