



Progress Report on Research Activities 2013

Hungarian Academy of Sciences
Centre for Energy Research

HUNGARIAN ACADEMY OF SCIENCES
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PROGRESS REPORT
ON RESEARCH ACTIVITIES
IN 2013

Dear Reader!

Welcome to the second yearbook published by the MTA Centre for Energy Research, summarizing the scientific results and other highlights. This booklet also provides a brief survey of the departments and research groups working in the Centre. The major task of the year 2013 in research organization was the fine tuning of the strategic research agenda. The management of half of the departments was also renewed, aiming at the long term smooth continuation of research activities.

The competitiveness of the present and future nuclear reactors with other energy producing technologies depends on the well-based but not unreasonably conservative definition of the safety margins for normal operation and incidental conditions. With this aim, the development of modelling of multi-physics phenomena in nuclear reactors is a priority area.

A new joint Korean-Hungarian laboratory was established in 2013, with the main objective of investigating the propagation of pressure waves induced by a pipe break in the primary circuit of a power plant. In order to keep the availability of our large scale experimental facilities (for fuel analysis and thermal hydraulics), the refurbishment of the equipment and the infrastructure has also been started.

The capacities of the Nuclear Security Department have been extended with a new laboratory capable for testing radiation detectors. In the framework of an EU project the results of the development of methods and instruments as well as their applicability for real accidental and terror attack conditions were demonstrated in an on-site exercise.

In-line with our long term strategy on nuclear research, the V4G4 Centre of Excellence was established among the nuclear research centres of the Visegrád 4 countries. The V4G4 Centre will coordinate the efforts for the future construction of a Generation 4 reactor, and hopefully V4G4 will be a cohesion force in the next decades for leading edge research and technology in this region.

The story of the spent nuclear fuel of the Budapest Research Reactor has arrived to its final stage. By the end of 2013 all highly enriched uranium (HEU) spent nuclear fuel was sent back to the Russian Federation, the country of its origin. According to internationally accepted view the presence of HEU material in a country increases its terror threat; therefore the removal of the spent nuclear fuel enhanced the security of Hungary.

The research reactor serves the scientific community with various analytical tools. In addition to the results published in material sciences, energy sparing catalysts and nuclear data, recent activities in archeometry are among the highlights.

Potable water – as much as energy – will be crucial for the sustainable future. Research aimed at cleaning waste water from chemically very stable drug molecules by energy thrifty radiation chemistry methods started several years ago, and is flourishing towards the realisation of a demonstration facility. In the last year the analytical chemistry equipment were upgraded and the research staff was expanded in this field.

Basic research and development in catalysts are directed towards the investigation of green, energy thrifty and economic chemical processes. A new direction of catalytic research has also been started in the field of visible-light photo-oxidation of water to produce hydrogen and the necessary experimental equipment for this area has been purchased too.

The Research Centre is committed to actively participate in the discussions on the energy supply, security and environmental safety, which was declared in its revised strategy in 2013.

Ákos Horváth

Director General

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I. NUCLEAR SAFETY RESEARCH



**DEVELOPMENT OF MULTI-PHYSICS MODELING AND ADVANCED
NUMERICAL SIMULATION TOOLS**

DEVELOPMENT AND VERIFICATION OF NEW NODAL METHODS IN THE KIKO3DMG CODE

András Keresztúri, István Pataki

Objective

In spite of the increasing computing performances, coarse mesh nodal methods play an essential role even nowadays for the tasks where the power distributions of the nuclear reactor must be determined many times. Core design and optimization or dynamic calculations of the safety analysis or training simulators are the most important applications in this respect. At the same time, the accuracy requirements are more and more demanding because the margins to be applied due to the calculation uncertainties can lead to economic burden in some cases. These are the reasons why the nodal methods are being developed continuously for a long time up to the present days.

Methods

Development and verification of the KIKO3DMG nodal multigroup code.

Results

Two classes of nodal methods were developed with the possibility of the automated mesh refinement leading to converged solutions. Two benchmark problems were solved for the verification, namely the static states of AER-2 (VVER-440) and the FCM-101 (VVER-1000) problem. (AER: Atomic Energy Research, VVER: well known Russian reactor type, Russian acronym). From practical point of view, the differences between the converged solutions and those from the CRONOS code fine mesh solutions are negligible, nevertheless, there are perceptible deviations. Only slicing the hexagon boundaries for more continuous conditions and parallel increase of the trial functions inside the node gives better performance regarding the computer time and accuracy than the method of subdividing the hexagon into triangles. Nevertheless, this latter method assures the possibility to take the heterogeneous structure of the node (burnup, temperature) into account.

Remaining work

There is no remaining work.

Related Publication

I. Pataki, A. Keresztúri: *Development and Validation of New Nodal Methods in the KIKO3DMG Code*, Proceedings of the 23rd Symposium of AER, Strbske Pleso, Slovakia, September 30 - October 4, 2013, Paper: pp. 49-64, ISBN 978-963-7351-22-8

FINITE ELEMENTS MODELLING USED TO CLARIFY SEPARATE EFFECTS

Katalin Kulacsy

Objective

1D and 1.5D fuel behaviour codes include either mechanistic or empirical models for the physical phenomena occurring in the fuel rods. Since it is in the nature of integral fuel behaviour tests and of real-life situations (e.g. licensing) not to provide detailed, local pre-characterisation of the rods, some sort of statistical averaging is inherently included in the modelling of the processes. Often applied averaging leads to assumptions of e.g. uniformity, homogeneity or axial symmetry.

Finite element codes, on the contrary, make it possible to study phenomena caused by local characteristics of the fuel rods without averaging. As post-irradiation examinations often reveal that the pellet fragments formed during normal operation are bonded to the cladding in some areas while they can move freely in others, the present work aims at studying what this arrangement causes in terms of cladding stress during a power ramp.

Methods

A 2D finite element model was built, consisting of two pellet fragments, the cladding and thin boundary layers on the interfaces between the pellet and the cladding. 90° symmetry was assumed. Realistic material properties (typical for a burn-up when pellet-cladding mechanical interaction is established) were implemented. A 100 s long power history was modelled with a ramp of 31 s. The pellet conserved its state during the simulation, i.e. no further crack opening was assumed.

Several models were built and tested: pellet with and without central hole, automatic meshing vs. manual meshing, coarse vs. fine meshing, completely vs. partially bonded pellet-cladding interfaces. The physical quantity of interest was the von Mises stress in the cladding.

Two cases were studied: the first where the fragment below the crack moved freely while that above the crack was bonded to the cladding, and the second where both fragments were bonded to the cladding. The calculations were performed by means of the finite element code MSC.Marc 2005 r3.

Results

The system reacted to the fast power rise with a characteristic time of approximately 3 s, i.e. the new equilibrium state was nearly reached in 10 s. In the partly bonded case, ovalisation could be seen in the x direction, i.e. the fuel element cross section was slightly elongated along the symmetry axis of the sliding pellet fragment. The partly bonded case and a blow-up at the vicinity of the crack tip in the completely bonded case are shown in Fig. 1. Complete bonding resulted in 1.5x higher cladding stress in front of the crack tip (the cladding stress reaching its maximum here) as compared to partial bonding (where the location of the maximum cladding stress was 45° away from the crack), as expected.

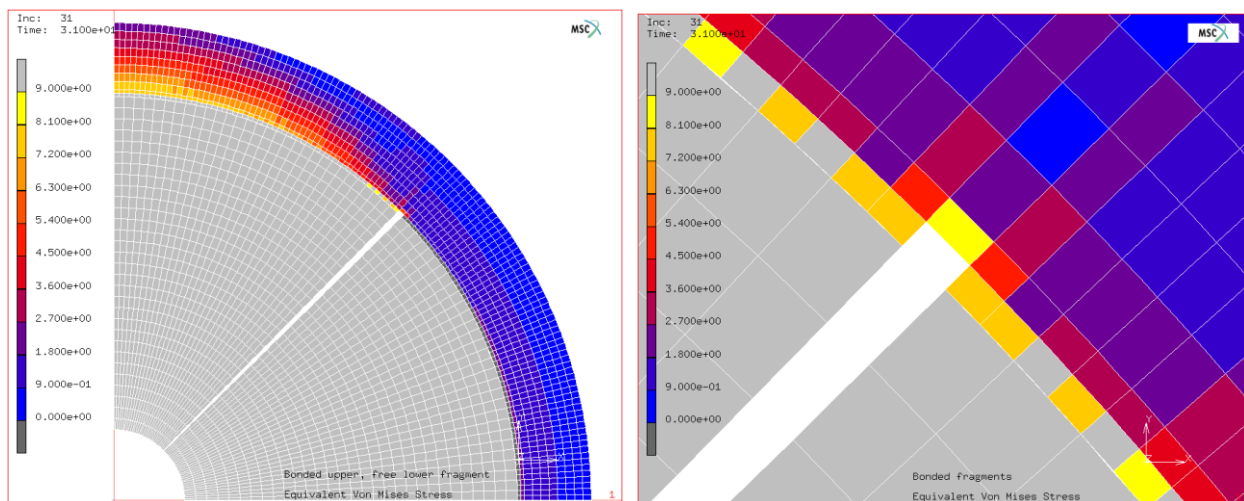


Figure 1: Stresses in the cladding in the partly bonded case (left) and at the crack tip in the completely bonded case (right)

Remaining work

The work has been completed.

Related publication

K. Kulacsy, D. Antók, T. Fekete and L. Tatár: *Finite Elements Modelling Used to Clarify Separate Effects*, Proceedings of the IAEA Technical Meeting on Modelling of Water-Cooled Fuel Including Design-Basis and Severe Accidents, 28 October – 1 November 2013, Chengdu, China

-Cooled Fuel Including Design-Basis and Severe Accidents, 28 October – 1 November 2013, Chengdu, China

DEVELOPMENT OF THE HOT CHANNEL ANALYSIS METHODOLOGY

A.Keresztúri, Gy.Hegyí, G.Hordósy, Cs.Maráczy, A.Molnár, I.Panka, E.Temesvári, Á.Tóta

Objective

The hot channel calculation is the important final phase of the safety analysis because the fulfillment of the acceptance criteria is investigated here. The safety reserve (margin) – which is intended to be applied in the analysis - depends on the calculation uncertainties. Although there are several sources of the uncertainties, our investigations in 2013 aimed at two special aspects only, namely the accuracy of the pin-wise power reactor physics calculation and – on the other hand - the calculation methodology of the coolant mixing from and to the sub-channels in the vicinity of the hot rod. The latter phenomenon is important because it significantly affects the heat transfer from the hot pin via the coolant thermal hydraulic state. Some few years back, a detailed methodology was elaborated for the RIA (Reactivity Initiated Accident) and ATWS (Anticipated Transient Without Scram) events, especially for the closed VVER-440 assemblies, which cannot be applied without further investigations in case of the open assemblies of the new NPP (Nuclear Power Plant) units and for some future VVER-440 assemblies either.

Methods

Concerning the first task, the “Full-Core VVER-440 Pin Power Distribution Calculation Benchmark” was proposed by P. Mikoláš on the 21st Symposium of AER. This is a 2D calculation benchmark based on the VVER-440 reactor core cold state taking into account the reflector explicitly. The main task of the benchmark is to test the pin by pin power distribution in selected fuel assemblies of the VVER-440 core. The k_{eff} , pin by pin power distribution, integral fission power made by the MCNP Monte Carlo code and those calculated by various core design codes – among others by the KARATE code system - were compared. Concerning the second task, computations with the COBRA-IIIIC thermal-hydraulic code were carried out for an ATWS event by using realistic pin power distributions derived from dedicated KARATE calculations. The shroud-less assembly was modeled by adding given numbers of pin and subchannel rows of the neighboring assemblies in an automated way. The computational domain was increased from a single assembly to a central assembly with several numbers of additional rows. We investigated the following questions:

1. Is the removal of the shroud advantageous concerning the DNBR (Departure from Nucleate Boiling Ratio)?
2. What is the sufficient computational domain of the geometry for the accurate thermal hydraulic modeling?
3. Can the closed assembly or sub-channel approximation be regarded as conservative for a DBA (Design Basis Accident) analysis?

Results

It was found that unambiguous answers for the above three questions don't exist, because the answers are depending on the pin power distributions. (It must be recalled that in our earlier investigations in case of the closed assembly, the closed sub-channel approximation proved conservative for arbitrary power distribution.) For example, the performed new computations show that the coolant flow rate is reduced in the high power central assembly; and the most significant difference between the shroud-less and the closed assembly models was observed in case of the symmetric pin-wise power distribution, where the coolant flow rate of the central assembly was about 20% less than in case of the closed assembly. The hot-channel DNBR was also changed unfavorable for the symmetric power distribution in case of the shroud-less assembly model: it was 5% lower in case of applying 7 additional rows than in case of the closed assembly. The investigations showed that considering shroud-less assemblies, a global power gradient can cause assembly-wise coolant cross-flows with significant changes in the hot-channel DNBR. Our conclusion is that a two level (combined coarse and fine mesh) thermal hydraulic model is necessary for the correct analyses, which will be developed in the frame of a next multi-physics project.

Concerning the pin power accuracy benchmark, the maximum relative deviation of the local power peaking factor by KARATE is 17.5% in a low power fuel assembly.

Remaining work

There is no remaining work.

Related Publications

- [1] E. Temesvári, Gy. Hegyi, G. Hordósy, A. Keresztúri, Cs. Maráczy, Á. Tóta: *Solution of the 'Full-Core' VVER-440 Calculation Benchmark by KARATE: Analysis and Conclusion*, Proceedings of the 23rd Symposium of AER, Strbske Pleso, Slovakia, September 30 – October 4 2013 pp.211-226 ISBN 978-963-7351-21-1
- [2] Á. Tóta, A. Keresztúri, A. Molnár, I. Panka, E. Temesvári: *Investigation of the Hot Channel Calculation Methodology in Case of Shroud-less Assemblies*, Proceedings of the 23rd Symposium of AER, Strbske Pleso, Slovakia, September 30 – October 4 2013, pp. 453-468, ISBN 978-963-7351-22-8, Accepted by the AER SC to be submitted in the special AER issue of Kerntechnik
- [3] V. Krýsl, P. Mikoláš, D. Sprinzl, J. Švarný, E. Temesvári, I. Póš, L. Heraltová: *"FULL-CORE" VVER-440 Calculation benchmark*, Accepted by the AER SC to be submitted in the special AER issue of Kerntechnik

EDUCATION AND DEMONSTRATION OF NOISE DIAGNOSTICS METHODS AND RESULTS IN THE NEW SIMULATOR LABORATORY

Sándor Kiss, Károly Krinizs, József Láz, Sándor Lipcsei

Objective

An education and demonstration methodology and package of noise diagnostics was developed in connection with the new simulator laboratory. The demonstrations have two main topics. The first is the interpretation of noise diagnostics measurements (demonstration of the measurement process, expert investigations and methods, in-situ estimation of the moderator temperature coefficient of the reactivity (MTC), demonstration of the localisation of core anomalies such as vibrations, methods and demonstration of the coolant velocity measurements in the core). The second topic covers the visualisation techniques of the measured and evaluated results (long term trends of the calculated results and demonstration of usefulness of information gained from noise diagnostics systems).

Methods

The education package consists of two main components: a PowerPoint presentation and a written scenario describing the details of demonstration steps connecting to the presentation shown with the noise measurement evaluation program package called PAZAR-K.

The tuition is further helped with the conference posters placed in the simulator laboratory. These posters well demonstrate the most important results of Reactor Monitoring and Simulator Department in the noise diagnostics field (see e.g. Fig. 1 and 2.).

Results

PowerPoint presentation as well as PAZAR (Paks Autonomous Noise Data Acquisition System) client and PAZAR-K program system were installed on the computer of the simulator laboratory, and a written scenario is assembled describing how PAZAR-K examples demonstrate the individual chapters of the presentation. Additionally, former conference posters were placed on the laboratory walls. New methods described in a new paper released in Progress of Nuclear Energy are also visualized in a new poster.

The package was used in the education of Budapest University of Technology and Economics students visiting MTA EK.

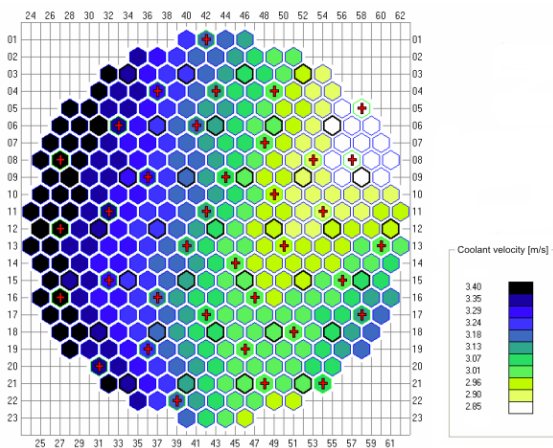


Fig. 1: Coolant velocity map of the core during crud deposition

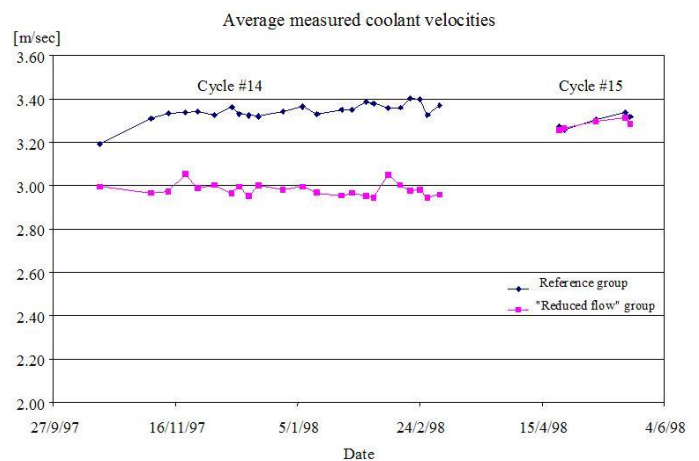


Fig. 2: Coolant velocity trends during and just after the core anomaly

Remaining work

The demonstration package will be continuously extended with future measurement, evaluation and research results [1].

Related publications

- [1] Kiss, S., Lipcsei S., 2014, Measurement of average circulation period of temperature fluctuations in the coolant of VVER-440 reactors' primary circuit, Prog. Nucl. Energy Vol. 71, pp. 188-194

DOSE CONSEQUENCES AND ENVIRONMENTAL RELEASE OF ACTIVITY PRODUCED AROUND THE REACTOR PRESSURE VESSEL

Sándor Deme, Tamás Pázmándi, Péter Szántó

Objective

Release of the activity from the containment originated in the leakage of the primary circuit has been calculated earlier. Another component of the atmospheric release is the activity produced due to the activation of air between the reactor pressure vessel and the biological shielding. Objective of this work was calculation of this activity component.

Methods

For the calculations, the volumes consisting of air around the reactor pressure vessel were split into four subvolumes:

- Volume between the reactor pressure vessel and the heat insulation
- Volumes in the heat insulation containing air
- Volume between the heat insulation and the biological shielding
- Cooling pipes of the ionization chambers inside the biological shielding

The production rates of ^{41}Ar , ^{14}C and ^{16}N in the unit air volume for the four sub - volumes were calculated by the staff of the Institute of Nuclear Techniques at the Budapest University of Technology and Economics.

Models were set in order to calculate the dispersion of the radioactive nuclides originated in the four subvolumes in the containment. Based on the calculations, the dose rates due to these nuclides in the rooms of the containment and in the TN02 ventilation system were calculated. The environmental release was also estimated.

Results

Figure 1 shows ^{41}Ar activity concentration in five nodes and in the TN02 ventilation system. Difference between the activity concentrations estimated for the nodes does not exceed 35%; the maximum deviation relative to the mean value is 24%. Estimated stack release rate of ^{41}Ar is $(2.0 \pm 0.4) \cdot 10^8 \text{ Bq}\cdot\text{s}^{-1}$. Release rate of ^{14}C is much lower: $(3.5 \pm 0.7) \cdot 10^4 \text{ Bq}\cdot\text{s}^{-1}$. Due to its short half-life, the ^{16}N has no contribution to the stack release.

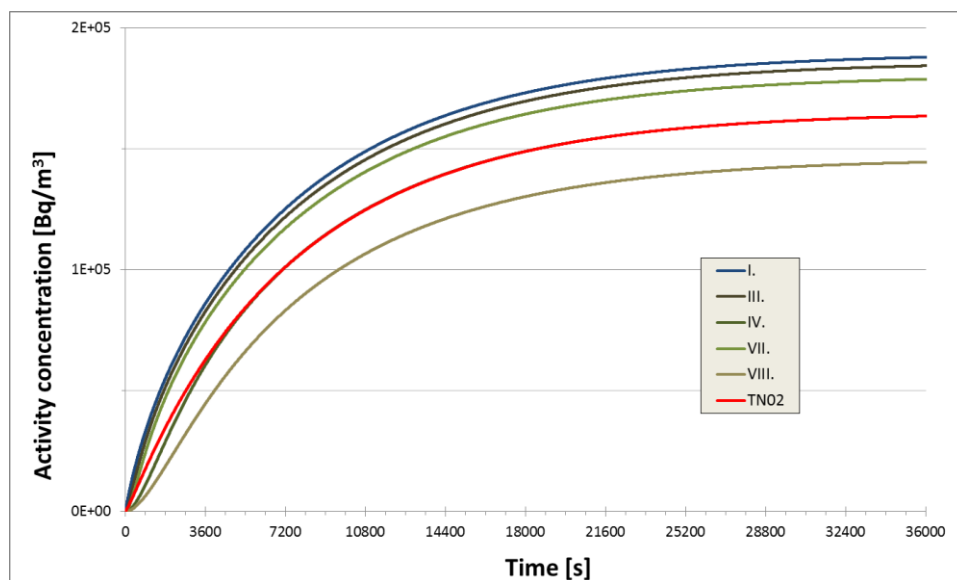


Figure 1: ^{41}Ar activity concentration in five rooms in the containment and in the TN02 ventilation system vs. time from the start of the activation

Remaining work

This work is completed.

Related publication

S. Deme, T. Pázmándi, P. Szántó: *Dose Consequences and Environmental Release of Activity Produced Around the Reactor Pressure Vessel*, Report, EK-SVL-2013-333-01-01-01 (2013)

CONTRIBUTIONS TO THE NURESAFE PROJECT

Gábor Házi, Valér Gottlasz

Objective

The major objective of the NURESAFE project is to develop a reliable software package usable for safety analysis needs and to provide guidelines based on a high level of expertise for the proper use of the most recent simulation tools. In the framework of NURESAFE, we study two-phase flow phenomena using highly resolved numerical simulation. To be more specific, CER is involved in Subproject 2 and work packages 2.2 and 2.3.

The aim of WP2.2 is to deal with the boiling phenomena, while WP2.3 is dedicated to develop models for the forces acting on bubbles in two-phase flow [1].

Methods

For the simulations of boiling and turbulent bubbly flows, we use our own solvers, which are based on the lattice-Boltzmann method.

Results

One of our solvers (called BOILI) has already shown the capacity to model boiling phenomena in 2D. During the project this code has been extended to 3D in order to be applicable for the simulation of boiling process in a turbulent background flow. A few years ago, we had also used a lattice-Boltzmann code for direct numerical and large eddy simulation of *single phase turbulent flow* in a subchannel of a triangular array of a rod bundle. Later this code was extended to simulate *laminar bubbly flows*. At the beginning of this project, we hoped that we can utilize this code for the simulation of *turbulent bubbly flows*. However, after a few unsuccessful attempts we have recognized that the code has certain limitations, which made impossible to step further without significant development of the model. These model developments have been done in 2013. Now, the code is able to simulate turbulent bubbly flow and some simulations (using coarse grid) have already been performed. In Fig. 1 a bubble moving in a subchannel in axial direction is shown, with the induced lateral velocity profile. Periodic boundary conditions are used in all lateral sides of the channels. More details about these simulations can be found in [2].

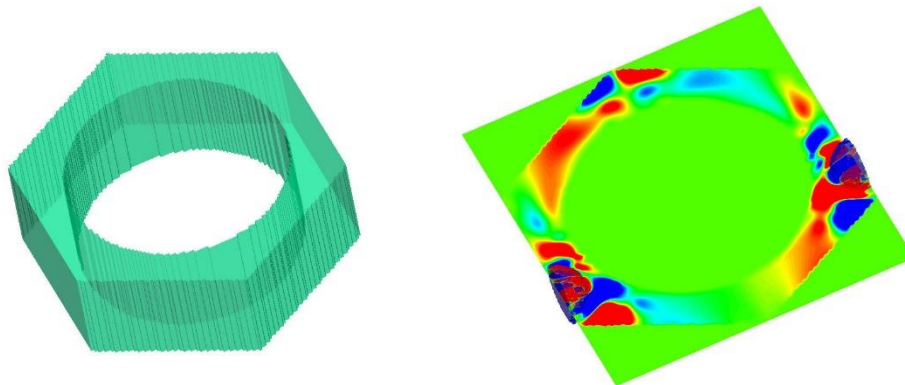


Figure 1: A layer of the subchannel and instantaneous lateral velocity contour in a cross section (periodic boundary conditions are used in lateral directions).

Remaining work

In 2014 and 2015 several simulations will be performed and the relevant quantities (mean velocity profiles, Reynolds stresses etc.) of bubbly flow simulations will be compared with single phase flow calculations.

Related publications

- [1] G. Házi, D. Lakehal, D. Bestion, NURESAFE delivery WP23.11: Benchmark definition for WP23 (2013, sept.)
- [2] G. Házi, V. Gottlasz, NURESAFE delivery WP23.21: Direct numerical simulation of bubbly flow in a channel, (2013, dec.)

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

András Keresztúri, György Hegyi, Lajos Korpás

Objective

In the last decades, KARATE-440 was elaborated and developed continuously to calculate VVER-440 reactor 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 analyzed by KARATE-440. The program 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 (Nuclear Power Plant) 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 is indispensable from year to year against the latest operational and start-up measurements for the establishment of the uncertainties and the margins for the calculated safety related frame parameters. In 2013, the cycles of Paks NPP finished in 2012 were used for the validation.

Methods

Model validation, comparison of the calculated and measured data.

Results

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. As an example, Fig. 1 shows the comparison of the measured and calculated differential control rod group worth for Unit 2 using high enriched Gd doped fuel. The deviation is about 10 %, which is in the range of the measurement scattering.

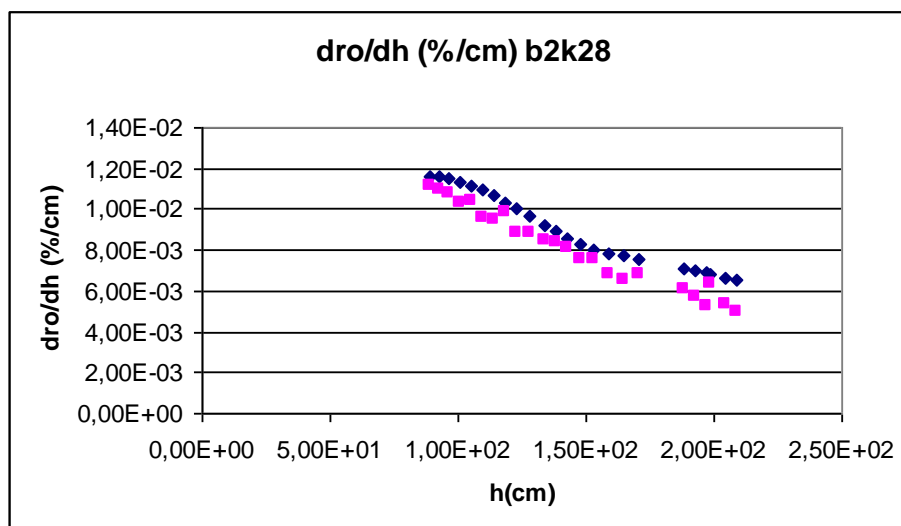


Fig. 1: Measured (lower curve) and calculated differential control rod worth for Cycle 28 of Unit 2 depending on the control rod axial position ("h")

Remaining work

There is no remaining work.

Related Publications

Gy. Hegyi, L. Korpás: *Comparison of the KARATE 5.0 results with the measurements and C-PORCA calculations for the last realized cycles of Paks NPP*, in Hungarian, MTA-EK-RAL-2013-706/1-M0.

SOURCE TERM OF SPENT FUEL POOL SEVERE ACCIDENTS

Zoltán Hózer, Richárd Nagy, Péter Szabó, András Vimi, Attila Nagy, Tamás Pázmándi, János Sebestyén Jánosy, Nóra Vér

Objective

In the earlier severe accidents studies the release of radioactive isotopes was considered only through the reactor hall from the open spent fuel pool. This conservative approach produced the maximum release to the environment in case of spent fuel pool severe accidents. In the present work, releases through other paths were estimated.

Methods

Eight different release paths were identified between the spent fuel pool and the environment. The simulation of transport phenomena was calculated in simplified way. The deposition of fission products on the cold surfaces was estimated on the basis of experimental data following the analyses of PHEBUS, VERCORS and RUSSET tests. The activity release from open reactor was determined using the MAAP code by NUBIKI Co. Ltd. In case of spent fuel pool accidents, the relative release rates of different elements was used from those MAAP calculations, and the absolute values were calculated using the isotope inventory of the fuel assemblies stored in the spent fuel pool.

Results

The calculations showed that the release of radioactive isotopes through new release paths are significantly lower compared to the case with open spent fuel pool and release only through the reactor hall.

The release through the filtered ventilation of chimney can decrease the release of iodine, cesium and other non-gaseous fission products by 99%, but the long term operation of these filters in severe accident conditions cannot be guaranteed.

The retention of closed spent fuel pool by concrete cover plates was estimated between 16-57% for different elements.

The use of local ventilation and the top of the spent fuel pool can force the release into the chimney and the height of release into the environment will be from 44 m to 100 m.

The release paths through the chimney without ventilation will lead to release at high elevation, and that decreases the environmental consequences. The temporary deposition inside the chimney and the delayed release will mean more time for mitigative actions.

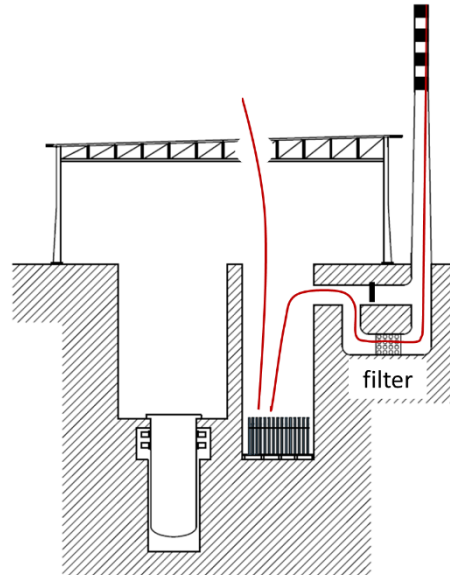


Figure 1: Release from the open spent fuel pool through the reactor hall and through the filtered venting of chimney

Remaining work

The planned work was completed. In long term, more detailed models of severe accident progression in spent fuel pool should be developed.

Related publication

Z. Hózer, R. Nagy, P. Szabó, A. Vimi, A. Nagy, T. Pázmándi, J.S. Jánosy, N. Vér: *Determination of Source Term of Spent Fuel Pool Severe Accidents*, EK-FRL-2013-748-01/01-M1 (in Hungarian)

CORE AVERAGE FISSION GAS RELEASE DURING DBA LOCA FOR A NEW FUEL WITH 4.7% AVERAGE ENRICHMENT

Katalin Kulacsy, Attila Molnár

Objective

During a design basis large break loss-of-coolant accident (DBA LB LOCA), fuel elements may become in hermetic and activity may be released to the primary circuit. There are two main sources of this activity, released when the cladding fails: the gaseous and volatile fission products stored in the rod free volume during normal operation (gap activity), and an extra release coming from the porosity of the high-burnup structure (HBS) due to LOCA. In the latter case pores in the HBS, filled with fission gases at high pressure, burst open as temperature rises and release their gas content, which is accompanied by the micro-fragmentation of the HBS (release due to fragmentation).

The present work was the follow-up of previous similar calculations performed for the current cores of Paks NPP (average enrichment: 4.2%, 3 gadolinia-doped rods per fuel assembly). The objective was to estimate the total (gap + fragmentation) activity release for the new, 15-month-cycle fuel of Paks NPP, for LOCA's occurring both during operation and in shut-down state. The fuel assemblies contain 6 gadolinia-doped fuel rods each and their average enrichment is 4.7%.

Methods

The fuel rod histories were calculated by means of the neutronics code KARATE developed at our Institute. The gap activities and the characteristics of the fuel rods (especially of the HBS) during normal operation were calculated using the fuel behaviour code FURROM, developed also at our Institute. As long-lived fission products have the highest release values and their release increases with burn-up, the break was assumed to occur at the end of the cycle. However, the gap activity of the short-lived fission products was considered when it was highest in the history of each individual rod, i.e. maximum values occurring at different times were summed up as if they had occurred simultaneously. The thermal-hydraulic conditions in the core during the accident were calculated by means of the system code ATHLET developed at the GRS institute in Germany, applying DBA conservatism. The transient behaviour of conservatively selected fuel rods during the accident was simulated by the code FRAPTRAN, developed at PNNL in the USA.

A conservative model was implemented for the release due to the fragmentation of the HBS: if the local burn-up exceeded 66 MWd/kgU and the local temperature reached 600 °C, then 20% of the local fission gas inventory was assumed to be released from the fuel pellet.

The gap activity for each fission gas nuclide and the extra release due to fragmentation were calculated for each rod, summed up and compared to the fission gas inventories also summed up for all the rods of the core, yielding the fission gas release fraction during LOCA. This released fraction remains in the fuel rods unless they become in hermetic, the proportion of in hermetic rods being a question for further studies.

Results

The total fractional fission gas release for each radioactive nuclide is shown in Fig. 1 for LOCA's occurring during operation and in shut-down state, compared to the conservative data proposed by the European Union (EU). The calculations were made applying a conservative gap width and a +4 MWd/kgU conservatism in the burn-up. The data proposed in the EU document are higher than the calculated release.

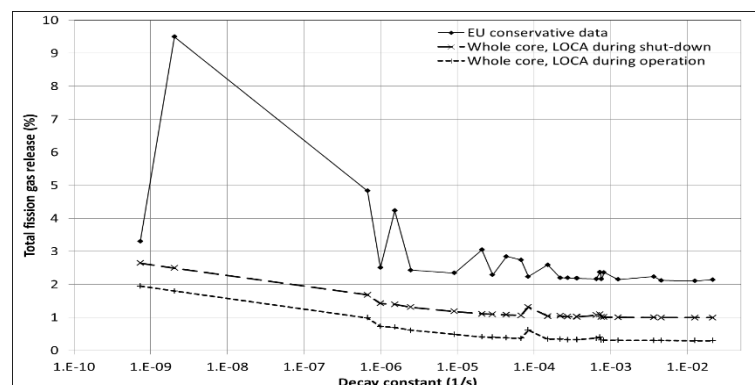


Figure 1: Total fractional fission gas release

Remaining work

The work has been completed.

Related publication

K. Kulacsy, A. Molnár: *Extra FGR due to Fuel Fragmentation during DBA LOCA for Higher Enriched Fuel Reaching Higher Burn-up*, EK-FRL-2013-754-01/01 (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 also in 2013. Measurements were carried out by means of the PAZAR System. PAZAR systems 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. There were also MTC-s calculated from long term (24/72 hour) measurements of in-core and primary loop thermocouples.

Methods

In the given year regular measurements were performed every month. Long term (1 day to 2 week) measurements were also carried out, usually two times monthly. 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.

Regular scenario of one hour long measurements was extended with transient monitoring: currently a large subset of the detector signals is virtually continuously measured.

Results

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

The possible vibrations of core internals were also investigated, but no anomalies were observed in 2013. Reports were compiled for the plant from all the measurements.

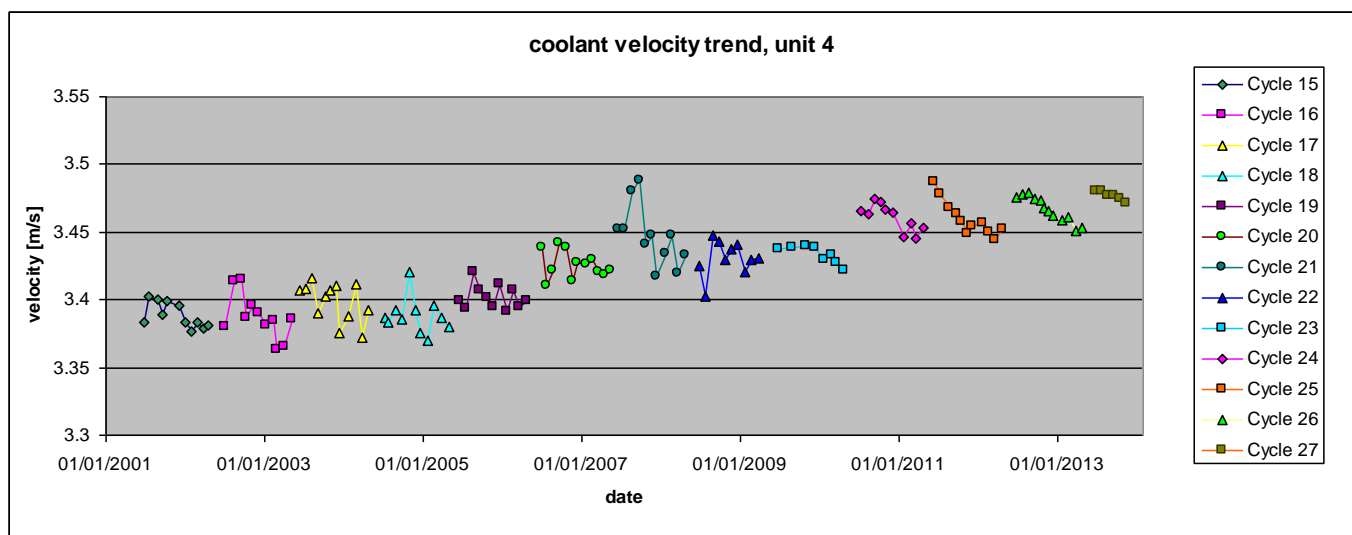


Figure 1: Twelve-year long trend of average core coolant velocity of Unit 4 at Paks NPP

Remaining work

Regular noise diagnostic measurements will be continued in 2014.

EVALUATION OF THE UNCERTAINTIES OF THE CALCULATED LOCAL LINEAR HEAT RATE, HOT CHANNEL ENTHALPY RISE AND BURNUP

András Keresztúri, István Panka, Lajos Korpás

Objective

Local power and burnup values are limited during the operation of the reactor due to safety reasons. Burnup dependent local linear power heat rate is limited in order to avoid the too high inner pressure in the gap. Too high linear heat rate at zero burnup can also lead to non-acceptable consequences in case of LOCA (Loss of Coolant Accident) events. The sub-channel enthalpy rise in the hot sub-channel must be limited to avoid the cavitation corrosion of the cladding. The pellet and pin burnup values are also limited because of fuel behavior. The operational maximum values must take into account the uncertainties of the determination, which had to be determined in the given project.

Results

The following uncertainties were obtained:

- linear heat rate
- sub-channel outlet temperature
- pin burnup
- pellet burnup
- assembly burnup

It was shown that the uncertainty of the burnup could be obtained from the statistical correlation of the power values at different times. The correlation was obtained from the evaluation of the deviation of the calculated and measured values.

Methods

First, the sources of the uncertainties were identified and the uncertainties of the primary (input) quantities were determined. One group of the sources is the uncertainties of the geometrical and material data in the calculations. The other group of the uncertainties, the calculational errors originating from the model approximations and from the uncertain nuclear data, were determined by using the validation results of the different codes. The limited quantities are determined as a result of the chain of the different codes and mathematical formulas. In order to simulate exactly the calculational process, the Monte-Carlo method was followed by generating the input data and perturbing the intermediate results between the calculational levels according to their statistics. Certain levels of calculations were imitated by models based on the generalized perturbation theory.

Remaining work

There is no remaining work.

Related publications

- [1] I. Panka, A. Keresztúri, L. Korpás: *Improvement of the burnup engineering safety factors*, in Hungarian, MTA-EK-RAL-2013-706/1-M0.
- [2] I. Panka, A. Keresztúri, L. Korpás. S. Patai: *Evaluation of the power related engineering safety factors*, in Hungarian, MTA-EK-RAL-2013-734/1-M0.

RESEARCH ON REACTOR MATERIALS

SORPTION PROPERTIES OF SILVER IONS IN THE PRIMARY CIRCUIT

Zsolt Kerner, Éva Kovács-Széles, Sándor Szabó, Zoltán Hózer, Nóra Vajda¹

¹ RadAnal Ltd.

Objective

Presence of silver contamination in the primary circuit of a nuclear power plant produces radioactive isotopes, for example ^{110m}Ag. Its half-life is 250 day, gamma energy is 117.6 keV. Silver ions adsorb on the surface of structural materials strongly. Accumulated ^{110m}Ag can cause gamma dose during the operating and the maintenance period. So minimization of the amount of the silver in the primary circuit is necessary. Adsorption properties of silver ions (and other forms) have to be known to describe the silver transport in the primary circuit. In this work the kinetics and the equilibrium of the silver ions adsorption was measured on steel and zirconium surfaces.

Methods

Ex-situ radotracer method was used. ^{110m}Ag isotope was produced by irradiation of 1 mg high purity silver wire in the Budapest Research Reactor. Activated silver was dissolved in nitric acid. The solution of the primary circuit was modeled with 8 g/L boric acid solution. pH was set to 5.06 and 7.15. (These values are approximately characteristic to the maintenance and operating period.) Stainless steel and Zr2.5%Nb samples with 2 cm² surfaces were steeped in 10 mL model solution containing 20, 100, 500 and 2500 ppb silver, during 10 minutes, 1, 24 and 69 hours, in closed PP (Polypropylene) test tubes, on a laboratory shaker. Oxygen was present. After the adsorption time the samples were rinsed by a small amount of ultrapure water. Quantity of the adsorbed silver was calculated based on the activity measured by Canberra HPGE gamma detector. Desorption was also examined in some tests.

Results

5-10 ng/cm² silver adsorbing on stainless steel at pH=5 from a solution containing 20-2500 ppb silver ion, the equilibrium is reached in 24 hours.

60-600 ng/cm² coverage was measured on stainless steel at pH=7. In case of higher silver concentrations the equilibrium was not reached even in 69 hours.

Supposing that the accumulation of silver is an electrostatic adsorption process, we can conclude that the stainless steel surface is positively charged at pH=5 (for example covered by hydrogen ions) and negatively charged at pH=7. The isoelectric point is between pH=5 and 7.

40-1100 ng/cm² coverage measurable on zirconium surface after 69 hours at pH=5 and 7. The adsorption equilibrium (maximal coverage) is probably reached in the experiment.

Zirconium surface adsorbs approximately twice as much silver at pH=7 again as stainless steel does. At pH=5 this ratio is 100:1.

The adsorption process is faster and the equilibrium can be reached in shorter time on zirconium surface than on stainless steel.

Adsorption equilibrium measured on zirconium surface can be described by a Langmuir-type isotherm (in case of pH=5 and 7).

At pH=7 half of the adsorbed silver can desorb in 106 hours from a zirconium or stainless steel surface. At pH=5 the desorbing ratio is just 0.25.

Remaining work

Long-term adsorption-desorption experiments are planned to find the equilibrium state. Adsorption of silver ions will be examined on pre-oxidized surfaces. Temperature dependence is planned to be measured up to 300 °C. Distribution of adsorbed silver will be characterized using SEM-EDX (Scanning electron microscope - Energy dispersive X-ray analysis).

Related publication

Zs. Kerner, É. Kovács-Széles, S. Szabó, N. Vajda: *Adsorption of silver ions on steel and zirconium surfaces*, EK-FRL-2013-753-01/01 (in Hungarian)

ROUND ROBIN ON ZIRCONIUM OXIDATION

Erzsébet Perez Feró, Tamás Novotny, Zoltán Hózer

Objective

The purpose of the work was to carry out parallel high temperature oxidation experiments and mechanical tests in several laboratories with the same Zr cladding alloy and to produce sufficient data to support the establishment of an ASTM-approved LOCA test procedure.

Methods

The six laboratories participating in the Round Robin received the same type of Zircaloy-4 cladding tubes. The samples included „as-received” and hydrogen charged cladding tubes. All participants carried out oxidation of Zircaloy-4 samples at 1200 °C. The oxidised samples were tested with standard tensile machines with ring compression at 135 °C. Laboratories used their own experimental facilities. The MTA EK experts collected the data from the participants and carried out evaluation of the measured data. The evaluation covered both oxidation and mechanical testing (total of 166 pcs).

In spite of the well-defined and previously agreed experimental conditions, the direct comparison of data from different laboratories was rather difficult because of several reasons:

- the oxidation times were not the same, because the range of CP-ECR (Cathcart-Pawel Equivalent Cladding Reacted) was specified only,
- the calculation of CP-ECR was performed in different ways, in some cases only the time at 1200 °C was considered, while in other cases the heat-up and cool - down periods were also taken into account,
- the specification of hydrogen content was confusing: in some cases the target values in other cases the real hydrogen content was assigned to the given sample.

Results

The oxidation tests indicated that:

- there was generally a good agreement between CP-ECR and measured ECR values (Fig. 1),
- due to the definition of oxidation times in different ways, the direct comparison of data on oxidation kinetics showed large scatter (especially in case of low oxidation times), the average values, could be approximated with a parabolic function.

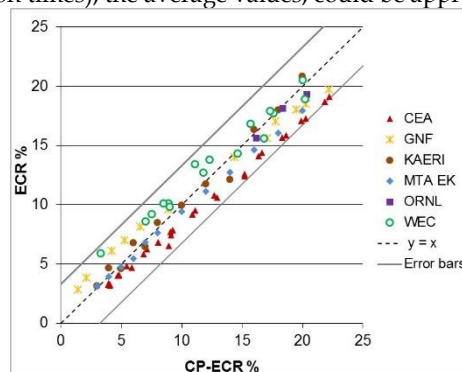


Figure 1: Measured ECR as a function of Cathcart-Pawel predicted ECR

The mechanical tests showed that:

- the as-received samples with 17 % CP-ECR produced different load-displacement curves, indicating that reproducibility of the determination of ductile-to-brittle transition cannot be guaranteed even in well-defined test conditions,
- the main trend of ductile-to-brittle transition can be determined as function of hydrogen content using the data produced in the Round Robin, the main differences between the measured points are associated to the uncertainty of the hydrogen content.

On the basis of Round Robin testing the development of a standard procedure can be initiated, but the examination of hydrogen content needs further measurements. Beyond the already agreed conditions, the exact calculation method of CP-ECR must be specified.

Remaining work

The evaluation of the measured data has been completed. The MTA EK will continue participating in the Round Robin tests and in the development of a standard procedure.

Related publication

E. Perez Feró, T. Novotny and Z. Hózer: *The evaluation of the results of Round Robin programme*, EK-FRL-2013-263-01/01 (in Hungarian)

HYDROGENISATION OF ZIRCONIUM SAMPLES IN SIEVERT VACUUM SYSTEM

Tamás Novotny, Erzsébet Perez-Feró, Anna Pintér Csordás

Objective

The aim of our project was to charge 5 pieces of cladding samples (E110G alloy) with hydrogen without huge surface hydrides for the hydrogen content of 1000 ppm. The length of the samples provided by UJP Praha was 30 mm. The requested charging temperature was 600 °C (below the phase transition temperature).

Methods

The samples were immersed in acetone separately to degrease the surfaces. The inside temperature of the furnace was set to 600 °C, which was checked before each charging. We measured the mass of samples and calculated the initial pressure of hydrogen. The pressure of the system was measured with a Vacuubrand DVR 5 and monitored online with PC (Fig. 1).



Figure 1: Picture of the vacuum system

The hydrogen transfer to the surface of zirconium depends on the diffusion in the gas system, generally it takes a long time. We made some preparatory experiments before this project and the results showed that the equilibrium of hydrogenisation was reached (after) about 16-18 hours. We wanted to guarantee that the calculated hydrogen was absorbed, that's why we left the samples in the furnace for 24 hours.

The vacuum system was uploaded with hydrogen (purity >99.999 %) and completed with argon (purity >99.999 %). This hydrogen was only the half of the total amount (corresponding to about 500 ppm), because we charged each sample in two steps to avoid any inhomogeneity. At the end of the hydrogen uptake the sample was withdrawn to the cold part of the quartz tube. After cooling the gas system we measured the mass of the sample and calculated the hydrogen concentration of the specimen.

Results

Table 1 contains the hydrogen concentration of the charged specimens. The target hydrogen content was 1000 wppm according to the order of UJP Praha. The maximum deviation from this value was 7%.

Sample CS-31 was used for control purposes and was cut into small pieces. Samples were delivered in their original form with hydrogen content specified in Table 1.

Table 1: Hydrogen concentration of the samples

sample	m ₀ (g)	m ₁ (g)	c (wppm)
CS-31	3.51232	3.51608	1069
CS-32	3.50927	3.51294	1045
CS-33	3.50840	3.51200	1027
CS-34	3.50714	3.51075	1030
CS-35	3.50709	3.51060	1001
CS-36	3.51771	3.52143	1057

Remaining work

The work is completed in the reporting year. Objectives in the project have been carried out.

ADVANCES IN THE MATTER PROJECT

Levente Tatár, Ferenc Gillemot, Attila Kovács

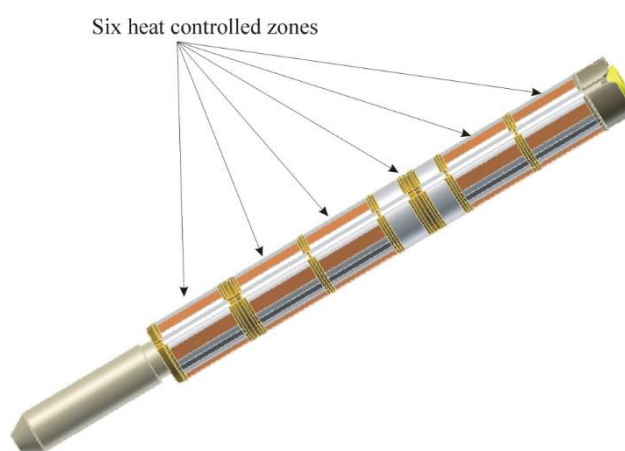
Objective

As a prerequisite for standardization, the MATTER project focuses on research for candidate materials for Generation IV reactors, especially for two demonstration reactor types: ASTRID (Advanced Sodium Technological Reactor for Industrial Demonstration) and MYRRHA (Multi-Purpose Hybrid Research Reactor for High-tech Applications). Supporting the design work, reliable and representative measurements of the mechanical properties of the candidate materials in aged state are required for these two reactors. Although these materials are generally not new, they are used in many industrial applications, the available database is incomplete and/or does not meet nuclear industry standards. Especially, it is not totally known how the material properties change by high temperature neutron irradiation. In the framework of the MATTER project these knowledge gaps have been identified. After a screening process for unknown, but necessary material properties a systematic research plan has been created. Practically all nuclear research institutes within Europe are co-operating to measure the required material properties. In the frame of this work MTA EK irradiated and will test two types of steels.

Methods

316 LN (18/8 type stainless steel with low impurities content) and it is welded joint, and P91 (9% Cr ferritic-martensitic steel) were provided by CEA (Commissariat d'Énergie Atomique). Irradiation conditions and type of post irradiation tests were agreed with workpackage leader. Specimen cutting and coding plan have been elaborated, and the specimens have been produced by milling and turning. All dimension of the specimens have been carefully recorded. Foil dosimetry program has also been developed and prepared.

For irradiation, an irradiation plan has been developed. The new BAGIRA 3 irradiation rig has been used for irradiation in the Budapest Research Reactor. The target holder of the rig has been designed in order to facilitate high temperature irradiations (this was the first irradiation in the Budapest Research Reactor at 550°C). The target holder has been machined from titanium alloy to withstand high temperatures and neutron irradiation. Changing the ratio of helium and nitrogen of the gas mixture within the rig controls the irradiation temperature, and electric resistance heating is applied for fine adjustments. Fine-tuning of the software controlling the irradiation temperatures was needed to allow precise control.



The titanium target holder of BAGIRA3 irradiation rig

Results

The specimens were machined, encapsulated and the irradiation (about 680 hours at 550°C) has been completed. The temperatures were kept within a ± 10 °C range from nominal temperature. After irradiation the specimens have been transported to the hot cell for PIE (post irradiation examination).

Remaining work

The freshly irradiated stainless steel specimens are highly radioactive. Two-three months decay time is necessary before mechanical testing can be started. Meantime the evaluation of the data acquired during the irradiation (temperature, gas mix, gas pressure etc.) will be evaluated. The activation analyses laboratory will measure the gamma activity and spectra of the dosimetry foils, and calculate the irradiation neutron fluence, dpa and spectra. Tensile testing at room temperature and at 550°C and Charpy impact testing of the specimens cut from the irradiated 316 LN will be performed. Fracture toughness testing and Master Curve evaluation is planned on the P91 specimens. Fractography and metallography testing will also be done. Evaluation of the results and preparation of final report is planned for the second half of 2014.

SIMULATIONS AND RESIDUAL STRESS MEASUREMENTS FOR NOZZLE MOCK-UP

Levente Tatár

Objective

The goal of the EU FP7 STYLE project was to assess integrity of PCPB-s (primary coolant pressure boundaries) except the RPV (reactor pressure vessel). In previous years, our institute manufactured the MU (Mock-Up) no. 6, which is a modified 1:5 scale replica of the primary feedwater nozzle of VVER-440 type RPVs. In 2013 we continued the work begun in previous years. We completed determination of missing material data, finalized simulations and made residual stress measurements.

Methods

Residual stress measurements by DHD (Deep Hole Drilling) were performed by Bristol University. For location of the hole see Figure 1a Figure 1b presents the measured axial and hoop stresses. Classic DHD and incremental DHD (iDHD) were applied.

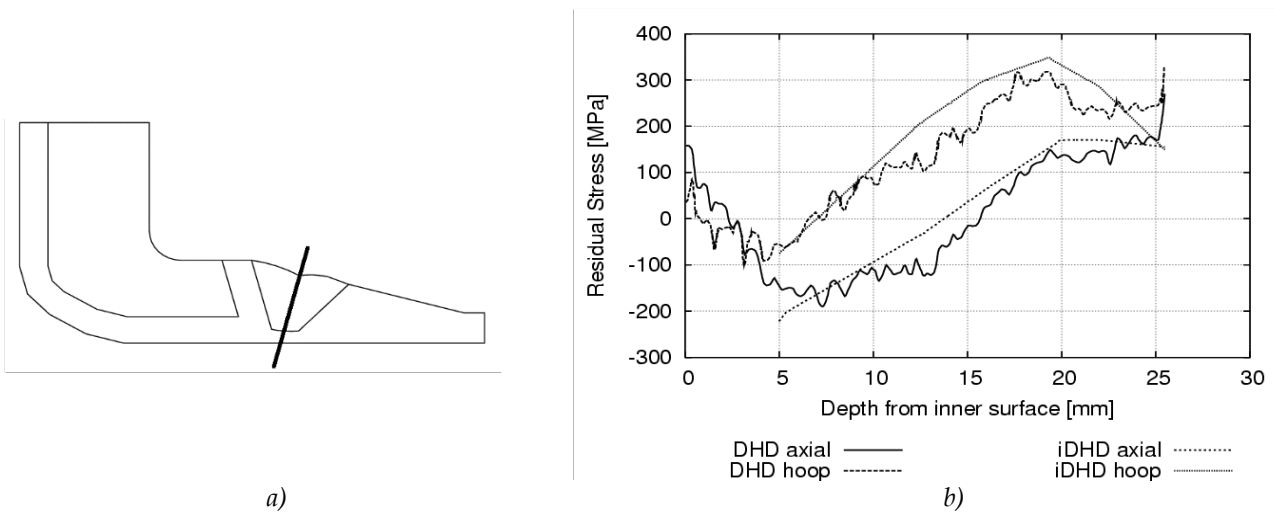


Figure 1: Location of the DHD measurement (a) and measured stresses (b)

ND (Neutron Diffraction) measurements for determining residual stresses were performed in the Budapest Neutron Centre by Wigner Research Centre for Physics. Figure 2a depicts a map of the measured axial stresses, Figure 2b shows the simulated values. Colours for both figures represent the same stress range.

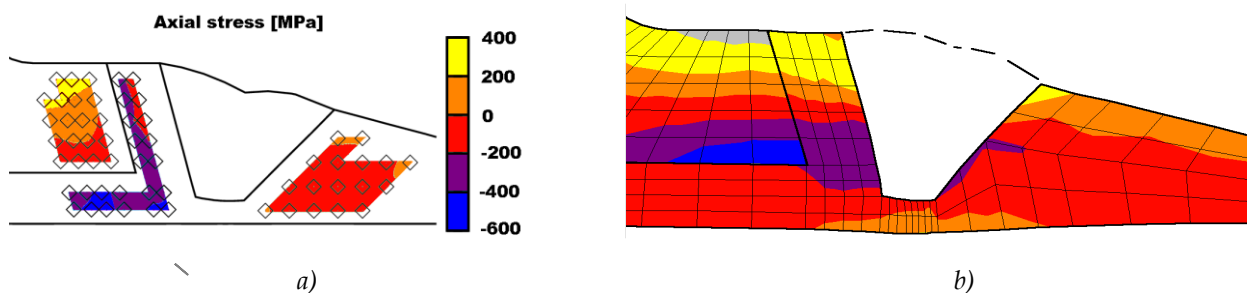


Figure 2. Measured (a) and simulated (b) residual axial stress components

Results

The simulation results of the manufacturing show a fairly good agreement with the measured temperatures and displacements. The measured and simulated residual stresses are within acceptable limits. Different residual stress measurement methods are not contradicting each other, however comparison of results is difficult to accomplish.

Remaining work

The STYLE project lasted for 3 years, it has been finished in 2013. The required deliverables were delivered, only administrative tasks have to be done.

Related publication

L. Tatár, Gy. Török, D. J. Smith, D. Son, C. Ohms, L. Kovács: *Manufacture, Residual Stress Measurement and Analysis of a VVER-440 nozzle Mock Up*, Proceedings of the ASME 2013 Pressure Vessels and Piping Conference (PVP2013), ASME Pressure Vessels and Piping Division, 2013.

IRRADIATION EFFECTS ON THE MICROSTRUCTURE OF RPV STEELS-LONGLIFE PROJECT

Ferenc Gillemot, Márta Horváth, Attila Kovács

Objective

LONGLIFE project is an European research project to study the expected material ageing of nuclear reactors after long term (60 years and beyond) operation. Twenty-one institutions participated in the project and studied the mechanical properties and the microstructure of the aged reactor wall steels [1].

Methods

MTA EK was the leading institute in Workpackage 2 (WP2). The elaboration and editing of the WP2 deliverables finished in the second period, but MTA EK supported the other workpackages using the collected information, taking part in their dissemination, and participated in the executive committee work. We also irradiated differently sidegrooved JRQ (reference steel of the International Atomic Energy Agency) steel to study the bias and constraint effects at use of Charpy size three point bending specimens for Master Curve evaluation, and elaborated a new model to understand the so called "flux effect".

Results

The reactor material group further developed the model of the so called "flux effect". This model shows that the effect caused by neutron irradiation is a combination of five different damage processes (stable and unstable matrix damage, segregations, occurrence of precipitations, thermal ageing and thermal recovery). These damage processes occur mainly by diffusion, that needs time to saturate and this time depends on temperature, spectra, chemical composition, etc. Simple use of the flux rate as a parameter may lead to high scatter, thus other boundary conditions should also be considered. The „flux effect” model explains why in many cases there is no effect observed even when the fluxes have different magnitudes, while in other cases this effect can be remarkable. (See Figure. 1)

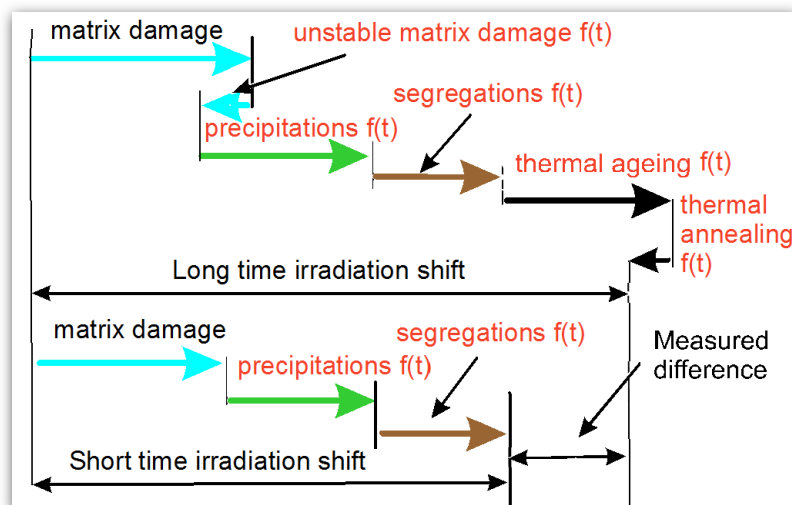


Figure 1: Explanation of the difference between short and long time irradiations[2]

MTA EK also compared smooth, 20% and 50% sidegrooved irradiated JRQ specimens for Master Curve determination according to the Russian proposal. The result shows that 20% sidegroove is advisable, and at 50% sidegroove the initial crack deteriorated from the original plan and ductile tearing occurred out of the maximum constraints [3].

Remaining work

The LONGLIFE project finished in January 2014. Continuation is planned in the "SOTERIA" project further studying the "Late blooming", the "Flux" effects during neutron irradiation and the application of the Master Curve.

Related publications

- [1] F. Gillemot, Á. Horváth, M. Horváth, A. Kovács et al: *Microstructural Changes in Highly Irradiated 15Kh2MFAA Steel* under publication in ASTM STP1572 on 26th Symposium on the Effects of Radiation on Nuclear Materials.
- [2] F. Gillemot, M. Horváth, A. Kovács: *Flux effect?* in proc. of LONGLIFE final workshop, 16-17 January 2014
- [3] F. Gillemot, M. Horváth, A. Kovács: *Effect of the notch size on irradiated 15H2MFA steel.* in proc. of LONGLIFE final workshop, 16-17 January 2014

DETERMINATION OF DISSOLUTION RATES FOR THE DAMAGED AND LEAKING VVER FUEL STORED IN WATER

MTA EK contribution to the FIRST-Nuclides Project

Emese Slonszki, Zoltán Hózer, Péter Szabó

Objective

The FP7 Collaborative Project FIRST-Nuclides (Fast / Instant Release of Safety Relevant Radionuclides from Spent Nuclear Fuel) aims to provide new and comprehensive knowledge of the fast release of safety relevant radionuclides from light water reactors' spent nuclear fuel after failure of the canister in an underground repository. The objective of MTA EK contribution to WP3 in the framework of the FIRST-Nuclides project is the determination of dissolution rates for several isotopes from damaged and leaking VVER fuel assemblies stored in water for several years.

Methods

Several isotopes were measured during and after the incident of Unit 2 of Paks NPP and during the wet storage of No. 70873 leaking fuel assembly of Unit 4 of Paks NPP. Concentrations of those isotopes were measured regularly and their decay corrected integrated releases were estimated in this work. It involves 11 isotopes and uranium in the first case and 13 isotopes and uranium in the second case. We used two methods for determination of the release rates:

1. First of all, we calculated the corrected integrated releases of every isotope from the measured activity data. After that, these data were divided by the total time which belongs to measurement (the elapsed time from the first measurement to the last one). The calculated release rate values are given by this method.
2. In the other case, linear fitting was applied to the corrected integrated releases data which resulted the fitted release rates.

Results

The dissolution rates for VVER fuel stored in water for long periods were determined on the basis of data from the Paks NPP. The two datasets provided information on slightly different conditions: in both cases the water temperature was similar, but in cases of damaged fuel the pH of coolant was significantly lower compared to the leaking fuel. This effect can explain the observed differences in dissolution rates (Fig. 1).

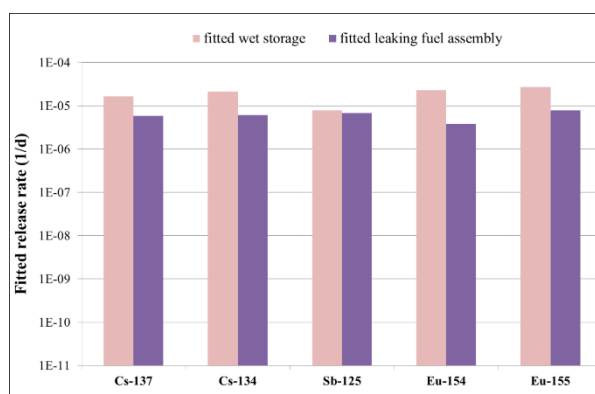


Figure 1: Comparison of the fitted release rates of long lived isotopes

During the wet storage of the damaged VVER fuel the fitted release rate range of long lived isotopes was $1 \cdot 10^{-5}$ - $3 \cdot 10^{-5}$ 1/d (only the release rate of ^{125}Sb isotope fell slightly short of this range with about $8 \cdot 10^{-6}$ 1/d). These values are three to six times higher than the release rates of leaking VVER fuel (Fig. 1). The release rates of ^{125}Sb isotope show the best agreement of all isotopes when comparing the damaged and leaking fuel under wet storage.

Following a review of the reliability of measured data, the dissolution rates were determined for eleven isotopes in case of damaged fuel and for seven isotopes in case of leaking fuel. Additionally, uranium dissolution rates were calculated in both cases. In most of the cases the release rates of individual isotopes were comparable to that of uranium.

Our calculated release rates may be regarded as conservative upper limits compared to the expected releases in the groundwater of deep geological repository since the release from the fuels took place in the spent fuel storage pool with high boric acid concentration.

Remaining work

Our calculating work in this project is finished. We will contribute to updating of the state-of-the-art report.

Related publication

E. Slonszki, Z. Hózer: *Determination of dissolution rates for damaged and leaking VVER fuel stored in water*, EK-FRL-2013-421-01/01-M1

THE MEASUREMENT OF THE MECHANICAL PROPERTIES OF E110 AND E110G ZIRCONIUM ALLOY CLADDING TUBES

*Márton Király, Dániel Mihály Antók,
Márta Horváth, Zoltán Hózer, Imre Nagy, Tamás Novotny, Erzsébet Perezné Feró*

Objective

The purpose of the work was to determine the ultimate tensile strength of the E110 and E110G cladding tubes and to assess the differences between these alloys. In order to achieve this target, ambient temperature tensile experiments were carried out on E110G (produced by new technology) and E110 (produced by current electrolytic method) alloy tubes, two-winged axial and short ring test samples in 2013.

Methods

Before the tensile tests, the behaviour of the cladding samples were analysed by MSC.Marc Mentat 2005r3 finite element simulation program in order to facilitate the selection of the final geometry of the axial and ring samples.

The samples were prepared by milling and slow cutting. The ring and axial tensile tests of the samples were carried out by Instron 1195 universal test machine. The load-displacement curves were recorded and evaluated.

In 2014, these tensile tests will continue with oxidised (1-3% equivalent cladding reacted) and hydrogenated (100-400 ppm) samples. After the preliminary oxidising experiments the oxidation temperature was fixed at 800 °C to avoid breakaway oxidation and to keep the surface of the samples intact. Some samples were prepared as well (Fig 1).

We set up an instrumented furnace to observe the thermo-mechanical creep of the cladding tubes at 300-500 °C temperature and 5-10 MPa inner pressure over a period of a few months. The creep will be registered by advanced laser distance meter.

The mayor steps of work conducted were:

- Modelling and analysing of the cladding sample geometries with finite element simulation program
- 3 ring, 2 axial and whole 1 tube tensile tests for each alloy were performed, ultimate tensile strength calculated
- Preliminary oxidising experiments and 8 ring samples of each alloy were prepared for future tensile testing
- Test matrix determined for the continuation of the project in 2014 and 2015.

Results

The axial tensile strength was uniform for the full tubes and the machined axial test samples. The E110G cladding samples' axial ultimate tensile strength is 11% higher than that of the E110 samples. The axial ultimate tensile strength of the E110G was $430,11 \pm 2,87$ MPa, for the E110 it was $385,92 \pm 5,06$ MPa at room temperature.

The E110G cladding samples' ultimate tensile strength in the hoop direction is 12% higher than that of the E110 samples. The hoop ultimate tensile strength of the E110G was $405,48 \pm 3,46$ MPa, for the E110 it was $360,65 \pm 3,31$ MPa at room temperature.

For both alloys the ultimate tensile strength in the hoop direction is about 6% lower than the axial ultimate tensile strength.

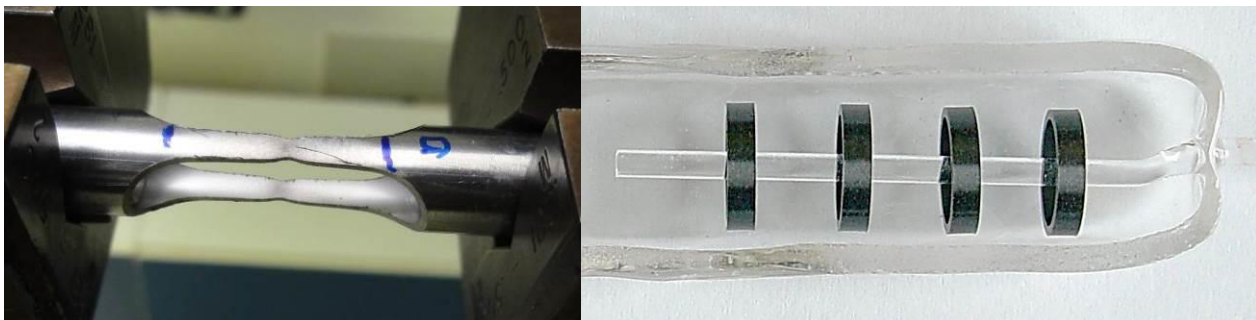


Figure 1: Axial tensile test sample during testing and oxidised ring samples in the furnace's quartz boat

Remaining work

The project will continue in 2014 and 2015 with tensile tests of oxidised (1-3% equivalent cladding reacted) and hydrogenated (100-400 ppm) axial and ring samples. We will perform ambient, elevated (150 °C) and in-service temperature (300 °C) tensile experiments of untreated, oxidised and hydrogenated axial and ring cladding samples of both alloys.

We will measure the thermo-mechanical creep of the cladding tubes at 500 °C temperature and 5-10 MPa inner pressure over a period of a few months. In 2015 we will repeat it at 300 °C temperature (expected normal service temperature).

ADVANCED MODELING OF CLADDING TECHNOLOGY

Tamás Fekete, Levente Tatár, Dániel Antók

Objective

The Reactor Pressure Vessel (RPV) is one of the most important components for safety and lifetime of the plant, accidental damage of which may cause serious environmental damages. 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. The vessels were manufactured from ferritic steels with austenitic anti-corrosion cladding from inside. The cladding was worked up by welding technology to the inside surface of the semi-products of the RPV. Thermal and mechanical properties (thermal expansion, thermal conduction coefficient and elastic-plastic properties) of the cladding significantly differ from thermal and mechanical properties of the low-alloyed base metal and weld seam, therefore, during welding Residual Stresses (RSs) occurred around the interface of cladding and the base material, and these stresses are significant even after the stress mitigating heat treatments. The RS fields are complex, caused by complex time history of thermal fields and different behaviour of structural materials during the technological process. The RSs play a significant role in structural integrity analyses. Defining the RS state for the cladding-base metal interface is still difficult and the differences between RS recommendations presented in commonly applied structural integrity guidelines are quite large. Typically, RS recommendations are overly conservative. The main goal of the study was to assess realistic residual stress field arising in the RPV wall near the cladding-base metal interface during and after the welding process.

Methods

A large scale Mock-Up (MU) was elaborated from a piece of RPV shell semi-product and the cladding was produced onto the inner surface of the test piece with same welding technology used by manufacturer of the RPV. The technological parameters, temperatures and displacements of the test piece during the experiment were collected by an advanced quality online measurement system. After the test, residual stresses were determined on the MU, and then material properties of cladding and the heat affected part of the MU were determined.

Before the experiments, a detailed 3D finite element model of the test was developed with the aim at enhancing quality of MU design and elaborating an advanced quality, validated simulation model for future applications. The methodology of calculations was developed by MTA EK, using elastic-plastic material models of the structural materials. Flow curves of the materials – describing real elastic-plastic deformation behaviour of the cladding and of the base material – were developed from tensile test results. Coupled thermo-mechanical calculations have been performed applying large deformation plasticity theory to model effects of geometrical and material nonlinearities that are locally present in the system during the technological process. Applied FEM mesh can be seen on Figure 1 (left). Numerical calculations were performed by using the Msc.MARC FEM code with updated Lagrange procedure. Selected results from calculations of the temperature field occurring during welding are depicted in Figure 1 (left), while the von Mises Stress field is shown on Figure 1 (right).

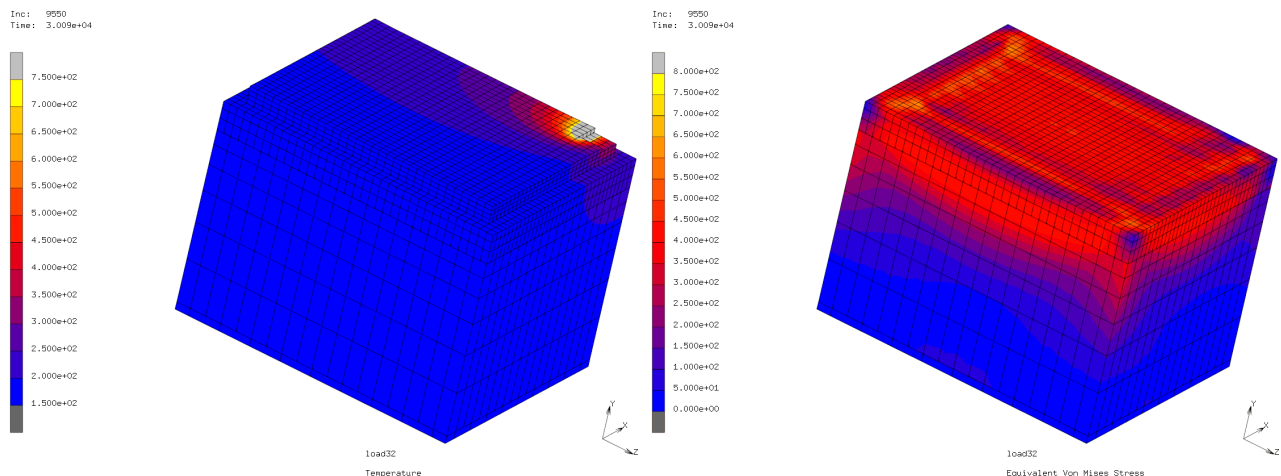


Figure 1: Temperature distribution (left) and equivalent von Mises stress field (right) at $t=30\,090$ s of the welding process

Results

Simulation results of the manufacturing process show a fairly good agreement concerning measured temperatures and displacements. Measured and simulated residual stresses are within acceptable limits.

Remaining work

Based on more recent material test results, some improvements of the simulation model are planned for the near future.

RECONSTITUTION TECHNOLOGY FOR IRRADIATED CHARPY-SIZED SPECIMENS

Tamás Fekete, Attila Kovács, Ferenc Gillemot, Márta Horváth, Gábor Uri

Objective

The Reactor Pressure Vessels (RPVs) are the lifetime limiting components of a Nuclear Power Plant (NPP) and irradiation embrittlement is the leading ageing mechanism of them. Evaluation of safety and structural integrity of long term operating RPVs requires good knowledge on fracture mechanics properties of their structural materials in aged state. Measurement of fracture properties of aged structural materials requires proper number of material specimens in aged state. The original monitoring (so called "surveillance") program contained large - but limited - number of specimens that provided measurement results, which served as a good database for lifetime extension, but these results have to be completed by further measurement results in order to cover all aspects of material characterisation required for later phases of the Long Term Operation (LTO). During the original surveillance program, the specimens were aged (irradiated) for years, replacement of them would either be impossible or extremely expensive. The reconstitution technology solves this problem. The reconstitution technology uses remnants of tested aged archive specimens, supplements them by welding new end pieces. These reconstituted specimens can be used at further material tests, so materials utilised during measurements of the original surveillance program can be reused. This way three times more information can be obtained from one original specimen. MTA EK has been using the reconstitution technology of Charpy and other small size specimens for more than 15 years. Presently, large number of reconstituted specimens is required by the life time management program of NPP Paks. The reconstitution of highly irradiated specimens and the high quality requirements prescribed by the current ASTM standard justified the present technology development.

Methods

The main phases of the applied technology (Figure 1) are as follows: identify the available irradiated remnants, make picture of the broken surface, cut the broken surface and deformed parts of the archive specimens, weld stud to new end pieces (Figure 2); machining the welded pieces, cutting the notch and graving the specimen code into the reconstituted specimens; quality assurance during the technology steps and of the final product. The irradiated archive specimens are highly radioactive. To avoid radiation harm to the staff, all operation must be performed in hot cells or behind proper shielding. Remote controlled welding and machining have been further developed and new equipment (e.g. saw cut machine, computer controlled graving machine, electric discharge wire cutting machine) have been introduced into the technology line to be able to produce large number of reconstituted specimen. The requirement to increase the specimen quality and reduce the quantity of the welding defects required new tool kits, development of temperature testing during welding, metallography checking the widths of the welds, mapping of the welding defects etc.

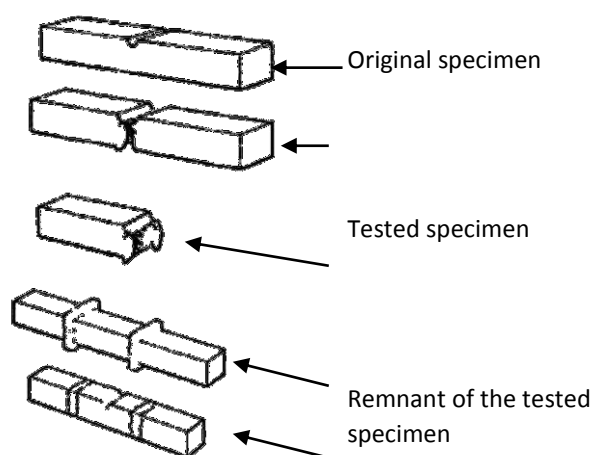


Figure 1: The technology scheme of the reconstitution

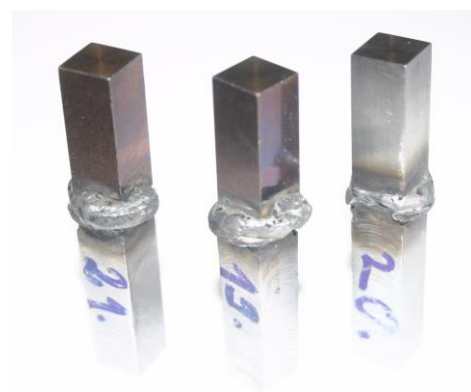


Figure 2: Reconstituted specimens after stud welding

Results

The results show that the reconstituted irradiated specimens fulfil quality criteria defined in the ASTM E-1253-12 standard.

Remaining work

MTA EK is planning to use the reconstitution technology partly for the extended surveillance programs of NPP-s and to reduce the volume of irradiated materials during radiation damage studies.

SECONDARY HYDRIDING OF E110 AND E110G CLADDINGS

Zoltán Hózer, Imre Nagy, András Vimi, Mihály Kunstár, Péter Szabó, Tamás Novotny, Erzsébet Perez-Feró, Zoltán Kis, László Szentmiklósi, Márta Horváth, Anna Pintér Csordás, Márton Balaskó, László Horváth, Gábor Benyács

Objective

Secondary hydriding can take place during a LOCA event after the ballooning and burst of Zr cladding. The oxidation and hydrogen uptake in the ballooned section can produce the weakest segment of the rod. This phenomenon was investigated in the past only for Zircaloy-4 cladding. The objective of the present work was the investigation of the effect of secondary hydriding in VVER reactors with E110 and E110G alloys.

Methods

High temperature facility was built to carry out high temperature treatment of fuel cladding samples. The burst of tubes was reached with inner pressurization at 750 °C and 800 °C. After burst the samples were oxidized in the same furnace for different periods and at different temperatures. The oxidized samples were examined in tensile test machine with four point bending tests (Fig. 1). The microstructure of samples was analysed by optical and scanning microscopy. The hydrogen content of the cladding was measured by hot extraction, prompt gamma activation analyses and neutron radiography methods.

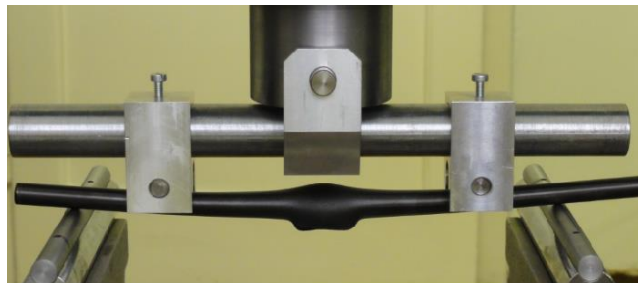


Figure 1: Four point bending of ballooned cladding sample

Results

The experiments indicated that after oxidation the ballooned section becomes the weakest segment of the VVER fuel, too. According to the mechanical testing, the cladding samples were brittle even after short oxidation time (200 s at 1000 °C) without any sign of ductile behavior. The samples oxidized to 10-18% ECR (equivalent cladding reacted) failed at low mechanical loads. The hydrogen content in the ballooned section reached 5000-7000 ppm value.

The comparison of E110 and E110G samples showed that the E110 tubes lost their load bearing capability or even integrity much earlier than the E110G samples treated under similar conditions (Fig. 2).

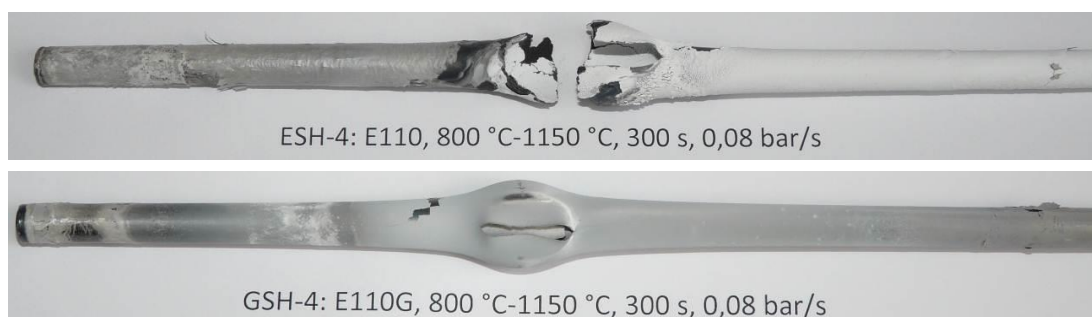


Figure 2: E110 (up) and E110G (bottom) cladding tubes after burst at 800 °C and oxidation at 1150 °C for 300 s

Remaining work

The experimental data will be included in the database of Zr1%Nb alloys.

Related publication

Z. Hózer, I. Nagy, A. Vimi, M. Kunstár, P. Szabó, T. Novotny, E. Perez-Feró, Z. Kis, L. Szentmiklósi, M. Horváth, A. Pintér Csordás, M. Balaskó, L. Horváth, G. Benyács: *Secondary Hydriding of Fuel Rod Cladding, Final report, EK-FRL-2013-759-01/07 (in Hungarian)*

ANALYSIS OF CORROSION PARTICLES ORIGINATED FROM THE PRIMARY AND SECONDARY COOLING SYSTEM OF PAKS NPP

Éva Kovács-Széles

Objective

Between MTA EK and Paks Nuclear Power Plant (NPP) there is a research contract which specifies analysis of corrosion particles originated from the primary and secondary cooling systems of the reactors to detect the origin or source of corrosion. For determination of the feature of these particles (size, morphology, activity, elemental composition, etc.), different techniques are used.

Methods

In this work several parameters of particle samples originated mostly from the block No. 2 from startup and shutdown period were determined using different analytical techniques: morphology by optical microscopy (OM) and scanning electron microscopy (SEM), activity by gamma-spectrometry, ^{63}Ni and ^{55}Fe content by liquid scintillation technique, corrosion products (Fe, Co, Ni, Cr, Zr, Ag) by inductively coupled plasma mass spectrometry (ICP-MS), calculation of the specific activity and the residence time of the particles in the reactor zone, analysis of the filtered particles and also the filtrates.

Results

During this work several particles originated from the primary and secondary cooling system of Paks NPP (with special regard to block No. 2) were investigated. Some pictures taken by SEM can be seen in Fig. 1 and Fig. 2.

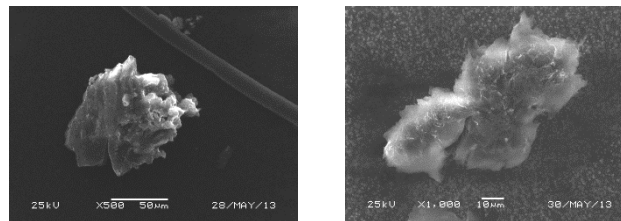


Figure 1: Particles from organic materials

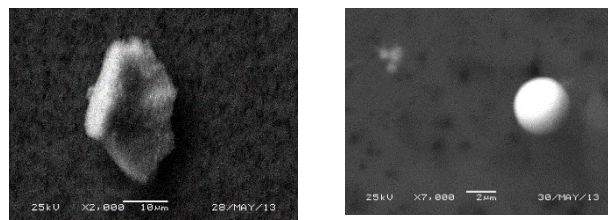


Figure 2: TiO_2 and Fe-oxide particles

In the samples only few corrosion particles were found which shows the efficiency of the electromagnetic filters in the system. The samples contained more silicate particles and in all of the samples Fe-oxides were also found. Difference was found among the blocks in the case of Fe-containing particles: particles originated from block No. 2 did not contain alloying elements (Cr, Ni, Mn); particles originated from block No. 3 contained Cr in higher amount and some Ni; particles originated from block No. 4 contained Mn. Organic particles in bigger size (larger than $100\ \mu\text{m}$) were always found in the samples.

The residence time of the corrosion products in the reactor zone can be calculated from the specific activity of the long-lived ^{63}Ni isotope (half-life: 100 years). The calculated value of residence time varied between 69 and 192 as well as 37 and 75 days, respectively.

Residence time measured determined by using the specific activity of the shorter half-life isotopes (^{54}Mn , ^{55}Fe , ^{60}Co) seems shorter compared to the residence time calculated from the previous method (^{63}Ni). It can be explained that the activation of the particles happened not only during the last campaign but also in earlier ones, therefore the shorter half-life isotopes have already decayed (assuming the long-term stability of the particles).

Remaining work

This work was a part of an ongoing research project for Paks NPP which will be running until 2016, therefore the analysis of the particles is continuing in the future.

Related publication

É. Kovács-Széles: Analysis of corrosion particles originated from primary and secondary system of NPP, research report for PAKS Zrt., EK-SBL-2013-766-01 (2013) [in Hungarian]

PELLET-CLADDING INTERACTION

Ágnes Griger, Anna Pintér Csordás

Objective

The objectives of our work were to overview and to re-evaluate the results originated from the open literature on the PCI (Pellet-Cladding Interaction), on the PCI-SCC (Pellet Cladding Interaction-fission product assisted Stress Corrosion Cracking) and on the PCMI (Pellet Cladding Mechanical Interaction) phenomena which have importance for the safe and more economic operation of nuclear reactors (higher burn-up, longer lifetime and wider manoeuvrability).

Methods

A lot of papers, reports including the ones of the Halden Reactor Project, the Studsvik experiments and others from the scientific literature dealing with these phenomena was collected and overviewed, as well as the available original measured data were newly evaluated. For practical reasons, the PCMI phenomena were primarily handled as the behaviour of cladding. This approach is admissible as the degrading effect of the PCMI on the cladding can terminate its further use because of the loss of its protective function.

Results

The manifestation of PCMI/PCI/PCMI-SCC phenomena strongly depends on several factors of the operation (heat generation rate, cladding temperature, burn-up, etc.) and on the properties and design of fuel pellets and claddings (grain size, texture, pellet-cladding gap, etc.).

The structural and dimensional changes of cladding caused by PCMI under irradiation were analysed, and the correlations determining the limit values of operating parameters - at which the cladding becomes failed and/or in - hermetic - were checked and partly revised.

From experiments carried out on VVER/PWR fuel rods/segments with various burn-up values (up to ≈ 70 MWd/kgU) the following results were gained:

- Two types of PCMI cases can be distinguished on the base of the circumstances and the duration of their presence:
 - PCMI at higher burn-up with lasting state
 - PCMI at lower burn-up merely during certain transient events, after which the gap can open again.
- Onset of PCMI is shifted to lower linear heat rates by increasing burn-up. During reactor operation the gradually closing pellet-cladding gap due mainly to the burn-up dependent pellet swelling, gives explanation to this experience. At smaller gap size a lower heat generation rate (a lower heat expansion of pellet) is enough to close the gap.
- Applying results of various ramp-tests, threshold values of the linear heat rate were determined as a function of the burn-up. Above these threshold values the cladding can be damaged with high probability and the fuel rod can become in-hermetic.
- Long lasting PCMI is expected only at high burn-up, which can result in irreversible cladding deformation.

The processes of dimensional changes of the pellet-column facilitating the PCMI-forming were reconsidered. The results are the following:

- The measure of the pellet densification decreases with increasing grain size of UO₂ pellet in connection with its high temperature creep properties.
- The actual measure of dimensional changes of the pellet is mainly controlled by the swelling caused by the solid and gas form fission products.

During PCI/PCMI several changes in the pellet-cladding microstructure can occur, which are very important from the point of view of the cladding corrosion, namely:

- Interaction region can form at the pellet-cladding interface during the long life PCI/PCMI which is completely or partly bonded to the inner side of the cladding and to the surface of the fuel pellet.
- Depending on the irradiation circumstances a continuously increasing oxide layer is formed and its thickness can reach 10 μm at high burn-up.
- At higher burn-up the large amount of the generated Cs may form precipitations at grain boundaries and at the same time it can migrate at high temperatures both axially and radially. From thermodynamic reasons, caesium-zirconate can form by slow kinetics only in the presence of ZrO₂. Otherwise Cs can be present in form of U(Cs)-oxide at the rim layer and it can occur as Cs-oxide-ZrO₂ mixed phases at the inner side of the cladding, respectively.

Remaining work

Objective of the work was fulfilled during the scheduled time period.

Related publication

- [1] Ágnes Griger, Anna Pintér Csordás: „*Pellet-Cladding Interaction*”, EK-RAL-2013-729-01/00 (2013 November) (in Hungarian)

HALDEN EXPERIMENTS AND FUROM SIMULATIONS

Ágnes Griger

Objective

The objective of the work was the investigation of the fuel element behaviour with high burn-up at different loading conditions by means of FUROM simulations with special attention to the fission gas release (FGR). Since the standard FGR model in FUROM provides unsatisfactory results in case of ramp tests, a new fission gas release (FGR) model was introduced and tested by simulating ramp experiments. The work was sponsored by MVM Paks NPP.

Methods

Ramp-tests carried on in the framework of the Halden Reactor Project (HRP) were reviewed and FUROM simulations were performed on the base of the irradiation histories. Proper data handling of the original raw data and data reduction were elaborated. The calculated (simulated) and measured values were compared.

Results

Ramp tests (IFA-519 rig) were performed in the Halden Boiling Water Reactor (HBWR) to study the thermal performance as well as the fission gas release of high burn-up (up to ≈ 90 MWd/kgU) PWR UO_2 fuels. The variation of the fuel temperature and the fission gas release (rod pressure) were measured under different power conditions (steady state, different ramps).

Applying a new local power (measured in mass rate, W/g) dependent FGR model, FUROM simulations were carried out for the rods of IFA-519 rig using best-estimate initial and boundary conditions derived from the experimental database. The fission gas release under different irradiation situations (steady state, rapid power changes (ramps), load follow tests) was analyzed. The analyses proved that the fission gas release of the high burn-up PWR fuel rods can be reasonably well predicted by the FUROM simulations with the new FGR model both in steady state and in transient cases. The calculated values of the fission gas release have matched the experimental data with adequate accuracy (+1.5 and +3%) (see Figure 1).

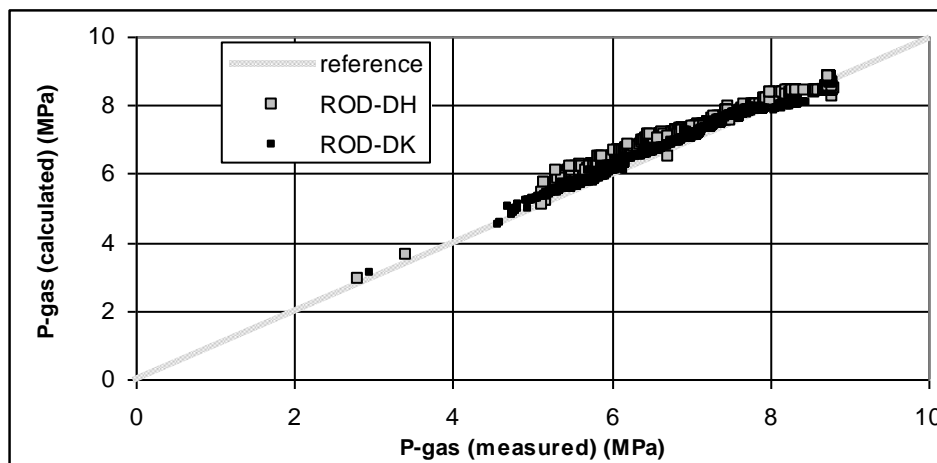


Figure 1: Calculated and measured values of rod pressure in the ramp tests

Remaining work

Objective of the work was fulfilled during the scheduled time period. However, the supervision, verification and validation of the newly introduced FGR model must be performed by simulating further VVER integral tests.

Related publication

Ágnes Griger: „Halden experiments and FUROM simulations. The test of the new FGR model”, EK-RAL-2013-729-02/00 (2013 November) (in Hungarian)

STRUCTURAL INTEGRITY CALCULATIONS OF VVER440 REACTOR PRESSURE VESSELS AT NPP PAKS

Tamás Fekete, Levente Tatár, Dániel Antók

Objective

The Reactor Pressure Vessel (RPV) is one of the most important components for safety and lifetime of a Nuclear Power Plant (NPP), accidental failure of which may cause serious environmental damages. RPVs have large cross-sections (VVER-440: 149 mm wall thickness with 3800 mm diameter); work at elevated temperatures ($\approx 270 - 290$ °C) and high pressures (≈ 12.2 MPa). 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 its lifetime, taking into account all possible modes of operation. Fracture - mechanical structural integrity calculations are tools to analyse mechanical behaviour of the RPVs under the influence of various loading cases. The goal of structural integrity calculations is the assessment of safety limits of RPVs for all defined loading cases. Two types of loading cases are relevant for fracture mechanical structural integrity calculations: normal operation conditions and postulated accident situations leading to Pressurised Thermal Shock (PTS). For normal operation, the start-up and shut - down process, as well as pressure testing situations have to be assessed by fracture mechanics analysis. These calculations lead to the construction of p - T limit curves that are valid during the operation of the RPV. PTS phenomenon can occur when in some accidental situations extra quantity of cooling water flows into the RPV, causing severe overcooling of the vessel wall. A PTS event can cause a dangerous situation regarding the integrity of RPVs, as high thermal gradient develops through the vessel wall, causing high thermal stresses, which are superposed to stresses originating from internal pressure. The thermal and stress fields in RPVs are very complex, caused partly by complexity of the pressure vessel geometry itself and partly by the complex thermal loadings. The main goal of PTS calculations is to assess allowable service time of RPVs from PTS point of view. During last years Paks NPP developed a strategy for introduction of a new generation of fuel elements that could affect ageing of structural materials and therefore allowable service time of the RPVs. The goal of the project is complete reassessment of allowable service time and p - T limit curves of the VVER 440-213 type RPVs installed at NPP Paks.

Methods

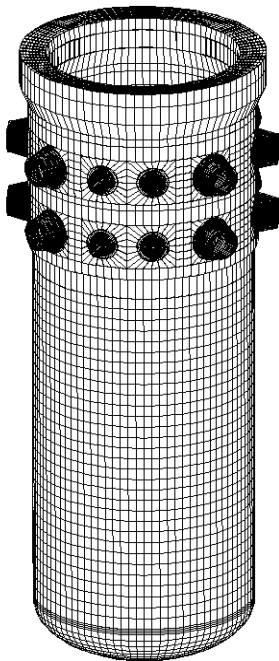


Figure 1. Model of VVER-440 RPV

The methodology of structural integrity calculations for normal operation was developed by MTA EK. At first, coupled 2D temperature field and linear elastic stress field calculations have to be performed for the lower cylindrical part of the vessel for start-up and shut - down conditions. The stresses include thermal stresses resulting from the start-up and shut - down transients, as it is prescribed in national guidelines. Fracture mechanics calculations are based on linear elastic fracture mechanics theory. The postulated defects are surface breaking flaws. The p - T limit curves of the reactor pressure vessel will be derived from results of fracture mechanics analyses and critical temperatures of brittleness (T_k) curves of aged structural materials. Critical temperatures of brittleness curves of RPVs will be derived from results of Charpy impact measurements performed in the frame of surveillance program of the RPVs.

For PTS structural integrity calculations, the methodology was developed by MTA EK. At first, detailed neutron fluence calculations are planned to provide input for the assessment of material ageing of irradiated parts of the RPVs. In a second stage, system thermal-hydraulics calculations have to be performed to provide thermal boundary conditions for the structural integrity calculations. For fracture mechanical structural integrity calculations a two level methodology has been developed. In first level of the calculations 3D finite element temperature field, linear elastic stress field calculations will be performed for the body of the vessel and for the nozzles, taking into account all transients analysed by system thermal-hydraulics calculations. Fracture mechanics calculations are based on linear elastic fracture mechanics (LEFM). In second level of the analyses 3D FEM temperature field, elastic-plastic stress field and nonlinear fracture mechanics calculations will be performed for the transient causing most severe situation in case of first level calculations - if it will be necessary.

Results

Neutron fluence calculations and system thermal-hydraulics calculations have been performed resulting in updated values for reassessment of allowable service time of RPV-s and the p - T limit curves of the vessels.

Remaining work

Fracture mechanical structural integrity calculations will be performed in the near future to provide updated values for the allowable service time of RPV-s and the p - T limit curves of the vessels.

RESEARCH RELATED TO NUCLEAR POWER PLANT TECHNOLOGY

HUNGARIAN SUSTAINABLE NUCLEAR ENERGY TECHNOLOGY PLATFORM

István Vidovszky

The Platform was launched in 2010. Its main goal 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 by now and also leads to some important further modifications, such as the refurbishment of the process control system. The government's decision concerning new units makes it actual to concentrate on related issues. The strategy concerning the nuclear fuel cycle should be reformulated due to the lifetime extension and the appearance of new units.

The platform is represented by MTA EK. The managers of the Platform members form the Governing Board. The Governing Board elaborates the main strategic documents, determines the direction of the activities. Two more bodies were established, the Executive Committee and the Mirror Group. The Executive Committee coordinates the everyday work of the platform, organizes the cooperation with European organizations, is responsible for the work plans and has to organize the conferences as well. Members of the Mirror Group are delegates from those member organizations which are responsible for the determination of the demands for research and development activities. The Mirror Group makes recommendations for the Governing Board aiming to fulfill the Hungarian and international demands and for determining the priorities of the R&D program.

The platform elaborated the detailed strategic research agenda (SRA). Unfortunately, financing of the platform's activities is still not solved. A few tasks which are financed by the Hungarian Atomic Energy Authority and by Paks NPP could start, however the major financing option by the government is still an open issue.

A NEW VIRTUAL CONTROL ROOM SYSTEM FOR THE PAKS NPP FULL-SCOPE TRAINING SIMULATOR

József Páles, Gábor Házi

Objective

The full-scope training simulator at Paks Nuclear Power Plant (NPP) is one of the most important educational and licensing tools of the plant operators and it contributes significantly to the safe operation of the plant. The Reactor Monitoring and Simulator Department is responsible for the development and upgrades of the simulation models in the system to face with the continuously changing requirements. In order to support better these activities, the replica simulator configuration has been extended significantly in MTA EK last year. With this extension our system became almost complete, the only missing component remained is the replica of the simulator control room. To make up for this deficiency we have developed a new interactive 3 dimensional virtual control room system and connected it to our simulator configuration.

Methods

A high fidelity 3 dimensional interactive model of the control room has been developed and connected to the full-scope training simulator. We used the open source 3D content creation software Blender (www.blender.org) and tools from the computer game industry to build up the model. The user can move freely within the model, interact with the switches and actuators, and read plant measurement data directly from the devices mounted on the panels just like in the real control room (Fig. 1).

To implement navigation methods and interactions in the system we used a game engine software and wireless game console devices. Since the model is highly programmable, it is easy to introduce further new interaction methods and devices into the system.

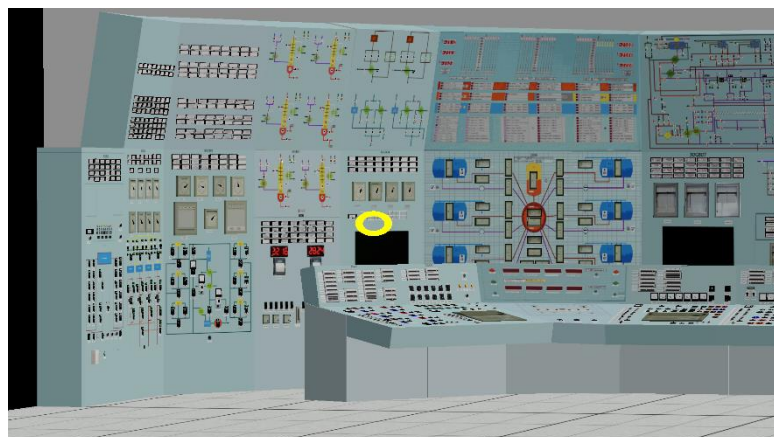


Figure 1: The viewpoint of the operator in the virtual control room

Results

A 3D interactive virtual control room system has been developed to facilitate the use of the full-scope training simulator configuration in MTA EK. The new virtual control room improves the efficiency of in-house simulation model testing and validation, but it can also be used to support other research and development activities, such as man-machine interface development and testing, or using the system to help solving engineering problems.

New methods have been developed to implement the navigation and interaction within the model by utilizing wireless game console devices. Besides the basic navigation methods, a prototype of a simple head tracking interface has also been developed by using low cost commercial off-the-shelf devices [1,2].

Remaining work

The new virtual control room system is functionally almost complete but it contains a special panel which uses a different kind of communication subsystem than the other panels for communication with the training simulator. Next year we are going to extend the system with this communication, and we will investigate and develop other new advanced interaction methods and devices, such as touch panels, and gesture recognition tools used in the computer game industry.

Related publications

- [1] G. Házi, J. Páles: *A New Virtual Control Room System for the Paks NPP Full-Scope Simulator*, EHPG Meeting Proceedings, HPR-379, Vol. 1 (2013)
- [2] G. Házi, J. Páles: *Virtual Control Room System for the Paks NPP Full-Scope Simulator*, Nukleon VI, 146 (2013)

MTA EK CRITICAL HEAT FLUX EXPERIMENT - CHERT

Gusztáv Mayer, Richárd Nagy, Imre Nagy

Objective

The critical heat flux (CHF) value at which the heat transfer decreases abruptly is often called burnout referring to the sudden temperature rise of the heated wall, which is generated by the onset of a constant vapor film between the wall and the bulk fluid, and usually causing the damage of the system. The CHF value depends on several parameters like: type of liquid, material and roughness of the heated surface, mass flux of the coolant and its surface tension, outlet quality, inlet subcooling, system pressure and geometrical data (length, diameter, orientation) etc. Exact prediction of CHF is an inevitable goal for many industrial areas and it has an especially great relevance in nuclear industry. The CHF phenomenon has a wide literature over the past decades. The engineering approach is based on empirical correlations. These correlations sometimes contain a lot of parameters and can be used only in limited parameter region. This fact inspired Groeneveld and his coauthors to develop a CHF lookup table for vertical 8 mm water cooled tube in 1995 and later in 2006, and using their work Doerffer and his coworkers extended its applicability to annuli. Park and his coworkers concluded that the Doerffer correlation show the most reasonable prediction published during the widest parameter ranges for annuli among the investigated correlations in literature. Park and his colleagues also concluded that no reliable correlations are available for very low pressure conditions ($P < 1000$ kPa), indicating a strong need for new correlations with enhanced prediction capability. To fulfill this gap, a low pressure low flow experimental mockup was built named CHERT (MTA EK Critical Heat Flux ExpeRiment).

Methods

The experimental test section consists of internally heated annuli. The heated length of the inner stainless steel solid rod is 464 mm and its outer diameter is 6 mm. The electrically heated rod is positioned concentrically into a Pyrex tube with an inner diameter of 16,3mm. The test section is positioned vertically and the deionized water coolant flows in upward direction. During the measurements presented in this paper the inlet subcooling was kept constant (3 °C below the current outlet saturation temperature). The investigated test section inlet pressure ranges from 1.1 bar to 2.25 bar and the mass flux rate is between 50 and 110 kg/(m²*s).

Results

111 CHF data points were collected on the MTA EK CHERT test facility. On Figure 1 the relative error of Doerffer correlation is depicted comparing to the current measurements in the function of mass flux. The results show good accuracy at around 70 kg/(m²*s) with the Doerffer correlation but they exhibit significant error both at lower and higher mass flux values. It also can be seen that Doerffer correlation gives better results using the older CHF look-up table of Groeneveld, which is not surprising knowing that the Doerffers' paper uses the older 1995 look-up table as a reference and they have not updated their correlations to the new 2006 look-up table yet.

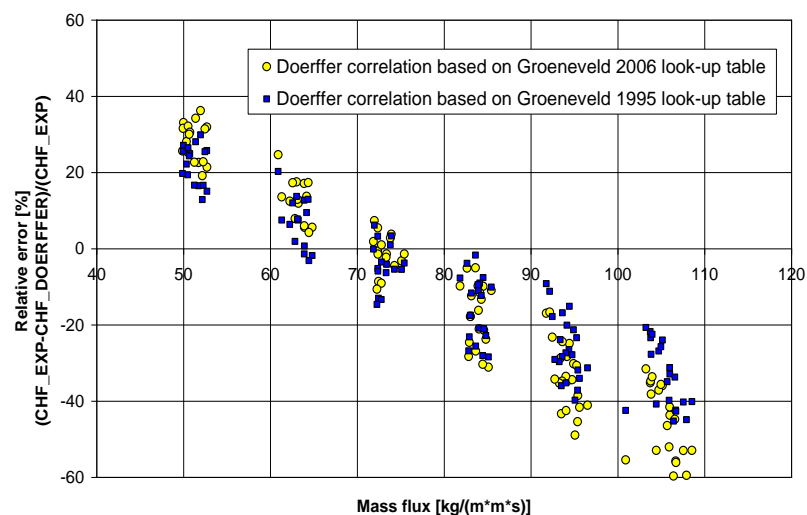


Figure 1: Relative error of Doerffer correlation comparing to MTA EK CHERT measurements

Remaining work

The above results confirmed the observation of Park and his colleagues - namely that there are no reliable CHF correlations available for very low pressure conditions ($P < 1000$ kPa) - and they exhibit high relative errors in certain ranges. This fact convinced us to continue our research in low flow and low pressure range conditions in order to give more accurate CHF prediction correlations.

CONCEPT FOR THE RENEWAL OF VERONA CORE MONITORING SYSTEM

János Végh, József Páles, Csaba Horváth, Gábor Házi

Objective

Paks NPP – in connection with the plan to extend the length of fuel cycles to 15 months from 12 months – has asked MTA EK to investigate the possible consequences of this plan regarding the VERONA core monitoring system.

Methods

We have prepared a study overviewing all possible aspects of the longer fuel cycles focusing on the VERONA system. Besides trivial consequences, like the necessity to introduce longer transient and campaign archives because of longer fuel cycles, we have also taken into account that there are other ongoing development activities in the plant. To be more specific, the renewal of the technological computer network and the design of a new plant computer system were taken into account as “boundary conditions” in our study.

Results

The major conclusions of the concept study are given as follows:

1. Development of reactor physics calculations of VERONA is needed before starting the first 15 months fuel cycle.
2. For the development of the calculations, the computational capacity of reactor physics servers (RPH) has to be increased roughly by an order of magnitude. Based on the experience we obtained in the VERETINA project, this objective can be achieved by using Graphics Processing Units (GPU) for the computations.
3. Standardization of hardware and software elements of the core monitoring system would be highly beneficiary from the point of view of operation and maintenance. Therefore, as far as possible, the same type of software and hardware elements should be used in all technological computational systems.
4. From the point of view of maintenance, the application of computer virtualization techniques would be extremely useful. Therefore, the virtualization should be applied wherever it is possible.
5. The ongoing renewal of technological computer network (TCN) in the plant implies the need to reconstruct both the local networks of VERONA and its connection to TCN. A significant change in TCN is the introduction of data diode, which will allow only one-way direction between TCN and the informatics network (IN) in the future. That is, users in the IN cannot influence anything in TCN. From the point of view of VERONA, it means that so-called mirror servers have to be located in the outer side of the data diode to provide data for non-operative users (outer users).
6. Network attached storage (NAS) should be introduced to modernize and standardize the archive system in the plant as a whole.

Related publications

- [1] T. Czibók, Cs. Horváth, J. Páles, J. Végh, P. Nagy, G. Fazekas, Cs. Korponai, L. Varga, V. Vörös, Modernization of VERONA core monitoring system for 15 months fuel cycles, Concept study, Version 2.0, EK-RMSzL-2013-744-00/01, 000000I01563KFA, (2013)

A COMPREHENSIVE DOSE ASSESSMENT FOR NORMAL OPERATION AND ACCIDENTAL SITUATIONS

Antal Fischer, Emese Homolya, Tamás Pázmándi, Péter Szántó, Péter Zagyvai

Objective

The European Committee revised its former recommendation on the use of Article 37 of the EURATOM Treaty and published a new recommendation (2010/635/Euratom C (2010) 6858) in 2010. The more detailed recommendation gave Hungary an opportunity to review the fulfilment of its obligation on data supply according to Article 37.

Methods

The Hungarian regulation has been reviewed and it has been shown that the system based on dose constraints and emission limit criteria can be fitted to the international practice. The dose burden of atmospheric and liquid releases for the population of the most affected EU country was calculated for normal operation and accidental scenarios as well.

The dose burden during normal operation was estimated by PC-CREAM 08 also for releases, into atmospheric and aquatic environment. With the lack of an accepted model for short term aquatic releases the PC-CREAM 08 program was used, which is basically suitable for estimating consequences of long term continuous emissions.

In case of short term releases to the atmosphere there is no accepted, validated programme that is able to make reliable calculations for larger distances in use in the Hungarian national practice, therefore, when analysing atmospheric emissions, a combined application of two different programmes was used. Dilution between the source point and the receptor point was calculated with HYSPLIT, then, knowing the atmospheric activity concentrations the doses were calculated with SINAC. For verifying the results additional calculations were performed with SINAC and PC-COSYMA programmes.

Results

Based on the estimations dose burden during normal operation in the most affected EU member state in case of aquatic and atmospheric releases were 5 nSv/y and 3 nSv/y, respectively. These values are by six orders of magnitude lower than the natural background radiation level.

Calculations were made for LBLOCA (large break loss of coolant accident) and PRISE (primary to secondary leakage) design basis accidents (DBA). In case of atmospheric release the results show that the radiation level in the most affected EU member state due to these events is lower than the annual natural background by one order of magnitude. According to the Final Safety Analysis Report of Paks NPP no aquatic release should be assumed for DBAs. However, test calculations were made assuming that a portion of the atmospheric emission is washed out to the Danube. The results of these calculations show that for LOCA and PRISE events the radiation burden is 3.2 μ Sv and 0.1 μ Sv, respectively.

The main pathway regarding accidental releases was found to be the food chain. Doses caused by these events can be significantly and effectively decreased by countermeasures.

Remaining work

The project is finished. The models for the atmospheric transport of radioactive pollutants in present use in the Hungarian practice are only reliable for short distances; therefore, accuracy of the calculations would be improved with the integration of more suitable methods and models.

Related publication

A. Fischer, E. Homolya, T. Pázmándi, P. Szántó, P. Zagyvai: *A comprehensive dose burden analysis for releases due to normal operation and accidental situations*, EK-SVL-2013-704-01-01-02 (2013) (in Hungarian)

RENEWAL OF THE FULL-SCOPE TRAINING SIMULATOR OF PAKS NUCLEAR POWER PLANT – PREPARATORY PHASE

Gábor Házi, József Páles, Csaba Páles

Objective

Paks NPP – in connection with the on-going service time extension of its VVER-440/V213 type power production units – has started the preparations to perform a full-scale renewal of its existing full-scope training simulator. As part of this preparatory phase, CER has been asked to gather information from experienced and internationally renowned *foreign* simulator suppliers on their capabilities and technical solutions offered for the complete renewal of the simulator.

Parallel with this activity, we have also started the implementation of some own, new graphics simulator development tools, which could be used during the renewal project by CER, as far as the project needs Hungarian contribution.

Methods

In order to obtain information from the foreign companies in structured and targeted manner, we had prepared a document with some guidelines. This document, called Request for Information (RFI), was sent to four potential foreign candidates: CORYS (France), L3 (Canada), WSC (USA), GSE (Sweden) [1]. The candidates were asked to provide information in the form of Supplier's Information Package (SIP). The form of this package (skeleton of SIP, issues to be addressed etc.) was specified by us in details. Due to the prescribed form of SIP, the evaluation of the collected information could be done easily on the same ground, in the form of Evaluation of the Requested Information [2].

Results

By evaluating and assessing replies received for the RFI, the staff of the training simulator could obtain a more or less clear picture on the technical characteristics of the proposed solutions.

Using this information they can also carry out preliminary studies to check the technical feasibility of the various proposals with respect to conditions existing in Paks and they can establish a preliminary project schedule, project implementation plan and simulator development resource estimate.

Parallel with the evaluation process and based on the information provided, the staff of the training simulator were able to get acquainted with the state of the art nuclear simulation technologies. Accordingly, a list of *general* requirements could be prepared enumerating all needs to be satisfied by the renewed simulator and its supplier [3].

The results of our own developments, a simulation system called SIMTONIA (SIMulation TOols for Nuclear Industrial Applications) were introduced in the 12th Nuclear Technique Symposium in Budapest. SIMTONIA provides a general graphics framework for the modeling of I&C (instrumentation and control) single and two-phase flow and electrical networks (see Fig. 1).

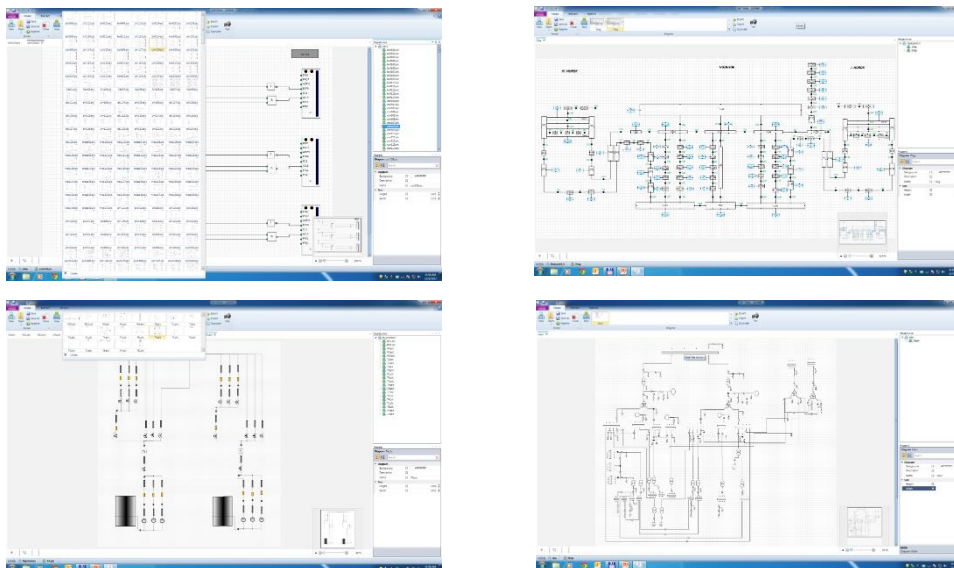


Fig. 1 SIMTONIA schemes for I&C (left-top), two-phase flow (right-top), single phase flow (left-bottom) and electrical networks (right-bottom).

Related publications

- [1] Renewal of full-scope simulator in Paks NPP, Request for Information, Doc. ID:000099A00030-KFA, MVM Paks Nuclear Power Plant Comp. Ltd., September, 2013
- [2] G. Házi, J. Páles, Renewal of full-scope simulator in Paks NPP, Evaluation of the requested information provided by foreign suppliers, EK-RMSZL-2013-708-00/03, December, 2013
- [3] Renewal of full-scope simulator in Paks NPP, Technical Specifications, MVM Paks Nuclear Power Plant Comp. Ltd., September, 2013

EXPERIMENTAL INVESTIGATION OF THE EFFICIENCY OF EXTERNAL COOLING IN THE CERES FACILITY

György Ézsöl, Gábor Baranyai, Valér Gottlasz, László Szabados

Objective

A research program has been going on at MTA EK to give scientific support to the in-vessel corium retention in the Paks NPP. Seven series of experiments had been performed for different critical gap sizes between vessel and cavity wall, without and with boron acid in the coolant. This report, however, focuses on the effectiveness of cooling by significantly increasing the axial heat flux distribution obtained from ASTEC code calculations. It was experienced in the former experiments that effectiveness is decreasing by increasing the coolant temperature up to saturation, changing the flow pattern in the critical gap region.

Methods

The measurements have been performed in the CERES facility, which is a scaled-down model of the external reactor vessel cooling, intended to apply in the Paks NPP, with 1:40 scaling ratio for the vessel external surface and 1:1 for the elevations, giving the driving force for natural circulation. To obtain coolant conditions relevant to the objective, the power to the elliptic bottom part of the vessel was increased from 48 kW obtained from ASTEC to 78 kW, with hot critical gap size of 9,7 mm.

Results

As a result of these measurement conditions, the coolant enters the critical gap region of cooling channel at saturated conditions.

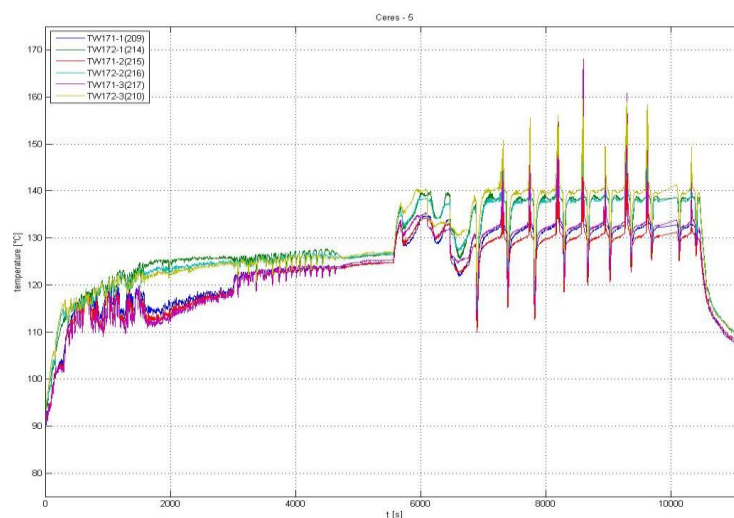


Figure 1: External surface temperatures

Figure 1 shows wall temperatures at the elevation of lower part of critical gap. Elevation of wall temperatures TW 171 and TW 172 is at the level of 1500 mm from the bottom. As shown, there is a stable cooling of vessel wall with a value of 410 K. Consequently, in spite of the much higher heat flux, the wall cooling is effective and it is not limited by the heat flux in the bottom part of the vessel in real heat flux ranges, however, the effectiveness is influenced by the flooding rate.

Remaining work

As experienced, the cooling effectiveness is highly influenced by the flooding rate, therefore, the continuation of the project is justified by this important research finding.

Related publications

- [1] Gy. Ézsöl, G. Baranyai, L. Perneczky, L. Szabados: *Research Results in Support of In-Vessel Corium Retention Program in the Paks Nuclear Power Plant*, ERMSAR-2012. Cologne (Germany), March 21-23, 2012. Paper No.15.
- [2] Gy. Ézsöl, G. Baranyai, V. Gottlasz: *Limits of Cooling Effectiveness by Different Axial Heat Flux Distributions in the CERES Facility*, Research Report: EK-THL-2013-717/02/M0

A NEW NUCLEAR REACTOR ANALYZER SYSTEM FOR VVER-440 REACTORS - VERETINA

J. Páles, G. Házi, Cs. Horváth, I. Pós, Z. Kálya

Objective

In order to have an interactive, fast and accurate time dependent reactor physics code for the analysis of operational transients of VVER-440 reactor units, a new coupled code systems has been developed, which is called VERETINA.

Methods

The two pillars of the system are the kinetics option of C-PORCA, a nodal neutron physics code developed in Paks NPP, and the RETINA two-phase thermohydraulic model system developed in CER. These two codes were integrated under a new platform called PCA (Plant and Core Analyzer), coupled with the VERONA core surveillance system of Paks NPP. The results of the system can be visualized by a new 3D core visualization system called CORE3DVIEW.

Results

To test the accuracy of the new coupled system, several calculations have been done, comparing the simulation results of VERETINA with measurements or other benchmark calculations.

As an example, here we recall the results of a control rod drop operational transient. The measured and calculated ex-core neutron fluxes were compared to each other, simulating control rod drop transients and taking the starting measurements in 24th fuel cycle of the 4th unit in Paks NPP as a reference. During the measurements the control rod in the position of 12-46 remained in its upper position and all other rods were dropped. One detector was near to the inserted control rod and two others were in far positions.

In Fig. 1 the linear power distribution in the core is shown by CORE3DVIEW. Here one can easily recognize the position of the stuck control rod, because the power near to this position is much higher than elsewhere.

Due to the symmetry of the problem, there was no difference between the measurements of the two detectors in far position, but the detector near to the stuck control rod experienced less significant changes than the others. Comparing the simulation results with measurement data we obtained very good agreement, the curves basically covered each other, proving the applicability of the neutron physic calculations in hot zero power. More details about benchmarking can be found in [1].

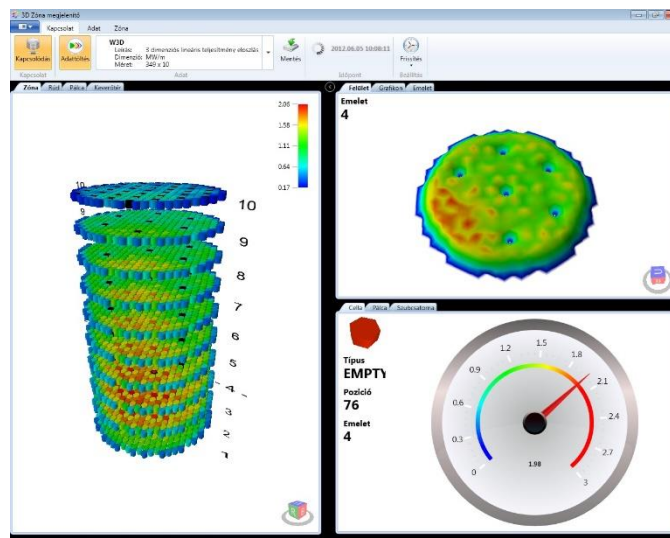


Figure 1. Linear power distribution in the core

Related publication

- [1] J. Páles, G. Házi, Cs. Horváth, J. Végh, I. Pós, Z. Kálya, Validation of VERETINA, a new nuclear reactor analyzer system for VVER-440, Proc. of 22th Symposium of AER, Pruhonice, Czech Rep., 1-5 Oct. , 2012

ENVIRONMENTAL DOSE ESTIMATION FOR 15-MONTH-LONG FUEL CYCLE WITH GADOLINIUM DOPED FUEL ASSEMBLIES IN PAKS NPP

Tamás Pázmándi, András Keresztúri, Péter Szántó, Péter Vértes

Objective

The Paks Nuclear Power Plant is planning to change to a new type of fuel assemblies with higher enrichment (4.7% in average), that makes the reactors capable of longer, 15-months-long fuel cycles. According to the plans, the number and the position of the fuel rods containing gadolinium burnable poison will also change. The excess reactivity caused by the higher enrichment of the fuel will be covered by six fuel rods containing gadolinium (instead of three). The geometrical parameters of the fuel rods and assemblies remain identical. The higher enrichment and the longer fuel cycle lead to higher burn-up, therefore environmental releases can also change.

Due to the differing potential releases, the revision of the Environmental Impact Assessment (EIA) was necessary. The conclusion of this revision was that the environmental parameters will not vary significantly, however recalculation of the dose estimations for accidental releases was necessary.

Methods

The public dose burden appearing in the EIA was recalculated considering the new fuel type. The calculations were also performed for releases caused by loss of coolant accident (LOCA) and primary to secondary leakage (PRISE) initial events. In order to compare the results of the current and the former calculations, the same methodology, software and parameters were used. For the same reason, the new dose estimations were performed considering also the best estimate nuclide inventory - calculated especially for this work - as it was done in case of the former analysis.

Two sets of weather conditions were considered during the estimations, one for dry and one for rainy weather. Besides the distances considered in the EIA, the calculations were performed also for 500 m. Short-term (7 days) and long-term (50 years) doses were also calculated.

Results

The long-term doses calculated for the new fuel type were less than 20% higher than the results of the former calculation. This might be caused by the increased activity of the long half-life isotopes (e.g. ^{134}Cs and ^{137}Cs) due to the higher burn-up levels at the end of the fuel cycle. The activity of these isotopes increased by up to 30% compared to the former inventory.

The new short-term doses were approximately 2% lower than the short-term doses calculated earlier.

Remaining work

The aims of the project are fulfilled, there is no remaining work.

Related publication

A. Keresztúri, T. Pázmándi, P. Szántó, P. Vértes: *Environmental dose estimation for 15-months-long fuel cycle with gadolinium doped fuel assemblies in Paks NPP*, Report, EK-SVL-2013-745/01-01-00 (2013)

REVISION OF RADIATION CRITERIA USED IN THE GENERAL EMERGENCY RESPONSE PLAN AT THE PAKS NUCLEAR POWER PLANT

Sándor Deme, Tamás Pázmándi, Péter Szántó, Péter Zagyoai

Objective

Revision of the general emergency response plan at the Paks Nuclear Power Plant became necessary in order to harmonize it with new recommendations of the International Atomic Energy Agency (IAEA) issued in 2011. This revision requested detailed calculation of the values of the criteria. Classification system and response actions recommended by IAEA are given in Table 1.

Table 1: Relationship of response actions under the classification system

Alert	Facility emergency	Site area emergency	General emergency
Immediate actions to analyse the situation and mitigate the consequences			
Immediate actions to protect those on the site			
Preparations to take protective actions off the site			
Immediate actions to protect the public off the site			

Criteria for alert, site emergency and general emergency are defined numerically by the IAEA. In most cases the ratio of radiation level is 1:10:100 for alert, site area emergency and general emergency. For example, the numerical values of the environmental gamma dose rate due to surface contamination for alert, site area emergency and general emergency are 0.01, 0.1 and 1 mSv/h consequently. IAEA has also recommended the numerical values of dose rate in the containment, in the rooms of the nuclear power plant and the effluent release rate.

Methods

Calculations of the dose rate in the containment, in the rooms of the nuclear power plant, the effluent release rate and the environmental dose rate were based on radionuclide ratio defined for the design basis accident. Other parameters of the calculation were the normal state of the ventilation system, 120 m effective height of the release, 5 m/s wind speed at 10 meters above the ground and dry weather conditions.

LOCAREL computer program developed in our Institute was used for calculation of radiation parameters inside the plant. Environmental calculations were based on PC COSYMA program.

Results

Environmental gamma dose rates due to dry deposition at a distance of 1.5 km from the stack in case of design basis accident are given in Table 2. These numbers show that in case of design basis accident environmental dose rate is in the range of natural background. Another conclusion is that the dose rate decreases about five times in one day and twelve times in one week.

Table 2: Environmental gamma dose rates due to dry deposition of gaseous halogens and aerosols at a distance of 1.5 km from the release point. Time periods are 1, 24 and 168 hours from the start of the radioactivity release.

Group	Dose rate (nGy/h)			Relative to 1 h value	
	1 h	24 h	168 h	24 h	168 h
halogens	38	7.0	2.2	0.18	0.06
aerosols	2.2	1.6	1.2	0.74	0.53
total	41	8.6	3.4	0.21	0.08

Based on these calculations the following 10-minute stack release limits were received:

- Alert: gaseous iodine or aerosols – $8 \cdot 10^8$ Bq, noble gases – $2.5 \cdot 10^{13}$ Bq.
(These data were calculated as 100 times the release limit.)
- Site area emergency: gaseous iodine – $3.6 \cdot 10^{14}$ Bq, aerosols – $1 \cdot 10^{15}$ Bq, noble gases – $6 \cdot 10^{15}$ Bq.
- General emergency: gaseous iodine – $1.5 \cdot 10^{16}$ Bq, aerosols – $6 \cdot 10^{16}$ Bq, noble gases – $2.4 \cdot 10^{17}$ Bq.

Remark: the facility emergency situation is not connected with the stack release rate, only with the dose rates in the rooms of the plant.

Remaining work

This work was finished during the period of the Progress Report.

Related publication

S. Deme, T. Pázmándi, P. Szántó: *Revision of radiation criteria used in the general plan for handling of the hazardous situations at the Paks Nuclear Power Plant*, Report, EK-TFO-2013-751-05/M1 (2013) (in Hungarian)

EXPERIMENTAL INVESTIGATION OF BEYOND DESIGN BASIS ACCIDENT TRANSIENTS

MTA EK PARTICIPATION IN THE OECD PKL3 PROJECT

Gábor Baranyai, György Ézsöl, Valér Gottlasz, Attila Guba, Iván Tóth, István Trosztel

Objective

The OECD PKL3 project will investigate safety issues relevant for current PWR (Pressurized water reactor) plants as well as for new PWR design concepts by means of transient tests under postulated accident scenarios and systematic parameter studies on thermal - hydraulic phenomena. The tests address current safety issues related to beyond design basis accident transients with significant core heat-up, e.g. station blackout scenarios or loss of coolant accidents in connection with failure of safety systems. The tests performed in the PKL facility will be complemented by tests in ROCOM, PMK and PWR PACTEL.

Methods

Tests are performed in the facilities listed above with the aim to create a data base covering current safety-related phenomena. The data base will be used both within and outside the project to validate computer codes for the thermal-hydraulic phenomena addressed.

Results

The scope of the 2013 activity included performance of two tests in the PKL test facility:

- Failure of the residual heat removal system during shut-down with open primary circuit
- Cool down under asymmetric natural circulation conditions with one or two steam generators isolated.

MTA EK was planning to perform the first test on the PMK facility, addressing pressure wave propagation following a larger loss of coolant from the primary system. In order to prepare the tests, pre-test analyses were carried out and - based on the results - a test matrix was proposed. The analysis was performed by the ATHLET code and the effect of break size, break opening time, sub-cooling in the cold leg and system pressure on the wave propagation was investigated. The results indicated that the amplitude of the pressure difference across primary components (e.g. between lower plenum and downcomer) strongly decreases as the break size decreases (Fig. 1) or opening time increases, but it is much less affected by the system pressure and temperature.

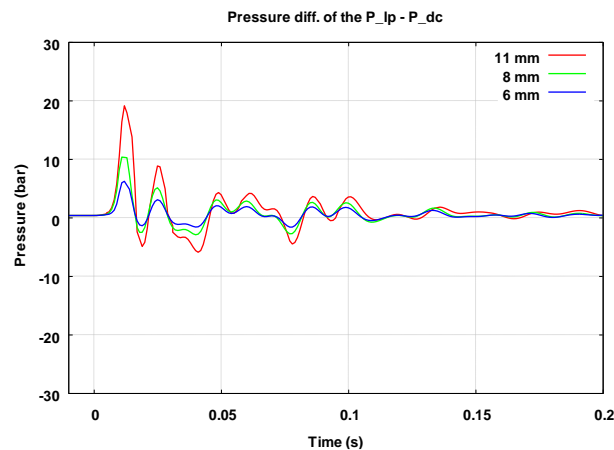


Figure 1: Calculated pressure difference between lower plenum and downcomer for different break diameters

The required modifications of the PMK facility were performed and besides the traditional instrumentation special pressure transducers, capable to resolve the pressure variation with a frequency of 4 kHz have been installed. Due to late arrival of the special quick opening valve (which allows adjustment of the break opening time between 10 and 100 ms), only scoping tests with rupture disks as break simulator could be performed.

Remaining work

Further tests will be carried out as defined by the common test matrix of the OECD PKL3 project and the Joint Hungarian-Korean Laboratory. The matrix contains tests at high pressure and temperature and they address the effect of the break opening time. At the same time preparation of the second PMK test for the project (simulating a station blackout transient) is underway.

NUMERICAL SIMULATION OF METHODS APPLIED FOR THE IDENTIFICATION OF LEAKING FUEL ASSEMBLIES

Zoltán Hózer, Barbara Somfai, Richárd Nagy, Péter Szabó

Objective

The main objective of the present work was the validation of the TSKGO code against measurements at Paks NPP and execution of a large series of calculations in order to analyze the relationship between TS (Telescope Sipping) and KGO (Russian abbreviation for the hermetic control of fuel assemblies) methods.

Methods

The improvement and validation of numerical models of TSKGO code was supported by special measurements. The MTA ATOMKI institute and the Isotoptech Co. Ltd. carried out calibration measurements with the TS facility using different mixtures of radioactive gases. The MTA EK performed experimental simulation of leaking fuel rods in the LEAFE facility. The new numerical models are based on the measured data from these experiments.

Results

The main new elements of the TSKGO models are as follows:

- Isotope specific correlations were developed to calculate the detector signal from gas activity data.
- Special transport model has been introduced to describe the time dependent detector signal. The model calculates the maximum signal and the integrated detector signal. The model is based on sipping measurements carried out in 2012 at Paks NPP.
- New model is used to simulate complex situations, when both water and gas can be released from the failed fuel into the coolant.
- The leakage rate during storage in the spent fuel pool is simulated using new correlation. The actual leakage rate depends on the linear heat rate and the size of the defect.
- Special nodalization has been applied to describe the axial variation of fission products inside the fuel rod during storage conditions.

The new version of TSKGO code was successfully applied to the simulation of TS and KGO examination of VVER-440 fuel. The comparison of calculated results indicated that more activity release takes place during KGO examination than that of TS examination. Due to the correction applied in the evaluation of ^{131}I activity measurements, the TS results do not depend on the time between shutdown and TS examination. The TS signal in case of upper hole position is significantly lower compared to positions in the middle or at the bottom of the leaking rod. The typical TS signal was identified for the leaking assemblies.

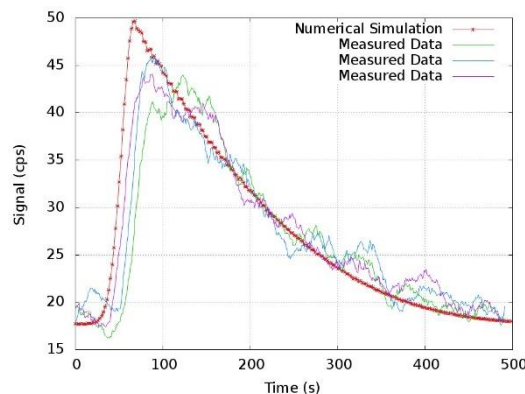


Figure 1: Measured data and numerical simulation of the signal of TS facility

Remaining work

The further development of TSKGO models will include a detailed description of fuel behavior in the reactor during normal operation. The Paks NPP will carry out TS examination of the leaking assembly, the code will be applied to predict the TS signal.

Related publications

- [1] Z. Hózer, B. Somfai: *Development of numerical models for the simulation of TS and KGO examinations*, EK-FRL-2013-738-01/01 (in Hungarian)
- [2] Z. Hózer, R. Nagy, P. Szabó: *Numerical simulation of TS and KGO examination*, EK-FRL-2013-738-01/02 (in Hungarian)

REACTOR VESSEL UPPER HEAD BUBBLE FORMATION

Attila Guba, Gábor Orbán

Objective

Previous studies examined the upper head coolability during natural circulation conditions in the Paks NPP. After plant shutdown if for any reasons the main circulation pumps are not operating the cooldown of the plant should proceed by natural circulation in the primary circuit. The operator initiates cooling by releasing steam from the secondary side. The primary pressure is reduced by pressurizer spray keeping the saturation margin in the hot leg between 45 and 55 °C. In the reactor vessel there is no flow above the hot leg elevation, the water in the stagnating parts remains hot. There is a possibility to remove heat by the CAGT cooling system and cold water injection of 5 t/h to the top of the reactor vessel head. If the pressure reduction in the primary circuit is too fast the cooling may be insufficient to keep the saturated conditions in the hottest parts of the upper head. In this case, steam bubble forms in the top of the vessel head pushing the water from the head to the circulation. The circulating primary water is much colder than the hot steam in the bubble, the considerable temperature difference in the boundary layer may result in sudden condensation and the bubble collapse. The resulting pressure wave may challenge the reactor internals. Therefore the bubble formation in upper head must be avoided.

In the previous studies the calculations used very coarse nodalization of the upper head. The resulting complete mixing did not let formation of hotter water packs which makes the calculation less conservative. The main objective of this project was to examine the effectiveness and the proper modeling of the heat removal by the CAGT cooling and the cold water injection to the reactor vessel head.

Methods

G6.1 experiment of the PKL2 aimed at examining the effect of aggressive cooling in the primary side with pressure reduction, which led to bubble appearance in the vessel head. Special measurements have been introduced to get detailed experimental evidence of the temperature distribution in the stagnating parts. In order to obtain the proper nodalization test, calculations have been performed to simulate the experiment. The conclusions of the modeling the PKL2 experiment have been introduced into the plant nodalization, with the validated model the plant behavior was examined.

Results

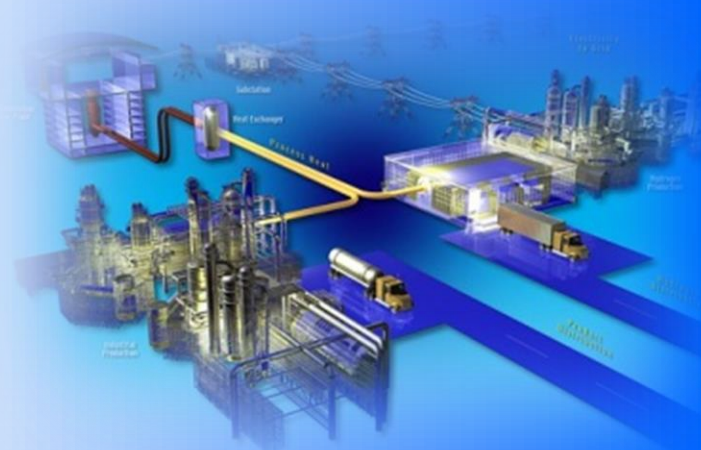
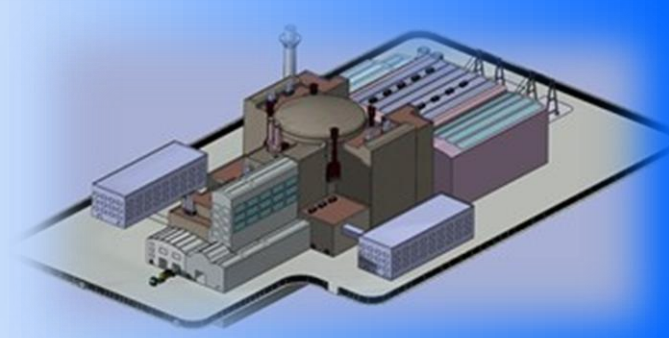
Four different upper head nodalizations were applied to the PKL2 G6.1 experiment. The original model of the facility was used in the first calculation. This coarse model was not able to predict the correct behavior of the experiment, it was used to set the proper operator actions sequence. The nine-node finer nodalization showed better agreement, but could not reproduce the inner circulations in the upper head, which could be seen in the experiment. A new nodalization with two parallel channels in the upper head was investigated to ensure mixing. The results showed good agreement with the experimental data up to the bubble formation. When bubble appeared in the upper head some discrepancies were found in the results. Mixing was somewhat less effective in the calculation, therefore this nodalization is conservative with regard to the effect of bubble formation. To overcome the previous shortages an even finer nodalization was tested with doubling the number of the nodes. The 20 part parallel channel nodalization gave excellent results for the measurements even with the steam bubble in the upper head.

The work done for the validation of the nodalization was applicable to the power plant calculations. In the power plant case the bubble appearance must be avoided, therefore the nine nodes parallel channel nodalization was the basis for the detailed modeling of the power plant vessel upper head.

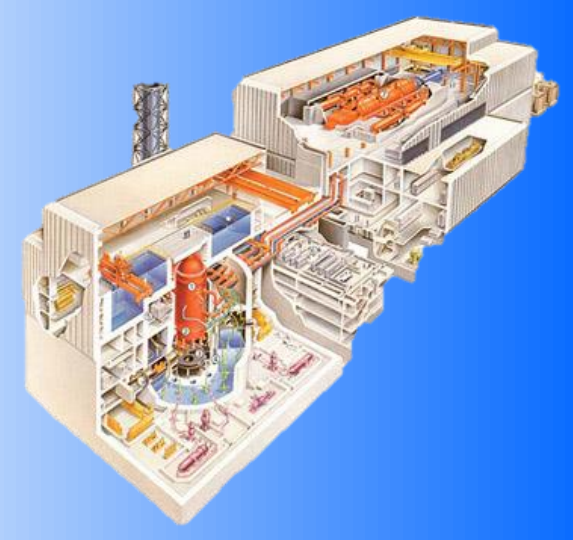
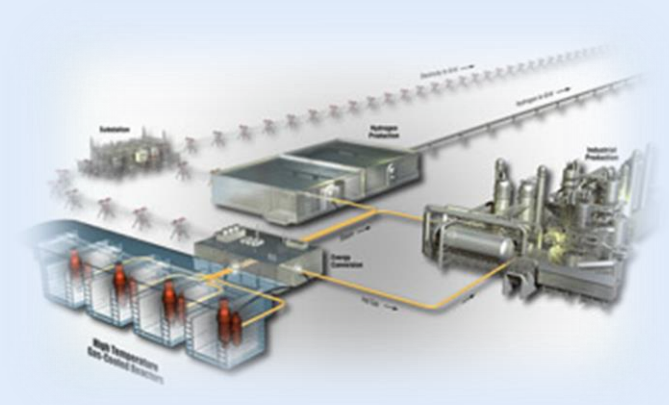
The power plant calculation was initiated by shutdown with all the main circulation pumps stop. The cooling and primary pressure reduction begins 1200 s after shutdown. Four calculations have been performed with different nodalization and cooldown rate. The results gave very good mixing with uniform temperature distribution in the upper head.

Remaining work

The project was finished.



II. Generation IV reactor system



APPLICATION OF EUROPEAN SAFETY METHODOLOGIES TO GENERATION IV REACTOR DESIGNS MTA EK CONTRIBUTION TO FP7 PROJECT SARGEN_IV.

Ákos Horváth, Iván Tóth

Objective

The EU project SARGEN_IV focuses on three types of fast neutron technologies, the sodium, lead and gas cooled fast reactors with the objective of future assessment of these advanced reactor concepts. The project gathers safety experts from European Technical Safety Organizations, designers and vendors as well as from Research Institutes and Universities to:

- develop and provide a tentative commonly agreed methodology for the safety assessment,
- identify open issues in the safety area,
- detect and underline new fields for R&D in the safety area and
- provide a roadmap and preliminary deployment plan for safety-related R&D, including cost estimation.

Methods

MTA EK was participating in Work Package 4, the test application of European safety assessment methodologies to the demonstrators of the fast reactor concepts listed above. It was decided that the work should focus on sample application of one of the tools of the Integrated Safety Assessment Methodology, the Objective Provision Tree (OPT). The purpose of the OPT is to document the provision of essential lines of protection ensuring successful prevention, control or mitigation of phenomena that could potentially damage the nuclear system. The levels of OPT are directly related to Defence in Depth (DiD) levels and at the same time related to the respective safety functions: control of reactivity, core heat removal and confinement of radioactivity, but the test application was only addressing the "core heat removal" safety function. MTA EK – based on its experience with the gas cooled ALLEGRO demonstrator – was responsible for the OPT development for ALLEGRO.

Results

An OPT had been developed for the ETDR (the predecessor of ALLEGRO) within the FP6 GCFR STREP project. When constructing the OPT for ALLEGRO, the main elements of this earlier work were retained, but the design changes made to ETDR to arrive at ALLEGRO were considered. The most important design changes are: a two-loop primary (and secondary) system instead of a single loop, a change in the safety approach, now relying partly on the main primary blowers in accidental conditions and – as a consequence – the review of the decay heat removal philosophy. When considering these changes in the OPT development, the status reflected by the most recent reports produced in the FP7 GoFastR project was taken into account.

The test application of the OPT addressing the Core Heat Removal safety function allowed a structured assessment of ALLEGRO safety. The results of the exercise are very different, depending on which level of defence was addressed. This can be explained by the present stage of the ALLEGRO design, which roughly corresponds to a pre-conceptual design. At this stage preliminary ideas exist about the requirements for the main systems and components, which might not be sufficient to judge the adequacy of the provisions at Level 1 of DiD. This is also true for the provisions to be deployed at Level 2, since the control system design is practically non-existing. At the present stage of design the most comprehensive insight could be gained at Level 3 of DiD, due to the fact that recent safety system developments and corresponding safety analysis results could be reviewed. When addressing the different mechanisms challenging the safety function investigated, the effectiveness of the provisions foreseen in the latest design was judged by the results of the safety analysis of the corresponding transients.

Remaining work

Within the next task of the SARGEN_IV project the open issues and areas relevant for safety research will be identified and the R&D resources needed to resolve these issues quantified. This review will also be used as a reference to provide guidelines on the structure and content of the Safety Analysis Report for innovative reactors.

Related publication

F. Puente Espel, J. Oldenburg, D. Beraha, L. Ammirabile, J. Holy, P. Bizek, K. Mikityuk, I. Tóth, A. Kaliatka, R. Alzbutas, D. Naidoo, C. Qeral, J. Gonzalez-Cadelo, J. Montero-Mayorga, G. Jimenez, E. Gallego: *Application of the harmonized safety assessment methodologies to the representative set of initiating events*, SARGEN_IV Deliverable D4.2, 2013

SCENARIOS FOR INTRODUCTION A GFR INTO THE HUNGARIAN REACTOR PARK

Áron Brolly

Objective

All four VVER-440 units of the first Hungarian nuclear power plant will be shut down by the end of the thirties. One option for managing the spent nuclear fuel of these units – beside placing it into a deep geological repository – is extracting the fissile material present in it and recycling into the nuclear fuel cycle. Our objective was to investigate the possibilities of the introduction of a GFR (gas-cooled fast reactor) into the Hungarian reactor park fuelled with reprocessed plutonium originating from the legacy spent fuel of the country's first nuclear power plant.

Methods

For the investigations the SITONG4 nuclear fuel cycle simulation code was used whose physical model was enhanced in 2012. Implementation of the new physical model was started in 2012 and was finished this year. SITONG4 takes into account all important facilities of the fuel cycle like material stocks, spent fuel interim storages, plants for uranium enrichment, fuel fabrication and spent fuel reprocessing and last but not least reactors. Facilities can be linked in a flexible manner, their number is not limited. Parameters which introduce lag time into the fuel cycle are taken into account (facility operation time, spent fuel cooling time).

Three scenarios were investigated: a „GFR only” scenario, where the new reactor park contains only GFRs; an „EPR only” (European pressurized water reactor) scenario as a reference one and a mixed scenario where GFRs and EPRs are present. It was assumed that the GFR is not commissioned before 2040 and its spent fuel is recycled as soon as possible. The GFR's electrical power is 1080 MW, its discharged fuel's composition was determined by a burn-up module developed by the Institute of Nuclear Techniques of the Budapest University of Technology and Economics. EPR's electrical power is 1550 MW, its discharged fuel's composition was determined from tabulated data based on the literature. Spent fuel's cooling time for all types of fuels ($T_{cool, GFR}$ and $T_{cool, EPR}$) was taken to be 2 or 5 years. Advanced reprocessing was assumed for all types of spent fuel with 0.1% loss for all actinides. For the GFR, fuel reprocessing and fabrication time was included into the spent fuel's cooling time. For both types of reactors 60 years lifetime was taken.

Results

Analysis of the „GFR only” scenario showed that the legacy spent fuel of the VVER-400 units contains enough plutonium to start one GFR in 2040. There is an intermediate period between the commissioning of the GFR and the recycle of its firstly discharged fuel. Plutonium need of the GFR in this period can be covered by the legacy plutonium only if $T_{cool, GFR} = 2$ years. To obtain the plutonium, reprocessing of the legacy spent fuel has to be started in 2035 with 236 t/year capacity. Reprocessing of GFR's spent fuel requires 17 t average annual capacity.

Mixed scenario showed that lack of plutonium found in the previous scenario when $T_{cool, GFR} = 5$ years, can be counterbalanced with reprocessed plutonium originating from the spent fuel of one EPR. The EPR must be started well before the GFR: in 2029.5 or 2032.5, depending on $T_{cool, EPR}$: 5 or 2 years, respectively. The supplementary plutonium for the intermediate period has to be accumulated during almost 10 years operation of the EPR. Beside this, almost the same amount of plutonium is needed until the operation of the GFR with its recycled fuel becomes self-supporting. If $T_{cool, GFR} = 2$ years then GFR's operation is independent from the operation of the EPR which decouples the commissioning date of the EPR from the GFR's one.

The „EPR only” scenario is simulated as a reference one. In this case two EPRs are assumed to be commissioned in 2035 and 2040. Operation of the EPRs is independent from each other and from the presence of the legacy spent fuel of the VVERs. The commissioning of the EPRs was chosen to fit to the shut down of the VVERs to keep the continuity of the energy production. Table 1 shows produced electrical energy (Erg.); consumed natural uranium (Nat. U); required average fuel fabrication (Fabr.) and reprocessing (Repr.) capacity; remained spent fuel (S. F.), irradiated uranium (Irrad. U) and plutonium (Pu); and accumulated waste (Waste) for the investigated scenarios.

Table 1: Important results of the investigated scenarios (abbreviations are given in the text)

Scenario	Erg. [TWh]	Nat. U [t]	Fabr. [t/y]	Repr. [t/y]	S. F. [t]	Irrad. U [t]	Pu [t]	Waste [t]
EPR only	1338	29378	50.0	0	5251.5	0	0	325.3
Mixed	1205	14689	44.3	298.0	1272.7	2518.2	0.3	242.7
GFR only	536	0	17.6	253.0	115.4	2095.6	3.4	59.2

Remaining work

Publication of the results.

Related publication

Á. Brolly: Closing the fuel cycle in Hungary using a GFR, EK-RAL-2013-122-01/01, 2014 (in Hungarian)

SUPERCRITICAL WATER REACTOR – FUEL QUALIFICATION TEST

Csaba Maráczy, György Hegyi, István Trosztel

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 pressure 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 for licensing of the FQT facility by the Czech regulator shall be the outcome of this project. MTA EK is participating in the 3D steady state and transient analysis of LVR-15 with the fuelled loop. The Reactivity Initiated Accident (RIA) analysis will be carried out with the KIKO3D-ATHLET coupled neutronic-thermohydraulic dynamic code.

Methods

- 3-D steady state coupled neutronic-thermohydraulic calculations of LVR-15 with the FQT facility.

Results

With KIKO3D-ATHLET the conservative analysis of the RIA events of the LVR-15 affecting the test section fuel bundle will be carried out. The conservative approach for the dynamic calculations means the use of worst case bounding parameters e.g. reactivity coefficients, control rod worth etc. The calculated bounding parameters cover the core loadings, technological and calculational uncertainties. Using the special tuning possibilities in the coupled KIKO3D-ATHLET code, the reactivity coefficients, rod worths etc. can be tuned to the bounding parameters allowing the conservative analysis. The tuning is based on the linear transformation of technological parameters affecting the few-group cross sections. The tuning factors affect both the cross sections of the IRT-4M fuel assemblies influencing the reactivity behaviour and the cross sections of the FQT. The calculations have shown that the FQT section parameters have low effect on the overall reactivity of LVR-15 with FQT, therefore the tuning here is focused on the conservatively high power in the fuel elements of the FQT section. The nodalization of both the LVR-15 pool and the FQT primary loop with the heat exchanger has been elaborated for the ATHLET code. Figure 1 shows the ATHLET model of the FQT assembly.

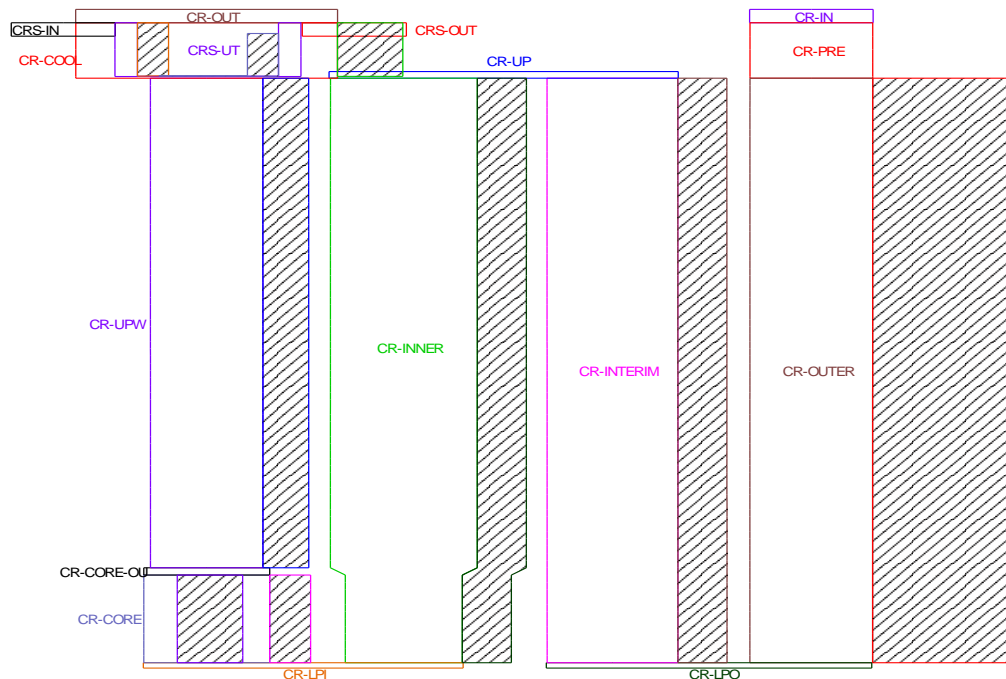


Figure 1: The ATHLET model of the FQT assembly in the LVR-15 research reactor. The zigzag path of the coolant of the primary loop inside the four meter long FQT section can be seen from the inlet (CR-IN) to the outlet (CR-OUT).

Remaining work

- RIA analysis with the KIKO3D-ATHLET coupled dynamic code.

Related publication

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 2, SCWR-FQT* (Contract Number: 269908) Deliverable E2.2

PREPARATION OF ALLEGRO - IMPLEMENTING ADVANCED NUCLEAR IN CENTRAL EUROPE (ALLIANCE PROJECT)

Ákos Horváth, János Gadó, András Keresztúri, Iván Tóth

Objective

Nuclear reactors with fast neutron spectrum (fast reactors) are to be developed and deployed in due time to make the use of nuclear energy sustainable by solving the closure of the fuel cycle. The Gas cooled Fast Reactor (GFR) is selected as an alternative reactor type for the Sodium Fast Reactor to be tested as a prototype in the 2020s.

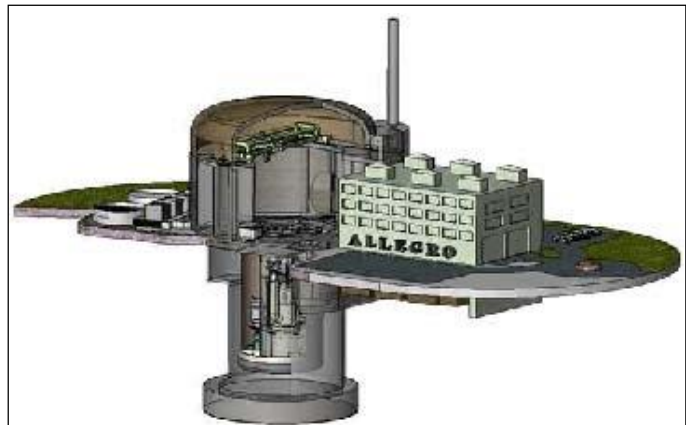
The ALLEGRO facility is designed as a demonstration reactor hosting GFR technological experiments, but also as a test pad of using the high temperature coolant of the reactor for generating process heat for industrial applications. MTA EK coordinates the EURATOM financed FP7 ALLIANCE project which was launched in 2012 with the aims

- to put together information on the feasibility of the construction, assessment of design needed following the GEN IV requirements and produce documents on the preliminary design, environmental impact, site identification, consortium and licencing issues,
- to serve not only as a technical guidance for future steps but as well as explanatory arguments for national and EU decisions makers, whose political and financial support will be needed for further development of the GFR demonstrator.

Methods

The main research and development areas for GFR technology were identified in the Strategic Research Agenda of the Sustainable Nuclear Energy Technology Platform (SNETP). For Gas Fast Reactor (GFR2400) to become an industrial reality, a pre-requisite step is the designing and construction of a demonstrator, named ALLEGRO.

The role of ALLEGRO reactor is to demonstrate the GFR concept, the GFR specific safety systems and to irradiate and qualify the innovative high-temperature fuel required for such reactors. ALLEGRO is a part of Strategic Energy Technology plan (SET plan) presented by European Sustainable Nuclear Industrial Initiative (ESNII). Safety methodology for innovative reactors issued from GIF (The Generation IV International Forum) Reactor Safety Working Group will be analyzed. Safety approaches adopted in European collaborative projects will also be used and disseminated within the Project.



Results

Preparation for constructing a reactor which can demonstrate the chosen fast reactor technology requires the solution of various technological and safety related questions on the basis of an extensive R&D program. Parallel to this, other types of difficulties (governance, financial, technical, etc.) should be also overcome to succeed in building ALLEGRO. In order to fulfil these tasks, four organizations of the *Visegrad* region (MTA EK (HU), ÚJV (CZ), VUJE (SK), NCBJ (PL)) created a legal entity in July 2013, the "V4G4 Centre of Excellence", which is in charge of the international representation of the project and of its technical coordination. The "V4G4 Centre of Excellence" is organized according to four areas, which are represented by four main pillars of the project. Each of these pillars is managed by one of the four organizations:

- Design & Safety Concept Research Laboratory – VUJE, a.s.
- GFR Technology Research Laboratory (Helium technology) – ÚJV Řež, a.s.
- GFR Fuel and Reprocessing Research Laboratory – MTA EK
- GFR Material Research Laboratory (except fuel) – NCBJ

Remaining work

The ALLIANCE project will end in 2015, however the preparatory phase of the construction of ALLEGRO will continue until the end of the decade. Strategic questions on the fuel supply and spent fuel management should be discussed in the short term, and the design work should follow accordingly. Besides the technical issues, legal and financial aspects of this regional project are still to be discussed with the respective authorities.

SAFETY ANALYSES FOR LICENSING OF A NEW FUEL TYPE AT NPP PAKS

András Keresztúri, György Hegyi, Gábor Hordósy, Csaba Maráczy, István Panka, Emese Temesvári, István Trosztel, László Perneczky, Tamás Pázmándi, Péter Szántó, Péter Vértes

Objective

In the near future, a new fuel assembly type enriched to 4.7 % is foreseen to be introduced at Paks NPP (Nuclear Power Plant) allowing more economic 15 month equilibrium fuel cycle length. The application of the new assembly modifies the power distributions essentially on all geometry scales; namely the distribution in the fuel pellet, the pin-wise and the assembly-wise distributions. The reloading schemes are modified to a great extent, too. The relevant parts of the Design Basis Analyses – where modified distributions are important – were repeated. Additionally, the subcriticality of the transport and storage devices of the NPP was investigated by using an advanced burnup credit methodology.

Methods

Safety analyses with coupled codes, subcriticality by using Monte Carlo Method.

Results

The following DBA (Design Basis Accident) initiating events were analyzed:

- Steam line break
- Inadvertent closure of 6 MSIV (Main Steam Isolation Valve)
- Seizure of one MCP (Main Coolant Pump)
- Inadvertent withdrawal of a control rod group
- Control rod ejection
- Stuck control rod in upper and lower position
- Inadvertent connection of one closed loop
- Large break LOCA (Loss of Coolant Accident)
- Erroneous loading of one fuel assembly
- Erroneous loading of one fuel pin
- Inadvertent withdrawal of a control rod group without scram

For checking the fulfillment of the PCI (Pellet Clad Interaction) requirement, the following analyses were performed

- Loading up to the nominal power after refueling
- Operation in the 100-0-100 % power range
- Operation in the 100-50-100 % power range
- Variation of the power in the 10 % range
- Inadvertent opening of one closed loop
- Control rod withdrawal
- Environment dose estimations for the large break LOCA using the conservative isotopic inventory
- Dose estimations of the transport and storage devices in case of abnormal events
- Thermal hydraulic analysis of the spent storage pool

Furthermore, the application of burnable poison makes it necessary to analyze the subcriticality of the storage and transport devices also for the burnt out fuel and as a consequence to apply burnup credit methodology. In case of all the above analyses, the acceptance criteria are fulfilled.

Remaining work

There is no remaining work.

Related Publication

40 MTA EK inner reports (in Hungarian).

BASIS FOR REGULATING NEW TYPES OF NUCLEAR INSTALLATIONS

János Gadó, Zoltán Hózer, Károly Késmárky,
András Kovács, Iván Tóth

Objective

The scope of regulating nuclear installations has to be extended because of the potential construction of both Generation 4 reactors and also fuel laboratories. At the request of the HAEA, the necessary changes in the regulation were studied without formulating the text of a new regulation. Construction of a Generation 4 gas cooled fast reactor demonstrator (ALLEGRO) is under discussion in the Visegrad 4 countries. In order to investigate the fresh and irradiated fuel of ALLEGRO and also the fuel of the potential new power reactor units in Hungary, the construction of a fuel laboratory is also under discussion. The aim of the work was to clarify the regulatory needs related to these new types of nuclear installations.

Results

Two separate reports were prepared on the above items. Both of them identify the basis for extension.

In case of the Generation 4 reactors the existing Hungarian regulation can be easily modified. The situation is rather simple since the existing regulation was prepared with careful attention on the construction of new power plant units. Henceforth only the items related especially to LWR reactors have to be modified. Another problem arises as a consequence of the purpose and future use of demonstrator reactors, namely the necessity of experimentation. Combining the existing regulations concerning power plant units and research reactors can solve this problem.

In case of fuel laboratory the situation is more complicated. A new separate volume of the regulation has to be developed. It can be partly based on the regulation of the spent fuel storage facilities but further very important items shall be taken into account, like proliferation problems, use of dangerous materials, treatment of highly radiating materials, special requirements on subcriticality etc. The appearance of plutonium and other transuranium elements has to be adequately addressed. The consequences of the probable siting of the fuel laboratory at the site of another nuclear installation were carefully studied. The starting point was that the operation of the fuel laboratory must not disturb the operation of the nuclear installations existing at the same site.

In both cases the international experience was widely used including the related IAEA documents and several national regulations. On the basis of the two reports prepared in the framework of this activity, the modification of the regulation can be developed.

Remaining work

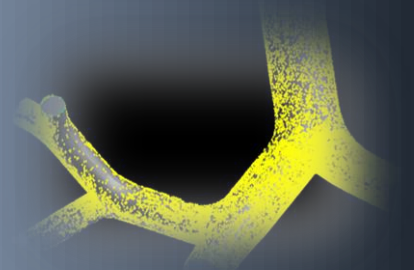
For the time being HAEA has not initiated the development of the corresponding modifications in the regulation.

Related Publications

- [1] J. Gadó, K. Késmárky, I. Tóth: *Preparing the extension of the existing nuclear regulation considering a Generation 4 gas cooled fast reactor*, EK-TSO-2013-276-01 report, September 2011
- [2] J. Gadó, Z. Hózer, A. Kovács: *Preparing the extension of the existing nuclear regulation considering a laboratory for the investigation of fresh and irradiated fuel*, EK-TSO-2013-275-01 report, September 2011



III. HEALTH PHYSICS , SPACE DOSIMETRY



REANALYSIS OF SPACE DOSIMETRY RESULTS

*Istoán Apáthy, Attila Hirn, József Pálfalvi, Tamás Pázmándi,
Péter Szántó, Márton Zagyvai*

Objective

The aim of this project was to reanalyse the results of the space dosimeter systems developed by our institute.

Methods

The Pille system was developed by the Hungarian Academy of Sciences Centre for Energy Research (MTA EK – former KFKI Atomic Energy Research Institute) as the first and to date the only thermoluminescent dosimeter (TLD) system containing an on board reader designed specifically for use by cosmonauts and astronauts while travelling in space. Since the first time it was launched in 1980, the Pille system has worked on board each space station. It has been continuously used on board the International Space Station (ISS) since October 2003 under the supervision of the Institute for Biomedical Problems, Moscow, as the service dosimeter system of the Russian Zvezda module. In the past six years the dosimeter system was utilized for routine dose measurements inside the ISS, and as personal dosimeter system during Extra-vehicular Activities (EVAs). With the system consisting of a lightweight reader device and a number of TL dosimeters, more than 35 000 read-outs were carried out until now. Solid state nuclear track detectors (SSNTDs) packed and evaluated in MTA EK were also launched in several spacecrafts including the ISS. The objective of SSNTD measurements is to obtain the dose map of the ISS and to measure the effect of the sun cycle on the dose levels on board.

The TriTel three dimensional silicon telescope is working onboard the ISS since 2012. The active TriTel system on board the ISS is capable of measuring the LET and energy spectra of the radiation field on low Earth orbit (LEO).

Results

The measurement results obtained by the Pille system between 2003 and 2012 were summarized during the work. During this time period more than 32 000 TL readouts were carried out on board the ISS.

The more than 36 000 automatic measurements have provided 90-minute time resolution dose monitoring data series. Based on these results, the South Atlantic Anomaly (SAA) crossings can be detected by the Pille System. The average dose rate measured outside the SAA was in the range of 3-7 $\mu\text{Gy}/\text{h}$, while the mean dose rates of orbits crossing the anomaly could reach 18 $\mu\text{Gy}/\text{h}$.

The Pille and TL measurements onboard stratospheric balloons were evaluated. The average absorbed dose measured by the Pille dosimeters was $13.1 \pm 1.5 \mu\text{Gy}$, while the absorbed dose measured by TriTel was $19.9 \pm 1.0 \mu\text{Gy}$ during the four-hours-long flight. The absorbed doses measured with TriTel for the balloon flight are higher than the one measured with Pille, as it was expected due to the low sensitivity of TL detectors to particles with LET higher than 10 $\text{keV}/\mu\text{m}$. Based on this measurements the correction factor of the Pille measurements in order to consider it is low efficiency on high LET radiation fields is 1.52 ± 0.2 .

Pille EVA measurements were re-evaluated. Between 2004 and 2012 more than two dozens of EVA measurements were carried out onboard the ISS. The excess dose rates of the EVA were between 16.6 $\mu\text{Gy}/\text{h}$ and 122 $\mu\text{Gy}/\text{h}$, 70% of the results were in the range of 40-70 $\mu\text{Gy}/\text{h}$.

Remaining work

Evaluation of the regularly received data obtained by the Pille System on board the ISS. New experiments are also under preparation on board the ISS.

Related Publication

B. Zábori, I. Apáthy, A. Csöke, S. Deme, A. Hirn, T. Hurtony, J. Pálfalvi, T. Pázmándi, *CoCoRAD and TECHDOSE cosmic radiation experiments on board BEXUS stratospheric research balloons*, Proc. '21st ESA Symposium European Rocket & Balloon Programmes and Related Research', 9-13 June 2013, Thun, Switzerland (ESA SP-721, October 2013) pp. 307-314, 2013

COMPUTATIONAL MODELLING OF THE EFFECT OF LOW DOSES

Imre Balásházy, Árpád Farkas, Balázs G. Madas

Objective

Our objectives were to elaborate an experimental setup for the investigation of radiation induced hyperplasia in collaboration with the Leiden University Medical Center, to quantify radio-aerosol distribution along the bronchial airways as a result of deposition and clearance, to analyse radiation induced cell death and mutation, and to apply our lung models.

Methods

Tissue doses and hit distributions in a tissue culture were estimated as the function of source-target distance, exposition time and mucus layer thickness in order to determine appropriate distance and exposition time for tissue experiments.

Analytical equations have been deduced and numerical techniques were implemented in order to model the dynamics of radioactive nanoaerosols after their deposition in the airways. Thermal diffusion and mucociliary clearance were simulated as leading mechanisms of the postdeposition particle dispersion. CFD techniques and stochastic models have been applied.

Results

Experiments for the induction of hyperplasia were performed based on our simulations. Individual alpha-tracks were visualised, and proliferation rate as the function of time was qualitatively determined.

Due to the special structural and physiological properties of mucus, deposited nanoparticles behave differently compared to micron-size aerosols. They encounter mucus viscosities up to three-four orders of magnitude lower than their micrometer sized counterparts. On the other hand, the fraction of radon progenies which is prone to mucociliary clearance decreases by the decrease of diameter. These findings have direct impact on future lung microdosimetry and risk assessment.

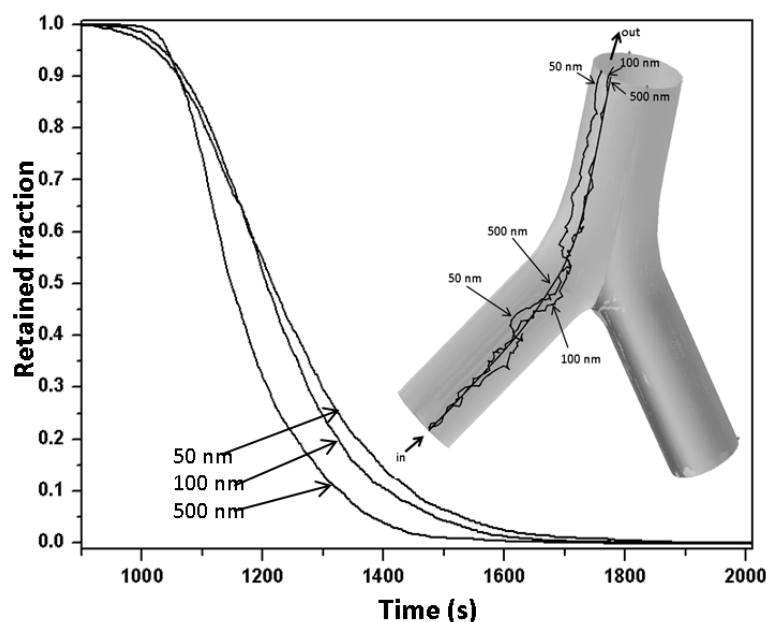


Figure 1: Retained mass fraction and individual trajectories of 50, 100 and 500 nm particles deposited in the deeper airways and clearing up along a selected model airway bifurcation.

Related publications

- [1] Á. Farkas and I. Szóke: *Simulation of bronchial mucociliary clearance of insoluble particles by computational fluid and particle dynamics methods*. Inhalation Toxicology 25(10): 593-605, 2013.
- [2] 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?* Submitted to Dose-Response Journal.
- [3] B.G. Madas and K. Varga: *Biophysical modelling of the effects of inhaled radon progeny on the bronchial epithelium for the estimation of the relationships applied in the two stage clonal expansion model of carcinogenesis*. Submitted to Radiation Protection Dosimetry, arXiv: 1308.2547.

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

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

Objective

The SINAC programme system was developed to follow the consequences of radioactive releases of a 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 in the software. Effects of the introduction of countermeasures are also taken into account.

The SINAC system – developed in AEKI (the predecessor of MTA EK) 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 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 present version of the programme system has been completed in 2012. In 2013 the reading method for the meteorological input files was altered and the countermeasure system was revised. Furthermore, minor changes in the graphical interface were carried out in accordance with the user's remarks. The programme system has been tested and the final version was delivered to the user. A study on the further development of SINAC has been finished and handed over to the user.

Methods

Due to the user's requests, the calculation and the representation of countermeasures has been modified. The module used for reading the input data has been reprogrammed to handle the altered files of meteorological data provided by the Hungarian Meteorological Service. Some graphical features have also been improved in order to provide a more suitable and perspicuous interface for decision-making. The developers carried out research on the further development of the programme system. Transport, depletion and dose calculation methods, parametrisation techniques and the countermeasure system applied in local dispersion models used in Hungary were reviewed and suggestions were made with the aim of making the puff model more effective. The list of calculated radionuclides was also reconsidered and the extension of the list was suggested with further radionuclides that effect environmental dose rates considerably.

Results

The development of the new version of SINAC is finished. Several programme tests have been carried out to ensure that the results of calculations are valid and adequate to previous versions. Modifications preferred by the user have been adapted. SINAC is suitable for estimating the environmental effects of short term releases with the help of a well-developed and perspicuous interface for decision-making.

Remaining work

Further development of the programme system requires a full reconstruction of transport and dose calculation methods. The adaptation of new methods applied in the most state-of-the-art models in the international use would result in a more accurate and reliable estimation of the environmental effects of potential accidental releases.

Related publications

- [1] S. Deme, I. Németh, T. Pázmándi and P. Szántó: *Models of the SINAC programme* (in Hungarian), EK-SVL-2012-262-01-01-02 (2013)
- [2] S. Deme, E. Homolya, I. Németh, T. Pázmándi and P. Szántó: *SINAC programme users manual (ver. 1.2.0)* (in Hungarian), EK-SVL-2012-262-01-02-04 (2013)

SHIELDING CAPABILITY STUDIES OF DIFFERENT MATERIALS USING A NEUTRON RADIATION SOURCE

József K. Pálfalvi, Tamás Pázmándi, Balázs Zábori, Attila Hirn

Objective

The main objective of the work was to study the neutron shielding capabilities of different building materials using the Biological Irradiation Facility of the Budapest Research Reactor as a neutron radiation source. The studied materials of unknown composition were provided by a construction company, all of them had the same geometrical parameters for easy comparison.

Methods

The samples were irradiated by neutrons in beam geometry. Identical activation detectors were mounted on the front and back sides of the cylindrical samples and the ratio of the measured absorbed dose rates or fluxes, called shielding ratio, were considered to characterize the shielding properties. Three different neutron energy ranges were selected as follows:

- thermal neutron energy range ($E < 0.5$ keV);
- intermediate neutron energy range (0.5 keV $\leq E < 100$ keV);
- fast neutron energy range ($E \geq 100$ keV).

The nuclear reactions used for the measurements were in what follows:

- $^{32}\text{S}(n,p)^{32}\text{P}$ in case of the fast neutron energy range;
- $^{197}\text{Au}(n,\gamma)^{198}\text{Au}$ in case of the intermediate and thermal neutron range.

After the irradiation, the surface gamma dose rate was monitored for several days in order to estimate the effective half life of the neutron induced radioactivity. Gamma activation analysis was also performed to determine the dominant radioactive isotopes of those samples that showed the highest surface activity.

Results

The shielding ratios (the ratio of the measured quantities on the front and the back sides of the sample) are summarized in Fig.1. Sample No. 3 was provided for reference purposes.

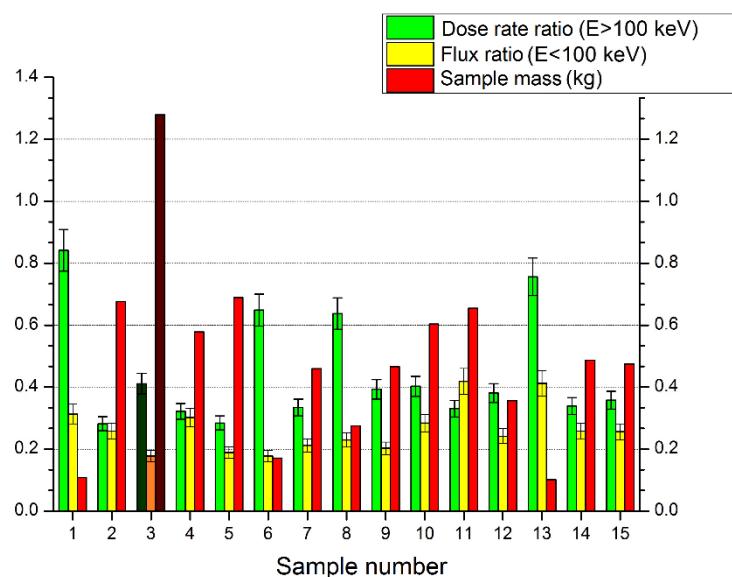


Figure 1: The measured shielding ratios and the masses of the samples. Although the reference material showed good shielding properties, considering to its quite large mass some other materials (samples No. 7, 9, 12 etc.) may be more favourable as new construction materials for neutron shielding.

The average effective half life of the induced activity of the samples was found to be about 4.5 h. According to the gamma activation the main radioactive isotopes were ^{82}Br , ^{56}Mn and ^{24}Na .

Remaining work

The study has been finished at the end of 2013 with the measurement of each sample. The obtained results have been evaluated and documented.

Related publication

J. Pálfalvi, T. Pázmándi, B. Zábori: *Shielding capability studies of different materials using a neutron radiation source (in Hungarian)*, MTA Centre for Energy Research, EK-SVL-2013-310-01-01-01 (2013)

PILLE, A PORTABLE TLD SYSTEM ON THE ISS

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

Objective

Exposure of astronauts to ionizing radiation in low Earth orbit is two orders of magnitude higher than that on the surface of the Earth. 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. The Pille space - qualified thermoluminescent dosimeter (TLD) system developed by MTA KFKI AEKI the predecessor of the MTA EK is providing accurate and high resolution absorbed dose data already on board the spacecraft. The Pille-MKS system launched in August 2003 to the Russian segment of the International Space Station (ISS) is operated in cooperation with the Institute for Biomedical Problems (IBMP) in Moscow in the frame of a bilateral contract. The objective of the Pille project is the evaluation and interpretation of on-board data, maintenance of the on-board system and the further development of the system.

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. Currently Pille-MKS consists of 8 original dosimeters transported to the ISS in 2003, 4 dosimeters delivered in 2009 and a TLD reader. The dosimeters are located at different locations in 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. For on-board sensitivity analysis, all Pille dosimeters are located on panel No. 327, and the quasi-homogeneous radiation field at that position is used as natural radiation source. The duration of the exposition is about two weeks. The correction factors for the individual dosimeters are then calculated from the results of the sensitivity measurements.

Results

Approximately 4000 on-board measurements were performed with the Pille-MKS system during ISS Expeditions 31-35. The data obtained were evaluated, analyzed, interpreted and presented at scientific conferences. On-board sensitivity and comparative measurements with NASA's tissue-equivalent proportional counter were fulfilled as well.

The development of a new type of Pille dosimeter with reduced shielding for EVAs was also continued. The prototype of the dosimeter was designed and manufactured (Fig. 1). [1]



Figure 1: Prototype of the new Pille dosimeters dedicated to EVA measurements: dosimeter "cartridge" of reduced shielding (left) and its read-out socket (right)

Remaining work

Evaluation and interpretation of on-board data as well as maintenance of the on-board system will be continued. Manufacturing and testing of the EVA dosimeters will be performed.

Acknowledgement

The authors wish to acknowledge the precious help provided by the colleagues at IBMP and RSC Energia. The work presented hereby was funded by the National Development Agency (contract number URKUT_10-1-2011-0009).

Related publication

- [1] A. Hirn: *Maintenance of the Pille dosimeter on board the International Space Station (in Hungarian)*, EK-SVL-2013-355-01-01-00 (2013)

RESULTS OF THE BEXUS TECHDOSE BALLOON EXPERIMENT

Balázs Zábori, Ágnes Gyovai, Tamás Hurtony, József Pálfalvi, István Apáthy, Antal Csőke, Sándor Deme, Attila Hirn, Tamás Pázmándi, Péter Szántó

Objective

The main scientific objective of the TECHDOSE student experiment performed on the 24th of September 2012 on board the BEXUS 14 stratospheric balloon launched from Esrange Space Center, Kiruna, Northern Sweden was to measure the effects of the cosmic radiation from dosimetric point of view at altitudes up to approximately 30 km where measurements with orbiting spacecrafts are not possible. The main technical objective was to develop a balloon technology platform for advanced cosmic radiation and dosimetry measurements. In year 2013 the main goal was the publication of the results obtained in the BEXUS TECHDOSE experiment and preparation for future radiation measurements on board sounding rockets STRATOS-II and REXUS 17/18.

Methods

The results of the TECHDOSE measurements performed with Geiger-Müller (GM) counters of mutually orthogonal axes and with TRITEL in similar geometry served as a baseline for preparing the preliminary design of the rocket experiments.

Results

Results of the BEXUS TECHDOSE experiment were presented at the '21st ESA Symposium on European Rocket & Balloon Programmes and Related Research' and were published in the Proceedings of the event [1]. A preliminary design was prepared for the radiation measurements on board the rocket STRATOS-II. With the support of the MTA EK a student team of M.Sc. and Ph.D. students from the Budapest University of Technology and Economics and the Eötvös Loránd University submitted a proposal for the REXUS 17/18 call of the Education Office of the European Space Agency (ESA). The proposal with title "GM Sounding Rocket Experiment to Measure the Cosmic Radiation and Estimate its Dose Contribution (REM-RED)" was preselected, and after a successful participation on the REXUS/BEXUS Selection Workshop, their experiment was finally selected as one of the payloads of the REXUS 17/18.



Figure 1: The two GM counters and their electronic unit mounted onto the REXUS rocket module (REM-RED)

Remaining work

The cross-comparison of the results obtained in the BEXUS TECHDOSE experiment and in the BEXUS CoCoRAD experiment of year 2011 will be published. Development of the rocket experiments in 2014 will continue in the frame of a new project named REXUS REM-RED.

Acknowledgement

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 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 vehicles. Experts from ESA, SSC and DLR provide technical support to the student teams throughout the project. The BEXUS TECHDOSE experiment was co-funded in the frame of the PECS contract No. 4000107210/12/NL/KML.

Related publication

- [1] B. Zábori, I. Apáthy, A. Csőke, S. Deme, A. Hirn, T. Hurtony, J. Pálfalvi and T. Pázmándi: *CoCoRAD and TECHDOSE cosmic radiation experiments on board BEXUS stratospheric research balloons*, Proc. '21st ESA Symp. on European Rocket & Balloon Programmes and Related Research', 9-13 June 2013, Thun, Switzerland (ESA SP-721) 307-314 (2013)

EXPERIMENTAL STUDY OF THE COSMIC RADIATION FIELD

MEASUREMENTS WITH THE TRITEL 3D TELESCOPE

Attila Hirn, István Apáthy, Antal Csőke, Sándor Deme, József K. Pálfalvi, Tamás Pázmándi, Péter Szántó, Balázs Zábori

Objective

A three-dimensional silicon detector telescope (TRITEL) was developed at MTA EK in the past years in cooperation with BL-Electronics Ltd. The instrument is capable of measuring 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 2013 the main objectives of the TRITEL-related projects were

- to provide on-ground support for the data download and de-installation of the TRITEL-SURE experiment comprising TRITEL and a passive detector package (PDP) of thermoluminescent (TL) and solid state nuclear track-etched detectors, and to perform preliminary evaluation of data obtained in the European Columbus Laboratory of the International Space Station (ISS);
- to provide on-ground support for the installation and operation of the TRITEL-RS instrument and an accompanying PDP delivered to the Russian Segment of the ISS;
- to continue the qualification testing 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

After inserting a USB (Universal Serial Bus) pendrive into any of the two USB slots of the TRITEL Electronic Unit, measurement data are immediately and automatically downloaded to the data storage unit inserted. The USB pendrive is then either retrieved directly from the ISS or its content is transferred to one of the Orbiter Communications Adapter (OCA) laptops on board and then transmitted to a ground server via the communication system of the ISS. The data received in these ways are displayed and evaluated using TRITEL's ground software. From the received total and the gated energy deposition spectra first the absorbed dose and the LET-spectra in water are derived. From the later then the average quality factors of the radiation field in three mutually orthogonal directions are calculated. The final output of the calculations is the dose equivalent.

The PDP travelled from Budapest to Baikonur and was returned to Budapest after retrieval from ISS together with a TRITEL Ground Reference Dosimeter in order to take into account the transport dose (e.g. due to X-ray exposure at the airport security). The TLDs included in the PDP record mostly protons of low LET ($<10 \text{ keV}/\mu\text{m}$). Considering the total shielding surrounding the detector cube (walls of the ISS, other instruments, etc.), only the relatively high energy protons reach the TL detectors from any direction. The carbon block inside the PDP further filters the protons. Considering that in space radiation the number of protons above 1 GeV is less than $\sim 1\%$ of the total number of protons, we may conclude that TLDs on one side of the carbon cube detect mostly those protons that are coming from $<2\pi$ solid angle in front of the surface of the cube. In this way the dose of low LET radiation can be estimated direction selectively. The $^6\text{LiF:Mg,Ti}$ (MTS-6) and $^7\text{LiF:Mg,Ti}$ (MTS-7) TL dosimeters of the PDP are read out with a Harshaw Laboratory TLD Reader system. The evaluation of the track-etched detectors is performed in a two-step etching procedure to distinguish the low and high LET particles. Etching is carried out in 6 N NaOH solution at $70^\circ\text{C} \pm 1^\circ\text{C}$; meanwhile N_2 bubble stirring is applied. In the first step, the detectors are etched for 6 hours, removing approximately $8 \mu\text{m}$ of the detector material, and hence making the tracks of particles with high LET ($>25 \text{ keV}/\mu\text{m}$) visible. In the second step, a 15-hour-long etching is performed, revealing the tracks belonging to particles with LET between 10 and $60 \text{ keV}/\mu\text{m}$. In this step approximately $20 \mu\text{m}$ of the detector material is removed. Inspection of the tracks is made with the VIRGINIA semi-automated image analyzer system and with an optical microscope. The tracks are distributed into groups, and their geometrical and optical parameters are measured. Manual track parameter measurements are also performed on very long tracks. From the measured major and minor diameters of the track's surface opening, the so called track etch rate ratio (V) is determined. The LET of the particles are then calculated by applying the appropriate calibration function on V. The LET values obtained are corrected for critical angle and background. Finally, the short- and long-etch spectra are combined and the absorbed dose, the dose equivalent, and the mean quality factor are calculated.

Results

The 6-month-long measurement with the TRITEL-SURE system was successfully completed in the Columbus Laboratory. On the 10th of May 2013 the raw data measured by the TRITEL 3D telescope and stored in the internal memory of the TRITEL Electronic Unit was copied to the dedicated USB Stick before de-installation and then downloaded to ground. The USB Stick and the Passive Detector Package were retrieved from the ISS with the Soyuz TMA-07M (ISS-33S) on the 14th of May 2013. After successful negotiations with the European Space Agency and the Russian Rocket Space Corporation Energia, the TRITEL Electronic Unit, the Detector Unit and the Interface Cable in their TRITEL Launch Bag were transferred to the Russian segment for future multi detector unit measurements. [1-2]

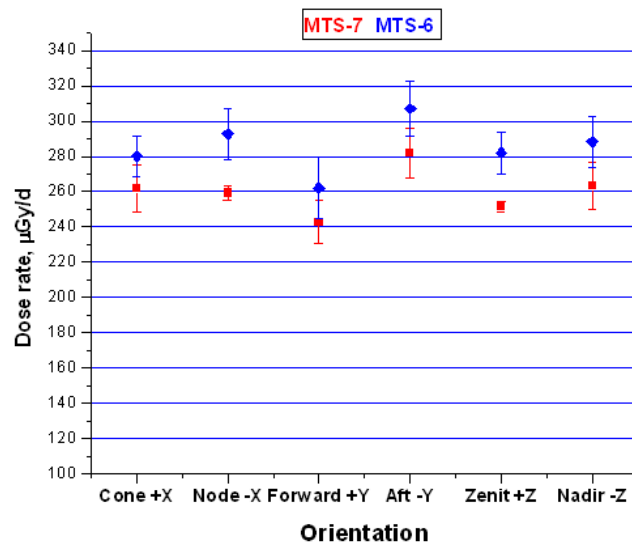


Figure 1: Results of the TL measurements performed with the PDP of the TRITEL-SURE experiment (with 1σ error bars)

Interpretation and evaluation of measurement data obtained in the Columbus Laboratory continued. Fig. 1 summarizes the results of the TL measurements for 6 different directions for the period between the 22nd of December 2012 and the 14th of May 2013. The values show significant direction-dependence.

The result of the preliminary cross-comparison of the LET spectra obtained from the CR-39 track-etched detectors in the PDP and from TRITEL gated energy deposition spectra for the aft direction is shown in Fig. 2. The results in the LET region between 15 keV/μm and 100 keV/μm in water agree nicely, therefore the LET spectra determined from CR-39 measurements can be used for correction of TRITEL results in the high-LET (>100 keV/μm in water) region.

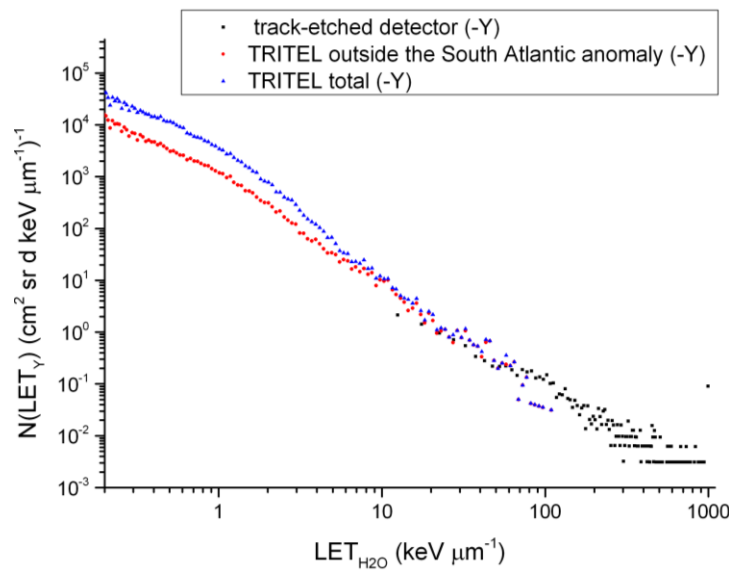


Figure 2: LET spectra obtained from the measurements with CR-39 track-etched detectors in the PDP and from TRITEL gated energy deposition spectra (aft direction)

The TRITEL-RS system was delivered to and successfully installed in the Russian Service Module of the ISS on the 5th of April 2013 (Fig. 3). TRITEL operated without any problem until the 17th of July. After this day, which coincided with an Earth-directed coronal mass ejection reaching the Earth, most of the measurement data stored got corrupted. Restart of the system failed. A detailed error analysis and development of scenarios for problem solving got underway. The analysis of measurement data obtained during the first three months of operation is in progress [3].

Due to a delay in the RISESAT program the qualification tests of the engineering model of TRITEL-JMS has been pending. Nevertheless, programming of the Remote Terminal Unit interfacing TRITEL to the Science Handling Unit of the satellite continued [4].

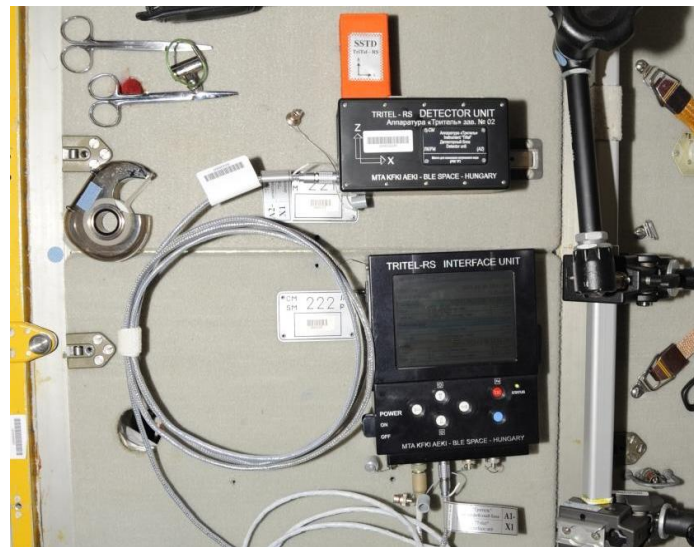


Figure 3: The TRITEL-RS system on the Russian Service Module of the ISS (credits: Rocket Space Corporation Energia/Roscosmos)

Remaining work

Comprehensive analysis of measurement data received in the TRITEL-SURE experiment will be performed in 2014.

The TRITEL-RS system will be either repaired on board or a new Interface Unit will be manufactured and delivered to ISS. After the problem will have been solved and the TRITEL system will be fully operational, connecting the Detector Unit of TRITEL-SURE to the TRITEL-RS system will be performed. 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.

New results of the measurements performed with the TRITEL space dosimetry system as well as the results of cross-comparisons with those of other dosimetry experiments performed simultaneously on board ISS 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.

Acknowledgement

The TRITEL-SURE experiment was co-funded by the EC project SURE, contract number RITA-CT-2006-026069 and by the Government of Hungary through ESA Contracts 98057 and 4000108072/13/NL/KML under the PECS (Plan for European Cooperating States). TRITEL-RS is operated on board the Russian Segment in frame of the Matroshka-R space experiment in cooperation with the State Scientific Center, Institute for Biomedical Problems, Russian Academy of Sciences, Moscow and it was funded by the National Development Agency (contract number URKUT_10-1-2011-0036). The authors wish to acknowledge the precious help provided by the colleagues at IBMP and RSC Energia.

The RISESAT project is led by the Space Robotics Laboratory of Tohoku University and is mainly granted by the Japan Society for the Promotion of Science (JSPS) through the "Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program)," initiated by the Council for Science and Technology Policy (CSTP). RISESAT project is also partly supported by Grant-in-Aid for Scientific Research on Innovative Areas KAKENHI:24760658 from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Related publications

- [1] A. Hirn, I. Apáthy, L. Bodnár, A. Csőke, S. Deme, T. Pázmándi, P. Szántó and B. Zábóri: *The first measurement results of the space dosimetry experiment TRITEL-SURE (in Hungarian)*, ŰRTAN évkönyv 2012, Az Asztronautikai Tájékoztató 64. száma, HU ISSN 1788-7771, 82-85 (2013)
- [2] A. Hirn, I. Apáthy, L. Bodnár, A. Csőke, S. Deme, T. Pázmándi, P. Szántó and B. Zábóri: *First measurements with the TRITEL space dosimetry system on board the International Space Station (in Hungarian)*, Sugárvédelem **6(1)** 1-6 (2013)
- [3] T. Pazmandi: *Development of the TRITEL three-dimensional silicon detector particle telescope (in Hungarian)*, Centre for Energy Research, EK-SVL-2013-354-01-03-00 (2013)
- [4] T. Kuwahara, A. Hirn, I. Apáthy, L. Bodnár, A. Csőke, S. Deme, T. Pázmándi, P. Szántó, G. Troznai and B. Zábóri, *TRITEL-JMS: A Three-Dimensional Silicon Detector Telescope Dedicated for Operation on Board Microsatellite RISESAT*, ISTS Special Issue of Transactions of the Japan Society for Aeronautical and Space Sciences, Aerospace Technology Japan, 2013-r-47[900383] (accepted for publication)

COSMIC RAY STUDIES ON BION-M1 AND ISS

József K. Pálfalvi, Andrea Strád, Julianna Szabó

Objective

The Russian made Bion-M1 satellite contains a recovery capsule holding the experiment payloads, including internal and external experiments. It was launched in Baikonur, Kazakhstan on 19th April, 2013 and stayed in orbit for 30 days, circling the Earth, at 575 kms altitude, with an inclination of 64.9°. Beside biological experiments, passive instruments for cosmic ray studies were located inside and outside of the capsule. The external detectors aimed at three purposes: to support the biological studies, to investigate the cosmic rays at high altitude and to study the behaviour of the detectors in a harsh environment, at vacuum and low temperature conditions. The MTA EK participated in both the internal and external measurements with thermoluminescent (TLD) and nuclear track detectors (NTD). In this report the results of the high charge and energy (HZE) particle measurements are compared to those ones obtained inside the International Space Station (ISS, altitude ~400 km, inclination 62°) nearly in the same calendar interval by MTA EK.

Methods

The TLDs are able to detect cosmic rays of low energy transfer (LET), while the NTDs detect the high LET ones, like HZE. The detectors were designed and prepared at the MTA EK in Budapest by the space dosimetry group, packed into two special boxes in Moscow by the Russian team of the Institute of Biomedical Problems (IBMP). The wall of the box simulated the space suit of an astronaut. The boxes were encapsulated in cylindrical holders (like pan), closed during the launch and landing, and open when in orbit. (See Fig. 1, left)

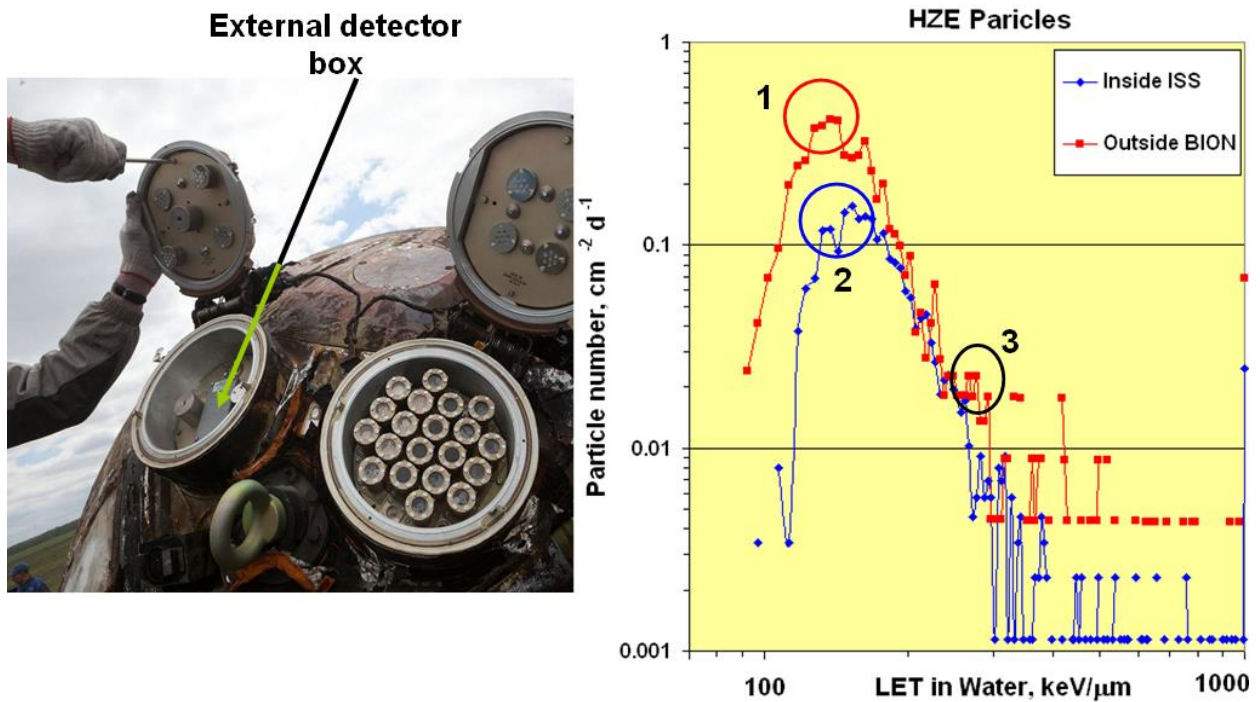


Fig. 1. Left: Removal of the external detector box after landing. Right: Comparison of the LET spectra of HZE particles obtained by the external detectors on the BION-M1 and measured inside the Columbus module of the ISS.

Results

The LET spectrum of HZE particles mostly depends on the shielding surrounding the detector. This shielding is composed of the effective thickness of the atmospheric air (altitude dependence) and man-made covers. The dominant particle of galactic cosmic rays (GCR) is the relativistic iron, having a characteristic LET value of ~137 keV/μm. Analyzing the LET spectra shown in Fig. 1 (right side), two remarkable differences can be observed: the flux of the iron on the BION-M1 (red circle 1) is higher by ~ a factor of two, and the relativistic iron peak shifted towards higher LET by ~ 15 keV/μm inside the ISS (blue circle 2), which means a ~10 GeV energy loss. Both effects were caused by the thicker air and the wall of the ISS. The black circle 3 shows the flux of the galactic helium particles (~260 keV/μm) on BION-M1. The same decrease appears again (blue curve below the red one).

Remaining work

The evaluation of the entire LET spectra inside and outside of the BION-M1 and inside the ISS is in progress.

DUST IMPACT MONITOR, SIMPLE PLASMA MONITOR

István Apáthy, Attila Hirn, Attila Péter, Balázs Zábóri

Objective

The *Rosetta* spacecraft of the European Space Agency is the first mission designed to both orbit 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 its implications with regard to the origin of the Solar System.

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* 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 an electrostatic, hemispherical analyser 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 $140^\circ \times 150^\circ$ for ions and $8^\circ \times 15^\circ$ 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 GRMs of *ROMAP* and *SESAME* (integrated with the GRM of the Lander) was continued at *DLR*, in Cologne, Germany.

In 2013, *Rosetta* was continuing its deep hibernation phase so there were no on-board payload checking campaigns but the planned *PHC* (*Post Hibernation Commissioning*) tests were executed on the *Philae* GRM to imitate the operation of *ROMAP* and *SESAME* just after wake-up. The evaluation of the data achieved during the *PHC* campaign proved the proper operation of the instruments.

In July, a *ROMAP* working group meeting was held at the Max Planck Institute für Sonnensystemforschung (MPS) in Katlenburg-Lindau, Germany, with the participation of MTA EK experts. The main topics were the application of *ROMAP* data for the altitude determination of the Lander and new SW developments for data evaluation.

During November-December, Attila Hirn was invited by MPS, where he performed tests by *DIM*'s mechanical GSE for investigating the impact parameters of the piezo sensor.

Experts of MTA EK participated in the activity of the *Lander Operation Working Group* (*LOWG*) as well as on the *ROSETTA Orbiter-Lander Joint Science Meeting*. On the *LOWG* meeting at *DLR* (October, 2013) reports were 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 on-ground calibrations of the sensors and tests of the GRM; to participate in the *PHC* on-board tests and *PDCS* (*Pre-Delivery Calibration and Science*); to participate in the *SDL* (*Separation, Descent and Landing*), *FSS* (*First Scientific Sequence*) and *LTS* (*Long Term Science*) activity of *DIM* and *ROMAP*; to take part in data evaluation.



IV. NUCLEAR SECURITY, NON PROLIFERATION



ELECTRON SPECTROSCOPY OF NUCLEAR MATERIALS

Zoltán Hlavathy, Tamás Bíró, Zoltán Schay

Objective

In characterisation of nuclear materials by surface analytical tools three regions can be considered. The 'as received' surface is characteristic to the handling of the material after manufacturing, the bulk, is characteristic to the chemical state of the fuel material and in between, after removing the outmost layer and before reaching the bulk we can get insight into the layer characteristic to the moulding of the pellets, i.e. traces of lubricants and/or binders can be found. Recovery of the intermittent layer needs very careful successive argon ion bombardment.

Methods

The pellets were investigated by X-ray photoelectron spectroscopy (XPS) in 'as received' state. Afterwards some of them were bombarded by argon ions and the XP spectra were taken again. Until now, the transition layer between the carbonaceous overlayer and the bulk was not reliably and reproducibly reached.

Results

We have found no significant differences between the pellets of different enrichment and suspected origin.

The main C 1s peak in 'as received' state was observed at 285-285.4 eV binding energy. On argon bombardment this peak decreased significantly and a second peak at 280.3 eV appeared which can be attributed to carbidic species.

O 1s peaks showed in 'as received' state two components, one at 530 eV and another at 532 eV. Upon argon bombardment the second component disappeared. The first one can be attributed to metal oxide, the second one to O in CO bond.

The U 4f peak exhibited a little shift upon Ar⁺ bombardment (380.5 → 380.2 eV); the black powder (UO_{2.9} and UO₃·2H₂O according to the supplier) and the yellow cake (end product at mining facilities) had a significantly lower binding energy (378.6 eV) which points to a different chemical state.

In a measurement aiming to reveal the composition of the transition layer we found Ca, Cl and Pb. Further systematic depth profile measurements are needed to map the significant differences between the particular pellets.

Remaining work

The investigations carried out until recently proved that characteristic differences between the chemical states of particular pellets and trace elements suitable for identification in the transition layer were found. Systematic investigations are needed to determine whether establishing of a data bank is feasible.

Acknowledgement

Special thanks are due to Attila Sulyok (MFA) for the depth profile measurement.

AGE DATING OF U-SAMPLES BY GAMMA SPECTROMETRY

C. Tam Nguyen, László Lakosi, Sándor Szabó, István Almási

Objective

The aim was to develop a non-destructive method for U age dating. Assay of items on the spot, or those from which it is not possible to take out a sample for destructive assay, may occur in combatting illicit trafficking of nuclear materials. The age of an unknown U sample, i.e. the time elapsed from the chemical processing or enrichment made for its production, is characteristic of the sample and may give a hint toward its origin.

Method

A novel and unique method was invented and developed at the Institute of Isotopes, one of the founders of MTA EK, applying high resolution gamma spectrometry (HRGS). It has been demonstrated that the daughter/parent activity ratio $^{214}\text{Bi}/^{234}\text{U}$ is obtained by directly measuring the count rates of their relevant gamma peaks by low background HRGS. The method does not require use of reference materials of known ages. The $^{214}\text{Bi}/^{234}\text{U}$ ratio of a U sample can be measured at least 2 weeks after separation, and its age T can be calculated to a good approximation as

$$\frac{A_{\text{Bi}214}}{A_{\text{U}234}} = \frac{A_{\text{Ra}226}}{A_{\text{U}234}} = \frac{1}{2} \lambda_{\text{Th}} \lambda_{\text{Ra}} T^2 .$$

Results

Summary of age results for undeclared U-samples obtained at the institute until now is shown in Fig. 1. The experimental results correspond to the ratio of the measured ^{214}Bi to ^{234}U activities and the age T of the sample determined from the equation. The continuous line is a theoretical curve resulting from calculation.

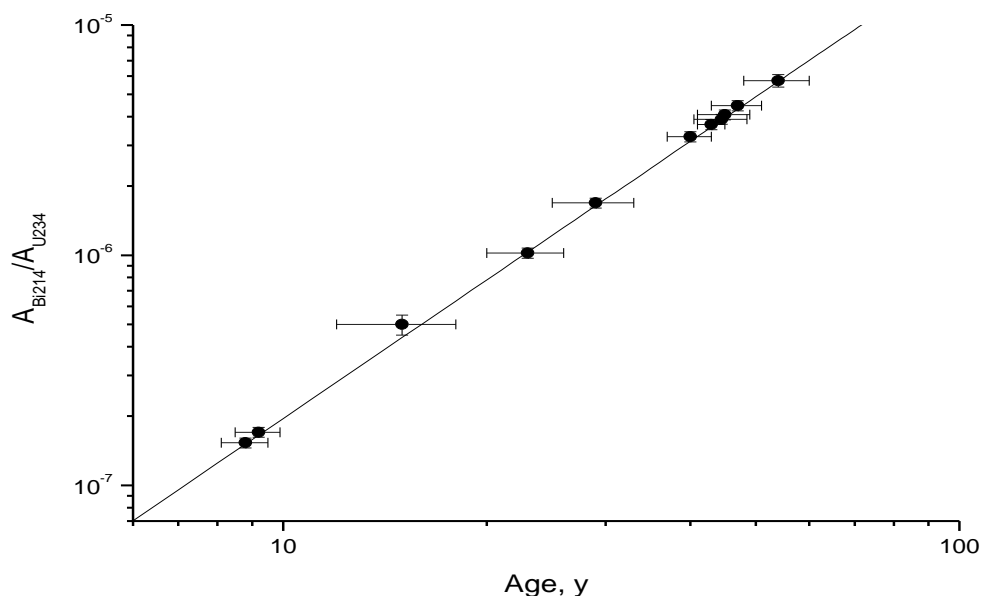


Figure 1: Age results of undeclared U samples assayed so far by HRGS

Data agree well with mass spectrometric results. Accuracy depends on the background, detector efficiency, measurement time, enrichment, amount of the sample and on its age. The least enriched U sample dated by our method was a 5% enriched oxide material, age of which was found to be 54 ± 7 yr. The youngest sample was a metallic U of 90.8% enrichment, found to be 6.7 ± 0.7 yr old.

Remaining work

Experiments are planned by a more sensitive well-type HPGe detector to be purchased. Lower limit of age dating could be 4 yr for samples enriched to 10%, whereas 15 yr for natural samples. Even lower limits are warranted for higher enriched samples.

Related publication

L. Lakosi, C. T. Nguyen, J. Zsigrai: *Characterization of uranium-bearing material of unknown origin by HRGS*. Int. Conf. on Nuclear Security: Enhancing Global Efforts, Book of Extended Synopses, Vienna, Austria, 1-5 July 2013. IAEA-CN-203/138

BURNUP MEASUREMENTS OF POWER PLANT FUEL ASSEMBLIES

István Almási, C. Tam Nguyen, Zoltán Hlavathy, László Lakosi

Objective

The aim was to support calculations performed by the nuclear power plant (NPP) for determining burnup of spent fuel assemblies by an independent experimental method based on high resolution gamma-ray spectrometry (HRGS). Measurements were required to indicate that the uncertainty of burnup determination is less than anticipated.

Methods

The measurements were carried out at Paks NPP by a 45 cm³ HPGe detector placed behind a collimator built into the concrete wall of the service pit. The spent fuel assemblies were transported to measurement position and moved up and down as well as rotated under water by the refueling machine in front of the collimator hole. Assemblies of 1.6, 2.4, and 3.82% enrichment burned for 1, 2, 3, and 4 y were measured in 8 height positions for 300 or 600 s on their 6 sides each. Gamma rays of ¹³⁴Cs and ²³⁷Cs were registered. Their activity ratio reflects well the burnup, taking into account irradiation history and decay times. Cs activity ratios were calculated theoretically. The apparent Cs activity ratios as seen by a Ge detector were calculated, considering the concentration of the specific nuclei in the individual pin nodes and the relative detector efficiencies.

Results

In order to check the agreement between experiment and calculation, axial and azimuthal Cs ratio profiles of assemblies were taken experimentally and by using the burnup calculation code, following the production and decay of Cs isotopes by the C-PORCA code on the basis of a simplified model. The calculated burnup and concentrations for an assembly comprise a dataset of 41 values for each of the 126 pins. Measured and calculated Cs activity ratios agree within to 3.4 % (STD), whereas the mean relative deviation is 0.77 %. This can be improved by longer measurements. As an example, the measured and calculated axial profiles on the 6 sides of a 39 GWd/tU burnup assembly are shown in Fig. 1. Measured and calculated values agree best for assemblies of cooling times of 2 – 4 y. It is expected that the currently assumed 4.5 % uncertainty of burnup calculation can be decreased by utilizing the data of the experimental results. This will facilitate observing safety limits more accurately in planning of the loading pattern of the core and during reactor operation.

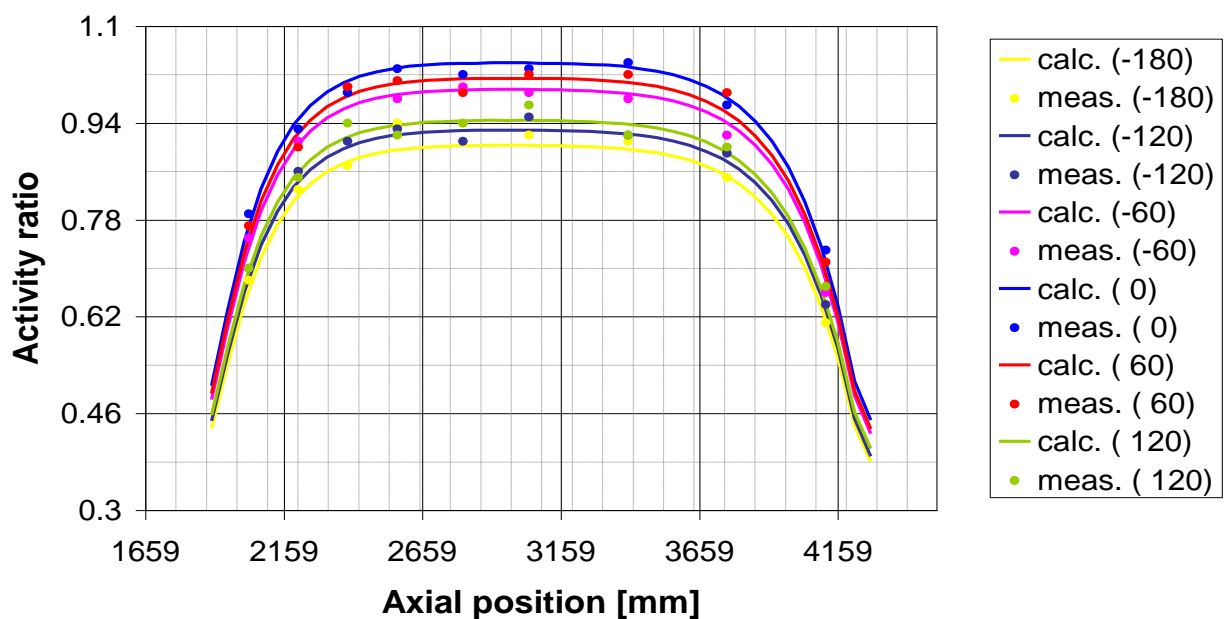


Figure 1: Measured and calculated axial profiles on the 6 sides of an asymmetrically burned 39 GWd/tU burnup assembly

Remaining work

Further measurements are planned for refining the agreement between experiment and calculation, thus further decreasing the uncertainty of burnup determination. The relation between the uncertainties of burnup and the Cs ratio is also to be examined at various operating parameters and cooling times.

Related publication

C. T. Nguyen, I. Almási et al.: *Monitoring burn-up of spent fuel assemblies by gamma spectrometry*, IEEE Transactions on Nuclear Science 60/2, 1107 (2013)

HANDBOOK FOR TRAINING OF SAFEGUARDS INSPECTORS

István Almási

Objective

The aim was to make a summarized curriculum about the necessary knowledge, without which the inspector cannot do an instrumental inspection.

Summary

The handbook is divided into two main parts.

Part one contains the basic knowledge. First of all radioactive elements are defined. The handbook contains necessary information about alpha, beta, gamma, X-ray, and neutron radiation, the differences among them. Then the frequently used radioactive materials are reviewed as NORM (naturally occurred radioactive material) like K-40, C-14, T-3, thorium, uranium and artificial radioactive isotopes like Cs-137, Co-60, Ir-192, Am-241. Next chapter introduces possible methods to detect these radiations.

In part two the knowledge necessary to perform instrumental measurements is described. It begins with the definition of 'nuclear material' and shows the importance of 'Safeguards'. Here is the review of frequently occurred radioactive materials (low activity calibrating sources: Co-60, Co-57, Cs-137, Eu-152, Am-241; sources like Co-60, Cs-137, Ir-192 for industry and therapy; sources for diagnostic use: I-132, I-125, Tc-99m; and neutron sources: Am-241-Be Pu-Be). The main characterizing gamma lines of these materials are also indicated. Category of nuclear materials is clarified. This part contains the review of the instruments ready to inspector's use. The handheld *IdentiFinder* and a portable multichannel analyzer with CZT detector are presented in this part. The most important parts of the users' manual are added here. Based on these data a trained inspector can perform the measurements.

Without practice the instruments cannot be handled, so the handbook contains a training program for the inspectors. Based on this program, a training was held at MTA EK in 2013 for four inspectors. They got a short training for handling of the instruments and also examined simple and mixed radioactive sources and different nuclear materials.

In the attachment are the spectra collected by these two instruments from the main important radioactive materials. These are useful for the inspectors, to compare them with the spectra collected at on-site inspections.



Figure 1: Instrumental training at the EK. A fuel pin and a depleted uranium container were measured

ANALYSIS OF NUCLEAR MATERIALS IN THE FIELD AND IN A LABORATORY BY LIBS SYSTEM

Éva Kovács-Széles, István Almási

Objective

Laser Induced Breakdown Spectroscopy (LIBS) is a type of atomic emission spectroscopic technique which is capable of detecting almost all elements from the periodic table in different sample types (solid, liquid or gas). Other advantage of the technique is that a LIBS analysis is much faster than a conventional laboratory technique, thanks to the absence of the sample preparation stage and due to the fact that portable LIBS systems are also available. Application of LIBS technique can be useful for analysis of materials, even in small particles originated from the environment of a terror attack or incident and to detect nuclear materials during a confiscation.

Methods

In this work a LIBSCAN25+ (Applied Photonics, England) type portable LIBS system was used and tested for detection of nuclear materials in the field and in a laboratory. The system contains a laser head with a strong (50 mJ) laser, a plastic aperture for positioning of the laser, a control panel and laptop with the evaluation software. For test measurements, the optimum parameters had to be found. During the tests real nuclear materials (low enriched and natural uranium-oxide pellets) were analyzed. After the optimization of the system, the test analysis could demonstrate that LIBS technique is applicable for detection and first analysis of nuclear materials in the field.

Results

During this work several nuclear samples (mainly uranium oxide pellets) originated from Hungarian confiscations were analyzed and the portable LIBS system was tested in the field and in laboratory use. Optimization of the measurements and analysis of real samples modelling a real confiscation were carried out. In-field and laboratory based LIBS measurements and a LIBS spectrum of a uranium-oxide pellet can be seen in Fig. 1.

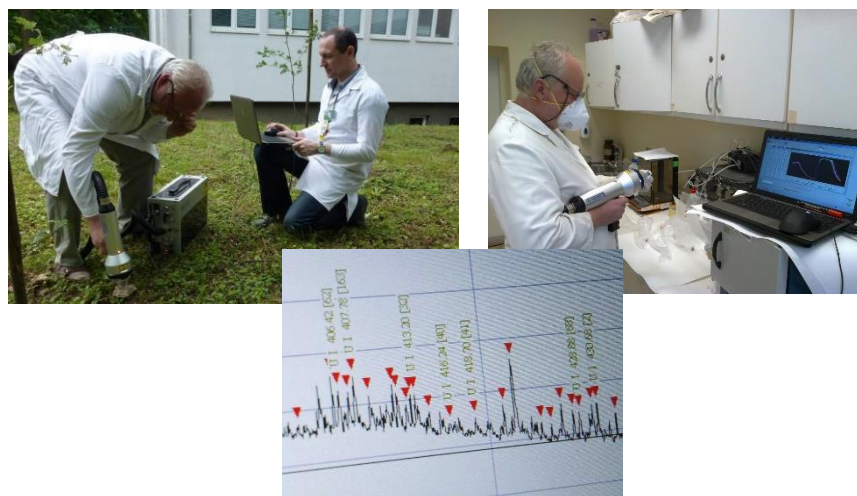


Figure 1: In-field and laboratory based measurements by LIBS and spectrum of a uranium-oxide pellet

The optimum parameters were the following: focus distance: 3 mm, energy: 50 mJ, repetition number for shots: 5. Detection limit for uranium was: 500 ppm. Reproducibility of the measurements was: $\pm 12\%$.

In the case of caesium, a calibration method was also developed for quantitative measurements from liquids in closed sample holders. Two wavelengths were investigated and 455.470 nm was found better. The detection limit obtained using this wavelength is: 38.1 ppm.

Remaining work

Testing and further development of the portable LIBS system for in-field analysis of nuclear materials is in progress. This work will be continued in the frame of a new OAH MMT project in 2014. The aim of the new project is to develop selective and rapid in-field sample preparation methods (like fast tests) for quantitative analysis of nuclear materials by LIBS in the field.

Related publication

É. É. Kovács-Széles, I. Almási: *Laboratory-based and in-field analysis of nuclear materials by portable LIBS system*, OAH MMT research report, OAH-NBI-ABA-16/13-M (2013) [in Hungarian]

SPECIALIZED SEM TRAINING FOR NUCLEAR FORENSIC PURPOSES

Éva Kovács-Széles, Anna Csordásné Pintér

Objective

The aim of the special course was to give a comprehensive and detailed training on scanning electron microscopy (SEM) technique in the field of nuclear forensics. The training was held for participants from the Russian Federation. The course included both the theoretical background and a practical hands-on training with nuclear materials. The suggested period for the training was October 2013. The training was organized by Institute for Transuranium Elements (ITU).

Methods

The training contained the following elements:

1. Presentations

- Basics: Introduction to nuclear forensics, Role of SEM, Working principle of SEM, Instrumentation, main parts of SEM, Capabilities of SEM (sample types, typical detection limits and other limitations), Comparison to other microscopic techniques with emphasis on nuclear forensics, Image analysis of SEM and other types of image
- Sample preparation: General methods for sample preparation, Special requirements for sample preparation and measurements for SEM and energy dispersive spectrometer (EDS), Sample preparation of nuclear materials
- Evaluation, data processing and software operation: Software overview, Semi-quantitative and quantitative energy dispersive X-ray microanalysis (EDS), Special requirements for quantitative electron beam microanalysis (quality and preparation of the samples, detection of elements in low amounts, separation of peaks of neighboring elements)
- Quality control: Certified reference materials (standards and tracers) with special focus on nuclear forensic applications, ISO-17025 laboratory quality management system

2. Practical part

- The training included the use of two distinct instruments: a Philips SEM 505 equipped with a LINK AN 10/55S type EDS, and a JEOL JSM 5600LV with an energy dispersive X-ray analyzer (EDS) and a wavelength dispersive analyzer (WDS).
- The training comprised microanalysis and picture analysis techniques using the two types of instruments listed above and included particle samples, powder samples and sections of larger samples.
- The training included a visit to a Transmission Electron Microscopy (TEM) of MTA EK.

Results

During the training the participants could get a basic and extensive knowledge about nuclear forensic and scanning electron microscopic technique as well as its special role and use for forensic purposes. Fig. 1 shows the training: participants and a presentation about the theory of SEM.



Figure 1: Training on SEM, presentation

Remaining work

Further trainings in the field are under organization. Next training will be held in August 2014, organized by International Atomic Energy Agency (IAEA) at MTA EK.

SPECIALIZED ICP-MS TRAINING FOR NUCLEAR FORENSIC PURPOSES

Éva Kovács-Széles, Kornél Fél

Objective

The aim of the special course was to give a comprehensive and detailed training on inductively coupled plasma mass spectrometry (ICP-MS) technique in the field of nuclear forensics. The training was held for participants from Ukraine. The course included both the theoretical background and a practical hands-on training with nuclear materials. The suggested period for the training was November 2013.

Methods

The training contained the following elements:

1. Presentations

- Introduction to nuclear forensics
- Introduction to ICP-MS: Role of ICP-MS in elemental and isotope analyses, ICP-MS instrumentation: sample introduction, plasma source, interface, mass spectrometer, adjoining instruments (cooling and vacuum system, ventilation, power supply), Capabilities of ICP-MS (sample types, typical detection limits and precisions), Comparison to the radioanalytical techniques with emphasis on nuclear forensics
- Sample preparation: General methods for sample preparation (liquid and solid samples), Dissolution techniques (leaching or total dissolution, hotplate vs. microwave-assisted dissolution), Special requirements for reagents and sample preparation environment for low-level analysis, cleaning of labware and chemicals, blank control (reagent and process blank), Sample preparation of nuclear materials, Sample preparation for laser ablation ICP-MS measurement
- Sample introduction techniques: Nebulizers and spray chambers, Desolvation-type sample introduction systems, Laser ablation for direct solid sample analysis
- Evaluation, data processing and software operation: Calibration techniques (external calibration, standard addition, isotope dilution, laser ablation analysis), Software overview (instrument, tuning, method editor, sequence editor), Special requirements for isotope analysis (mass discrimination, detector dead time)
- Quality control: ISO-17025 laboratory quality management system, Certified reference materials (standards and tracers) with special focus on nuclear forensic applications

3. Practical part

- Laboratory practice on different types of sample preparation covering the radiochemistry
- Uranium isotope ratio analysis of dissolved uranium-bearing materials
- Measurement of trace-level impurities in uranium matrix. Sample preparation, calibration approaches. Use of extraction chromatography separation for detection limit improvement (trace-level rare-earth, plutonium and common impurity measurement)
- Direct isotope analysis of a uranium-oxide sample by laser ablation ICP-MS. Comparison with the liquid measurement methods

Results

During the training the participants could get a basic and extensive knowledge about nuclear forensic and mass spectrometric technique as well as its special role and use for forensic purposes. Fig. 1 shows a picture from the training: participants and the introduction of the air-handling system of the ICP-MS laboratory.



Figure 1: Training on ICP-MS, air-handling system on the roof of building 17/A

Remaining work

Further trainings in the field are under organization. Next training will be held in August 2014, organized by International Atomic Energy Agency (IAEA) at MTA EK.

BIO-DOSIMETRIC TOOLS FOR TRIAGE TO RESPONDERS (BOOSTER)

Éva Kovács-Széles, István Almási, András Kovács

Objective

In the FP7 BOOSTER project 5 research centres from France, Germany, Hungary, Ireland, Spain, one French company, Canberra, producing nuclear instrumentation and a national authority, the Hungarian Atomic Energy Authority worked together. The aim of this work was the development of bio-dosimetric and nuclear analytical methods suitable for rapid triage of exposed persons of an incident (e.g. terror attack using dirty bombs) involving exposure to large number of people to radioactive material.

Methods

In the frame of this work the following methods and tools have been developed:

- Low background gamma spectrometric tool box for the measurement of environmental and human samples.
- ICP-MS (Inductively coupled plasma mass spectrometry) methods for the analysis of human samples containing radioactive and/or nuclear materials.
- Retrospective dosimetry methods for personal monitoring and analysis of environmental samples.
- Construction of Laser Induced Breakdown Spectroscopy (LIBS) equipment for in-field applications.
- Testing of novel gamma detectors and portal monitors to detect nuclear and radioactive materials.

Results

Low background gamma spectrometry methods have been developed for the in-field determination of uranium from biological samples (blood and urine) using outer calibration. A chemical separation based analytical method has been developed for the determination of americium, uranium and plutonium from biological samples (blood and urine) using ICP-MS instrument. By using this equipment with a laser ablation unit, another method has been developed for the measurement of uranium from one dried droplet of blood or urine applying outer calibration. A portable LIBS system was built and tested in the field for the mapping of the contaminated environment as well as for the measurement of one droplet of blood or urine using closed sample holder.

The testing of the Canberra produced portal monitors, the GPS-COM and Colibri gamma detectors, as well as that of the low background gamma spectrometers (of MTA EK) have been completed successfully.

Retrospective dosimetry using thermoluminescent (TL) and optically stimulated luminescent (OSL) methods have been developed to estimate dose absorbed by victims. Surface mounted devices (e.g. resistors) originated from mobile phones and environmental materials (e.g. dolomite) for dose monitoring in the vicinity of the incident have been investigated and found suitable for retrospective dosimetric purposes up to 100 mGy and 10 Gy respectively. The results of the BOOSTER project have been successfully demonstrated in the frame of an in-field exercise held in the premises of MTA EK with the participation of several experts from the IAEA and the EU and with end users from Hungary.



Figure 1: Live presentations of the retrospective dosimetry and the LIBS system

Remaining work

After the closure of the BOOSTER project in 2013, further research to develop mass spectrometric and gamma spectrometric methods for the analysis of human samples containing radioactive and nuclear materials is planned. Participation in other EU projects is also planned in the field.

Related publications

- [1.] D. Mesterházy, M. Osvay, A. Kovács, A. Kelemen: *Accidental and retrospective dosimetry using TL method*, Radiation Physics and Chemistry 81, 1525-1527, 2012.
- [2.] É. Kovács-Széles: *Development of fast quantitative analysis for biological samples using LA-ICP-MS technique*, European Winter Plasma Conference on Plasma Spectrochemistry, 10-15 February, 2013, Krakow, Poland, Abstract CD
- [3.] I. Almási István, É. Széles: *Method development for determination of long-lived actinides in biological samples for analysis of victims of terror attacks and nuclear accidents using distractive and non-distractive methods* (OAH-ÁNI-ABA-11/12, Oct., 2012) [in Hungarian]

SAFEGUARDS MEASUREMENTS IN PAKS NPP

István Almási, Zoltán Hlavathy, Sándor Szabó

Objective

The aim was to verify the enrichment of the incoming fuel assemblies before they are packed into the reactor core, and to perform attribute testing of spent fuels and other objects in the spent fuel storage ponds.

Methods

The fresh fuel measurements were carried out in the fresh fuel storage at Paks NPP by a 95 cm³ HPGe (high purity germanium) detector placed to the detector holder rack at the fresh fuel assembly, and a 20 mm³ CZT (Cadmium-Zinc-Telluride) detector placed into the assembly central hole. The method is based on measuring the 186 keV energy gammas of ²³⁵U and comparing it to those of fuel assemblies of homogeneous configuration consisting of uniformly enriched pins, considered to be standards. Spent fuel measurements were carried out underwater by the SFAT (Spent Fuel Attribute Tester) equipment, inside in it with a 500 mm³ CZT detector. The 662 keV gamma lines of ¹³⁷Cs, 605 and 795 keV ones of ¹³⁴Cs, and the 1173 and 1332 keV ones of ⁶⁰Co isotopes from the assemblies were detected. ¹³⁷Cs is one of the highest activity fission products of uranium.

Results

About ten percent out of every shipment of fresh fuel assemblies were measured from outside by the HPGe detector and inside by the CZT detector. The results of inside and outside measurements were different since assemblies were ‘profiled’, i.e. of heterogeneous configuration consisting of different enrichment pins. The results agreed with the MCNP calculations (for assemblies made of 4.2%, 3.91% (outside), and 4.34% (inside) enriched pins. The precision of the measurements is 0.1 % in enrichment (2 STD).

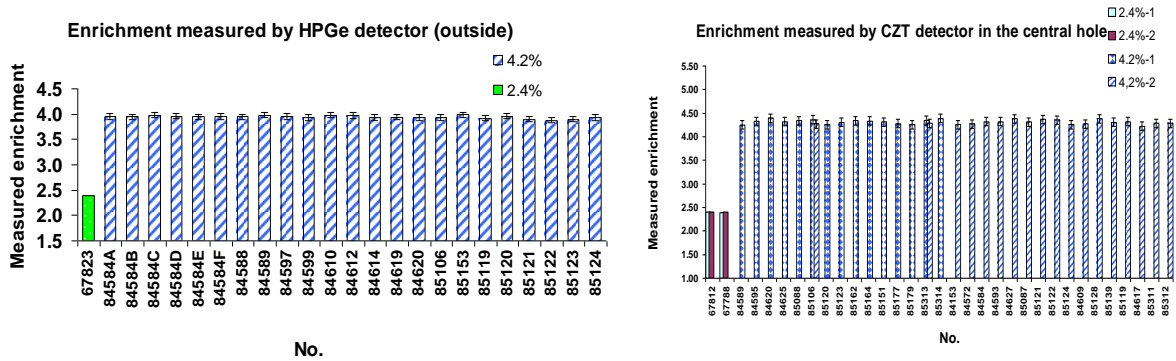


Figure 1: Enrichment of fresh fuel assemblies measured by the HPGe and CZT detector

The SFAT tests were carried in all four spent fuel storage ponds, both with ordinary fuel assemblies and special containers (canisters) filled with nuclear material from damaged assemblies as well. Cesium peak(s) are well detectable at various cooling time and burnup values.

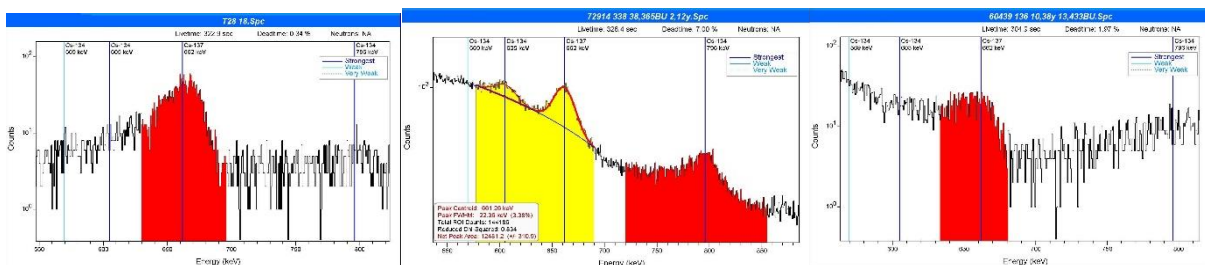


Figure 2: Spectra of some objects with various cooling times

Remaining work

We have a long term contract for routine measurements with the Paks NPP. The method should be further developed for better precision and/or shortened measuring time, so as to measure more than 10 % of fresh fuel.

DEVELOPMENT OF NATIONAL NUCLEAR FORENSICS LIBRARY

Éva Kovács-Széles, István Almási, László Lakosi

Objective

Illicit trafficking of nuclear and other radioactive material is a subject of serious concern due to the radiological hazard to the public and the environment, as well as the security risks associated with nuclear and other radioactive material out of regulatory control. The availability of tools to prevent and respond to incidents of nuclear smuggling resulted in the development of a new field known as nuclear forensics which can assist in law enforcement investigations and nuclear security assessments associated with a nuclear security event. Through nuclear forensic analysis, information on the history and on the potential origin of intercepted nuclear material can be obtained by investigating the characteristic parameters of such material. Analysis of data characteristics (e.g. isotopic composition of uranium, morphology features, age or production date, impurities, etc.) of this material provides insight to the industrial processes used in their manufacture. Despite the availability of these data characteristics, the experiences indicate that it is difficult to determine the origin and history of unknown samples without comparison with data from known samples to facilitate the identification. To increase confidence in determining the origin and history of questioned materials, analysis of numerous comparison samples from the same and also different confiscations and batches with different origin is necessary. Another necessary element is the development by the States a National Nuclear Forensics Library to aid on national level comparison of material out of regulatory control.

Methods

In the frame of the project, investigation of the most important and informative/characteristic parameters (signatures) for nuclear forensics purposes was planned and to find novel methods to fully characterize the seized materials originated from Hungarian confiscations. As a first step, a comprehensive review of relevant publications was performed to include a search for promising new methods in other scientific disciplines. During the next step, analysis of confiscated materials was started using different techniques, such as optical microscopy, gamma-spectrometry and mass spectrometry for creation of a relatively large and informative database.

Results

During this work several nuclear samples (mainly uranium oxide pellets) originated from Hungarian confiscations were analyzed. Hereinafter an example of the results is showed as a part of the future database and national nuclear forensic library.

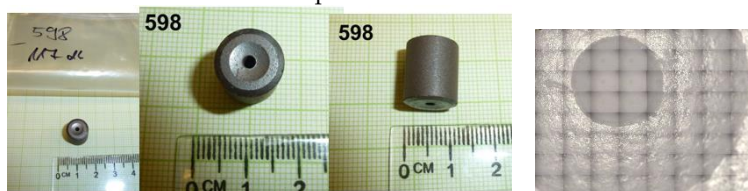


Figure 1: Physical parameters of a uranium-oxide pellet (No. 598) and a microscopic picture

In Table 1 the results of the isotopic composition of the uranium-oxide pellet (No. 598) analyzed by mass spectrometry can be seen. There is also a reference value from former gamma-spectrometric measurement. The good agreement between the analyzed and the reference value is obvious.

Table 1: Isotopic composition of a uranium-oxide pellet (No. 598) and the reference value for comparison

Sample ID	U-234	U-235	U-236	U-238
5	0,0153	1,99	0,0068	97,9821
REFERENCE		1,98		

Remaining work

Full characterization of the confiscated materials using further different techniques as scanning electron microscopy or X-ray diffraction technique needs more years. Therefore, this project is an ongoing work together with IAEA in a Coordinated Research Project which is running until 2015. The extended analysis of seized materials will yield both conventional parameters (isotope ratios, enrichment, production date, morphology, surface, structure, physical parameters, impurities, reprocessing, etc.) as well as new parameters obtained during the method developments or adaptations. Finally, this database will be compiled relevant to the development of a national nuclear forensics library.

Related publication

É. Kovács-Széles, I. Almási: *Establishment of national nuclear forensic library by analysis of confiscated materials*, OAH MMT research report, OAH-NBI-ABA-19/13-M (2013) [in Hungarian]

DEVELOPMENT OF NEW MATERIALS AND MEASURING METHODS IN LUMINESCENCE DOSIMETRY

András Kelemen, Dávid Mesterházy

Objective

Luminescent methods: thermoluminescence (TL) and optically stimulated luminescence (OSL) are well known and widely used procedures in several fields of dosimetry. However, the improvement of their capability and the aim of their application in new situations need continuous development of the measuring methods and elaborating and synthesizing new detector materials.

Radiation therapy is an important method mainly in treatment of various tumors. The precise determination of the dose applied during the treatment is a basic and important task in order to maximize the effect and at the same time to minimize the risk of the intervention. That is why production of new tissue-equivalent TL and OSL detector materials are so important in clinical dosimetry. The family of the differently doped lithium tetraborates (LTB) means materials owing tissue equivalency and having favorable luminescence properties. Synthesizing new material, its characterization from optical and dosimetric point of view and then new synthesis with changed composition based on the results, these are the steps of the material development.

Luminescent methods have proven their capabilities in dose estimation after unexpected events causing uncontrolled ionizing radiation. Our aim is to find materials which are suitable for accidental detectors, and characterize them from dosimetric point of view.

Methods

Differently doped LTB materials (LTB:Cu, LTB:Mn, LTB:Ag and LTB:Ag, Eu), single- and poly-crystals were grown by the Czochralski method at the Institute of Surface Chemistry in Ukraine. The new materials were then subject to optical and luminescent investigations. Photoluminescence, radioluminescence, optical absorption measurements were applied to both unirradiated and irradiated samples. TL properties of the materials were also investigated thoroughly.

Common materials that frequently occur in the natural and human environment were chosen for testing their suitability for retrospective dosimetry. Limestone, dolomite and rock-salt (common salt, kitchen-salt) were the candidates. TL properties of the chosen materials, with special respect to the fading properties were investigated.

Results

Thermoluminescence dose characteristic and kinetic parameters of the newly developed $\text{Li}_2\text{B}_4\text{O}_7:\text{Mn}$ single crystal were investigated. It shows good TL properties for use as a TL detector. It has a simple and well separated glow curve which is composed of 105 and 220 °C peaks although 105 °C peak rapidly fades, in hours. The dosimeter shows good linearity in the 33 mGy to 60 Gy dose range. There is no significant variation in 15 measurement cycles, revealing that reproducibility of TL is also excellent. It shows low fading in 10 days, when it was stored in dark at room temperature. TL sensitivity $\text{Li}_2\text{B}_4\text{O}_7:\text{Mn}$ was found to be considerably less than that of TLD-100, which makes it suitable for high dose environment such as radiotherapy. The kinetic parameters of the main peak were calculated using the various heating rates method. The activation energy and frequency factor were found as 1.21 eV and $3.75 \times 10^{11} \text{ s}^{-1}$, respectively.

The first results on the double-doped LTB: Ag, Eu revealed that:

- high-dose irradiation of LTB:Ag causes the reduction of Ag^+ ions to Ag^0 with further aggregation to $n\text{Ag}^0$. Radiation induced Ag-nanoparticles formation is evidenced by the appearance of wide (300-400 nm) surface plasmon resonance (SPR) band in the optical absorption spectrum.
- radiation induced Ag^0 -nanoparticles in LTB: Ag, Eu samples lead to enhanced Eu^{3+} phosphorescence, while irradiation of mono doped LTB:Eu causes decreasing of the Eu^{3+} phosphorescence intensity.

Common rock-salt (NaCl) shows nice glow curves in the dose region under 10 Gy. TL peaks occur at about 100 °C, 240 °C and 280 °C. Glow curves can be evaluated even at 50 mGy dose. The 100 °C peak fades rapidly while the two others make possible the posterior dose estimation. Dolomite needs higher dose irradiation for showing TL response; it can be used as accidental dosimeter in the 1-30 Gy region. Limestone shows TL only in the several kGy region. Its glow curve shows a complex structure that needs further investigations. With these features, limestone can be an interesting material in geological dating.

Remaining work

Based on the results of the investigations on LTB materials, synthesis of new samples with modified composition are planned. The detailed dosimetric characterization of some of the existing samples is also to be completed.

Fading properties in case of various circumstances (temperature, humidity) of both the natural material (salt, dolomite etc.) and the industrially produced objects (SMD resistors) need further investigations.

Related publications

- A. Kelemen, I. Kása, P. Mell, D. Mesterházy: *Effect of the Cu co-activator on the charge-carrier trapping efficiency in $\text{CaSO}_4:\text{Tm,Cu}$* , Radiation Measurements, **56**, 232 (2013)
- E. Ekdal, T. Karalı, A. Kelemen, M. Ignatovych, V. Holovey, C. Harmansah: *Thermoluminescence characteristics of $\text{Li}_2\text{B}_4\text{O}_7$ single crystal dosimeters doped with Mn*, Radiation Physics and Chemistry, **96**, 201 (2014)
- E. Ekdal, T. Karalı, A. Kelemen, V. Holovey, M. Ignatovych: *Evaluation of kinetic parameters of $\text{Li}_2\text{B}_4\text{O}_7:\text{Mn}$ single crystal*, Journal of Alloys and Compounds, **588**, 413 (2014)



V. RENEWABLES AND FOSSIL ENERGY PRODUCTION



STUDYING SMARTGRID: INTELLIGENT ELECTRICITY NETWORK

János Sebestyén Jánosy

Objective

It became necessary for MTA EK to look around and start studying energy-related topics we did not deal with earlier. Smartgrid – a well established name for intelligent electricity distributing networks – is a very challenging topic. A decision was taken that a study has to be prepared as a starting point describing the actual situation worldwide and the most promising methodologies and experiments.

Methods

At the beginning, data and publications were collected from the Internet. There are thousands and thousands of them available. First, a selection method had to be introduced; finally a top-down approach has been applied. First the standards and terminology established by the authorities of the US Government and the EU were studied. These standards usually refer to several studies ordered by the authorities; next, there were links to different international projects, referring to conference proceedings, journals etc. containing the most advanced and detailed information available.

Results

There are two ways to compose smart grids. The first one looks a little easier: it can be used in undeveloped rural territories of some countries where no power grids exist – like parts of Australia, Argentina, Indonesia, etc. With the financial and methodical help of the government, small local villages can establish small but intelligent networks - so called mini- or microgrids - containing traditional (e.g. diesel) and renewable (windmill, photovoltaic, biogas etc.) energy sources, some kind of energy storage and intelligent computer-optimized consumption. Long-distance power lines are too expensive to establish for these communities.

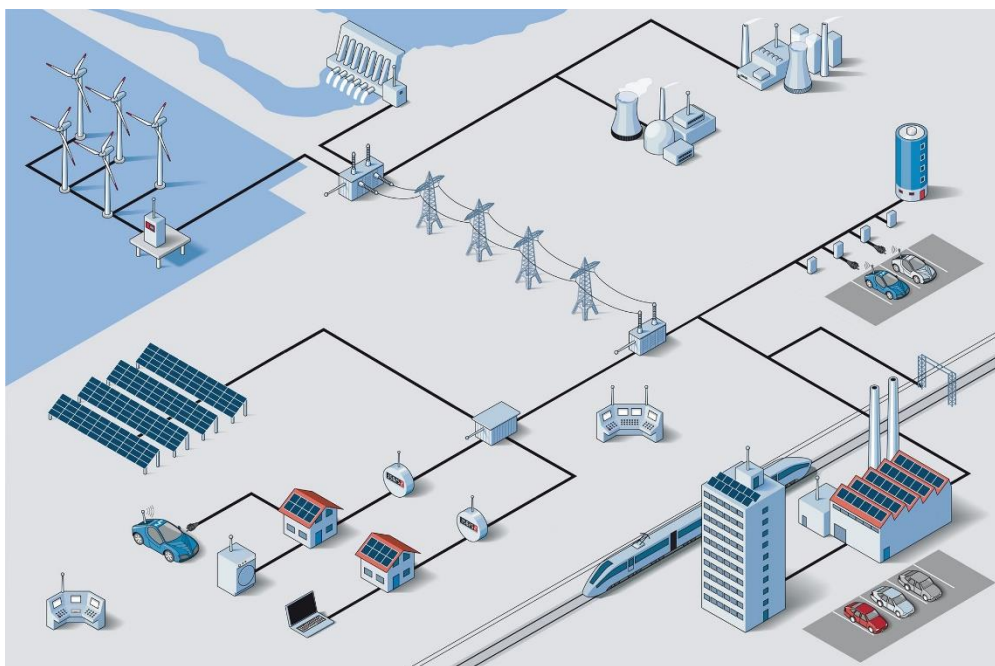


Figure 1: The Smart Grid Concept

The second method can be used for existing old power grids as well. As a beginning step, all meters should be replaced by intelligent new ones, calculating the consumption cost taking into account the actual tariffs, changing rapidly and continuously according to the momentary grid load. It becomes sensible for the customers to optimize the power-sensitive activities. Later on, mini- and microgrids can be formed for villages, suburbs etc. with local energy production, storage and consumption optimized to connect the state grid with minimal operational costs.

Remaining work

As the prepared study shows [1], the problems of the smart grids and minigrids are mostly practical, to be solved by technical, engineering methods, not fully by scientific research. There are some problems however, where scientific approach would be very useful: advanced control strategies, optimization and stability issues of distributed, diverse and redundant smart power grids and minigrids, mathematical modeling of them, including verification and validation, simulation studies and evaluation of the results. (Nowadays everything starts with simulation.) As these issues are only parts of the mostly technical problems, these particular scientific activities probably should be exercised in the framework of large international projects financed by the EU or by some governmental institutions.

Related publication

[1] János Sebestyén Jánosy: *Smart Grids*. Study prepared in Hungarian for the MTA EK researchers (32 pages).

CO₂ GEOLOGICAL STORAGE: ENSURING LONG-TERM SAFETY

Zsuzsanna Szabó, Árpád Farkas, Dániel Breitner, Margit Fábián, Szabina Török

Objective

To reduce greenhouse gas emission, carbon capture and storage (CCS) technology is considered to be necessary. The Hungarian regulation obligates the Geological and Geophysical Institute of Hungary (MFGI) to collect and regularly update all geological complexes that are potentially suitable for CO₂ geological storage in Hungary. Based on the available information, the most abundant potential storage formations are saline aquifers of the Great Hungarian Plain (SE-Hungary), with sandstone reservoir and clayey caprock. It is known that geochemical reactions are taking place in the caprock for the effect of injected CO₂. In long-term, these can affect the caprock integrity via porosity, permeability and geomechanical changes. Studies proved that CO₂ is present in the caprock both in dissolved (CO₂-saturated pore water) and free (H₂O-saturated CO₂ or wet CO₂) form. So far, the very few experimental studies are focused on CO₂-saturated water. In this work we study both the effect of CO₂-saturated water and the H₂O-saturated CO₂ on potential Hungarian caprock samples via laboratory experiments. Beside this, we also contributed to the study of sandstone samples from a potential CO₂ reservoir formation in Spain [1] and performed computational fluid dynamics (CFD) simulations of CO₂ behavior in saline aquifer by the available FLUENT code in order to analyze the ability of the code for such purpose.

Methods

In collaboration with MFGI, two potential caprock samples originating from different boreholes of the Great Hungarian Plain were investigated. These have been micronized to increase their specific surface area (SSA). The one month long laboratory experiments were carried out in simplified artificial pore water, CO₂-saturated pore water and H₂O-saturated CO₂ at the Department of Geosciences, University of Oslo. The CO₂ treatments were going on at 180 °C temperature and 130 bar pressure. The samples before and after treatments and in different environments are compared. The SSA value is estimated based on laser grain size analysis results. X-ray diffraction (XRD) analysis on bulk samples and on oriented clay preparations has been carried out, as well as scanning electron microscopy (SEM) was applied. Artificial pore water samples taken during and after experiments were analyzed by Ion-Chromatography and UV/VIS Colorimetry to determine their Na-, K-, Mg- and Ca-ion concentration and silicate content. The potential Spanish reservoir rock samples originated from different sedimentary basins in Spain. The mineralogy and texture were studied by optical microscopy and SEM before and after a close-well injection simulation [1]. The volume of fluid (VOF) two phase model of FLUENT code has been applied to model the evolution of CO₂ after its injection in the aquifer. User defined functions have also been implemented to adapt the code to the special case of CO₂-salt-water system.

Results

The XRD results of potential Hungarian caprock samples show the most significant presence of quartz and microcline, and that the muscovite and illite are also important phases. Minor amounts of albite, calcite and kaolinite were also identified. Differences were found in the presence of chlorite, smectite, dolomite and ankerite [2]. After the experiments the SSA is changing with a maximum of 10% due to the dissolution of the finest grains. In the artificial pore water compositions the increase of Na-, K- and Mg-ion concentration and the decrease of Ca-ion concentration was observed for the effect of CO₂ [2]. The values of dissolved silicate content are varying. The comparison of XRD analyzed mineral compositions before and after experiments refers to mineral dissolution and reprecipitation. All results certainly show that the CO₂ dissolved in the artificial pore water has significant effect on the geochemical processes even in such a short time-scale. The small amounts of samples treated in the H₂O-saturated CO₂ seem to have elevated reactivity matching literature indications. Regarding the Spanish sandstone samples, the results indicate the intergranular clay matrix detachment and partial removal from the reservoir rock in the close-well environment for the effect of CO₂ injection [1]. CFD test calculations revealed that in contrast to the codes developed for and focusing on the specific problems of CCS (e.g. THOUGHREACT), FLUENT is not suitable to model the long-term processes, especially trapping of CO₂ by different minerals. However, it can capture some short-term aspects of CO₂ fate after its injection into the deep geological formations.

Remaining work

Further evaluation of the Hungarian caprock XRD and SEM results is needed together with geochemical modeling (PHREEQC) of determined mineral compositions under experimental conditions.

Related publications

- [1] E. Berrezueta, L. González-Menéndez, D. Breitner and L. Luquot: *Pore system changes during experimental CO₂ injection into detritic rocks: Studies of potential storage rocks from some sedimentary basins of Spain*, International Journal of Greenhouse Gas Control 17, 411-422 (2013)
- [2] Zs. Szabó and Sz. Török: *The September-December 2013 contribution of Centre for Energy Research to the research of CO₂ geological storage (in Hungarian)*, Report to the Geological and Geophysical Institute of Hungary, MFGI (2013)

AN ECONOMICAL APPROACH OF THE INTEGRATION OF WIND AND SOLAR PHOTOVOLTAIC GENERATION

Endre Börösök, Bálint Hartmann, Veronika Oláhné Groma, Szabina Török

Objective

Current financing of renewable based electricity generation is unsustainable in the long run. The economic burden, created by the present rules of the obligatory electricity take over, is a significant obstacle of the utilisation of the renewable potential of the country. The present tariff structure allows a much shorter return of the investment, however, investors may undertake a longer return period in exchange for a simpler licensing process. The goal of our work is to elaborate a dynamic tariff structure, based on spot (day-ahead) electricity prices, which would preserve the effect to encourage investments, and would decrease the public burden at the same time. The authors aim to estimate the potential benefits of using energy storage units and meteorological data as well. Electricity generation data are to be obtained from the 100 kW solar photovoltaic system of Tesco Megapark and the cumulative wind generation data, recorded by MAVIR (MAVIR Hungarian Independent Transmission Operator Company Ltd.). Spot prices are aimed to be modelled using prices of HUPX (Hungarian Power Exchange).

Methods

Processing of the electricity generation data was performed using a 15-minute temporal resolution, since scheduling of renewable power plants is currently performed in such time resolution. Using these data, production of the plants was normalised to the built-in capacity, creating characteristic production curves for both the solar photovoltaic and the wind units. Both units were assumed to have a nominal power of 500 kW. Potential income of these plants was calculated using two different tariff structures; first the current electricity feed-in tariffs were used, then spot pricing was implemented. A transformation of the spot prices was introduced in all cases when spot prices were above the yearly average, thus ensuring that the estimated income of the plant was equal for both tariff structures. The calculated factor was 8.83 in case of solar photovoltaics and 6.84 in case of wind generation. The second phase of the examinations focused on the utilisation of a Li-ion battery, with a nominal energy set between 0.1 and 1 MWh. Four assumptions were made concerning this battery: only renewable energy is used to charge the battery, forecasting error of renewable is assumed 10%, one discharge (lasting at least one hour) was allowed every day, and charge-discharge power was set as 50% of nominal power. Using these assumptions, return of the investment was calculated for the battery using cost-benefit analysis.

Results

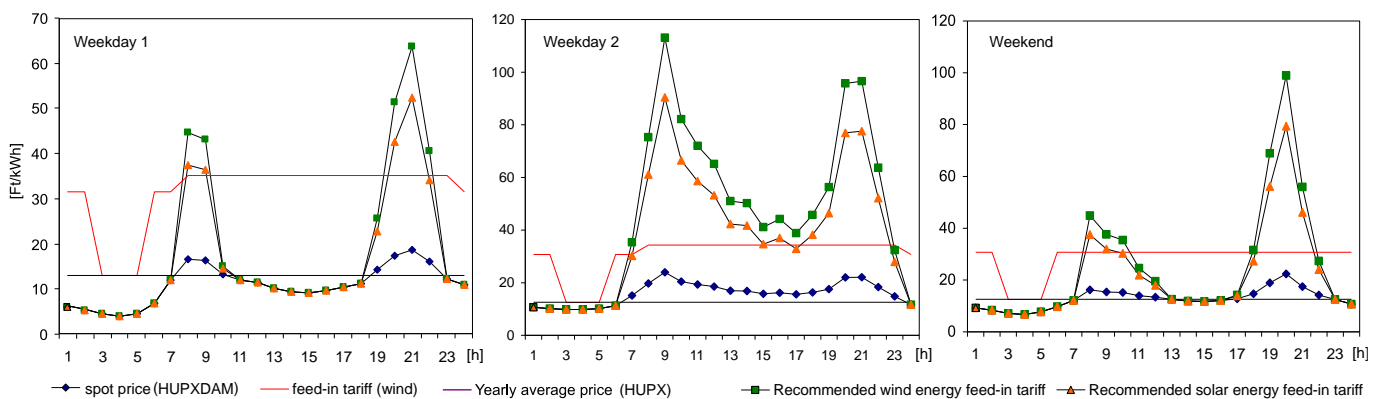


Figure 1: Resulting prices according to the proposed new tariff system

Cost-benefit analysis results have shown that by using energy storage, payback time of the storage is significantly shorter (2-2.5 years), thus the multiplier of spot prices may be decreased, and the estimated income of the investors would still be equal for both tariff structures. It also has to be noticed that current spot prices do not facilitate such investments, since payback time is over 10 years. In connection with our study, a report was prepared on the renewable energy purpose reutilisation of a brownfield site, which focused on the technological and economical potentials of the site.

Remaining work

The experience gathered during the in-depth examination will be utilised in future work.

Related publications

- [1] B. Hartmann, Sz. Török, E. Börösök, V. Oláhné Groma: *Complex Method of Energy Purpose Redevelopment of Brownfield Sites*, Journal of Cleaner Production – submitted
- [2] B. Hartmann, Sz. Török, E. Börösök, V. Oláhné Groma: *Energy Purpose Redevelopment of Brownfield Sites – an Examination and Evaluation Method*, World Energy Engineering Congress (WEEC 2014) – submitted

NUMERICAL SIMULATION OF AEROSOL DRUG DELIVERY TO THE HUMAN AIRWAYS

Árpád Farkas, Imre Balásházy, Ágnes Jókay, Péter Fűri

Objective

The primary objective of the work was to quantify the transport and airway deposition of inhaled therapeutic aerosols. A further aim was to reconstruct the 3D geometry of airways from 2D slices acquired by medical imaging techniques.

Methods

The Stochastic Lung Deposition Model has been adapted to the case of medical aerosols. This task basically implied the development of physical models of particle evaporation and hygroscopicity, and their inclusion into the code. In addition, the improvement of some of the existing algorithms of the software package was also necessary. Data handling of the code and the configuration of input and output data have also been improved. The code has been applied to quantify the distribution of aerosol deposition along the airways for both spray and powder inhalation drugs commercialized on the domestic market, like Foster, Symbicort and Seretide. For this purpose, realistic lung function curves acquired from healthy volunteers and asthmatic patients were used. These curves describe the breathing patterns during the delivery of drugs.

Concomitantly to the above work, three dimensional geometries of the upper and central human airways were reconstructed from planar computer tomography images. The digital geometries were handed over to our consortium partners for 3D printing and measurements in the printed - out hollow physical replicas. These measurements are necessary for the validation of our numerical simulations.

Results

Our computations revealed that currently recommended breathing modes may not be appropriate for some aerosol drugs, especially for those with large particle diameter ($> 4 \mu\text{m}$). However, a personalized breathing mode ensuring high deposition on the targeted area and low deposition elsewhere could be determined by taking into account individual lung function data and applying our numerical models. Based on the simulations, the optimization of breathing parameters and particle size can lead to a more efficient treatment and less side effects.

Segmentation of 2D medical images yielded three-dimensional upper and central airway geometries, which were printed out by a 3D printer. Reconstructed and printed - out models of a segment of the bronchial tree are depicted in Fig. 1.



Figure 1: Reconstructed digital (left side) and physical, printed out, (right side) geometries of the central airways

Remaining work

Acquisition of data concerning the inhalers, aerosol drugs and drug receptor distributions, reconstruction of diseased airways and aerosol deposition computations for asthmatic patients are foreseen for the next period. Comparison of simulated and measured deposition distributions and optimization of drug delivery will also be performed.

Related publications

- [1] A. Kerekes, Á. Farkas, I. Balásházy and A. Horváth: *Experimental measurement and numerical simulation of airway deposition of the inhaled aerosol drugs*, *Medicina Thoracalis* **66**, 11-20 (2013), [In Hungarian].
- [2] Á. Jókay, Á. Farkas, I. Balásházy and P. Fűri: *Optimization of aerosol drug deposition within the airways by numerical techniques*, XIth. Hungarian Aerosol Conference Debrecen, Book of Abstracts 44-45 (2013), [In Hungarian].

INITIAL DECOMMISSIONING PLAN OF THE EUROPEAN SPALLATION SOURCE

Péter Zagyoai, Szabina Török, Zsófia Kókai

Objective

Several approaches of the preliminary decommissioning plan (DP) of the European Spallation Source (ESS) were elaborated in the previous periods of its design process. The DP shall be in compliance both with authority requirements defined for non-nuclear research facilities in the appropriate Swedish legislation and with current international (IAEA, EU) guidance. During the "Target Design Review" (TDR) phase in 2012 - 2013 an initial decommissioning plan (IDP) had to be submitted to the Swedish authority SSM. The IDP [1] was compiled in the frame of TDR Work Package #11 by these authors.

Methods

According to international guidance, a graded approach should be applied to the development of the decommissioning plan. The type of information and the level of detail shall be commensurate with the type and status of the facility and the identified health and other hazards associated with the decommissioning procedure. As the envisaged period for the decommissioning of the ESS facility is 2065 - 70 after an expected 40 years of lifetime, the form of an initial decommissioning plan (IDP) seemed quite satisfactory at present. Technical and financial details do not have to be defined in the IDP since many factors are likely to change substantially over the lifetime period of the facility.

Results

The IDP comprises the following main chapters: Decommissioning strategy, Waste inventory and management, Licensing conditions, Staffing and training, Organization and control, Engineering aspects for efficient dismantling and disposal in the design phase, Cost estimation, Emergency management, Radiation and physical protection, Monitoring, Specific problems of ESS materials (graphite, beryllium). As a result of a detailed analysis, the "immediate dismantling" (ID) option was selected as the primary strategy. According to the widely accepted IAEA guidance Safety Standard Series GSG-1 (2009) the

characterization of radioactive waste is recommended to be based on the "Waste Index" or "Clearance Index" $WI = \sum_i \frac{c_{A,i}}{CL_i}$

where $c_{A,i}$ represents the activity concentration of the i -th component in the actual waste stream (Bq/g for mass, Bq/cm² for surface contamination), CL_i is the respective clearance level for bulk (>1 t) material. Clearance levels are applied in Swedish regulatory control but some of the neutron-poor activation products of the proton-driven spallation source were not available even in exhaustive compilations so these values had to be deduced by the authors.

Waste indices were determined for each eligible component of the ESS structure: accelerator, target and assemblies, moderator, reflector, steel monolith, neutron guides and beam dumps etc. Activation was calculated with appropriately set versions of FLUKA and MCNPX codes. The following table summarizes the calculated WI values for 1 and 150 years after shutdown. The waste is clearable if $WI < 1$, it is considered as low level waste for $1 < WI < 1000$; intermediate level waste falls between $10^3 < WI < 10^6$ and high level waste (HLW) is considered if $WI > 10^6$.

Structural element	WI (1 year from shutdown)	WI (150 years from shutdown)
Tungsten target	4.10 ⁷	9.10 ⁵
Be reflector	1.10 ⁸	1.10 ⁸
Concrete shielding of accelerator	40	<1 in 50 years
Soil around accelerator shielding	3	<1 in 20 years

Table 1: Waste indices of various ESS materials

The characteristic radionuclide responsible for the high WI value of the Be reflector is ¹⁴C. The most important long-lived radionuclides of the W target are generally rare earth metal radionuclides like ¹⁴⁸Gd or ¹⁵⁸Tb. The total amount of HLW (considering conservatively that the tungsten targets will be classified as HLW) is only 35 t (3.3 m³) for the whole lifetime of the ESS facility.

Remaining work

The activation calculations of all important ESS components constitute the PhD task of Zs. Kókai, she spends two years of her research term at ESS Lund. As construction works of ESS commence in 2015, renewal of IDP is also envisaged with special respect to the significance of decommissioning requirements in engineering design and implementation. Hopefully our activities will be covered by the future Hungarian in-kind contribution agreement.

Related publication

- [1] http://www.stralsakerhetsmyndigheten.se/Global/ESS/ESS-ansökan/Kompletteringar/SSM2012-131_130724_3.pdf

ENVIRONMENTAL ECONOMIC EVALUATION OF ELECTRICITY AND HEAT GENERATION TECHNOLOGIES FOR REVISION OF SCENARIOS

Endre Börcsök, Veronika Oláhné Groma, Bálint Hartmann, János Osán, Szabina Török

Objective

At present days, 97.75% of Hungarian electricity is produced by thermal power plants (nuclear and fossil), and no significant change is expected in the long run, thus generation of heat and electricity is strongly connected, furthermore these technologies usually utilise the same fuels for both purpose. Because of the effect of the economical crisis on the Hungarian energy sector, the heat and electricity generation scenarios published in the white paper "Energy Strategy 2030" of the Ministry of National Development need to be revised. The revision of the scenarios was aided by multi-criteria decision analysis (MCDA) ranking of all potential renewable technologies and their respective fuels. First the results of Hungarian initiatives aiming at the increase of the share of renewables were examined, then by analysis of technological and economical trends of recent years, new scenarios were set to reach the targets set by adopting the 2009/28/EC directive.

Methods

Five main criteria were considered in the MCDA evaluation: economy, environment, climate, job creation and innovation. Properly quantified indicators and expert weighting were assigned to these five criteria. The aspect of economy included investment and operation and maintenance costs; Hungarian and international values were compared, and learning curves were created for each technology to show their future potential as well. The aspect of environment and climate included the examination of life-cycle health effects and greenhouse-gas emissions, respectively. The effect on job creation was considered as the number of new jobs normalized to the amount of energy generation during the operation of the power plant. Finally, the number of related patents was chosen as the measure of innovation. When examining the electricity and heating/cooling sectors, regional potentials (wind, hydro, solar, forestry and agricultural by-products, municipal waste, geothermal energy) and demands (heat demand of family houses, apartment houses and blocks of flats) were assessed. A dynamic MCDA ranking of the potentials and demands was introduced, in order to enforce market saturation and potential depletion during the optimisation. Based on the MCDA results, regional renewable quotas and shares were calculated.

Results

Based on our LCOE (average lifetime levelled cost of electricity generation) calculations, the technologies with the lowest costs besides biogas based CHP plants are solar thermal and geothermal heating (9-11 HUF/kWh), biomass combustion (15 HUF/kWh) and wind power (19 HUF/kWh). More expensive alternatives are hydro power (25 HUF/kWh) and solar photovoltaics (35 HUF/kWh). Hydro and wind power generation was found to have the lowest health and climate effects. Most jobs are expected to be created by low energy density solar PV due to the high labour demand of the installation. Solar collector and wind energy were found to be the most innovative. The resulting MCDA ranking (Fig. 1) shows preference for solar collector, biogas, wind and hydro, however these alternatives have limited potential in Hungary. For this reason, larger portion of renewable energy consumption have to be based on biomass. Because of the complex expectations of the future energy supply, the electricity and heat generation scenarios have to be carefully balanced.

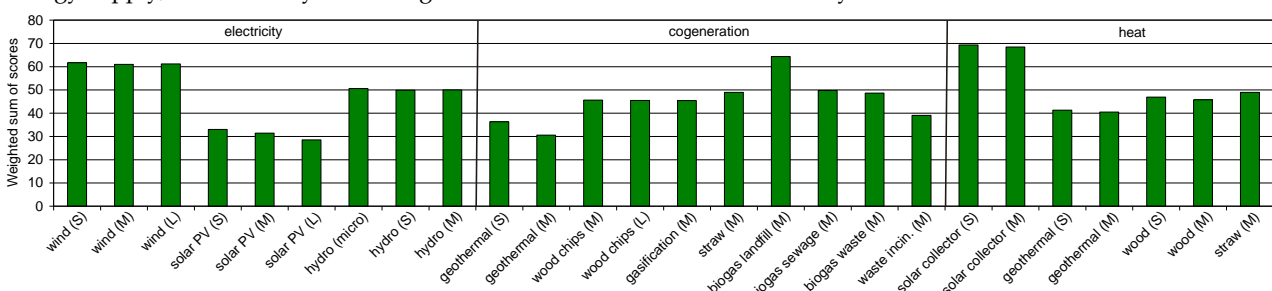


Figure 1: Result of MCDA for heat and electricity generation technologies (S: small, M: medium, L: large facilities)

Remaining work

Finalization and evaluation of the revised scenarios for renewable electricity and heat generation.

Related publications

- [1] E. Börcsök, J. Osán, Sz. Török: *Decisions in energy sector with stakeholder involvement using multi-criteria decision analysis*, European Energy Conference, Budapest, 2013.
- [2] E. Börcsök, B. Hartmann, I. Kitzinger, V. Oláhné Groma, J. Osán, Á. Szabó, A. Talamon, Á. Török, Sz. Török: *Comparison of renewable energy generation technologies based on economical and environmental criteria*, Report to the Ministry of National Development, 2013. [in Hungarian]
- [3] B. Hartmann, Sz. Török, J. Osán, A. Talamon, E. Börcsök, V. Oláhné Groma: *Complex Evaluation of renewable energy sources*, World Energy Engineering Congress (WEEC 2014) - submitted

CH₄ CONVERSION VIA DRY REFORMING: CATALYST DEVELOPMENT AND REACTION STUDIES

Anita Horváth, Norina Nagy, Miklós Németh, László Borkó, Dávid Sránkó, Tamás Ollár, Zoltán Schay

Objective

Highly active nanostructured catalyst systems were to be developed or investigated in two related catalytic processes aiming at methane (biogas) conversion. The two research topics were as follows: i) dry reforming of methane with CO₂ to yield CO and H₂ mixture on Ni or Pt/ZrO₂ catalysts with special attention to the issue of undesired surface coke formation and ii) conversion of methane with N₂O in the presence or absence of CO traces on multifunctional microporous M/Ga/H-ZSM-5 catalysts. Short literature surveys on some catalysis-related issues of non-fossil H₂ production routes were planned as well.

Methods

For the preparation of catalyst samples, traditional impregnation or newly developed liquid phase sol reduction methods were applied. For the structural and surface characterization of the catalysts, temperature programmed oxidation or reduction, X-ray diffraction and normal or high resolution transmission electron microscopy (TEM) were carried out. Catalytic reactions (dry reforming: CO₂+CH₄=2CO+2H₂; dinitrogen monoxide conversion with methane and/or carbon monoxide: 5N₂O+CH₄+CO=5N₂+2CO₂+2H₂O) were carried out under different conditions (see the related publications for details). Subatmospheric circulation system with isotope tracing ability (¹³CO₂ or ¹³CH₄) was applied to study the reaction mechanism and the coke formation routes during dry reforming of methane on ZrO₂-supported samples.

Results

As for dry reforming, the main results on Au-modified Ni catalysts were published. Next, ZrO₂-supported Ni, Pt and NiPt catalysts were prepared, which after catalyst pretreatment at 600°C (calcination, reduction) contained metal particles of around 1-15 nm in size. The NiPt bimetallic sample was a true alloy with about 10-30 atomic% Pt. During catalyst screening in flow system at 1 atm with 30%CO₂+69%CH₄ mixture, Ni containing samples deactivated more and produced the most deposited carbon, impregnated Pt sample lost some of its activity due to sintering, while Pt sample prepared by sol method did not deactivate at all. The bimetallic NiPt sample performed as a real combination of Ni and Pt: it showed higher initial activity and deactivation tendency (resembling Ni), produced intermediate amount of surface carbon but gave the same H₂/CO ratio as the pure Pt samples. Catalytic results in circulation system at ~50 mbar pressure using isotope labeled reactants revealed significant back reaction at as low as 450°C (proving the scrambling of surface carbon species). The measurements determined that CO originating from CO₂ reactant is formed and gasified first. The thermodesorption studies after reaction showed that coked catalyst desorbed CO and H₂, while coke-free Pt samples produced only CO₂ and H₂ desorption peaks.

Investigations on N₂O decomposition or reduction by methane were carried out on metal-modified Ga/H-ZSM-5 samples. Studies focused on the redox and acidic properties of the catalysts suggested that low CO adsorption capacity and acidic sites with medium strength could be the best combination for successful conversion of N₂O and CO. The presence of CO caused the irreversible and reversible deactivation of Fe and Pt samples, respectively, while Ir sample lost only some of its original activity. When the reaction mixture contained CH₄ as well, a complex redox mechanism was suggested to prevail. Due to the presence of CO, instead of methoxy species that are the active intermediates in N₂O conversion, surface formate (ZOOCH) species may be formed and so deactivation happens.

Short literature search on the thermochemical sulfur-iodine (SI) cycle to produce H₂ from water was done. After the exothermic SO₂ gas-absorbing Bunsen reaction (I₂ + SO₂ + 2H₂O = 2HI + H₂SO₄), the separated HI and H₂SO₄ solutions are need to be decomposed to produce H₂ from HI and O₂ from H₂SO₄ at high temperature. With regard to heterogeneous catalytic decomposition of HI, noble metal catalysts supported on Ce-Zr-oxides could be employed. The other literature screening was concerned about H₂ production from electrolytic water splitting. The hydrogen evolution reaction (HER) can be enhanced by lowering the reaction overpotential with Pt catalyst. Since Pt is too expensive, highly dispersed nanostructured MoS₂ on graphene or graphite looks an ideal protocol to lower the activation potential. Mechanism studies of HER reaction at the MoS₂ modified electrodes could offer other new areas of research.

Related publications

- [1] A. Horváth, L. Guzzi, N. Nagy, G. Sáfrán, V. La Parola, L. F. Liotta, G. Pantaleo, A. M. Venezia: *The effect of preparation on the structure of Au-modified Ni/MgAl₂O₄ catalysts and its methane dry reforming activity*, 10th Natural Gas Conversion Symposium, Doha, Qatar, 2013.03.02-2013.03.07.
- [2] A. Horváth, M. L. Németh, N. Nagy, Z. Schay, Zs. Kasztovszky, I. Sajó, G. Sáfrán: *Carbon dioxide reforming of methane on nanostructured nickel-based catalysts*, 3rd European Energy Conference, Budapest, Hungary, 2013.10.27-2013.10.30.
- [3] A. Horváth, L. Guzzi, A. Kocsonya, G. Sáfrán, V. La Parola, L. F. Liotta, G. Pantaleo, A. M. Venezia: *Sol-derived AuNi/MgAl₂O₄ catalysts: Formation, structure and activity in dry reforming of methane*, Appl. Catal. A: Gen. 468, 250 (2013)

POSSIBILITIES OF THE UTILISATION OF RENEWABLE AND FOSSIL ENERGY SOURCES AT THE SITE OF TISZA II POWER PLANT

Endre Börcsök, Bálint Hartmann, Veronika Oláhné Groma, Ábel Szabó, Szabina Török

Objective

In recent years a new approach has appeared that aims at the energy purpose redevelopment of brownfield sites, which is usually carried out by deploying renewable energy technologies. Several advantages of such redevelopment can be found, for example the proximity to both utility grids and consumers, the utilisation of existing infrastructure, the availability of lands with few competing investments, etc. It has also to be noted that several financial incentives are available for developments aiming at the utilisation of renewable energy sources. The owners of a gas power plant (Tisza II, temporarily out of operation) asked for a detailed investigation on the possibilities of the company to redevelop the power plant site by installing new renewable and/or fossil units.

Methods

The first step of the examination focused on the assessment of baseline conditions at the brownfield site. This included the collection of available information about the history of the site, which was both written (maps, past operating licenses, past operation profiles, etc.) and oral (operational experience, field knowledge, etc.). A visit was also held at the site to clarify all issues and misunderstandings. The second phase of the first step was to gather relevant information on the area and the region of the brownfield site, which included the examination of present states and future options as well. Such information included climatic conditions, land cover and land use, and the state of existing infrastructure. Local climatic conditions were analysed and compared to national characteristics. Land cover and land use data contained indirect information on the expedient redevelopment of the brownfield; for example, biomass potential of the surrounding region could be estimated. Finally, data on the existing infrastructure included the aspects of transportation (railroads, roads, and waterways), energy utilities (transmission and distribution lines, hydrocarbon pipelines), competing and cooperating industry, etc. were analysed.

The second step of the examination focused on the potential of all energy sources that can be utilised at the redevelopment site. Of course, priorities can be given to certain technologies (for example renewable or non-intermittent sources), but the authors' view is that a comprehensive examination is necessary in almost all of the cases. The second step had three phases, which are more or less independent from each other. The first phase was to determine the amount of available "fuel", be it renewable (wind speed characteristics, solar irradiation, geothermal heat) or be it combustible (biomass, biogas, coal, waste). If "fuel" supply is not sufficient for this capacity, the certain technology has to be dismissed. The second phase was the estimation of the electricity and heat generation potential, according to the various capacities and technologies that the investor may select. Such analysis was carried out by either using data of existing power plants to derive the results or by approximations and performing simplified calculations using the available baseline conditions.

The third step of the method was the calculation of space requirements. Since brownfield developments usually have space constraints, detailed analysis has to be carried out to find the potential (and preferable) sites for the newly installed units. For example, existing buildings may be used to mount solar panels on them, but only if the roofs have southern orientation. Space requirements represent a less significant issue in case the existing infrastructure is being converted. Beside the above listed three phases, the examination may also provide space for innovative ideas, for example reinterpretation of existing functions and operations. The possible number of such ideas is of course largely determined by the conditions of the site.

Results

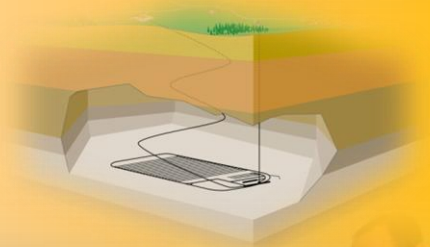
The authors examined several different power generation technologies, and also came up with ideas for converting part of the existing infrastructure to reinterpret the operation. Beside technical issues, feasibility of the technologies was also analysed. Based on the results, a recommendation was offered for the investor, detailing the advantages and disadvantages of each energy source, and choosing the technologies that might draw the interest for further research and/or are feasible enough to perform an in-detail business analysis as well. In general, mostly due to the laws in force and the limited budget, renewable generation technologies were selected; small-scale wind and solar power being the best solution, closely followed by the gas-to-coal conversion of the existing power plant. The conversion of the oil tanks into a pumped hydro facility was the fourth option that the authors have recommended for the investor.

Related publications

- [1] B. Hartmann, Sz. Török, E. Börcsök, V. Oláhné Groma: *Complex Method of Energy Purpose Redevelopment of Brownfield Sites*, Journal of Cleaner Production – in submission
- [2] B. Hartmann, Sz. Török, E. Börcsök, V. Oláhné Groma: *Energy Purpose Redevelopment of Brownfield Sites – an Examination and Evaluation Method*, World Energy Engineering Congress (WEEC 2014) – in submission



VI. ENERGY SAVING AND ENVIRONMENT STUDIES



NEW ENERGY SAVING TECHNOLOGIES FOR WASTEWATER TREATMENT: HIGH-ENERGY IONIZING RADIATION INDUCED DEGRADATION OF ORGANIC IMPURITIES

László Wojnárovits, Erzsébet Takács, Péter Hargittai,
Renáta Homlok, Erzsébet Illés, Krisztina Kovács, Viktória Mile, Tamás Csay

Objective

The main aims are: to establish clear structure–reactivity relation and by that to show the advantages and limits of application of radiation technology in water purification, to compare the degradation with different Advanced Oxidation Processes (AOP) and to establish the technological parameters for industrial application.

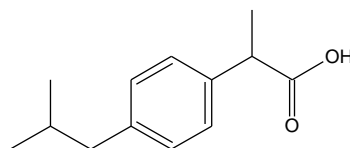
Methods

The chemical changes caused by irradiation 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. Such technological parameters as the changes in chemical oxygen demand (COD), total organic carbon content (TOC) and toxicity were also followed by using the standard methods.

The intermediates of radiolytic reactions were studied by pulse radiolysis with transient optical detection. Solutions were irradiated by a Linac type 4 MeV electron accelerator.

Results

Experiments were made with several water contaminants, here we show the results only with ibuprofen (IBP) ((*RS*)-2-(4-(2-methylpropyl)phenyl)propanoic acid, $C_{13}H_{18}O_2$). The investigation with IBP started in 2012 and was continued in 2013. IBP as the most popular "pain-killer" is used for relief of symptoms of arthritis, primary dysmenorrhoea, fever and as an analgesic. It is most often sold with trade names Nurofen, Advil and Motrin. IBP shows little absorbance in the wavelength region of the solar spectrum, its photodegradation in surface waters is limited and its biodegradation is also slow. IBP is regularly detected in the effluents of wastewater treatment plants and in surface waters at $ng-\mu g\ dm^{-3}$ level. IBP and its probably more harmful metabolites together with other drugs may present a potential hazard for human health and also for the aquatic ecosystem.



Ibuprofen

The results of this work show that the degradation of initial IBP molecules is more efficient under oxidative conditions than under reducing conditions and in air saturated solution than in the absence of dissolved oxygen. The first degradation products observed in radiolysis, hydroxylated molecules, were the same as found in other advanced oxidation processes: in all these reactions hydroxyl radicals are the main degradation inducing intermediates. Using irradiation technology, a complete ibuprofen mineralization can be achieved. In some of the other AOP techniques only partial degradation takes place. Combination of the different methods may show synergistic effect. A summary of the radiolytic reactions of IBP solutions and a comparison of IBP degradation in different AOP was given in a book chapter published in 2013 [1].

In our experiments the changes in the toxicity during the irradiation treatment were mainly followed by the *Vibrio fischeri* luminescence tests. In this test the decrease of luminescence is related to the mortality of the bacteria, and thereby is related to the toxicity of the solution investigated [2]. Practically in all irradiated solutions with different organic molecules, and also in the solutions of ibuprofen, at the beginning of the treatment an increase of the toxicity was observed. This increased toxicity has generally two reasons. The hydroxylated molecules (the first degradation products) are more toxic than their non-hydroxylated counterparts. The other reason of the increased toxicity is the hydrogen-peroxide formation during irradiation. H_2O_2 may form in reactions of two hydroxyl radicals, produced nearby to each-other (in the track), or in the reactions of the $O_2^{\cdot-}/HO_2^{\cdot}$ pair that is always present in aerated solutions with hydroxyl radicals as the main reacting intermediate. When catalase enzyme was added to the solutions after irradiation strong decrease in toxicity was observed due to the destruction of H_2O_2 by the enzyme [3].

The degradation of ibuprofen was compared with the reactions of the other popular "pain-killer" molecule ketoprofen. In spite of the stability of ketoprofen (two aromatic rings, connected by a carbonyl group), its decomposition in radical reactions is highly similar to that of ibuprofen. Both molecules can be efficiently degraded by irradiation in their aqueous solutions. Similar and efficient degradations were also found in other AOP for these molecules [4].

Remaining work

The experiments with ibuprofen are finished, however the investigations with other pharmaceuticals that are dangerous for the environment should be continued.

Related publications

- [1] K. Gajda-Schranz, E. Arany, E. Illés, E. Szabó, Zs. Pap, E. Takács, L. Wojnárovits: *Advanced oxidation processes for ibuprofen removal and toxicological risk assessment of degradation intermediates. Ibuprofen: Clinical Pharmacology, Medical Uses and Adverse Effects*, Editors, Wilton C. Carter and Brant R. Brown, Nova Science Publishers, pp. 152-232 (2013) (ISBN: [978-1-62618-659-0](https://doi.org/10.1080/978-1-62618-659-0))
- [2] R. Homlok, L. Szabó, E. Illés, E. Takács, L. Wojnárovits: *Change in toxicity during the ionizing radiation induced decomposition of organic pollutants, (in Hungarian)*, Autumn Radiochemical days, 2013, Eger, Hungary, 2013.10.16-2013.10.18. Budapest: Radiochemical Committee, HAS, pp. 101-104 (2013) (ISBN: 978-963-9970-42-7)
- [3] E. Takács, L. Wojnárovits, R. Homlok, E. Illés, T. Csay, L. Szabó, G. Rácz: *Radiation treatment of wastewater containing pharmaceutical compounds*, in Report of the 2nd RCM on Radiation Treatment of Wastewater for Reuse with Particular Focus on Wastewaters Containing Organic Pollutants Jeongup, Republic of Korea, 2013.10.29-2013.11.02, Working Material, IAEA, Vienna, pp. 67-79 2013. http://www-naweb.iaea.org/napc/iachem/working_materials/RC-1188-2-report.pdf
- [4] E. Illés, E. Szabó, E. Takács, L. Wojnárovits, A. Dombi, K. Gajda-Schranz: *Ketoprofen removal by O₃ and O₃/UV processes: kinetics, transformation products and ecotoxicity*, Science of the Total Environment **472**, 178-184 (2014)

MODELS AND CALCULATIONS ABOUT THE ACCIDENTAL ACTIVITY EMISSION TO THE ENVIRONMENT OF THE NPP PAKS

Attila Nagy, Zoltán Hózer

Objective

The nuclear power plants in operation necessarily produce radioactive materials, potential threat to the environment. The plants have a multi-barrier protection to prevent environmental release. In an accidental condition the primary circuit can be damaged, in this case the containment is the final barrier to the environment. To determine the amount and composition of the radioactive materials leaving the plant in this case, we must use computer codes.

Methods

This work is about modelling the possible activity emission in a case of a LOCA (Loss Of Coolant Accident) in the Paks NPP. Calculations and physical models were made for this purpose. The HERMET code was used for different LOCAs and the results of the calculations were analysed. The physical models found by the HERMET program were examined and developed:

- The HERMET program steam-water-air state calculating algorithm was changed to a new one and was checked with the help of CONTAIN calculations.
- Volume-work calculation algorithm for the HERMET program was added and was compared to CONTAIN calculation successfully.
- New wall heat convection model for the HERMET code was made. The new model is much simpler than the old one, and it gives more detailed simulation of the heat conduction, it works with two phases and considers radiation heat transfer as well.
- Emission to the environment is possible from the hermetic rooms through other rooms of the NPP at a LOCA, if their internal pressure is higher than the atmospheric. To calculate this emission, a new reactor hall model was made and several different analyses were carried out considering different LOCA scenarios. These calculations were made for the three most important isotopes from radiation protection point of view. The new reactor hall model was used to examine the effect of the different fuel failure starting time on the emission. This study was made from 0 s fuel damage delay to 60 s delay. The results were presented in detail in graphic and table form, and were compared to the earlier calculations.

Results

1. The calculation accuracy of some models of the HERMET code was determined. It was found that the parameters describing the state of the nodes and the wall heat model must be further developed.
2. An algorithm was developed to calculate the air-steam-water state parameters in the nodes by appropriate precision.
3. Expansion work was integrated to integral calculation of node state.
4. New wall heat transfer model was created. It proved that the modified model can be used for long term LOCA simulation.
5. A new model for the reactor hall was created. Dilution, filtration and retention are simulated, and follow the path of the radionuclides towards the environment.
6. The new reactor model was used to calculate the impact the different fuel damage starting times on the emission through the chimney.

Remaining work

To integrate the new physical models to the new HERMET 2 code that can handle different nodalizations, and to develop further physical models.

Related publications

- [1] Attila Nagy, Zoltán Hózer, János Sebestyén Jánosy: *Modelling of VVER-440/213 hermetic rooms in training simulator*, Annals of Nuclear Energy Volume 55, May 2013, Pages 272-278
- [2] Attila Nagy, Sándor Deme, Zoltán Hózer: *Activity emission model for VVER 440/213 reactor LOCA*, Annals of Nuclear Energy, Volume 62, December 2013, Pages 413-420
- [3] Attila Nagy: *Models and calculations about the accidental activity emission to the environment of the NPP Paks*, PhD thesis, 2013

MODELLING THE TRANSPORT OF RADIONUCLIDES IN SURFACE WATER

*Barbara Brockhauser, Emese Homolya, Tamás Pázmándi,
Péter Szántó, Péter Zagyvai*

Objective

In order to determine radiation burden in the vicinity of an emission source, modelling the transport of radioactive material in the environment is crucial. To determine the environmental effects of a possible radioactive emission we also need to pay attention to the radionuclide transport in surface water. Our objective is to create a transport model of radionuclides in rivers that gives more accurate results than the currently used and accepted ones. Primary focus will be given to the section of the Danube under Paks. The current work is the initial task of a 5-year-long project, which started at the beginning of 2013.

Methods

In the first year of the work the national and international literature and recommendations as well as national regulations were overviewed in order to select appropriate methods for the transport module of our model. During the model construction phase different source types of the releases (e.g. point source, continuous source) were reviewed and considered. Processes that influence the advection and diffusion of pollutants in water bodies (e.g. river flow parameters, river geological parameters, shear stress) were also analyzed. The essential parameters of the Danube (e.g. mean river depth, flow rate) with special regard to the section under Paks were considered during the calculations.

Results

An overview of the literature and also a summary of transport models being in use have been completed. Processes that influence the advection and diffusion of pollutants in a water body were analyzed. The transport equations from different models were selected and a comparison was made. The fundamental equations for the advective-diffuse motions in rivers were selected according to the reviewed literature. Basic algorithms for the radionuclide transport model in surface waters were set with more accurate data in the region of Paks. First version of the program has been written in order to make sensitivity analyses of each data set. A publication is under preparation.

Remaining work

The main task in the next year of the project is to investigate the interactions of the nuclides with the bed and the suspended sediment (e.g. adsorption, sedimentation, erosion, deposition, resuspension).

During the following years the internal and external pathways of the radiation burden, such as direct radiation coming from the river or the shore sediment, effects of incorporated isotopes, direct contact with the contaminated water will be determined. The factors and parameters that influence these processes will be defined by sensitivity analysis.

Related publications

- [1] B. Brockhauser, T. Pázmándi, E. Homolya, P. Szántó, P. Zagyvai: *Modelling the transport of radionuclides in surface water* (in Hungarian), EK-SVL-126-01-01-00 (2013)
- [2] B. Brockhauser, S. Deme, E. Homolya, T. Pázmándi, P. Szántó: *Modeling radionuclide transport in major rivers*, IRPA2014, Accepted for publication (2014)

HIGH ENERGY RADIATION INDUCED DESTRUCTION OF PESTICIDES IN AQUEOUS SOLUTIONS

Krisztina Kovács, Viktoria Mile, Tamás Csay, Erzsébet Takács, László Wojnárovits

Objective

Phenylurea herbicides (such as fenuron) act as inhibitors of photosynthesis and they are used for control of weeds in many crops and also on non-cultivated areas such as roads and railways. These herbicides are highly persistent; they degrade in soils with half-lives of several months. By dissolution the phenylureas continuously contaminate surface waters. The decompositions of phenylureas were investigated by direct photolysis in order to study their degradation by sunlight. The elementary steps of hydroxyl radical reaction with fenuron were investigated in our laboratory.

Methods

The elementary steps of hydroxyl radical reaction with fenuron were investigated using radiation chemical methods (pulse radiolysis, UV-Vis spectroscopy, toxicity, chemical oxygen demand, liquid chromatography-mass spectrometry technique).

Results

The main reaction is $\cdot\text{OH}$ addition to the ring forming hydroxycyclohexadienyl radical (Fig. 1). These radicals readily react with dissolved O_2 forming peroxide intermediates which may transform either to phenols or disintegrate to smaller oxidized products.

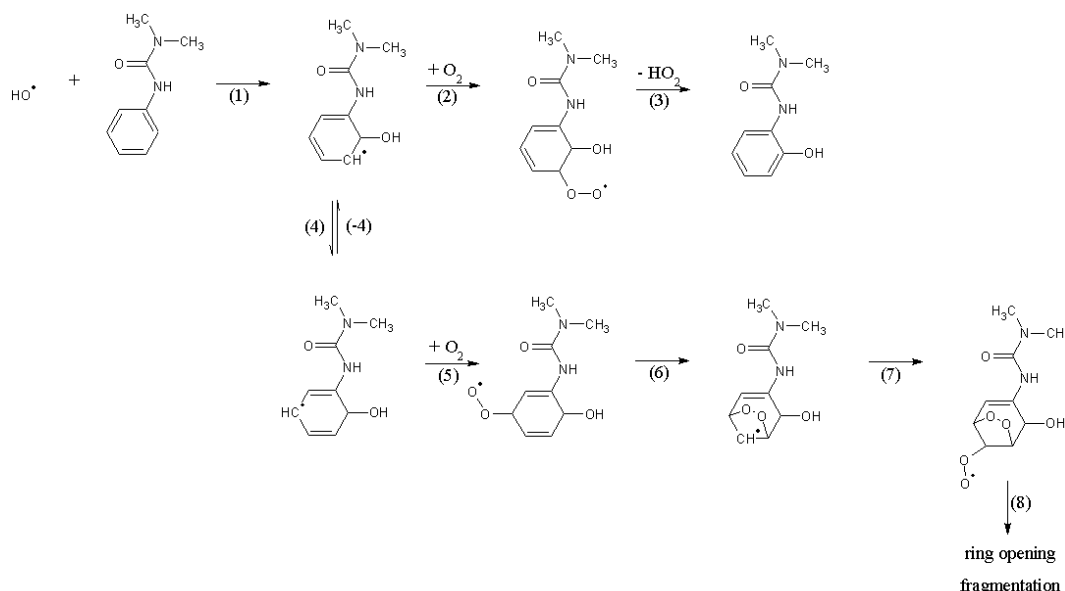


Figure 1: First steps of $\cdot\text{OH}$ induced degradation in the presence of dissolved O_2

$\cdot\text{OH}$ reactions with $-\text{NH}-$ or $-\text{CH}_3$ groups and also the reactions of hydrated electrons or the $\text{O}_2^{\cdot-}/\text{HO}_2\cdot$ pair have low contribution to degradation. The toxicity first increases with absorbed dose, then decreases. The increase is partly due to phenol formation during the first degradation period. H_2O_2 also significantly contributes to toxicity. Our experiments were made in the 10^{-4} – 10^{-3} mol. dm^{-3} concentration range, the practical concentrations in biologically treated waters are some 4–5 magnitudes lower. Considering also the presence of other contaminants ($\text{COD} \approx 50 \text{ mg dm}^{-3}$), less than 1 kGy dose is sufficient for degradation.

Remaining work

The experiments with phenylurea herbicides (e.g. monuron, diuron) should be continued.

Related publications

- [1] Krisztina Kovács, Viktoria Mile, Tamás Csay, Erzsébet Takács, László Wojnárovits: *Hydroxyl radical induced degradation of Fenuron*, Environmental Science and Pollution Research submitted.
- [2] Kovács Krisztina, Mile Viktória, Takács Erzsébet, Wojnárovits László: *High-energy radiation induced degradation of fenuron, in Hungarian*, Autumn Radiochemical Days, 2013, Eger, Hungary, 2013.10.16-2013.10.18. Budapest: HAS Radiochemical Committee, 2013. pp. 91-95. (ISBN: 978-963-9970-42-7)

LOOKING FOR INTERESTING RESEARCH TOPICS ON THE FIELD OF LITHIUM ION BATTERIES

Ildikó Harsányi, Viktória Mile

Objective

MTA EK has a recently extended mandate to expand non-nuclear research topics in the energy sector. Lithium ion batteries or energy storing devices or techniques were identified as one of the promising research fields. The electrochemical history of MTA EK forms a strong basis for this research direction.

Methods

As the literature on the field of energy storing devices is broad, we decided to focus only on selected segments of lithium ion batteries research. As they are belonging to the most important energy storing devices of our age, the corresponding literature has been critically reviewed. After having an overview on the most developing fields and based on the available knowledge, the prosperous research questions/topics were identified. In order to establish an up-to-date knowledge base we read fresh scientific papers, reviews and some books, and the conclusions are collected in a report.

Results

Lithium ion batteries in general, battery materials, research areas and problems are summarized in a report. Some interesting topics are emphasised here.

The scientifically most interesting batteries today are found to be Li-air and olivine (nanophosphate) types. There is a patent of the idea of Li-CO₂ batteries by Károly Németh. Such batteries work with pure CO₂, and the produced material is LiCO₃. The reactions of usage are very safe in this case, but the storage of CO₂ gas is the problem that should be solved. Another advantage of this type of battery is that its temperature dependence is low.

Nanostructured batteries seem to be the most promising type, but the research is already advanced, also supported by companies, so that the technology is under patent. They work with Ni and Sn covered electrodes of Ni and LiMnO₄ in some glassy electrolyte, and use the advantage of nanosized structure to get higher power. This model is to be used in micromechanics.

The situation of nanophosphate or olivine types of batteries are the same: already enormous background exists behind the developments. The advantages of these batteries are the low weight and high capacity; the problems are usually the cooling and the loss of power after several charging cycles.

The solutions for these problems are to be found in the structure itself or in structural or chemical changes inside the battery and/or on the SEI. That is why we suggest to connect the chosen area with answering basic research questions like how the structure looks like, where are the lithium ions and what structural changes can we find behind changes of physical properties. When choosing a new project, one must take into account the possibilities and advantages of our research centre and collaborations with nearby institutions and laboratories.

Another very evident research area would be the battery waste treatment. Lithium is expensive, not to mention its most commonly used salt, cobaltite. Both metals have high abundance in the waste material, hence proper recycling technics could be developed. The existing ones work with acidic digestion by citric acid. Later both hydrated metal ions can be precipitated from the solution. The process is basic chemistry, not complicated to set up and have low cost to gain – promising not too remarkable scientific, but economically important results. As environmental research fields also have history and knowledge in our research centre, it would fit in its profile.

In the autumn a scientific committee discussed the report and chose the problem of examining the structure, conductance etc. properties of the metal – metal-oxide/-hydroxide layers system on lithium as a starting point. The work will be a shared project in collaboration with the Surface Chemistry and Catalysis Laboratory. The present authors will contribute to laboratory work and calculations, simulations as well, as the project needs to be continued. Some of the calculations will be done in collaboration with co-workers at the Wigner RCP, with whom close collaboration is ongoing on aqueous electrolyte structures.

Remaining work

The project was accepted by the scientific committee of MTA EK, the actual laboratory work has to be started with procurement and preparation of the necessary materials. Bases of the calculations are being studied in the meantime.

During the process of the report we found out that in addition to lithium ion batteries, the research area of fuel cells should be overviewed, with specially focus on the advantages of the PGAA instrument. This work is still to be done.

Related publication

[1] Project report *MTA EK NAL 135*, 30. June, 2013.

HYDROXYL RADICAL INDUCED DEGRADATION OF SALICYLATES IN AERATED AQUEOUS SOLUTION

Erzsébet Takács, László Szabó, Renáta Homlok, László Wojnárovits

Objective

Salicylic acid and its derivatives are often used in the industry (pharmaceutical, cosmetic) and in households (food preservative). Due to the frequent use they are regularly detected in wastewater and surface waters. Therefore, it seems to be necessary to remove salicylates and other harmful organics from the biologically purified wastewaters before releasing to the environment. To solve this problem, ionizing radiation based simple, energy saving and economical technique was developed for wastewater treatment. The aim of this work was to use this technique for the radiolytic degradation of salicylic acid and its derivatives.

Methods

Dilute solutions with 0.25–0.5 mmol dm⁻³ concentrations were prepared from acetylsalicylic acid (ASA), salicylic acid and 5-sulpho-salicylic acid. Irradiation was done by a ⁶⁰Co γ -irradiation facility with 11.5 kGy h⁻¹ dose rate. Irradiation induced changes were evaluated either by taking UV-Vis spectra or by HPLC separation. Two HPLC systems were used: one with diode array detection, the other with Triple Quad LC/MS equipment.

Results

In hydroxyl radical reactions with all the three compounds in the first step hydroxylated products form. This is illustrated for ASA in Fig. 1. In the analysis of ASA solutions the parent ion with m/z 179 eluted at 6.1 min while salicylate ion with m/z 137 at 7 min. The chromatogram is dominated by products with m/z 195, belonging to the hydroxylated form of the starting molecule. With prolonged reaction, dihydroxylated derivatives of salicylates are also observed (with m/z 211). Hydrated electrons destroy salicylates with lower efficiency; the products do not have aromatic character. Chemical oxygen demand measurements in aerated solutions revealed that the one electron oxidant hydroxyl radical induces 2–4 electron oxidations due to the reactions of intermediate radicals with O₂. The experiments showed that salicylates can be effectively degraded by using irradiation technology.

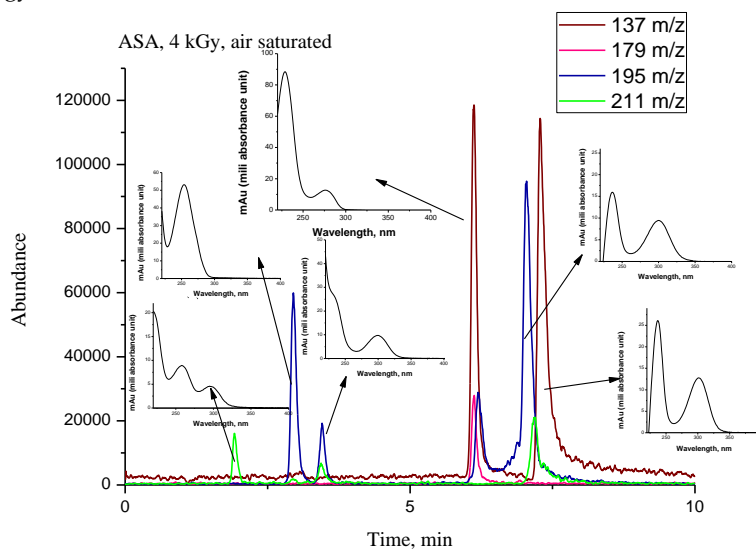


Figure 1: Chromatogram of air saturated 0.5 mmol dm⁻³ ASA solution irradiated with 4 kGy dose. Detected mass/charge numbers were 137, 179, 195 and 211. The insets show the absorption spectra of some of the compounds taken with diode-array detection

Remaining work

We plan to continue this work studying the degradation of antibiotics as target molecules.

Related publications

- [1] L. Szabó, T. Tóth, R. Homlok, G. Rácz, E. Takács, L. Wojnárovits: *Radiation induced degradation of salicylic acid derivatives*, in *Hungarian, Autumn Radiochemistry Days 2013*, Eger, Hungary, 2013.10.16-2013.10.18. Budapest: HAS Radiochemistry Committee, pp. 105-108. (ISBN: 978-963-9970-42-7) (2013)
- [2] L. Szabó, T. Tóth, R. Homlok, G. Rácz, E. Takács, L. Wojnárovits: *Hydroxyl radical induced degradation of salicylates in aerated aqueous solution*, *Radiation Physics and Chemistry* **97**, 239 (2014)

ANALYSIS AND IMAGING OF URANIUM SAMPLES IN LEAD CONTAINERS

László Szentmiklósi, Zoltán Kis

Objective

A R&D program, financially supported by the Hungarian Atomic Energy Authority, was established to work out methodology for the non-destructive analysis of nuclear materials in sealed containers, using the combination of PGAA and Neutron Tomography.

Methods

Application of the prompt gamma activation analysis (PGAA) and neutron imaging methodology as described in the "Standard Operating Procedure of the Budapest PGAA-NIPS/NORMA-DÖME facility" (NAL-PGAA-01). Monte-Carlo calculations with MCNP5. Image processing, tomographic reconstruction.

Results

PGAA – thanks to the high penetration power of neutrons and energetic gamma rays – is capable of the identification, the qualitative and quantitative analysis of nuclear material, as well as the determination of the enrichment, even if it is encapsulated in a sealed shielding container. The experience showed that the most important uncertainty arose from the uncertain geometry of the material inside the container. To overcome this limitation, we combined PGAA with neutron imaging, in order to achieve in-situ visualization of the container's content. The present work was the continuation of our efforts in 2008.

We recorded projections at every 0.3 degree for neutron tomography reconstruction and created 3D visual representation of the objects placed in sealed lead containers. The dimensions of the samples, being accurate to about 0.2 mm, could be measured with the calliper tool of the visualization software VG Studio. It was shown using uranium pellets of various enrichments that the gray value of image pixels can be related to the enrichment of the sample, if the thickness is known.

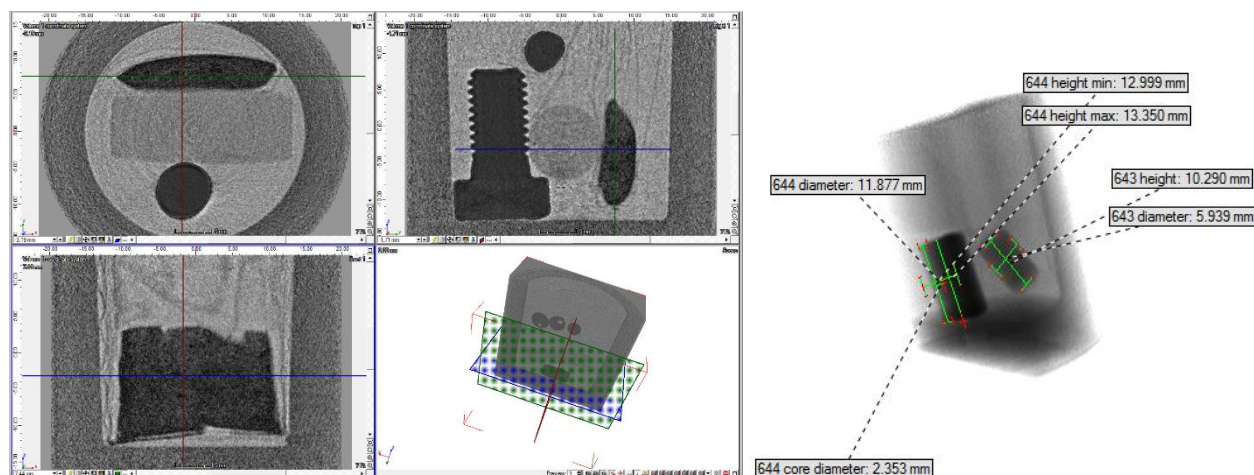


Fig.1: The top, side and cutaway views of the sealed uranium sample (left); determined dimensions (right)

Quantitative equations were deduced to analyse ^{235}U and ^{238}U based on their 6395 keV and 4060 keV peaks. As the geometry of the sample became known from the neutron imaging, more accurate correction of the neutron self-shielding and gamma self-absorption could be carried out. We also managed to reproduce the measured radiographic projections by simulations. The most challenging task was the definition of the iso-centre, i.e. the intersection of the neutron beam and the gamma collimator's solid angle. Here, an inaccuracy of 1-2 mm can result in an error of 10-20% in the final mass estimation.

The ultimate motivation of the study was the mass estimation of the pellets. For samples in the enrichment range of 0.72%-2.64%, results better than 8% was achieved. With the reinterpretation of earlier results it was concluded that the validity of the method could be extended towards higher enrichments up to 36%.

Remaining work

The comparison of the novel methodology to competing methods and explore the limits of applicability.

Reference

László Szentmiklósi, Zoltán Kis: Investigation of uranium samples in sealed lead containers using Prompt gamma activation analysis and neutron tomography. OAH-ABA-21/13-M project report [in Hungarian]

CATALYTIC PROCESSES IN ENVIRONMENTAL PROTECTION, SUSTAINABLE FINE CHEMICAL, PHARMACEUTICAL INDUSTRY: SCREENING AND UTILISATION OF LIQUID WASTES

Antal Tungler, Erzsébet Takács, Arezoo M. Hosseini, Erika Szabados, Chamam Mounir, Tamás Csay

Objective

Elaboration of characterization methods for process wastewaters with respect to their biodegradability and development of treatment methods (wet oxidation and high energy radiation) for elimination of their toxicity.

Methods

The suggested characterization methods (total organic carbon (TOC), chemical oxygen demand (COD), biological oxygen demand (BOD), special respirometry, special anaerobic digestion test, Zahn-Wellens test, qualitative and quantitative determination of volatile content with distillation and gas chromatography-mass spectrometry (GC-MS), liquid chromatography-tandem mass spectrometry (LC-MS/MS) for determination of non volatile, high molecular weight contaminants) are in our daily practice, their applicability has been proven. Reaction rate determination of the wet oxidation in the presence of catalyst and in the thermal reaction was carried out. Advanced oxidation process (AOP) experiments (high energy radiation induced and photo-Fenton) were carried out investigating the possibility of intensification of the oxidation processes.

Results

In the traditional wet oxidation (WO) of model compounds complete mineralization could be achieved. The wet oxidation of different models (containing dimethyl formamide and diclofenac) and real wastewaters has been carried out by design of experiments (DOE). Advanced oxidation of model and real wastewaters were investigated including the ionizing radiation induced degradation of diclofenac and chloramphenicol, photo-Fenton degradation and ultrasonic+AOP treatment of micropollutants. The AOP experiments and the water radiolysis induced degradation tests were successful as the pollutants could be eliminated with good conversion into harmless materials, in most cases complete mineralization occurred. The methods were tested also in continuous reactors.

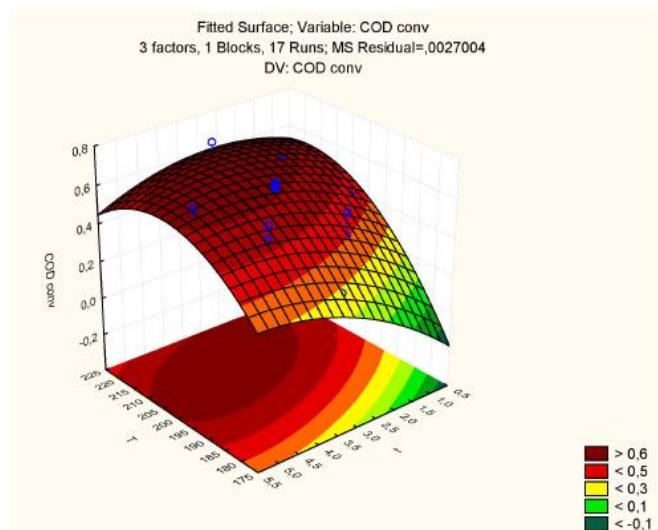


Figure 1. COD decrease in the function of temperature and time



Figure 2. Wet oxidation combined with high energy electron beam radiation

Remaining work

The intensification of wet oxidation at concentrated wastewaters and the development of AOPs for degradation of emergent pollutants will be continued.

Related publications

- [1] N. De la Cruz, L. Esquius, D. Grandjean, A. Magnet, A. Tungler, L.F. de C. Alencastro and C. Pulgarín: *Degradation of emergent contaminants by UV, UV/H₂O₂ and neutral photo-fenton at pilot scale in a domestic wastewater treatment plant*, *Water Research*, **47**(15), 5836-5845 (2013)
- [2] R. Homlok, E. Takács and L. Wojnárovits: *Degradation of organic molecules in advanced oxidation processes: Relation between chemical structure and degradability*, *Chemosphere*, **91**, 383-389 (2013)
- [3] A. M. Hosseini: *Intensification of wet oxidation of industrial process wastewaters*, PhD dissertation (2013)

CATALYTIC PROCESSES IN ENVIRONMENTAL PROTECTION, THIOPHENE HYDRODESULFURIZATION AND HYDROTREATMENT OF OLEIC ACID

Tamás Ollár, Tibor Szarvas, Pál Tétényi

Objective

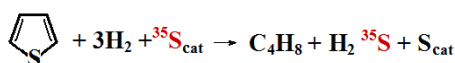
Transition metal sulfides, especially molybdenum sulfide, are widely used to produce cleaner energy carriers: **hydrodesulfurization (HDS)** of crude oil, **hydrotreating of natural triglycerides and oleic acids** are nowadays successfully used as active **electrodes for hydrogen evolution** from water. To understand how molybdenum sulfides are working we have to study the catalytic mechanisms.

Methods

For the study of the mechanism of two different catalytic processes (hydrodesulfurization of thiophene and hydrotreating of oleic acid) gas recirculation system, catalytic flow-through microsystem, microcatalytic pulse system, gas chromatography and radioisotope tracer technique (H_2^{35}S , oleic-acid- $1\text{-}^{14}\text{C}$) have been used. Measurements of the radioactivity were carried out by liquid scintillator. Catalytic processes were investigated over industrial (different Ni, Mo and P containing) catalysts.

Results

1. A linear correlation was observed between the sulfur exchange capacity and HDS activity of new generation catalysts containing phosphorus. The amount of phosphorus has no influence on this correlation. Thiophene recyclization also takes place under inert conditions over sulfided molybdenum based catalysts. Thiophene adsorption over labeled sulfur sulfided Mo $^{35}\text{S}_2$ catalyst produced H_2^{35}S in the presence and in the absence of hydrogen, too, while HDS reaction did not occur. The fact that hydrogen sulfide leaves the catalyst surface during the adsorption of thiophene, points to the absence of inhibitory effect of hydrogen sulfide, unlike previous claims that hydrogen sulfide may block active sites. Two types of inhibitory mechanisms are suggested, on the one hand the reaction between butadiene (or other diolefins) and hydrogen sulfide - the formation of thiophene (or thiophene derivatives), on the other hand hydrogen sulfide can displace thiophene already adsorbed on the active sites, but not reacted yet. Taking into account also the findings and results of other researchers, we developed further the current view on the mechanism of thiophene desulfurization process. According to our proposed reaction mechanism, thiophene desulfurization takes place via the exchange of surface sulfur.



2. Decarboxylation, decarbonylation and hydrodeoxygenation pathways of oleic acid over sulfided supported MoP and NiW catalysts were studied in a microcatalytic system applying oleic acid- $1\text{-}^{14}\text{C}$. It was stated that only CO, CO $_2$, and CH $_4$ were radioactive among the gas products of conversion of oleic acid- $1\text{-}^{14}\text{C}$. The carboxyl group of this compound was converted by hydrodeoxygenation pathway into a radioactive alkane: C $_{18}\text{H}_{38}$. There was not observed any radioactivity among the alkanes with a lower number of carbon atoms (e.g. 5-8) formed as products of cracking or hydrogenolysis. This indicates that no interaction took place between the gas and cracking products. The C $_{18}\text{H}_{38}$ alkane - formed in hydrodeoxygenation pathway - was not cracked. ^{14}CO and $^{14}\text{CO}_2$ were converted partly into $^{14}\text{CH}_4$ and the extent of this process was higher on NiW than on the MoP catalyst. This means that more hydrogen is required for hydrotreating of vegetable oils on NiW catalyst in comparison with MoP. The ratio of ΣC_1 production was lower, and its energy barrier was higher than these values, characterizing the production of C $_{18}\text{H}_{38}$. The decrease of the sulfur content of the sulfided MoP was somewhat higher than that of NiW. This, however, influenced considerably the catalytic activity only in longer time on stream.

Remaining work

Revealing the whole mechanism of thiophene hydrodesulfurization using DFT calculations. Studying the mechanism of hydrogen evolution from water over molybdenum sulphide electrode.

Related publications

- [1] T. Szarvas, Z. Eller, T. Kasza, T. Ollár, P. Tétényi, J. Hancsók: *Investigation of radiocarbon (^{14}C) labeled oleic acid hydrotreating over sulfided alumina supported MoP and NiW catalysts*, Applied Catalysis A., submitted
- [2] T. Ollár: *The effect of the sulfur mobility over sulfide catalysts in thiophene desulphurisation process (in hungarian)*, PhD dissertation (2013) [in Hungarian]
- [3] T. Ollár, T. Szarvas, P. Tétényi: *Transition metal sulfides for cleaner energy*, 3rd European Energy Conference – E2C 2013, October 27-30. Budapest, Hungary
- [4] T. Ollár, T. Szarvas, P. Tétényi: *A probable mechanism of thiophene HDS: as calculated from the correlation between sulfur exchange capacity and thiophene HDS activity (poster 1), Butadiene interactions on the HDS catalysts surface (poster 2)*, VI. International Symposium on Molecular Aspects of Catalysis by Sulfides (MACS), 12-16. May 2013. Satillieu, France

AU-CONTAINING BIMETALLIC CATALYSTS IN HIGHLY SELECTIVE AEROBIC OXIDATION REACTIONS

Tímea Benkó, Zoltán Schay, Dávid Srankó, László Borkó, Andrea Beck

Objective

Selective oxidation processes leading to chemical intermediates and fine chemicals represent a large class of organic reactions where the development of clean and efficient “green chemistry” processes can have a significant positive economic and environmental impact. A wide range of oxidative transformations using molecular oxygen are promoted by gold at relatively low temperature and with very high selectivity. Also bimetallic Au-based catalysts are highly promising, but relatively unexplored systems. Different bimetallic combinations as Au-Ag, Au-Cu, Au-Ru, Au-Ir are studied and compared in selective aerobic oxidations of model substrates, as glucose, benzyl-alcohol and toluene in the frame of our OTKA project #101854. The effect of the second metal and the structure-catalytic effect relationship is investigated.

Methods

Truly bimetallic nanoparticles and analogous monometallic ones were prepared by liquid phase reduction using NaBH_4 and stabilized by polyvinyl alcohol in aqueous sols. The nanoparticles were deposited on silica or alumina support by adsorption, the total metal loading was $1 \text{ mmol/g}_{\text{cat}}$. The colloids and the supported samples were characterized by UV-vis spectroscopy, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) equipped with EDS and high resolution electron microscopy (HRTEM) and EELS. (TEM studies were performed in MTA TTK MFA by G. Sáfrán and O. Geszti.) The supported samples were tested in glucose oxidation after calcination ($400^\circ\text{C}/\text{air}$) applied for removal of organic contaminations and also after consecutive reductive treatment ($350^\circ\text{C}/\text{H}_2$) providing metallic state of the active components. The selectivity towards gluconic acid was 100%.

Results

Earlier synergetic activity increase was observed for calcined AuAg/SiO₂ catalysts containing bimetallic nanoparticles of Ag/Au \leq 0.5 atomic ratio. In 2013 the effect of treatment in hydrogen at 350°C on the structure and catalytic performance of the calcined samples were investigated. The UV-vis, TEM, HRTEM and XPS measurements suggested that both in the calcined and calcined+reduced state dominantly alloyed particles in metallic state were present, only in the calcined form could several Ag-oxide decorations on AgAu metallic particles be identified. On the effect of reduction treatment the mean particle diameters (3-5 nm), the wavelength of the single band of surface plasmon resonance (SPR) and the binding energies in the XPS of bimetallic samples hardly changed, the Ag/Au atomic ratio measured by XPS somewhat decreased, while the catalytic activities varied only slightly and their order did not change. A possible reaction mechanism was proposed based on our results and literature data including also DFT calculations, and as the role of Ag the acceleration of decomposition of the O₂ activation intermediate H₂O₂ was supposed.

AuCu nanoparticles of Cu/Au=1/1 molar ratio with different structure were successfully prepared by co- (Au&Cu) and consecutive reduction of the precursor ions, Cu reduction on Au NPs (Cu \rightarrow Au) and vice versa (Au \rightarrow Cu). According to the UV-vis and HRTEM results, alloyed AuCu and Au core-Cu-oxide shell type particles were formed in Au&Cu and Cu \rightarrow Au samples, respectively, while in Au \rightarrow Cu alloyed AuCu of less Cu-concentration than in Au&Cu was suggested with Cu-oxide decoration. The oxidative and reductive treatments induced some restructuring of the particles. For example, in Au&Cu/Al₂O₃ calcination lowered the Cu/Au ratio in the alloyed phase and formed Cu-oxide around its surface; H₂ treatment resulted in redissolution of some Cu possibly formed by reduction of CuO, into the alloyed phase. XPS also indicated the appearance, then disappearance of CuO in this sample during oxidation and reduction treatment, respectively. The mean particle sizes of all of the samples both in oxidized and reduced state were between 2.7-3.7 nm. The activity order was Au/Al₂O₃>Au&Cu/Al₂O₃>Au \rightarrow Cu/Al₂O₃>Cu \rightarrow Au/Al₂O₃, and Cu/Al₂O₃ was inactive between the test conditions. Among the AuCu/Al₂O₃ catalysts only Au&Cu/Al₂O₃ showed some synergistic activity increase, however its extent was much lower than in the case of AuAg/SiO₂ (Ag/Au \leq 0.5). Surprisingly, there were no significant differences between the activity of calcined and calcined+reduced bimetallic samples. The reason might be the modification of the catalysts in the reaction mixture that will be checked by investigation of the structure of the used catalyst.

For the study of the further bimetallic combinations, AuRu and AuIr colloids were prepared with 1:1 atomic ratio by co-reduction and adsorbed on alumina support.

Remaining work

The structural and catalytic characterization of Al₂O₃ supported AuRu and AuIr catalysts. Variation of the Au/M (M:Cu, Ru, Ir) ratio and study of the support effect.

Related publications

- [1] T. Benkó, A. Beck, K. Frey, D. F. Srankó, O. Geszti, Gy. Sáfrán, B. Maróti, Z. Schay: *Bimetallic Ag-Au/SiO₂ catalysts: Formation, structure and synergistic activity in glucose oxidation*, Applied Catalysis A, submitted
- [2] T. Benkó, K. Frey, A. Beck, O. Geszti, L. Guczi, Z. Schay, *Silica-supported bimetallic Ag-Au nanoparticles: Formation, structure and high activity in glucose oxidation*, 11th European Congress on Catalysis, Lyon, France, Sept. 1-6 (2013)

MANGANESE-PROMOTED COBALT OXIDE IN PROX REACTION

Andrea Beck, Zoltán Schay, László Borkó, Dávid Srankó, Krisztina Frey

Objective

The development of novel power generation systems, such as fuel cells, has increased the interest towards hydrogen as energy carrier during last years. In particular, PEM fuel cells appeared the most suitable technology for distributed power generation. Catalytic preferential CO oxidation (PROX) reaction can be the most economical way to remove traces of the electrode catalyst poisoning CO from H₂ originated from natural gas, biogas, hydrocarbons - including (bio)diesel - and (bio)alcohols. In our earlier studies, Mn-Co mixed oxide catalyst prepared either via oxalate or carbonate precipitation presented synergetic effect in PROX reaction compared to the Co₃O₄ and MnOx prepared via oxalates. It was suspected to be originated in the presence of crystalline Co₃O₄ spinel partially substituted by Mn cations or the presence of amorphous oxide phase. Further studies were performed to ascertain the key structure responsible for the improved catalytic performance. The research was supported by the OTKA project # NNF2-85631.

Methods

Cobalt oxide (CoOx) and manganese-promoted cobalt oxide with Mn/Co=5/95 and 12/88 atomic ratio (5Mn95CoOx, 12Mn88CoOx) were prepared by precipitating Co-oxalate and MnCo-oxalate, respectively, followed by calcination (360°C/20 min/10%O₂ in He). For increasing the crystallinity of the samples, a treatment was applied at 700°C in air for 2 or 3 h. The catalysts were characterized by BET, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and temperature programmed reduction (TPR) measurements. (The BET and XRD measurements were performed at BME VBK by K. László and at MTA TTK by I. Sajó, respectively.) Temperature programmed catalytic tests were performed with quadrupole mass spectrometry (QMS) and gas chromatography (GC) analysis in PROX reaction (20 mg catalyst, 20 ml/min 1%CO+1%O₂+50%H₂/He, 6°C/min) running several heating-cooling cycles typically up to 250°C, in several cases up to 360°C. The extent of reduction of the catalyst during the course of TP-PROX process was characterized by temperature programmed oxidation (TPO) measurements up to 360°C.

Results

On the effect of the treatment at 700°C the crystallinity of 12Mn88CoOx increased, the 25-35% amorphous phase content decreased below 10% and in the crystalline Mn substituted Co₃O₄ spinel (Mn_mCo_{3-m}O₄) larger Mn ratio was detected. CoOx contained well crystallized Co₃O₄ also in its as prepared state, the high temperature treatment increased its crystalline phase content by 5% at the most. The thermal treatment was accompanied with the reduction of the specific surface area of the samples to different extent (CoOx: from 50 to 10 m²/g, 5Mn95CoOx: 70 to 30 m²/g, 12Mn88CoOx: from 79 to 20 m²/g).

The activity of the high temperature treated 12Mn88CoOx catalyst dropped dramatically, much more than that could be caused by the surface area loss. This highlights the importance of the amorphous phase in the improved PROX performance of the mixed oxide catalyst. 5Mn95CoOx also deactivated, but to much less extent, while CoOx activity related to surface unit was retained in the treatment at 700°C. Surprisingly, the 700°C treated mixed oxide catalysts could be reactivated in a temperature programmed PROX test up to 360°C followed by a TPO up to 360°C. In a subsequent PROX reaction these samples presented activity related to surface unit close to that of the original catalysts. The unit surface related activity of the CoOx did not change significantly in these subsequent treatments. The PROX reaction up to 250°C caused a partial reduction of CoOx to a larger, of the mixed oxides to a smaller extent as evidenced by TPO and XPS results. In CoOx, but not in mixed oxides also reduced sites having methane formation (CO+3H₂=CH₄+H₂O) activity appeared. In PROX up to 360°C also the mixed oxides suffered such a deep partial reduction to appearing methanation activity. It is suggested that in the reactivation of the 700°C treated mixed oxide samples this deep reduction followed by reoxidation plays important role.

Based on all these results, the PROX properties of the mixed oxide surpassing that of CoOx can be likely attributed besides to the optimal extent substitution of the Co₃O₄ by Mn, rather to the amorphous oxides and the larger defect concentration in the lattice. The ordering of these structures during the high temperature (at 700°C in air) treatment might have caused activity decrease. During the reactivating (reducing followed by oxidizing) treatments at 360°C the defect sites rich mixed oxide phase may be reformed, but in CoOx, where the formation of the well-ordered Co₃O₄ phase is easier, this method does not provide a more active defective lattice.

Remaining work

The preparation of a publication is in progress, which needs several additional experiments.

Related publications

- [1] A. Beck, K. Frey, Z. Schay, L. Borkó, I. Sajó, G. Sáfrán, N. Kruse, D. Teschner, *Manganese-promoted cobalt oxide in PROX reaction*, 11th European Congress on Catalysis – EuropaCat-XI, Lyon, France, September 1st-6th, 2013
- [2] OTKA project #NNF2-85631 final report, chapter 3



VII. RESEARCH REACTOR UTILISATION



INVESTIGATION OF THE NATURAL FLOW OF SUPERCRITICAL WATER BY NEUTRON RADIOGRAPHY

CONSTRUCTION OF THE CONTROL EQUIPMENT OF THE ANCARA LOOP

László Horváth, Márton Balaskó, Ákos Horváth, Attila Kiss and Attila Aszódi

Objective

The aim of our work is to construct a model of a cooling channel in a fuel element of the super critical water-cooled reactor. We would like to study the streaming of the super critical water in it.

Methods

The investigated object is the ANCARA (MTA EK-BME NTI Budapest supercritical water test facility) natural circulation loop. It is essentially a bended pipe with many different measurement equipment mounted on a robust frame. The pipe was made of stainless steel the inner diameter of which is in the same order of magnitude as the equivalent diameters in an individual cooling channel of a fuel assembly in a current SCWR design. The warm side of the model is heated by five special heaters with a total heating power of 5000W (5x1kW). The heating power is supplied by five remote controlled power supplies. The thermodynamic parameters of the loop will be measured by twelve pieces thermo-couples, two pieces absolute pressure transducers, two pieces differential pressure transducers and a SITRANS FC 300 type mass flow meter. The power supplies and the signal conditioner units have been assembled in a common frame. This frame is located near by the ANCARA loop. It provides a high degree of immunity from electrical noise. It communicates over a RS485 data line with the data acquisition software running on a PC. The circulation loop is monitored continuously by this software. The temperatures and the pressures are displayed on graph and flowchart, furthermore they are stored on hard disc. The heating powers are controlled by the software.

Results

The photo of the closed circulation loop and of the signal conditioner frame is visible in Fig.1.

Screenshot of the data acquisition and control software is visible in Fig.2.



Figure 1: The ANCARA loop and the signal conditioner frame

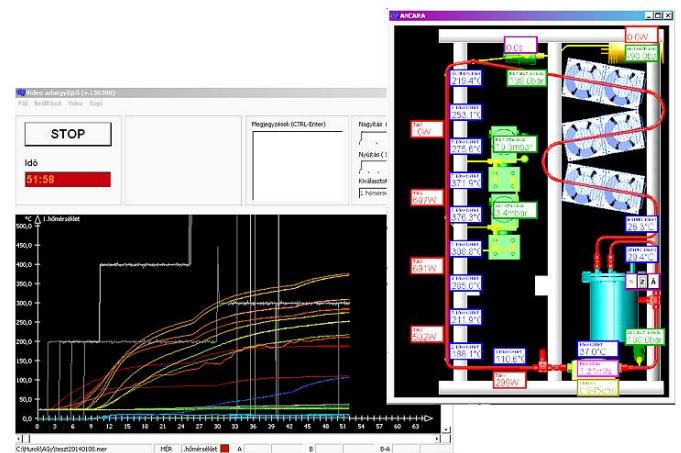


Figure 2: Screenshot of the software

Remaining work

The cooperation between MTA EK and BME NTI will be continued as experimental and education work using the ANCARA loops.

Related publication

Márton Balaskó, László Horváth, Ákos Horváth, Attila Kiss, Attila Aszódi: *Study on the Heat Transfer of Supercritical Pressure Water Flowing in a Closed Loop using Dynamic Neutron Radiography*, ISSCWR-6, March 03-07, 2013, Shenzhen, Guangdong, China

NEW ADVANCED OXIDATION PROCESSES IN WATER TREATMENT

László Wojnárovits, Erzsébet Takács, Renáta Homlok

Objective

This research is aimed at contributing to develop ionizing radiation based simple, energy saving and economical technologies for wastewater treatment. In the Advanced Oxidation Technologies (AOT) the transformation of organic molecules is principally made by hydroxyl radicals. Here, the structure dependency of hydroxyl radical reaction rate constants is investigated with a large number of aromatic molecules.

Methods

Dilute solutions with 0.1–1 mmol dm⁻³ concentrations were prepared. The solutions were pulse irradiated by a Linac type 4 MeV electron accelerator and the formation and decay of intermediates was followed by optical detection. Computer programs were used for fitting to the experimental curves.

Results

The rate constants of hydroxyl radical addition to the rings of aromatic molecules (k_{OH}) were evaluated based on the data measured in our laboratory and literature values. By analysing the methods of k_{OH} determination and the obtained data, the most probable values were selected for the k_{OH} 's of individual compounds and thereby the most reliable dataset was created for monosubstituted aromatics and *p*-substituted phenols. For aromatics the k_{OH} 's fell in a range between 2×10^9 and 1×10^{10} mol⁻¹ dm³ s⁻¹. Although the values show some regular trend with the electron donating/withdrawing nature of substituent, the log k_{OH} - σ_p Hammett substituent constant plots do not give straight lines because these high k_{OH} 's are controlled by both the chemical reactivity and the diffusion (Fig. 1a). However, the logarithms of the rate coefficients of the chemical reactivity controlled reactions (k_{chem}), calculated by $1/k_{OH} = 1/k_{chem} + 1/k_{diff}$, and accepting for the diffusion controlled rate coefficient $k_{diff} = 1.1 \times 10^{10}$ mol⁻¹ dm³ s⁻¹, show good linear correlation with σ_p (Fig. 1b) [1]. The structure-rate coefficient relation, observed for simple molecules, was also shown to be valid for the more complex, practically very important pesticide molecules [2].

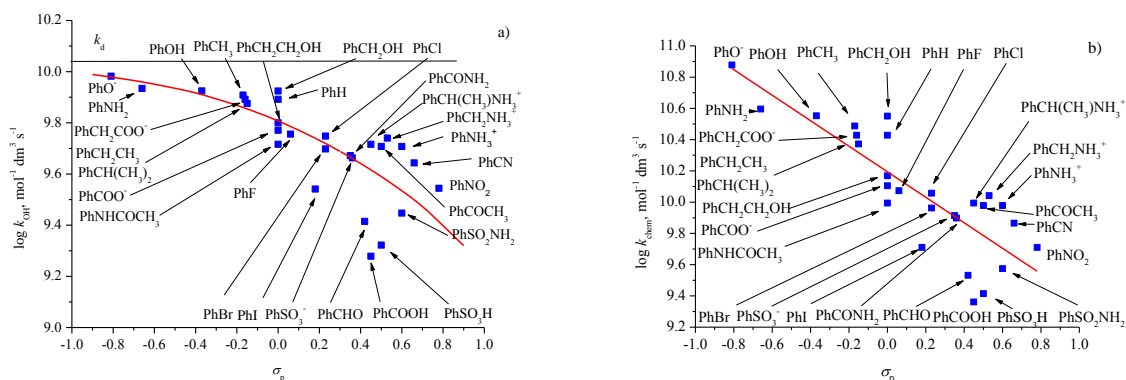


Figure 1: Dependence of k_{OH} (a) and k_{chem} (b) on the Hammett substituent constants for monosubstituted benzenes

Remaining work

The good correlation between k_{chem} and the σ_p is really surprising and encourages us to continue the work with involving in the research several other classes of organic compounds e.g. pharmaceuticals.

Related publications

- [1] L. Wojnárovits, E. Takács: Structure dependence of the rate coefficients of hydroxyl radical + aromatic molecule reaction, Radiation Physics and Chemistry **87**, 82 (2013)
- [2] L. Wojnárovits, E. Takács: Rate coefficients of hydroxyl radical reactions with pesticide molecules and related compounds: a review, Radiation Physics and Chemistry **96**, 120-134 (2014)

PROVENANCE STUDY OF LITHIC RAW MATERIALS OF STONE TOOLS FOUND IN THE CARPATHIAN BASIN

Zsolt Kasztovszky¹, György Szakmány², Zsolt Bendő², Katalin T. Biró³, András Markó³, Bálint Péterdi⁴,
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Objective

Prompt Gamma Activation Analysis (PGAA) has successfully been 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 report is about the second year of an OTKA* project, 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, 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 the elements H and B. Occasionally, we plan to perform complementary measurements using XRF, INAA, EPMA or ICP-AES, ICP-MS. Other very important new methods were also developed, partly in the framework of the current OTKA project, notably the non-destructive SEM-EDX analyses, which we also use to analyse polished stone tools.

Results

In the second year of the present project, we have continued the work with PGAA investigations of archaeological and geological samples made of obsidian [xx], flint, metabasite, eclogite, hornfels and various silex-type rocks from Hungary and – thanks to field works organized within the project, as well as to the CHARISMA Transnational Access – from Poland, the Czech Republic and Romania. Approximately 150 samples – both artefacts and raw materials – have been measured on PGAA and NIPS-NORMA stations of the Budapest Research Reactor. We have started the first measurements of a complete set of greenstone stone tools by SEM-EDX methods.

On the basis of our continuously increasing obsidian database, various artefacts from North-West Romania, as well as the famous Nyírlugos cores from the Hungarian National Museum (HNM) have been undoubtedly ascertained as belonging to the “Carpathian 1” type (North Tokaj Mts, Slovakia). From the Lithoteca collection of the HNM, we have widened the range of investigated obsidian raw materials with new samples from Melos, Antiparos, Tolcsva and its environs.

We have started to investigate the stone tools of a very important Copper-Age culture of Erőd, which is represented in settlements of Eastern Transylvania and over the Carpathian mountains.

We have continued 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 two 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 prehistoric stone tools with preference on long distance trade items and building our comparative database.

Related publications

[1] Kasztovszky Zsolt, T. Dobosi Viola, T. Biró Katalin, Szilágyi Veronika, Maróti Boglárka: *Prompt-gamma activation analysis of jpanese obsidians in the lithoteca collection of the HNM (in Hungarian)*, Archeometriai Műhely 2012 9/4 247–254.

[2] Szakmány György, T. Biró Katalin, Kristály Ferenc, Bendő Zsolt, Kasztovszky Zsolt, Zajzon Norbert: *Long distance import of polished stone artefacts: HP Metamorphites in Hungary (in Hungarian)*, Archeometriai Műhely 2013 10/1 83-92.

[3] Péterdi B., Szakmány, Gy., Judik, K., Dobosi, G., Kasztovszky, Zs., Szilágyi, V., Bendő, Zs., G. Gil: *Results of petrographic and geochemical investigation of a nephrite adze of Late Copper Age - with a view on known European nephrite occurrences (in Hungarian)*. In: Dályay V. – Sámson, M. – Hámos, G. (szerk.): IV. Kézttani és Geokémiai Vándorgyűlés Kiadványa, Orfű, Hungary, 2013. szeptember 12-14. pp.: 100-105. (ISBN 978-963-8221-52-0)

[4] Szakmány Gy., Bendő Zs., Kasztovszky Zs., Kristály F., Zajzon N.: *HP metaophiolite polished stone tools in Hungarian archaeological finds (in Hungarian)*. In: Dályay V. – Sámson, M. – Hámos, G. (szerk.): IV. Kézttani és Geokémiai Vándorgyűlés Kiadványa, Orfű, Hungary, 2013. szeptember 12-14. pp.: 95-99. (ISBN 978-963-8221-52-0)

- [5] B. Constantinescu, D. Cristea-Stan, Zs. Kasztovszky, B. Maróti: *PGAA analysis of some Neolithic obsidian samples from Romanian regions (poster)*, NINMACH 2013, 2013.09.09-12, Garching, Németország.
- [6] Zs. Kasztovszky, B. Maróti, Z. Kis, K. T. Biró : *Prompt Gamma Activation Analysis of the Nyírlugos obsidian core depot find (poster)*, 2013.08.20-24 Iasi, Romania 5th Arheoinvest Symposium, 'Stories Written in Stone'
- [7] I. Sobkowiak-Tabaka, Zs. Kasztovszky, J. Kabacinski, K. T. Biró: *Trans-Carpathian contacts of the late glacial societies of the Polish Lowlands (poster)*, 19th EAA Annual Meeting, 2013.09.4-8, Pilsen, Cseh Köztársaság.
- [8] F. Bernardini, A. De Min, D. Lenaz, Z. Kasztovszky, P. Turk, A. Veluscek, C. Tuniz, E. Montagnari Kokelj: *Petrographic and geochemical comparison between the Copper Age "Ljubljana type" axes and similar lithotypes from Eisenkappler Diabaszug complex (southern Austria)*, *Journal of Archaeological Science* **41** (2014) 511-522.



Figure 1: An obsidian core in the sample holder of the Budapest NIPS station

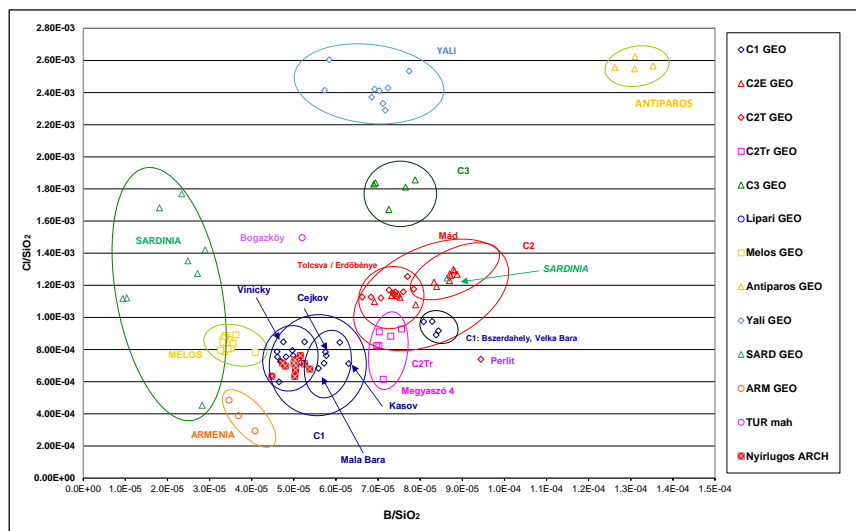


Figure 2: Characterisation of obsidian samples, based on their B- and Cl-contents

CHARISMA - CULTURAL HERITAGE ADVANCED RESEARCH INFRASTRUCTURES: SYNERGY FOR A MULTIDISCIPLINARY APPROACH TO CONSERVATION/RESTORATION

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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 instrumentations and knowledge allowing scientists, conservators-restorers and curators to enhance their research at the field forefront. Transnational Access programs 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 (Wigner RCP) and in cooperation with the Centre for Energy Research (MTA EK) - 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 PGAI/NT unit): applicable for determination of bulk elemental composition with optional tomography and elemental mapping of large objects - at MTA EK
- Time of Flight Neutron Diffraction, Triple Axis Spectrometer and Small Angle Neutron Scattering: applicable for non-invasive micro structural- and phase analyses - at Wigner RCP
- External milli-beam PIXE and compact XRF: applicable to determine the near-surface elemental composition - at Wigner RCP.

Results

In 2013, 12 various projects, proposed by European scientists, have been completed. The material investigated comprises Prehistoric stone objects and raw materials, Celtic and Medieval silver coins, various glazed pottery, lapis lazuli, Medieval armor and a sealed Egyptian jar. 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 2013 can be found in Table 1.

Remaining work

The CHARISMA project will be finished in the spring of 2014. The last experiments are performed before March 2014. Evaluation of the experimental data, as well as dissemination of the results and preparation of the final report is in progress.

Related publications

- [1] M. Mödlinger, P. Piccardo, Zs. Kasztovszky, I. Kovács, Z. Szőkefalvi-Nagy, Gy. Káli, V. Szilágyi: *Archaeometallurgical characterization of the earliest European metal helmets*, *Materials Characterization* **79** 22-36 (2013)
- [2] T. Rehren, T. Belgya, A. Jambon, Gy. Káli, Zs. Kasztovszky, Z. Kis, I. Kovács, B. Maróti, M. Martín-Torres, G. Miniaci, V. C. Pigott, M. Radivojevic, L. Rosta, L. Szentmiklósi, Z. Szőkefalvi-Nagy: *5,000 years old Egyptian iron beads made from hammered meteoritic iron*, *Journal of Archaeological Science* **40** 4785-4792 (2013)
- [3] D. Watkinson, M. Rimmer, Zs. Kasztovszky, Z. Kis, B. Maróti, L. Szentmiklósi: *The use of neutron analysis techniques for detecting the concentration and distribution of chloride ions in archaeological iron*, *Archaeometry*, 2013, (in press)
- [4] F. Bernardini, A. De Min, D. Lenaz, Z. Kasztovszky, P. Turk, A. Veluscek, C. Tuniz, E. Montagnari Kokelj: *Petrographic and geochemical comparison between the Copper Age "Ljubljana type" axes and similar lithotypes from Eisenkappler Diabaszug complex (southern Austria)*, *Journal of Archaeological Science* **41** 511-522 (2014)
- [5] E. Abraham, M.C. Hervé, Z.M. Bessou, Z. Kasztovszky, L. Szentmiklósi and Zs. Kasztovszky: *3D Neutron Imaging of a XVIIIth Dynasty Egyptian Sealed Pottery* (poster), NINMACH 2013, 2013.09.09-12, Garching, Németország
- [6] Rosta László, Belgya Tamás, Káli György, Kasztovszky Zsolt, Kis Zoltán, Kovács Imre, Maróti Boglárka, Szentmiklósi László, Szőkefalvi-Nagy Zoltán, Alblbert Jambon, Thilo Rehren: *„VASGYÖNGYÖK AZ ÉGBŐL” A legősibb ember által készített vastárgyak meteorit eredetének igazolása röntgen- és neutronanalízissel*, *Magyar Régészet* (online magazin, 2013 tél).

• Table 1: Summary of CHARISMA projects in 2013.

BNC Proposal Nr.	Principal Proposer	Principal Proposer's Affiliation	City, Country	Proposal Title	Experiment Date	BNC Instrument	Main achievements
316	Emmanuel Abraham	University of Bordeaux, Laboratoire Ondes et Matière d'Aquitaine	Bordeaux, France	Investigation of a XVIIIth Dynasty Egyptian sealed Pottery by cold Neutron Tomography	2013.04.08-11	NIPS-NORMA	3D neutron imaging clearly reveals that the stopper of the jar is made of a ball of linen. 3D images also provide representations of the mobile content of inhomogeneous dried materials. By semi-quantitative analysis at NIPS, we concluded that the jar content is composed of H, C, N, S and Cl elements, which supports the assumption about its organic nature.
321	Judit Zöldöldi	University of Stuttgart, Institute of Materials Testing	Stuttgart, Germany	Provenance analysis of lapis lazuli	2013.05.21-24	TOF-ND, PGAA, External m-PIXE	PGAA database of lapis lazuli were extended with samples from Tadjikistan, Usbekistan, Turkistan, Pakistan and Pamir. Additionally, TOF-ND analyses were done. The abundance of mineral phases, the crystal structure of each phases, the grain sizes and orientations could provide important clues to the deformation history, and help to uncover historic production steps.
345	Ewa Panczyk	Institute of Nuclear Chemistry and Technology	Warsaw, Poland	A comparative study of medieval silver coins from Poland and Central Europe	2013.06.20-28	PGAA, External m-PIXE, XRF	An overall aim was to determine the provenance and dating of a few groups of the early medieval (13th-14th c.) Central European coins. Widely known and already described types of coins have been chosen. Knowing the elemental composition determined by PGAA and PIXE, we aimed to determine provenance of the coins and to show whether they were struck in one mint or produced in various centers.
346	Johannes Sterba	Vienna University of Technology, Atominsttitut	Vienna, Austria	Obsidian Least Destructive Analysis Provenancing System	2013.03.19-21	PGAA, NIPS	Complementary to a larger project using INAA, LA-ICP-MS, PIXE and PIGE, obsidians from main European sources were analysed by PGAA. The overall chemical fingerprints of each sources are greatly enhanced and allow an easier distinction between sources (e.g. from the Greek islands of Melos).
344	Maria Isabel Prudencio	CTN, Instituto Superior Técnico, Universidade Técnica de Lisboa	Lisbon, Portugal	Evaluation of the degradation state of ancient Portuguese glazed tiles...	2013.07.01-04	PGAA, External m-PIXE, XRF	Chemical composition of numerous ceramic bodies of glazed tiles and the glaze was obtained combining PGAA, PIXE and XRF. Detailed characterization of the tile bodies allow to distinguish different raw materials / provenances. This kind of approach have an impact on the enhancement of the diversification of used raw materials and tiles production recipe in central Portugal from the 17th till the 20th century.
343	Jacopo Corsi	University of Torino, Physics Department	Torino, Italy	Ancient silver-copper alloy coins: from Celtic to Roman times	2013.07.02-05	TOF-ND, PGAA	Major composition of 40 Celtic and Roman coins partly from the Hungarian National Museum were determined by PGAA. The results show very clearly the presence of a general silver debasement in the Celtic coinage. Moreover, a significant loss of silver content is detected also within some series, as seen on similar coins from the Archaeological Museum of Turin
342	Michael Brandl	University of Graz	Graz, Austria	Characterization of radiolarites from the Northern Calcareous Alps and the Carpathian Basin in an archaeological context	2013.05.08-10	PGAA	Characterisation of selected radiolarite sources from Northern Calcareous Alps (Austria), the Carpathian Mountains (Slovakia, Poland) and the Bakony Mountains (Hungary) used for prehistoric raw material procurement and distribution was aimed using PGAA. Combining PGAA and LA-ICP-MS results, a finer resolution of provenancing is expected
331	Massimo Rogante	Rogante Engineering Office	Civitanova Marche, Italy	SANS and TOF-ND Investigation of ancient and modern Linen cloths	2013.11.18-21.	TOF-ND, SANS	9 ancient - pre-dinastic (3500-2000 B.C.) and Ptolemaic ages - and 5 modern linen samples were studied by SANS. A relatively high number of scattering was observed in case of all (old and modern) samples. In case of the old samples, no orientation was observed. This could be explained by the degradation of the samples and the destruction of cellulose fibrils. The modern samples, on the other hand, showed anisotropy along the linen wire axis.
347	Alan Williams	The Wallace Collection	London, UK	Non-destructive structural and compositional analysis of swords and helmets by TOF-ND and PIXE techniques	2013.11.06-10.	TOF-ND, External m-PIXE	Five Indo-Persian blades were analysed by TOF-ND, a useful method of identifying high-carbon steels. The detection of anisotropy in patterned blades has proved to be more complex. Some blades with clearly visible patterns show less anisotropy than might have been predicted.
353	Thomas Birch	Dept. Of Archaeology, University of Aberdeen	Aberdeen, UK	Iceland's early crucible metallurgy: a new investigation into Viking Age technology	2013.11.19-23.	PGAA, NIPS-NORMA, External m-PIXE	It was aimed to resolve questions associated with the technical ceramics (crucible fragments) found in Iceland, associated with metallurgical activity. The results provide an unprecedented insight into non-ferrous metallurgy in Iceland with an understanding of development in technological practices.
350	Hágó Attila	Satu-Mare County Museum	Satu-Mare, Romania	The provenance of the obsidian, silex and other ge archaeological materials from the Middle Neolithic	2013.09.23-26.	PGAA	Middle Neolithic archaeological objects made of obsidian and silex from Carei Plain (NW-Romania) were analyzed by PGAA. Based on major components as well as B and Cl content, obsidians were identified as Carpathian-1 type of a raw material source in North Tokaj. One piece which was thought to be an obsidian, finally was proved to be a silex.
352	Nikolaos Zacharias	Archaeometry Laboratory, Univ of Peloponnese	Kalamata, Greece	Technology and Provenance Studies of Byzantine Glazed Pottery from Corinth, Greece	2013.11.10-14.	PGAA, External m-PIXE	PGAA was applied for the bulk analyses of the ceramic body free from any decoration/glazed material. We hope to distinguish the groups of different origin ceramics, based on the elemental composition measured by PGAA. Additionally, PIXE was able to identify the colorant agents of copper, iron and lead that produce green, red, yellow colorations.

ERINDA – EUROPEAN RESEARCH INFRASTRUCTURES FOR NUCLEAR DATA APPLICATIONS

Tamás Belgya, László Szentmiklósi, Zoltán Kis

Objective

The EUROATOM FP7 ERINDA project aims to form 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, aiming to reduce nuclear waste production.

Special emphasis is on the improvement of all varieties of nuclear data related to actinides and structural materials. Finally, we are committed in the continuation of our activities in a future EURATOM project similar to ERINDA.

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 Compton-suppressed spectrometer system. We also accommodate custom setups to carry out more sophisticated experiments, provided that it is shipped to our experimental site.

Results

In 2013 we hosted 3 projects that were accepted by peer-review proposal evaluation body (PAC) of ERINDA:

1./ PAC 4/1 Spokesperson: Andreas Oberstedt (CEA/DAM, France). *First ever correlation measurements of prompt fission γ -rays and fission fragments from the reaction $^{241}\text{Pu}(n_{\text{th}}, f)$.* Requested beam time: 200 h. Measurements were done in 11-22 June 2013 with four participants from JRC IRMM, Belgium and CERN, Physics Department, Geneva.

2./ PAC 4/2 Spokesperson: Olivier Serot (CEA-Cadarache, France). *Ternary ^6He : a possible way to explain the tritium excess problem observed in spent nuclear fuel reprocessing.* Requested beam time: 200 h. Measurements were done in 16-26 April 2013 with two participants from CEA-Cadarache, France and JRC IRMM, Belgium.

3./ PAC 4/1 Spokesperson: Matthias Rossbach (Forschungszentrum Juelich GmbH). *Characterisation of prompt gamma signature of actinides.* Requested beam time: 120 h. Measurements were done in 10-17 May 2013 with two participants from Institute for Energy and Climate Research, IEK-6, Jülich, Germany.

The prompt fission spectrum from $^{241}\text{Pu}(n_{\text{th}}, f)$ reaction taken in Experiment 1. can be seen in Figure 1.

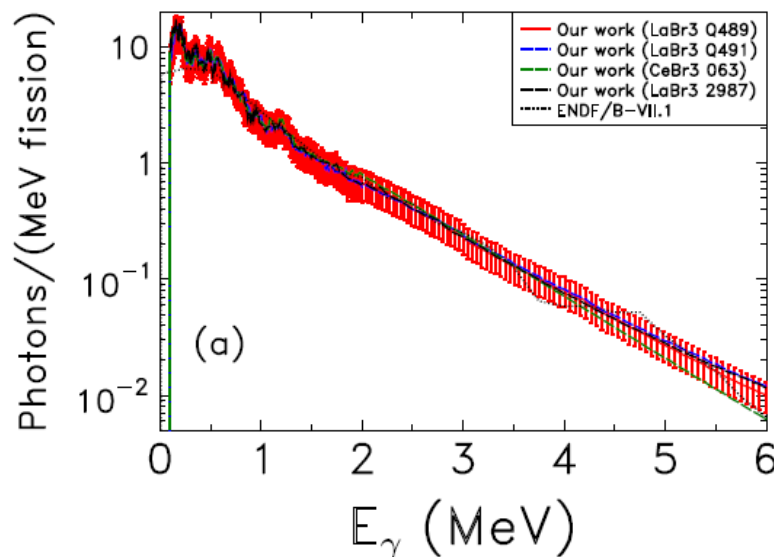


Figure 1: The prompt fission γ -ray emission spectrum for the neutron-induced fission on ^{241}Pu taken with our four lanthanide-halide detectors. All spectra agree very well with each other.

Remaining work

Preparation of publications.

Related publication

S. Oberstedt, R. Billnert, T. Belgya, T. Bry, W. Geerts, C. Guerrero, F.-J. Hamsch, Z. Kis, A. Moens, A. Oberstedt, G. Sibbens, L. Szentmiklósi, D. Vanleeuw, and M. Vidali; *High precision prompt spectral γ -ray data from the reaction $^{241}\text{Pu}(n_{\text{th}}, f)$* , Phys. Rev. C., submitted.

APPLICATIONS OF PROMPT-GAMMA ACTIVATION ANALYSIS

Zsolt Kasztovszky, László Szentmiklósi, Boglárka Maróti, Katalin Gmélíng

Objective

To apply the prompt-gamma activation analysis (PGAA) method for determination of samples' elemental composition, in the fields of catalysis, material science, geochemistry 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, neutron activation analysis, X-ray fluorescence.

Results

Chemical catalysis

With a customized in-beam catalysis setup 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 are on-going since 2008, in close collaboration with the Fritz-Haber Institute, Berlin. Based on these results, we can make highly relevant statements for the mechanism of heterogeneous catalytic processes. An environmental-friendly process to replace the conventional NaCl electrolysis for producing chlorine is the so-called Deacon-reaction, based on the heterogeneous gas phase oxidation of HCl. CeO_2 , and Hf, Zr, La, Y-doped CeO_2 catalysts ($\text{Ce}_{99}\text{Hf}_1$, $\text{Ce}_{97.5}\text{Hf}_{2.5}$, $\text{Ce}_{95}\text{Hf}_5$, $\text{Ce}_{90}\text{Hf}_{10}$; as well as $\text{Ce}_{95}\text{Zr}_5$, Ce_{95}Y_5 , $\text{Ce}_{95}\text{La}_5$) were measured and the results were compared to the RuO_2 , which was studied in 2011. The Cl to Ru/Ce molar ratios were measured by PGAA, while the Cl_2 production was monitored by iodometric titration. The experiments indicate the lowest Cl uptake for undoped CeO_2 , the largest uptake for catalysts with trivalent dopants. It was found that the intrinsic reactivity of ceria can be improved by a factor of two when doping with Hf in appropriate quantities, whereas trivalent dopants are detrimental. Since oxygen excess in the reactant stream enhances the reaction rate, the variation of the feed (HCl/O_2) composition allowed us to correlate the reaction rate and the degree of chlorination. Results indicate that chemisorbed Cl is a poison of the catalytic reaction.

Material science

As a continuation of our experiments in 2012, a second batch of Co-Re based alloys was prepared at the TU Braunschweig to supplement Ni-base Superalloys at ultra-high temperature ($>1200^\circ\text{C}$) applications, such as turbines. We quantified the B content of Co-Re-Cr(-Ta) alloys by PGAA, whereas the spatial distribution of the boron in the alloys was mapped with the solid state nuclear track detector (SSNTD) technique. Thanks to the high cross-section of the $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction, we could quantify boron already in a few ppm quantity, based on its 477.6 keV gamma-ray peak, 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].

Elemental fingerprinting to identify source-of-origin has become an important aspect of classifying high quality wool, mohair and cashmere. Since the hair takes up trace elements found in the animals' local environment, it should be possible to construct trace element matrices that could be used for verification of source-of-origin of textiles and identification of blending of fibres from different locations. PGAA has been applied with success on a suite of fibre samples of wool, mohair and cashmere from various sources around the world to assess the viability of developing a fingerprint profile for the respective fibres. The study was complemented with parallel SANS measurements for the structure analysis.

In collaboration with the Semmelweis University, the composition of a dental cement sample and its change over time was measured during the settlement. It has been found that the hydrogen content is gradually changing. This can be a significant addition to the interpretation of earlier neutron diffraction measurements.

Archaeometry

A 18th -16th B.C. bronze statuette from the Egyptian Collection of the Museum of Fine Arts has been studied by PGAA and Neutron Radiography. The aim of the study was to decide whether the different parts of the statuette were manufactured separately, and whether meteoritic iron was used for the fabric. In another project, corrosion mechanism of ancient iron objects through their Cl distribution has been studied with PGAI, NR and NT. This research has been published in 2013 and will be continued in 2014, too. Additionally, composition of different archaeological objects (17th-20th c. Portuguese and 12th-17th c. Greek glazed ceramics, 9-13th c. ceramics crucibles, silver coins) have been measured, in order to survey their present conditions and/or to determine their origins or technology of production. The bulk PGAA has been combined with neutron radiography at the NIPS-NORMA station, as well as with PIXE and portable XRF. Results of previous research on polished stone axes, on bronze helmets and on 5,000 years old Egyptian iron beads made from hammered meteoritic iron have been published in 2013.

Besides scientific papers and presentations, review papers about the use of neutron methods in Cultural Heritage research have been published. In addition, numerous archaeometric applications are summarized in the CHARISMA and OTKA project reports.

Geochemistry

We participated in the IAEA coordinated inter-comparison test (IAEA TC project RER 4/032/RER1/007, 2011-2013), WEPAL (WAGENINGEN Evaluating Programs for Analytical Laboratories), measuring the composition of four soil samples. It was interesting to compare PGAA results with the results of numerous NAA laboratories and other ICP-MS and XRF laboratories from all around the world. Comparable elements (all major elements and some trace elements, which are possible to measure with NAA and also PGAA) corresponded well with each other. It should be emphasized that few elements (e.g.: Si, H, B, Cl and Gd) could only be measured with PGAA, even these elements are well measurable with PGAA, could not be compared.

Volcanic rock samples from Antarctica (Deception Island) were measured with PGAA in a framework with a Polish Scientific Cooperation. Samples are waiting for NAA measurement at the beginning of 2014, and some of them are under K/Ar-measurement. Publications from the combined results are expected in 2014.

Comparison and combination of the PGAA and NAA laboratory started in 2013 materials, related to geological reference were measured in both laboratories. The comparable elements showed good agreement, while NAA and PGAA proved to be good complementary analytical procedures to each other. Results were published on the 6th k0-Users Workshop (22-27. Sept. 2013, Budapest) and in the related special issue of JRNC.

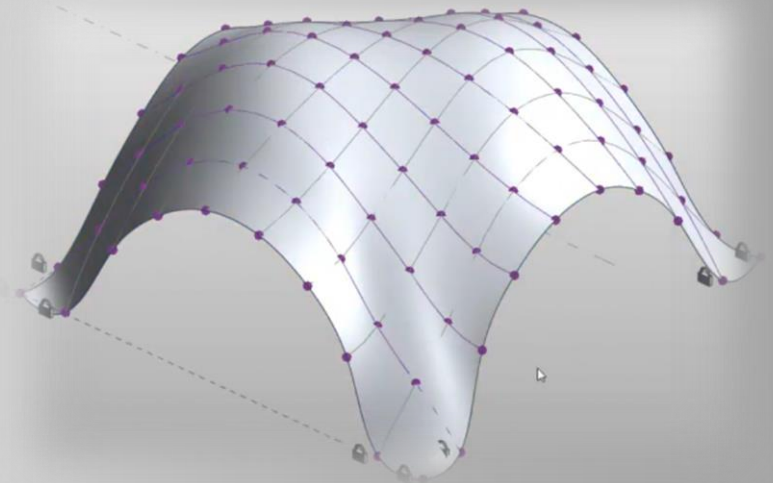
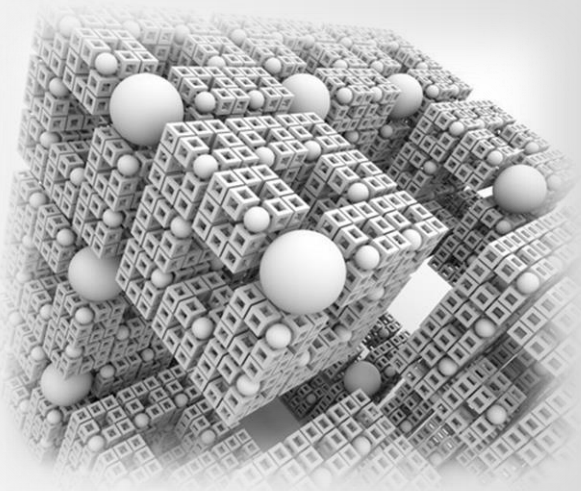
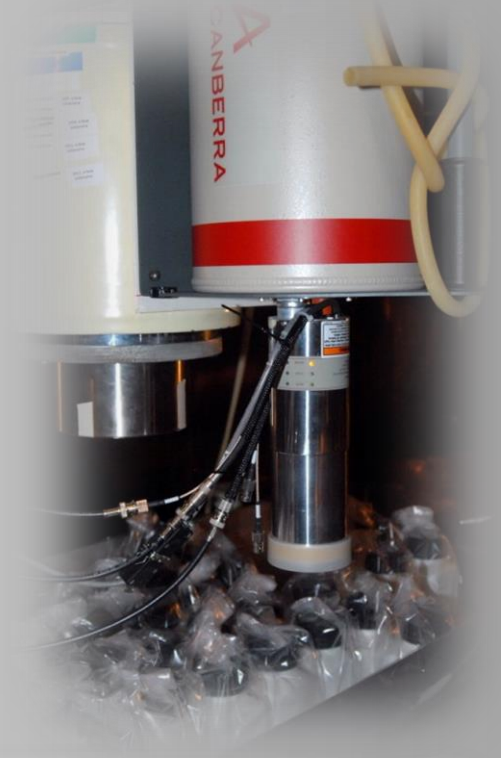
Remaining work

The data analysis of the completed experiments is in part still in progress. The continuation of several experiments is foreseen for 2014.

Related publications

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- [3] 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 production*, Applied Catalysis B: Environmental 132-133 (2013), 123-131.
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- [9] T. Rehren, T. Belgya, A. Jambon, G. Káli, Z. Kasztovszky, Z. Kis, I. Kovács, B. Maróti, M. Martín-Torres, G. Miniaci, V.C. Pigott, M. Radivojević, L. Rosta, L. Szentmiklósi, and Z. Szőkefalvi-Nagy: *5,000 years old Egyptian iron beads made from hammered meteoritic iron*, Journal of Archaeological Science 40:(12) (2013), 4785-4792.
- [10] Rosta László, Belgya Tamás, Káli György, Kasztovszky Zsolt, Kis Zoltán, Kovács Imre, Maróti Boglárka, Szentmiklósi László, Szőkefalvi-Nagy Zoltán, Alblbert Jambon, Thilo Rehren: *Proof of the Meteoritic Origin of Mankind's Earliest Iron (in Hungarian/in English)*, Hungarian Archaeology (E-journal, 2013 Winter).[in Hungarian]
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- [12] K. Gméling, A. Simonits, I. Sziklai-László, D. Párkányi (2014): *PGAA and NAA Results of Geological Samples and Standards (6th International k₀-Users' Workshop, Budapest, 22-27. September, 2013.)* J. Radioanal. Nucl. Chem. (Accepted)

VIII. MISCELLANEOUS



DIGITAL GEOMETRY

Attila R. Imre

Objective

Fractal geometry can be used to simplify problems related to complex shapes, lines, etc. During the analysis of digitalized version of an irregular line with loops describing a complex track or trajectory, it is sometimes forgotten that the discrete points are forming a sequenced set, i.e. one can define a first, second, ... Nth, (N+1)th... point. Omitting the sequencing during digital length measurement with variable yardstick, a systematic error will be introduced, causing erroneous fractal dimension values. In this project, the extent of this error is demonstrated.

Results

There are several scientific problems, when the knowledge of the length and the fractal dimension of a „curve” is crucial information. In most cases, these curves are not real curves, i.e. they are not continuous lines, rather a set of discrete points. The discretization can be the result of data processing (digitalization) or can be originated from the used method itself (like GPS tracking). Besides the length and shape (fractality, tortuosity), there is a third property which can be important for several curves, namely the direction. A curve describing the movement of an object has not only length and shape, but also a direction. In a discretized curve, the direction will be represented by the sequencing (chronological order of points). Depending on the source and/or process, there are some cases, where the sequencing are lost or cannot be determined. The lack of proper sequencing can cause unavoidable problems in length and fractal dimension measurements, when the original curve is tortuous (see Fig. 1).

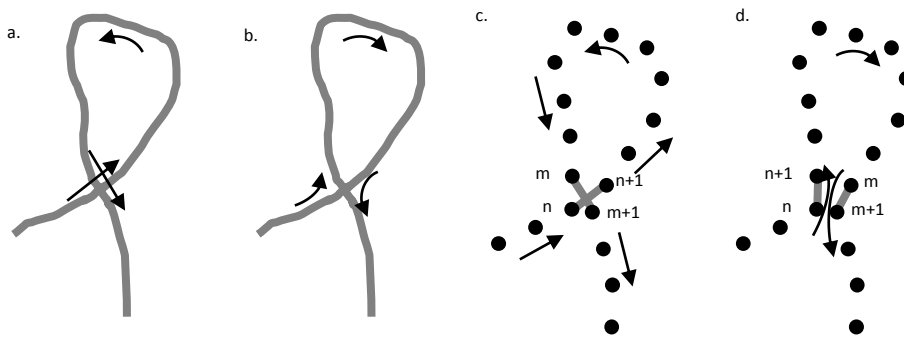


Figure 1: The effect of sequencing on the length measurement in two geometrically identical tortuous lines. Dataset c and d are the digitalized versions of curves a and b, respectively. Due to the different sequencing, the distance measured between points n and n+1 differs.

As an example, GPS track of a herding dog was analyzed [1]. Points with proper and improper sequencing were analyzed. The fractal dimensions were calculated from the two different length measurements. The error of the estimated fractal dimension was around 0.1, which is 10% of the whole fractal-range (the fractal dimension in this case has to be between 1 and 2). This error can be too high and may mask the difference between two, physically or biologically different cases. To avoid these problems, one should always use properly sequenced data set.

Remaining work

Applicability of the results on areas relevant for energetics should be tested. Further mathematical problems related to digital geometry should be studied.

Related publication

Attila R. Imre and Owen R. Bidder: *The importance of proper sequencing in estimating the length- and fractal dimension of tortuous curves*, Acta Biotheoretica, submitted

PREPARATION OF SUPERABSORBENTS BY IONIZING RADIATION INDUCED CROSS-LINKING OF CELLULOSE DERIVATIVES

*Erzsébet Takács, László Wojnárovits,
Tamás Fekete*

Objective

Superabsorbents are three-dimensional polymer networks capable of absorbing large amounts of water. Conventional superabsorbents are usually petroleum based synthetic polymers. Natural materials like cellulose are intensively studied for the substitution of synthetic materials by natural ones. In the present work cellulose based superabsorbents were synthesized using high energy irradiation.

Methods

Hydrogels were prepared by γ -irradiation in aqueous solutions of four cellulose derivatives (carboxymethylcellulose sodium salt - CMC-Na, methylcellulose - MC, hydroxyethylcellulose - HEC and hydroxypropylcellulose - HPC). Dried, weighted hydrogels were immersed in deionized water for 48 hours. The gel fraction (GF) was calculated by the equation: $GF (\%) = W1/W0*100$, where $W0$ and $W1$ are the sample weight before and after extraction, respectively. After the removal of the sol fraction, gels were immersed again in deionized water (L:G = 1000:1). Swollen gels were removed by using a sieve. The degree of swelling (Q) was determined using the formula: $Q = (Ws - Wd)/Wd$, where Ws and Wd are the masses of the swollen and dry samples.

Results

Hydrogels with high water uptake were successfully prepared from four cellulose derivative solutions by ionizing radiation induced crosslinking. Synthesis parameters had a major effect on the gel properties. The gel fraction increased with the absorbed dose, while the water uptake decreased. Over a critical dose the gel ratio slightly decreased due to the radiation induced degradation - the water uptake did not change. Due to the increasing crosslink density, the water uptake was continuously decreasing with increasing dose. The lower uptake at high concentrations can be explained with the low water content, resulting in lower polymer chain mobility and inhomogeneity. The difference between various derivatives can also be attributed to different molecular weights besides the chemical structure.

The swelling rate was the highest in the first 4-5 hours after which it gradually slowed down. CMC and HEC gels reached equilibrium after 24 hours, while HPC and MC gels required longer immersion times. In pure water, CMC gels showed the highest water uptake, while HPC and MC gels took up significantly lower quantity of water than the other derivatives. The derivatives showed different sensitivity to the ionic strength of the swelling solution. The water uptake of CMC gels decreased significantly with the salt concentration, while HEC gels showed smaller response. At high ionic strength, the swelling properties of HEC gels were much better than those of the other three gels. Thus different cellulose derivative based gels may be preferred at various applications depending on the environment.

Remaining work

As a continuation of the work we intend to improve the mechanical properties of the synthesized polymers by adding monomers to the solutions of the cellulose derivatives before irradiation. The results will be summarized in a PhD thesis.

Related publications

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- [2] T. Fekete, J. Borsa, E. Takács: *Functionalization of cellulosic fibres by high energy irradiation. 23rd IFATCC International Congress, Budapest, Hungary, 8-10 May, 2013. Proc. p. 39-47. ISBN: 9789639970335 CD P1 17, ISBN 978-963-9970-33-5, Abstracts, ISBN 978-963-9970-32-8* [3]
- [3] T. Fekete, E. Takács, L. Wojnárovits, J. Borsa: *Radiation induced synthesis of cellulose based hydrogels. in Hungarian. Autumn Radichemical Days 2013, Eger, Hungary, 2013.10.16-2013.10.18. Budapest: HAS Radichemical Committee, 2013. pp. 87-90. (ISBN: 978-963-9970-42-7)*
- [4] T. Fekete: *Synthesis and characterization of cellulose based hydrogels. MSc thesis. 2013. January.*

A BROAD RANGE ANALYSIS OF WASTEWATER MODEL SYSTEMS TREATED WITH ADVANCED OXIDATION PROCESSES

Tamás Csay, Gergely Rácz, Gyuri Sági, Erzsébet Takács, László Wojnárovits

Objective

Utilizing advanced oxidation processes (AOPs) like γ -radiation is a promising way to degrade toxic and persistent organic pollutants from pretreated wastewater. Liquid chromatography – tandem mass spectrometry (LC-MS/MS) is a progressive method to qualify and quantify remaining components and degradation products from effluents. The aim of this work was to follow the radiation induced degradation of clofibric acid and suggest a possible degradation mechanism after comparing the results obtained with LC-MS/MS and other analytical techniques.

Methods

Dilute aqueous stock solutions of pharmaceuticals were prepared with different concentrations. The solutions were irradiated under precisely adjusted reaction conditions (pH, atmosphere, dose, etc.) by a ^{60}Co gamma source. Effects of several reactive species ($\cdot\text{OH}$, e_{aq}^- , $\text{O}_2^{\cdot-}/\text{HO}_2^{\cdot}$, $\cdot t\text{BuOH}$) generated during irradiation of water were followed by various analytical methods, like LC-MS/MS, ion chromatography (IC), UV-Vis spectrophotometry, chemical oxygen demand (COD), total organic carbon content (TOC), adsorbable organic halogens (AOX) and toxicity measurements.

Results

Clofibric acid (CFA) is the bioactive metabolite of several world-wide used lipid regulator medicines. Due to its high persistence, it has been detected both in the aquatic environment and in drinking water. After ionizing radiation treatment, CFA decomposes effectively in aqueous solutions rather by hydroxyl radical than by hydrated electron or $\text{O}_2^{\cdot-}/\text{HO}_2^{\cdot}$. Various hydroxylated, dechlorinated and fragmentation products have been identified and quantified, and possible degradation pathways have been proposed (Figure 1). In order to follow the formation of hydroxylated derivatives of CFA a new and unique LC-MS method was developed based on ^{18}O isotope labelling. The mineralization of CFA was monitored by determination of sum parameters like COD, TOC and AOX. It was found that the organic chlorine cleaves very effectively prior to complete mineralization. After the treatment no toxic effect was found according to *Vibrio fischeri* tests. However, at early stages some of the reaction products were more harmful than the clofibric acid.

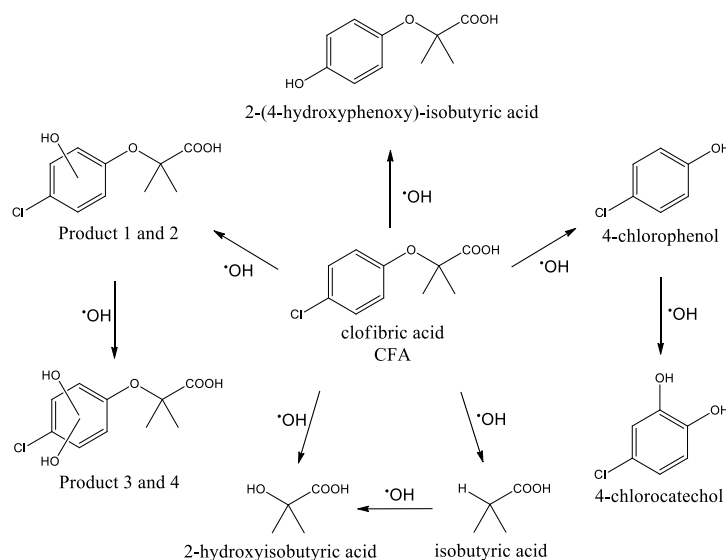


Figure 1: Suggested reaction scheme and identified metabolites generated from CFA in the presence of $\cdot\text{OH}$

Remaining work

Other types of pharmaceuticals like sulfonamides have also been subjects of our preliminary investigations. Sulfonamides are a large group of persistent antibiotics with more or less similar structures. They provide a good opportunity to examine relationships within structure, reactivity and toxicity.

Related publications

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- [2] Gy. Sági, T. Csay, L. Wojnárovits, E. Takács: *Oxidative and reductive degradation of sulfamethoxazole in aqueous medium* [in hungarian language], Radiochemical Days in Autumn 2013, 16-18. October 2013, Eger, Hungary. Budapest: Radiochemical Committee of the Hungarian Academy of Sciences, pp. 96-100 (2013) (ISBN: 978-963-9970-42-7)

DEVELOPMENT OF NUCLEAR ANALYTICAL AND IMAGING TECHNIQUES, NUCLEAR DATA MEASUREMENTS, AND RELATED TRAINING ACTIVITIES

László Szentmiklósi, Tamás Belgya, Zoltán Kis

Objective

To develop our analytical and imaging capabilities and know-how in PGAA (Prompt-Gamma Activation Analysis), PGAI (Prompt Gamma Activation Imaging) / NT (Neutron Tomography) and low-level counting, to accurately determine related nuclear data, and to provide training and education for guest researchers and students.

Methods

(n,γ) measurements, evaluation of data and comparison to literature, computer programming, Monte Carlo modelling, teaching.

Results

We performed highly accurate (n,γ) measurements on elemental targets, such as K, enriched isotopes of tungsten, lead and iron samples. The evaluation of such data is completed in close collaboration with colleagues at the Berkeley National Lab., Institute for Reference Materials and Measurements and Charles Univ. Praha. The results were published in several papers [1-3].

With colleagues at the Helmholtz-Zentrum, Dresden-Rossendorf, the unfolding of the $^{195}\text{Pt}(n,\gamma)$ spectrum has been completed and published [4-5]. Significant progress has been made with the unfolding of the $\text{Cd}(n,\gamma)$ experiment, as the methodology was implemented with the PGAA detector system, and the trueness of the earlier calculation could be significantly improved.

In the framework of the TANDEM collaboration, a new set of prompt gamma measurements, decay spectra and neutron radiographies were completed on ^{237}Np , ^{242}Pu and ^{238}U samples to extend the PGAA spectroscopic library and establish nuclear data for spent fuel characterization and transmutation.

We finalized the construction of and published a paper about the design details of the Neutron Induced Prompt-gamma spectrometry (NIPS) Compton suppressed spectrometer. The methodology of the 3D PGAI-NT method has been described in a Journal of Analytical Atomic Spectrometry paper, co-authored by the FRM-II PGAA group.

In the DÖME low level counting facility, the specific activities of various natural and artificial construction materials were measured and published. These results will contribute to a Ph.D. thesis at the ELTE University.

The Monte Carlo simulation code for the calculation of the detector response function was implemented for the Ge13 and LiGe detectors. Efficiency and full spectrum calculations were made, and the results were compared to the experimental gamma spectra. A close agreement was found. The partial results were presented at the 6th k_0 NAA workshop.

We started research to benefit from the complementary character of the PGAA, NAA and X-ray fluorescence techniques. This was found to be a great potential in our future element analyses capabilities. So far this has been tested on soil and some metallic samples.

We participated in domestic and international training of students and scientists:

- 6th Central European Training School on Neutron Scattering 14 May - 19 May: Nuclear Analytical Techniques and Neutron Imaging: lectures and lab exercises
- We hosted undergraduate lab exercises for students of Budapest University of Technology and Economics, ELTE University and University of Debrecen (7 occasions, altogether about 60-70 students)
- Summer training (4 weeks) for an M. Sc. IT student of University of Pannonia: developing control software for NORMA Imaging station in C# language
- In Hungarian-Moroccan bilateral inter-governmental research collaboration (TÉT-10-1-2011-0492), two fellows from CNESTEN, Morocco were hosted for two weeks training and two of our PGAA staff members visited Rabat in order to establish a PGAA facility there

Remaining work

The above described international collaborations and development directions are prosperous, so further experiments and data analysis are foreseen.

Related publications

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- [15] T. Belgya, L. Szentmiklósi: *Thermal neutron capture cross sections of $^{54,56,57}\text{Fe}$* , In: Garrett PE, Hadinia B (szerk.), Capture Gamma-Ray Spectroscopy and Related Topics: Proceedings of the Fourteenth International Symposium, Kanada, New Jersey; London: World Scientific Pub Co Inc, 2013. pp. 450-455. (ISBN:978-981-4383-63-9)
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- [22] Z. Kis, P. Völgyesi, and Z. Szabó, DÖME: *Revitalizing a low-background counting chamber and developing a radon-tight sample holder for gamma-ray spectroscopy measurements*, Journal of Radioanalytical and Nuclear Chemistry 298:(3) (2013), 2029-2035.
- [23] Z. Szabó, P. Völgyesi, H.É. Nagy, C. Szabó, Z. Kis, and O. Csorba: *Radioactivity of natural and artificial building materials - a comparative study*, Journal of Environmental Radioactivity 118 (2013), 64-74.

MICROSCOPIC X-RAY FLUORESCENCE ANALYSIS OF METAL UPTAKE BY ARGILLACEOUS ROCKS USING MULTIVARIATE METHODS

János Osán, Annamária Kéri, Dániel Breitner, Margit Fábián, Szabina Török

Objective

Argillaceous rocks are considered in most European countries as suitable host rock formations for the deep geological disposal of high-level radioactive waste (HLW). In Hungary the Boda Claystone Formation (BCF) is considered as a possible formation for the 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 quantify the geochemical and physical processes that influence the mobility of the radionuclides in the deep geoenvironment imposed by the host rock. The present study deals with the interaction between the host-rock surrounding the planned HLW repository and the ions which represent the HLW (natural U(VI), Cs(I), Ni(II), Nd(III)). Synchrotron radiation microscopic X-ray fluorescence (SR μ -XRF) has sufficient sensitivity to study these processes on the microscale without the necessity of the application of radioactive substances. Multivariate methods were found to be efficient tools for extracting information from the elemental distribution maps even when the clayey matrix and fracture infilling regions were examined in the same measured area. By using positive matrix factorization (PMF) as a new approach, the factors with higher sorption capacity could be identified and with additional mineralogical information the uptake capacity of the different mineral phases could be quantified. The results of PMF were compared with the ones got from cluster analysis and microscopic X-ray diffraction (μ -XRD).

Methods

Thin sections were prepared from representative core samples selected from two areas of BCF, i.e. West-Mecsek Anticline Block (Sample D-11) and Gorica Block (Sample Ib-4). Thin sections were subjected to 24–72 hour uptake experiments with one ion of interest added, using synthetic porewater for Cs and Ni, and a 0.1 M NaCl solution for Nd and U as background electrolyte. The μ -XRF/XRD experiments were performed at the FLUO beamline of ANKA (see next page), using monochromatic excitation at a primary beam energy of 17.5 keV ($\Delta E/E = 10^{-2}$). Compound refractive lens was used for focusing a beam down to a spot size of $2 \times 5 \mu\text{m}^2$. Elemental maps were recorded for the adsorbed element (Cs, Ni, Nd, U) as well as for the major and minor elements of the rock measurable by XRF (e.g. K, Ca, Fe, Rb, Sr), using a $5 \mu\text{m}$ step size and 4–10 s counting time per pixel. The elemental concentrations were calculated using the fundamental parameter method, taking into account the thickness of the sample ($50 \mu\text{m}$) and the average density of the rock (2.7 g/cm^3). Several μ -XRD images were collected by a 130 mm diameter CCD detector from selected positions of interest. Many multivariate methods are known from which factor analysis (FA), positive matrix factorization (PMF) and cluster analysis (CA) were tested in this work. Since all multivariate methods work with two-dimensional matrices (variables–observations), the 2D elemental maps for each element (variable) were unfolded to 1D vectors. The resulting factor maps or cluster maps were created after refolding the resulting data to 2D matrices.

Results

The examination of micro-XRF elemental maps and pairwise elemental correlations is a useful tool in identifying the main groups of mineral phases responsible for the uptake, but it works also well for simple cases, when one of them binds the majority amount of the element of interest. For every measured sample the intensity of Ni and Cs shows the most significant correlation with the clayey matrix that could be deduced by correlation between the given element and K as well as Fe. U and Nd was found to be bound not only to the clayey matrix, but the cavity filling minerals also played important role in the uptake. Multivariate methods were found to be efficient tools for extracting information from the elemental distribution maps obtained by μ -XRF both for the clayey matrix and fracture infilling regions. Conventional FA already delivered information on the possible mineral phases responsible for the uptake.

By using positive matrix factorization as a new approach, the factors with higher sorption capacity could be identified and with additional mineralogical information the uptake capacity of the different mineral phases could be quantified. In case of Ni, $170 \mu\text{g/g}$ was bound to the factor representing the clayey matrix, in accordance with the clay content and the average load of $100 \mu\text{g/g}$. For U, a separate factor with the contribution map similar to the uranium map was formed, having high loading in Ca, Mn and Fe apart from U (Fig. 1). This factor could be associated to ankerite $[\text{Ca}(\text{Fe}^{2+}, \text{Mg}, \text{Mn})(\text{CO}_3)_2]$ mineral, which was verified by point μ -XRD measurements. The uptake capacity of ankerite was estimated as $400 \mu\text{g/g}$ U, much higher than the average U load of the sample ($20 \mu\text{g/g}$).

Cluster distribution maps resulting from CA showed the best correspondence with elemental maps of potassium feldspar, carbonates and silicates. After the identification of the main mineral phases of each cluster, the uranium binding capability of the phases could be calculated. The cluster that could be related to the ankerite has the highest uranium content of $40 \mu\text{g/g}$ that is lower than the result obtained by PMF. However, micro-XRD results show that the ankerite content at pixels belonging to U-rich rings was 5–30%, the rest was albite, calcite and dolomite. Therefore the average uranium content of the cluster was in accordance with the average ankerite content of the pixels assigned to it.

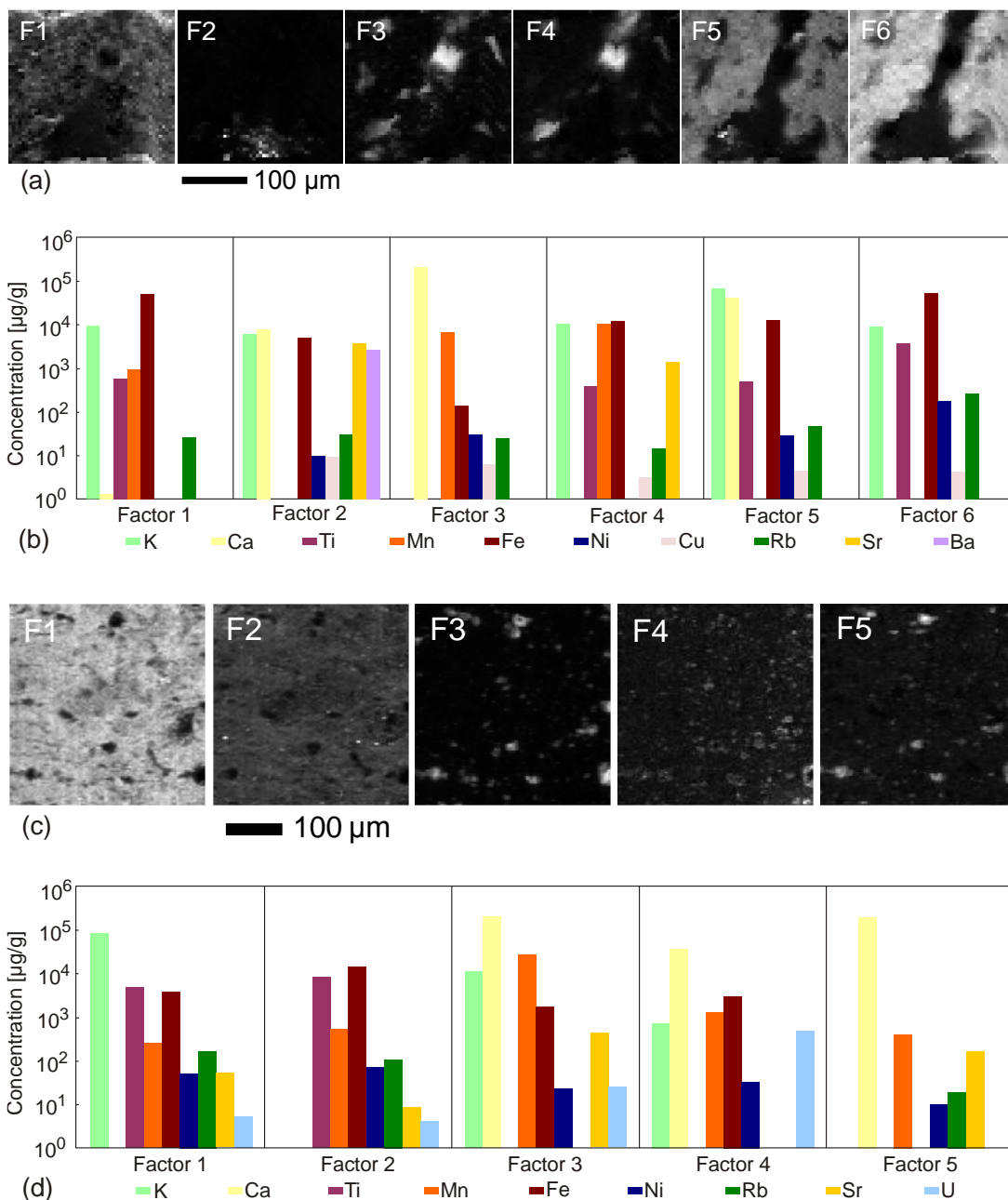


Figure 1: Factor contribution maps (a) and profiles expressed as elemental concentrations (b) for selected area of sample D-11 treated with Ni(II) and U(VI) (c, d). The results were obtained using PMF. Ni was connected mostly to the clayey matrix (Factor 6), while U was found to be accompanied with Ca, Mn and Fe as main elements (Factor 4)

Remaining work

Comparison of macroscopic and microscopic studies of the uptake representative ions by BCF, with verification of the uptake mechanism using X-ray absorption spectrometry.

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 publications

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- [2] D. Breitner, J. Osán, M. Fábíán, P. Zagyvai, C. Szabó, R. Dähn, M. Marques, I. Sajó, Z. Máthé, S. Török: *Effect of mineralogical characteristics on the U(VI) uptake of Boda Claystone Formation as the candidate host rock of high activity and long lived nuclear waste repository in Hungary*, Environmental Earth Sciences, submitted

PRODUCT DEVELOPMENT FOR CONTROLLED HOUSEHOLD RIPENING OF FRUITS

Erzsébet Takács

Objective

The project's aim is the development of a product line that allows controlled ripening of fruits at household level using ethylene gas. This gas acts as a hormone accelerating ripening. It is a project with five participants and our task was to find the proper method for ensuring constant ethylene gas concentration in the ripening box. The production of the prototypes was the final purpose for 2013.

Methods

Pastilles were pressed from the homogenized mixture of NaOH powder and CMC (carboxymethyl-cellulose). Cerone SL 480, a spray in agriculture containing chloroethylene phosphoric acid was used for ethylene gas evolution. Ethylene gas concentration in the ripening boxes was followed by using gas chromatograph with flame ionization detector.

Results

The amounts of CMC, NaOH, Cerone in the pastilles were changed one by one, in separate experiments. 400 - 600 ppm ethylene gas was measured in the ripening boxes for two days with pastilles of the optimum composition. To avoid the difficulties in obtaining permission for manufacturing the chemical gas evolution device (containing NaOH), it was decided to find a completely new way for gas evolution. The idea was to release the ethylene gas from a cartridge. The purpose was to substitute the expensive valve by developing a special membrane that controls the rate of ethylene gas diffusion. The gas diffusion through this membrane ensures a proper and constant ethylene gas concentration in the ripening box. After measuring the diffusion rate of ethylene gas through various kinds of polymer membranes, silicone rubber was found to give the desired ethylene gas permeability. We developed the fruit ripening box and we are able to ensure proper ethylene gas concentration using both by chemical gas evolution method and by cartridge.



Figure 1: Fruit ripening boxes produced by the industrial partner (PEMÜ)

Remaining work

The project has been completed successfully. In case of development of boxes with different sizes some more experiments will be necessary to check the ethylene concentration in the boxes.

Related publications

- [1] E. Andersen, I. Rácz, A. Erős, Gy. Bánhegyi, É. Fenyvesi, E. Takács: *Development of synthetic and natural mineral based adsorptive and filter media containing cyclodextrin moieties*, IOP Conf. Series: Materials Science and Engineering **47** (2013) 012038 DOI: 10.1088/1757-899X/47/1/012038 (2013)

PHASE TRANSITIONS IN SUPERHEATED LIQUIDS

Attila R. Imre

Objective

Overheated liquids are metastable for the liquid-vapour phase transition. When the transition occurs, it is fast and violent (called explosive- or flash-boiling). The knowledge of the properties of overheated liquids as well as the location of the final limit of overheating is important in several fields handling high temperature-high pressure liquids.

Methods

Analytical methods and the ThermoC program (developed in the University of Cologne) were used to calculate stability limits and energy balance. For interface study, molecular dynamic methods were used.

Results

The limit of overheating or expanding is an important property of liquids, which is relevant for the design and safety assessment of processes involving pressurized liquids. Upon accidents (like a LOCA, Loss of Coolant Accident), stable high temperature- high pressure liquids might endure pressure drop, transforming them into metastable, superheated state [1,2]. Traditional equation of states – developed for stable liquids – can be used for metastable states only with limitations [3,4].

Two different systems were investigated, n-nonane and water. For both liquids, molecular dynamic study was used to calculate the thermodynamic limit of stability, which is the limit where metastable, overheated liquid cannot exist anymore and the system must relax into a stable state. The relaxation process is an explosion-like boiling and the final stable state might be an equilibrium liquid-vapour mixture or pure pressurized vapour. Overheated liquid – depending on the extent of metastability – can store some extra energy, which will be partly or fully released upon relaxation. This uncontrolled energy release might cause further accidents; therefore from safety point of view, the knowledge of the location of the limit of overheating is important.

The thermodynamic stability limit—the so-called spinodal—of water were calculated by molecular dynamics computer simulation, using the molecular potential model of Baranyai and Kiss. The spinodal pressure was obtained from the maximal tangential pressure within a liquid–vapour interface layer. The results were compared to predictions of various equations of state. Based on these comparisons, a set of equations of state is identified which gives reliable results in the metastable (overheated or expanded) liquid region of water down to –55 MPa [1]. Using the selected equation of states, we were able to estimate the energy release for some conditions relevant in VVER reactors [5], required by the Hungarian Atomic Energy Authority (OAH).

The spinodal for n-nonane was estimated using a similar method. The choice of n-nonane as investigated molecule was originated from the question whether a deviation from the spherical symmetry affects the prediction of the stability limit data. It was found that the estimated stability limit data for n-nonane are consistent with the experimental data available for the homologous series of the n-alkanes. It turned out that the slight alignment of the molecules parallel to the interface reported in the literature does not affect the method of transferring interface properties to the bulk phase stability limit [2].

Remaining work

- Extension of the calculations for more fluids, including carbon dioxide.
- Calculation of the mass-balance during explosive boiling, i.e. estimation of the fraction of vapourization.
- Study of the reverse process - vapour-liquid transition - with special emphasis on Condensation Induced Water Hammer, (CIWH).
- Further works on the theory of metastability and nucleation.

Related publications

- [1] A.R. Imre, A. Baranyai, U. Deiters, P.T. Kiss, T. Kraska and S. E. Quiñones Cisneros: *Estimation of the Thermodynamic Limit of Overheating for Bulk Water from Interfacial Properties*, International Journal of Thermophysics, 34(2013)2053–2064, doi 10.1007/s10765-013-1518-8.
- [2] S. Braun, A. R. Imre, T. Kraska: *Stability limits of n-nonane calculated from molecular dynamics interface simulations*, Journal of Chemical Physics, 138(2013)244710; doi: 10.1063/1.4811197.
- [3] A. R. Imre: *Stability and negative pressure in bulk and confined liquids*, NATO Science Series, Alternative Water Resources in Arid Areas by retrieving Water from Secondary Sources (Eds.: L. Mercury, N. Tas and M. Zilberbrand), Springer (2013)151-157.
- [4] A. R. Imre, J. S. Sperry: *Front Matter: Part III In-Pores/Channels Cavitation - Cavitation in metastable liquids*, NATO Science Series, Alternative Water Resources in Arid Areas by retrieving Water from Secondary Sources (Eds.: L. Mercury, N. Tas and M. Zilberbrand), Springer (2013)127-130.
- [5] A. Imre: *Energy release during phase transition of superheated liquids: dynamics, trajectories and energy distribution*, (in Hungarian), OAH report, OAH-NBI-ABA-13/12-M (2013).

GAMMA-SPECTROMETRY

András Kocsonya

Objective

The main task of the Environmental Protection Service (EPS) is the radiological environmental monitoring of the KFKI Campus. The liquid emission monitoring is also the task of the Service. Due to multi-nuclide character and the simple sample preparation, gamma-spectrometry is a substantial tool in analysis of environmental samples. The gamma-spectrometry analyses at the EPS have two main aspects:

- quick and effective analysis of the samples from the routine environmental monitoring
- reliable analysis of special or unique samples or irregular cases

Methods

Three gamma-spectrometers of the EPS are devices of analyses accredited by the Hungarian Accreditation Board. Two of them were moved to the building 4/6 due to the moving of the Service. These spectrometers have been reinstalled, their calibration and specific characteristics were checked.

This year two handheld gamma-spectrometers were tested by the EPS. These devices were provided by the representatives of their manufacturer. The spectrometers were calibrated and the evaluation processes were developed for the specific tasks of the EPS. The devices were tested for different analytic problems.

This year the EPS took part in 3 proficiency tests and interlaboratory comparisons involving water samples. These exercises definitely improved the analytic skills of the laboratory. This knowledge became rather useful when water samples were measured even at normal releases or at the incidents of the waste water system.

The routine environmental monitoring programme was extended to regular sampling and analysis of the released waste water of the isotope laboratories (1-2 releases/month). From the end of 2013 two samples, a pre-release and a prompt one are collected from each release. The analysis results are compared with those of the emission monitoring laboratory of the Institute of Isotopes Co.

The environmental monitoring programme was extended to the analysis of ^{125}I at the monitoring station no. 6, which is situated near to the isotope laboratories. 1-10 Bq/m²/week of ^{125}I is almost continuously detectable in these samples. The determination of its origin is in progress.

Results

Due to the large amount of environmental samples, quick but effective spectra evaluation processes are necessary to reduce the time and human resource needs. Since a significant part of environmental monitoring are the fall-out samples, an automatic evaluation algorithm has been developed which evaluates only the selected key nuclides and detects the irregular cases. Evaluation of the routine environmental measurements are performed by the Genie-2000 software. From former experiences we know, that this software sometimes makes mistakes in the analysis (mainly incorrect nuclide-identification). These cases are collected and discussed. The reasons of these failed nuclide identification were determined. In a few cases software errors can be expected. This observations were reported to the software manufacturer.

For complicated cases the Hypermet PC and FitzPeaks (demo version) computer codes are also applied for spectrum evaluation. In these cases the results and the capability of the codes are compared for specific analytical problems.

This year two incidents happened in the radioactive waste water handling system of the Campus. The waste water storage tank of the Isotope laboratories in bld. XVII. and XXI. was overflowed due to pump error. Both the overflowed water and the contaminated soil were analysed by gamma-spectrometry. The extent of the contamination was determined. The countermeasures were based on the results of these analyses. In the other case a pipeline of the radioactive waste water system of an isotope laboratory was broken. Building materials were contaminated. The radiation protection aspects of the reconstruction was continuously monitored. Both the laboratory and the portable spectrometers were applied in these cases. Where it was possible the two results were compared. Rather good agreements were detected.

A set of unique samples were analysed under the frame of collaborations with other laboratories and institutes. An example of these works is the determination of specific activity of activation products in irradiated concrete.

Remaining work

The optimisation of the detection limits of water samples is in progress. This is a new requirement of the supervising authority. The application of the mobile aerosol sampler is depending on the monitoring programme of the workplaces.

Related publications

- [1] A.K.: *Disturbing effects in gamma-spectroscopy analysis of organic ^{125}I in air* (poster at ICRM-2013)
- [2] A. Kocsonya, K. Bodor: *On the field measurement experiences with portable NaI scintillation spectrometers* (lecture at 6 December 2013)

STRUCTURAL STUDIES PERFORMED WITH NUCLEAR TECHNIQUES

Károly Lázár, Sándor Stichleutner, János Megyeri

Objective

Structures of various substances were analysed with nuclear techniques. Namely, porous and layer silicates, carbon nanotubes, metallic electrodeposits and amorphous alloys have been studied.

Methods

Two nuclear techniques were applied, Mössbauer spectroscopy (with two nuclei, ^{57}Fe and ^{119}Sn) and positron lifetime measurements.

Results

The dominant part of the work was devoted to studying various mesoporous silicates. Effects of the difference between SBA-15 and SBA-16 structures were analysed by comparing the properties of these mesoporous supports loaded with CuFe bimetallic oxide particles. Their structures were analysed by XRD, BET, TEM and Mössbauer spectroscopy, their catalytic performances were compared in oxidation of toluene. Most of the oxide particles were finely dispersed in the channels of the SBA-15 structure. In contrast, more coarse particles were formed on SBA-16, resulting in partial blocking of the entrances of channels [1]. Related nanostructures, layered double hydroxides (LDHs) were also analysed. Effects of the intercalation of Ca^{2+} and Fe^{3+} ions were investigated. Formation of single phase structure was observed at $\text{Ca}^{2+}/\text{Fe}^{3+} = 2$ ratio. Increase of the Ca^{2+} content (e.g. $\text{Ca}^{2+}/\text{Fe}^{3+} \sim 3$) results in improved high temperature stability of the structure which may be advantageous for further catalytic applications [2]. Similar studies were performed on Mg^{2+} , Fe^{3+} containing LDHs [3]. A concise review was also prepared on the application of in situ Mössbauer spectroscopy for studying catalysts [4]. Another nuclear technique, positron lifetime (PLT) measurement, was combined with Mössbauer spectroscopy to characterise the pore structure of micro- and mesoporous ferrisilicates. PLT component of longer lifetime with noticeable contribution (indicating the presence of larger pores and channels) was detected only in Fe-SBA-15 sample [5]. PLT measurements were also applied to characterise the pore structure of multi-wall carbon nanotubes [6].

Thin layers of electrodeposited metastable amorphous trimetallic Sn-Ni-Fe alloys were analysed with ^{57}Fe and ^{119}Sn conversion electron Mössbauer spectroscopy. The structural disorder provides a certain stability in the layers. Galvanostatic charge-discharge cycling was carried out in a model Li ion cell indicating that the ternary Sn-Ni-Fe alloy has a potential as perspective electrode material [7]. Short-range structural rearrangements due to swift heavy ion irradiation were also analysed in these electrodeposited ternary layers [8]. Structure of samples of an industrially important amorphous soft magnetic alloy, FINEMET, was also analysed with ^{57}Fe Mössbauer spectroscopy. Correlation of permeability with magnetic anisotropy in $\text{Fe}_{73.5}\text{Si}_{13.5}\text{Nb}_3\text{B}_9\text{Cu}_1$ samples was investigated by estimating the average angle of magnetisation (related to the surface plane of melt-spun ribbons) with comparing the relative intensities of 2, 5 lines to the 1,3,4,6 ones in the magnetically split Mössbauer spectra [9].

Remaining work

Further application of these nuclear techniques is intended for structural analysis of perspective substances in the future.

Related publications

- [1] Á. Szegedi, M. Popova, K. Lázár, S. Klébert, E. Drotár: *Impact of silica structure of copper and iron-containing SBA-15 and SBA-16 materials on toluene oxidation*, Microporous and Mesoporous Materials, **177**, 97-104 (2013).
- [2] M. Sipiczki, E. Kuzmann, Z. Homonnay, J. Megyeri, I. Pálkó, P. Sipos: *The structure and stability of CaFe layered double hydroxides with various Ca:Fe ratios studied by Mössbauer spectroscopy, X-ray diffractometry and microscopic analysis*, Journal of Molecular Structure, **1044**, 116-120 (2013)
- [3] M. Sipiczki, E. Kuzmann, Z. Homonnay, J. Megyeri, K. Kovács, I. Pálkó, P. Sipos: *Mössbauer and XRD investigations of layered double hydroxides (LDHs) with varying Mg/Fe ratios*, Hyperfine Interactions, **217**, 145-149 (2013)
- [4] K. Lázár: *Mössbauer spectroscopy in catalysis*, Hyperfine Interactions, **217**, 57-65 (2013)
- [5] T.Q. Dung, K. Lázár, K. Havancsák, Zs. Kajcsos: *o-Ps lifetimes in iron containing micro- and mesoporous media*, Materials Science Forum, **733**, 197-202 (2013).
- [6] L.A. Tuyen, Zs. Kajcsos, K. Lázár, T.D. Tap, D.D. Khiem, P.T. Phuc: *Positron annihilation characteristics in multi-wall carbon nanotubes with different average diameters*, Journal of Physics, Conference Series, **443**, 012065 (2013)
- [7] G.B. Lak, E. Kuzmann, M. El-Sharif, C.U. Chisholm, S. Stichleutner, Z. Homonnay, L. Sziráki: *Galvanostatic charge-discharge tests. ^{57}Fe and ^{119}Sn Mössbauer and XRD measurements on novel Sn-Ni-Fe electrodeposits*, Hyperfine Interactions, **218**, 145-150 (2013).
- [8] S. Stichleutner, E. Kuzmann, G.B. Lak, M. El-Sharif, C.U. Chisholm, K. Havancsák, V.A. Skuratov, L. Sziráki, Z. Homonnay, A. Vértes: *Effect of swift heavy ion irradiation on the short range order in novel electrodeposited ternary amorphous alloys*, Radiation Physics and Chemistry, **91**, 166-169 (2013)
- [9] E. Kuzmann, S. Stichleutner, A. Sápi, Z. Klencsár, M.I. Ostrakh, V.A. Semionkin, S. Kubuki, Z. Homonnay, L.K. Varga: *Mössbauer study of FINEMET with different permeability*, Hyperfine Interactions, **218**, 145-150 (2013)

LONG-LIVED ^{135}Cs

*Péter Nagy, Nóra Vajda, Ibolya Sziklai-László, Éva Kovács-Széles,
András Simonits*

Objective

Our aim was to develop/adopt an adequate radiochemical method for the determination of ^{135}Cs in waste samples. The method is based on the selective separation of Cs and the detection of ^{135}Cs by two independent measuring methods, i.e. neutron activation analysis (NAA) and inductively coupled plasma mass spectrometry (ICP-MS).

Methods

Cesium was concentrated in waste samples to increase measurement accuracy for ^{135}Cs in both measurement techniques. The sample matrix had to be removed to get a pure concentrated cesium fraction and to get rid of salt content that is tolerated neither by the ICP-MS technique nor by NAA due to precipitation in the spray chamber or the activation of various interfering components, respectively. The separation of barium from samples was very important, because stable ^{135}Ba causes the basic isobaric interference in the determination of ^{135}Cs by ICP-MS. The separation of Na and K is essential for NAA determination due to their high activation cross sections, high gamma emission rates and their long half-lives as compared to that of ^{135}Cs . For the separation of cesium from other elements, ammonium-molybdophosphate (AMP) precipitation and cation exchange chromatography were used. The chemical yield of the method was about 60-100 %.

Results

NAA and ICP-MS techniques were comparatively evaluated and a good agreement between the results was found (Fig. 1). The activity concentration of ^{135}Cs in a couple of waste samples originating from VVER-440 type nuclear reactors was in the range of 1-5 Bq/Liter (20-120 ng/L) while ^{137}Cs activity concentrations varied between 0.1 and 1 MBq/L.

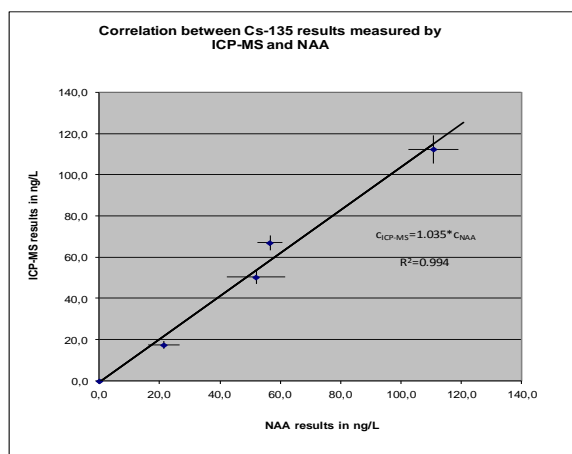


Figure 1: Results obtained by ICP-MS and NAA

Parameters of the regression line fitted to the measured ^{135}Cs concentration data are shown in the figure.

Remaining work

The method will be applied to various sample types, such as coolant and wastes.

Related publications

- [1] P. Nagy, N. Vajda, I. Sziklai-Laszlo, E. Kovacs-Szeles, A. Simonits: *Determination of ^{135}Cs in nuclear power plant wastes by ICP-MS and k_0 -NAA*, Journal of Radioanalytical and Nuclear Chemistry, DOI: 10.1007/s10967-013-2875-2 (2013).
- [2] P. Nagy, N. Vajda, I. Sziklai-Laszlo, E. Kovacs-Szeles, L. Lakosi: *Determination of ^{135}Cs in coolant and waste samples from a nuclear power plant*, Radiobiology and Radiochemical Measurements Conference, 21-25 October 2013, Rohnert Park, California, USA.
- [3] P. Nagy, N. Vajda, I. Sziklai-Laszlo, E. Kovacs-Szeles, A. Simonits: *Determination of ^{135}Cs by radiochemical NAA and ICP-MS*. 6th International K_0 -Users' Workshop. 22-27, September, 2013, Budapest.
- [4] P. Nagy, N. Vajda, I. Sziklai-Laszlo, E. Kovács-Széles, A. Simonits: *^{135}Cs isotope in coolant and radioactive waste samples*. XII. MNT Nuclear Technical Symposium, 05-06.12.2013, Budapest. [in Hungarian]

APPLICATIONS OF NEUTRON ACTIVATION ANALYSIS

Ibolya Sziklai-László, Katalin Gméling, Dénes Párkányi, László Szentmiklósi

Objective

Neutron Activation Analysis (NAA) has extensive application in various fields: material and environmental sciences, archaeology and geochemistry. The technique has also been used to support the operation of the research reactor.

Method

NAA laboratory consist of: high resolution gamma-spectrometers with HPGe detectors, low background sample chambers, clean lab, fast rabbit system. The method requires software: Hypermet-PC for spectrum deconvolution, INAA-CNC for concentration computation. NAA facility is part of the BNC.

Results

Material science

To investigate the status of fuel cladding integrity during the fuel conversion (from HEU to LEU), samples from the primary cooling water were measured in every reactor cycle. The activity concentrations of characteristic fission and corrosion products in the water and the chemical concentrations of different impurity components in various water systems of the BRR were measured to monitor the water quality. The control and data acquisition electronics and software of the fast rabbit system has been upgraded. In order to extend the irradiation period, a new sample holder capsule was used. The cleanliness of it and its surface contamination during irradiations, the sample temperature inside, the neutron flux characterizations, and the reproducibility/reliability of the irradiations were tested.

Archaeometry

Provenance study of lapis lazuli is not absolutely possible from the results of PGAA analysis. To bring up to the solution NAA method was used, which gives the results for much more trace elements. As an experiment two lapis lazuli samples and four pigments were irradiated and measured by NAA. The evaluation of spectra is in progress.

Maintenance and validation

We participated in the inter-laboratory comparison rounds (IAEA TC project RER 4/032/RER1/007, 2011-2013) organized by the IAEA WEPAL measuring the composition of four soil and four plant samples. We also measured the soil samples by PGAA. Results of elements which could be measured with both techniques corresponded well. NAA results were compared with the participating NAA, ICP-MS and XRF laboratory results. Our NAA laboratory performed really well.[1] Comparison and combination of the PGAA and NAA laboratory started in 2013. Geological reference materials and other synthetic multi element standards were measured in both laboratories. The elemental concentrations showed good agreement. NAA and PGAA proved to be analytical procedures complementary to each other.[2]

Geochemistry

Five mantle xenoliths from the Balaton Highlands were measured with NAA. NAA results showed good agreement with previous XRF results.

Biology and Environmental Sciences

In the framework of the NMI3 coordinated projects, the elemental composition of iron bacteria was measured. The NAA results should help in revealing an optimized scheme for isolation and enrichment of bacteria in laboratory conditions and possible implications for nanotechnology. We developed/adopted an adequate radiochemical method for the determination of ^{135}Cs in nuclear waste samples that is based on the selective separation of Cs and the detection of ^{135}Cs by NAA and ICP-MS methods. NAA and ICP-MS techniques were comparatively evaluated regarding accuracy, precision and detection limit. Trace elements in energy grass were determined. Zn, Br, and Fe concentrations of the treated and the control plants show remarkable differences. NAA was suitable also to determinate major components (Fe, Ca, Na) and 26 trace elements in a red mud sample, including minor elements (La, Nd, Sc).

Organized workshop

6th International k_0 Users' Workshop (September 22–27, 2013, Budapest)

A successful workshop was organized at Budapest (in Hotel Gellért). The main purpose of the meeting was to discuss the latest developments and applications of neutron activation analysis and also prompt gamma activation analysis using the k_0 approach.

Related publications

- [1] I. Sziklai-László, K. Gméling (2013): *Results of the k_0 -based instrumental neutron activation analysis (k_0 -INAA) for WEPAL plant and soil IPE/ISE 2013 in Hungary*. Accepted in Annex on CD-ROM of IAEA TECDOC (under preparation). TECDOC and Annex connected to IAEA TC project RER1007: Workshop on Inter-Comparison Feedback of NAA and other Analytical Techniques Proficiency Tests Performed in 2012-2013.
- [2] K. Gméling, A. Simonits, I. Sziklai-László, D. Párkányi (2014): *PGAA and NAA Results of Geological Samples and Standards* (6th International k_0 -Users' Workshop, Budapest, 22-27. September, 2013.) J. Radioanal. Nucl. Chem. (Accepted)

STRUCTURE ANALYSIS OF POROUS IRON-CONTAINING SUBSTANCES

Károly Lázár

Objective

A chain of fruitful bilateral cooperations with colleagues from National Institute of Chemistry, Ljubljana, was commenced in 2006. These cooperations obtained support from TÉT fund. Among them, the first half of 2013 was the last period of TÉT_10-1-2011-0624 project entitled "Structure studies of porous iron-carboxylates". The main target of the bilateral work was completion of structure studies on various porous iron containing substances. In previous years of the specified project MOFs (Metal-Organic Framework compounds, namely, MIL-45(Fe) and MIL-101(Fe)) and various ferrisilicates have been studied. For finalisation, structure analyses of two types of novel compounds, mesoporous Fe- KIL-2 and Fe(II)citrate-carboxylate were performed.

Methods

In principle, wide variety of methods have been applied in investigations carried out in National Institute of Chemistry, Ljubljana (X-ray diffraction, BET (Brunauer-Emmett-Teller)/sorption, scanning electron microscopy, FTIR (Fourier transform infrared spectroscopy), UV/VIS spectroscopies, TPR-TG (temperature-programmed reduction - thermogravimetry) and magnetic susceptibility measurements). In addition, catalytic performances of Fe-KIL samples were also tested in oxidation of a volatile pollutant organic compound, toluene. The principal contribution from the MTA EK side was the completion of in situ Mössbauer measurements, which are primarily suitable to determine the oxidation state and coordination environment of iron and changes in them under various in situ experimental conditions.

Results

In correspondence, structures of two types of compounds have been investigated in detail. The first substance was synthesized with mesoporous KIL structure (KIL stands for the name of the place of the very first synthesis - Kemijski Institut Ljubljana) with Fe/Si atomic ratios 0.005, 0.01, 0.02, 0.05, their specific surface area values ranged from 210 to 560 m²/g. Samples with the novel structure were characterised with a variety methods. Mössbauer spectroscopy, in particular, confirmed that significant part of iron is incorporated into the silica host matrix, and may participate in reversible Fe²⁺ ↔ Fe³⁺ redox transformations, important in catalytic reactions, e.g. in the studied case of oxidation of toluene [1].

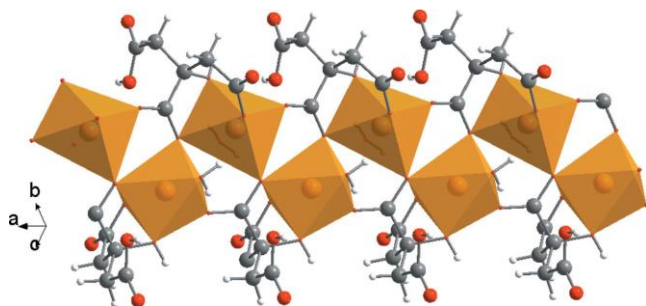


Figure 1: Projection of the $[Fe(H_2cit)(H_2O)]_n$ showing a chiral helical chain of corner-sharing FeO_6 octahedra (spheres: grey: carbon, red: oxygen, white: hydrogen and brown: iron) [2]

Synthesis of another novel compound, carboxylate-linked $[Fe(II)(H_2cit)(H_2O)]_n$ has also been completed at the Kemijski Institute. Its structure was solved primarily from single crystal X-ray diffraction studies. In addition, thermal stability and magnetic susceptibility measurements have also been carried out. A slight difference in the environment of the FeO_6 octahedra was also confirmed from 77 K Mössbauer spectra, displaying two Fe^{2+} doublets. Structure of the studied coordination polymer with the chiral helical chain of FeO_6 octahedra along the a axis is represented in Figure 1 [2]

Remaining work

The tasks scheduled in TÉT_10-1-2011-0624 project have been completed, no remaining work is left for further studies.

Related publications

- [1] M. Popova, A. Ristic, K. Lázár, D. Maucec, M. Vassileva and N. Novak Tusar: *Iron-functionalized silica nanoparticles as a highly efficient adsorbent and catalyst for toluene oxidation in the gas phase*, *ChemCatChem* **5**, 986-993 (2013)
- [2] T. Birsa Celic, Z. Jaglicic, K. Lázár and N. Zabukovec Logar: *Structure and magnetic properties of a new iron(II) citrate coordination polymer*, *Acta Cryst. B* **69**, 490-495 (2013)

DEVELOPMENT, CHARACTERIZATION AND MODELLING OF SELF-POWERED NANOGENERATORS ON FLEXIBLE FIBROUS ASSEMBLIES

Erzsébet Takács, Viktória Míle

Objective

The aim of the 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. In this work, large-scale single-crystalline ZnO nanotube arrays were deposited on viscose substrate from aqueous solution. This year our task in the project was the radiation induced modification of the nonwoven cellulose based material (viscose) and the characterization of the samples by using SEM and element analysis instrument.

Methods

The surface morphology of the ZnO array films was studied by JEOL JSM-6700F scanning electron microscope (SEM) operating at an accelerating voltage of 5 kV.

Results

ZnO nanorods were formed by electrodeposition method and by hydrothermal deposition on the surface of the previously grafted samples. All morphologies produced by the electrodeposition method on viscose substrate were found to deposit primary cabbage-like structures connected into secondary belt structures (Fig. 1). The ZnO nanowires, deposited by hydrothermal method, exhibit a perfect hexagonal faceted morphology (wurtzite crystals) with a diameter of 250 - 500 nm, and lengths of about 3-7 μm (Fig. 2).

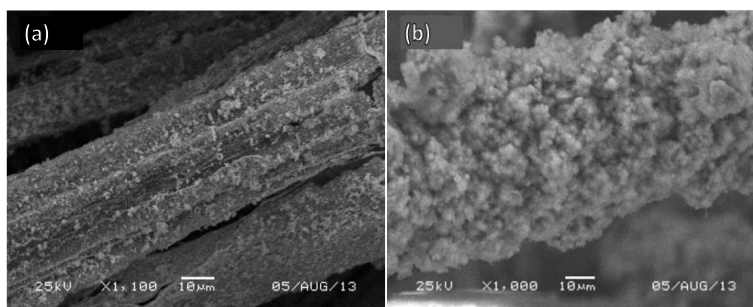


Figure 1: SEM image of the ZnO nanostructured film prepared by electrodeposition method (a) deposition onto silver coated viscose (b) deposition onto copper coated viscose from 5 mM ZnCl_2 + 0.1 M KCl + H_2O_2 without oxygen bubbling

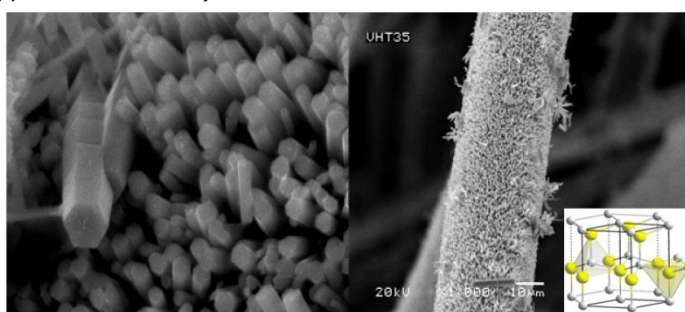


Figure 2: SEM micrographs of samples prepared via hydrothermal synthesis on a viscose substrate using, 50 mM $\text{Zn}(\text{NO}_3)_2$ and 50 mM hexamethylenetetramine precursor solution

Remaining work

The project is close to finalization. Fine tuning of the deposition methods is necessary.

Related publication

[1] M. Furkó, E. Fazakas, E. Takács: *Deposition of nanostructured ZnO with variable morphology by electrochemical and hydrothermal methods onto nonwoven materials*. Material Science Forum, submitted.



X. INTERNATIONAL ACTIVITIES



AER (ATOMIC ENERGY RESEARCH)

István Vidovszky

AER is a loose organization of 24 institutions (utilities and research institutes) from eight countries. Two of these organizations (Paks2 Hungary and Fennovoima Finland) joined AER during last year. Both are companies planning to build new NPP units. 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 2013 the Symposium was organized in Štrbské Pleso, Slovakia, 30 September - 4 October. The participants presented 59 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. They 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. Nuclear Fuel Cycle Perspectives and Sustainability, 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 MTA EK, Budapest. The secretariat organizes a yearly meeting for making organizational and financial decisions. In these meetings every participating organization is authorized to be represented.

COMMERCIAL MEASUREMENTS OF THE PGAA GROUP IN 2013

Boglárka Maróti, László Szentmiklósi, Tamás Belgya, Katalin Gméling

Objective

The objective is to provide analytical service to customers on a commercial basis, using PGAA (prompt-gamma activation analysis), and XRF (X-ray fluorescence) techniques.

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). Prompt gamma activation analysis is a nuclear analytical technique for non-destructive determination of elemental and isotopic compositions. The sample is irradiated in a guided neutron beam, and the gamma-rays from the radiative capture are detected. All elements can be analysed (except helium), without any prior information on the analyte. The energies and intensities of the peaks are independent of the chemical state of the material; hence the analytical result is free of matrix effects. Both neutrons and gamma-rays are highly penetrating; therefore the average composition of the illuminated volume is obtained. Every step of the measurement and the evaluation can be described with statistical methods, therefore uncertainties of the concentrations can be estimated already from one measurement.

X-ray fluorescence (XRF) is a non-destructive analytical method, based on the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis of metals, glass, ceramics and building materials, and for research in geochemistry, forensic science and archaeology. The penetrating depth of the X-rays depends on the composition of the samples. We use the Olympus Delta Premium InnovX type handheld XRF device, which is appropriate to analyse elements with atomic numbers higher than Mg.

Results

We completed the following commercial measurements in 2013:

- Concentrations of boron (B) have been determined in nine silicon samples by PGAA. The B content of all samples could be quantified with 2-3% accuracy. The samples can be classified to three groups. Group 1 appears to be almost pure silicon with trace amounts of B. Group 2 contains Ti, Fe and Gd, in addition to B. Group 3 differs from previous groups due to its detectable H, Mn and Co content. [1]
- As a follow-up, concentrations of boron (B) have been determined in three additional silicon samples by PGAA. All samples were almost pure silicon with trace amounts of B. The B content of all samples could be quantified with 3-3.5% accuracy. [2]
- In-situ, non-destructive XRF measurements on thirty archaeological brass samples were performed at the Hungarian National Museum [3]. In all samples Fe, Ni, Cu, Sn, Sb and Pb concentrations could be successfully determined. In addition, in most of the samples it was also possible to detect Bi and Cd. The goal of the measurements was to define the ages and origins of the objects via the elemental concentration data.

Remaining work

We continue to offer our analytical services (PGAA [Prompt gamma activation analysis], NIPS/NORMA [Neutron induced prompt-gamma spectroscopy/Neutron tomography], DÖME [Damn heavy measuring equipment], XRF [X-ray fluorescence], NAA [Neutron Activation Analysis] and DNR [Dinamic radiography]) for customers and adapt our methodology to the requests.

Related publications

- [1] B. Maróti, L. Szentmiklósi: *Analysis of silicon samples by PGAA*, REPORT NAL-2013/20, 10 pp (2013)
- [2] B. Maróti, L. Szentmiklósi: *Analysis of silicon samples by PGAA*, REPORT NAL-2013/93, 6 pp (2013)
- [3] B. Maróti: *Analysis of 30 archaeological brass samples in the Hungarian National Museum by Handheld-XRF*, REPORT NAL-2013/255, 14 pp (2013)

ADVANCED COHESION IN EURATOM RESEARCH – MTA EK CONTRIBUTION TO NEWLANCER PROJECT

Ákos Horváth

Objective

Three major handicaps to the integration of European research capacity may be observed today: fragmentation, imbalance of resources, and mutual ignorance. The new member states (NMS) were allowed to participate in Euratom Programmes starting with the FP5. With FP6, NMS involvement increased continuously but slowly and often being carried out predominantly by one or few research institutes or universities in each country. The European Commission (EC) considered that NMS participation in the Euratom Framework Programme 7 (FP7) is still low compared to the old member states' (OMS) involvement despite initiatives to facilitate greater contributions to European research (such as the NCP (Network Control Program) network, bonus evaluations for the proposals including NMS partners, events promoting Euratom FP in each NMS, etc.).

Greater involvement of NMS is seen by the EC as a part of necessary efforts in the nuclear energy area to increase cooperation, reduce fragmentation and avoid duplication, and also to improve the standard of research, to reinforce safety and environmental issues within projects, to improve operations, emergency planning, etc.

NEWLANCER is a Coordinated Action project, which proposes to identify and implement effective and efficient actual solutions leading to enlarged New Member States involvement in future Euratom Framework Programmes by strengthening and catalysing the full R&D potential at national level, by increasing cohesion between New Member States institutions, and by improving their cooperation with Old Member States research centres.

Methods

The work in this Coordination Action is distributed in the following work packages:

- Analysis of skills and current participation of NMS in Euratom Projects - Review and assessing NMS research capabilities and participation in Euratom R&D Programmes (key issues, gaps, good practices and barriers, challenges, etc. with increased attention to the risk, safety and environmental aspects).
- Network for advanced cohesion in NMS nuclear research - Creating a multi-level regional network having as mission to enhance cohesion and interact with national and European levels in order to strengthen future participation in European research.
- Good Practices and Recommendations - Collect and analyse relevant cases on New and Old MS participation in Euratom Programmes in order to draw up good practices and recommendations addressed to a large end-users spectrum: scientists, research managers, national authorities, EC structures (SNE-TP, IGD-TP, EERA, ESNII) – interested in better use of entire research potential.

Results

National expert groups were formed in the specific fields and prepared reports on the national research strategies. MTA EK presented the work done within the frame of the Hungarian Sustainable Nuclear Energy Technology Platform and the ALLEGRO project.

All information on research potential of NMS and OMS partners of NEWLANCER organized in the "Catalogue of NMS Research Potential for Broader Participation in EURATOM Programmes" was widely disseminated among OMS research centres with view to help for an extended NMS' participation in Euratom programmes.

The first results of the NEWLANCER approach became already visible: 4 new ongoing projects MACSIMA, EAGLE, and ASAMPESA_E and ARCADIA rooted in NEWLANCER activities and embarking the NMS partners ensure continuity in NMS participation in FP7 Euratom and contribute to the enlargement of their future involvement.

Remaining work

The project finished in 2013, no other work remains.

JOINT HUNGARIAN-KOREAN LABORATORY PROGRAM FOR ADVANCEMENT OF NUCLEAR THERMAL-HYDRAULICS SAFETY

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Iván Tóth, István Trosztel*

Objective

The objective of the Joint Laboratory is to advance scientific knowledge in two areas important for nuclear power plant safety: the effect of pressure waves on pressure vessel internals and coolant mixing in cold legs and in the pressure vessel downcomer, as well as to increase nuclear safety assessment capabilities via validation of computer codes.

Methods

The scope of the first year activity includes performance and evaluation of tests in the PMK test facility addressing the pressure wave propagation phenomenon and application of codes computer available at MTA EK and KAERI to the test cases with the aim to validate these tools for the given phenomenon. The validation effort was extended to the following computer codes: ATHLET, MARS and WAHA.

Results

The phenomenon of pressure wave propagation following a larger LOCA was systematically addressed by experiments in the integral-type test facility PMK-2. Besides the normal instrumentation of PMK-2, special pressure transducers capable to resolve the pressure variation with a frequency of 4 kHz have been installed. Four experiments were performed with two different break orifice diameters and changing the initial system pressure and temperature. In all cases the break was simulated by the burst of a rupture disk downstream of the orifice. A number of important conclusions could be deduced from the tests. During the first 100 ms of the transient a recovery of the system pressure can be observed, which can be explained by the fact that the flow coming from the pressuriser is temporarily able to compensate the break flow. This leads to a low-frequency (about 6 Hz) oscillation of the pressure that dies out after a few cycles. A higher frequency oscillation (with a half wave length of about 12-15 ms) is superimposed on the system pressure, which represents the reflection from the point, where the rarefaction waves travelling via the downcomer and the cold leg meet somewhere in the hot leg. The value of the first amplitude of the pressure difference across different parts of the system is of highest importance from the point of view of stresses on vessel internals. The test results indicate a strong increase of the amplitude with increasing break size, while the effect of system pressure and temperature is of second order of importance.

A first series of calculations performed indicate that the propagation of the first rarefaction wave from the top of the downcomer to the upper plenum is very well calculated by all the three codes: in spite of first order discretization in ATHLET and MARS no numerical diffusion can be observed. The calculated pressure differences between two different locations in the system are of primary interest, since they define the loads on primary system internals. ATHLET somewhat overestimated the amplitude of the pressure difference pulses, while in the case of MARS they were slightly underestimated. The frequency of oscillations was fairly well described by both codes. Both codes calculate a slower attenuation of the pressure oscillations as compared to test results: this can be the consequence of rigid walls assumed in the analyses.

Remaining work

Further tests will be performed as defined by the common test matrix of the OECD PKL3 project and the Joint Laboratory. The matrix contains tests at higher pressure and temperature and they address the effect of the break opening time.

Related publications

- [1] G. Baranyai, Gy.Ézsöl, V. Gottlasz, A. Imre, I. Tóth, I. Trosztel, S. J. Yi, X. G. Yu: *First Year Technical Report*, EK-THL-2013-442-01/M0, November 2013
- [2] I. Trosztel, I. Tóth, Gy.Ézsöl: *Validation of ATHLET Code by LOCA-Induced Pressure Wave Propagation Tests*, Paper No. 30706, Proceedings of ICONE22, July 7-11, 2014, Prague, Czech Republic, to be published.

BUDAPEST NEUTRON CENTRE - 20 YEARS OF INTERNATIONAL USER OPERATION

Rózsa Baranyai, Mihály Makai

20 years ago a consortium named Budapest Neutron Centre (BNC) was formed to coordinate the utilization of the Budapest Research Reactor (BRR) and provide scientific infrastructure and manage the access programme for the international user community.

BNC offers 15 instruments located around the BRR through the international user programme. It 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). The newly developed BNC homepage serves the users; provides detailed information on the application procedure, on the instruments and on the science that can be performed on various systems and materials. Scientists who want to get access to BNC's instrumentations are requested to submit proposals. Beam time applications can be submitted twice a year and in special cases "urgent beam time application" is also accepted. Proposals are evaluated and ranked by the International Selection Panel.

New NMI3 project named NMI3-II started in February 2012. The continuation of the project was essential for the user community and for the facility as well. It makes possible for BNC to run the user programme smoothly. The financial support through the beam fee system contributes to the infrastructure and instrument developments.

In the frame of NMI3-II project, BNC received in 2013 38 eligible proposals. From these, 21 projects were carried out using 112 beam days. 23 scientists visited BNC and almost all of them received travel and accommodation support. The main scientific fields of the supported projects were physics, chemistry, and engineering.

An international board called International Scientific Advisory Committee (ISAC) assists BNC work in strategic issues. ISAC had an annual meeting on the 15-16th November, 2013. Major discussions were about

- BNC contribution to the renewable energy research
- The new European Commission call: Horizon 2020
- European Spallation Source (ESS) status.

User Selection Panel (USP) also had a review meeting during these days. The panel members evaluated 27 proposals requesting 173 reactor days for the first half of 2014. All proposals were accepted.

We continued the tradition and organized the 5th User Meeting connected with the ISAC meeting. On the meeting 7 user projects were presented, providing possibility to the ISAC and USP members to get more information about the scientific work done at BNC.

In 2013, the 7th Central European Training School on Neutron Scattering was organized with the participation of about 30 young scientists. The training consists of 5 days lectures and experimental works including hands-on-training at the Budapest Research Reactor facilities. The participants are divided into groups. Each group of 5-6 students performs one or two neutron scattering experiments per day and each group works at 6 different instruments. The aim of this training programme is to bring together young physicists, chemists, biologists and potential neutron users.

ABBREVIATIONS

AER	Atomic Energy Research
ANCARA	MTA EK-BME NTI Budapest supercritical water test facility
AOT	Advanced Oxidation Technologies
ASA	acetylsalicylic acid
ASTM	American Society for Testing and Materials
ATWS	Anticipated Transient Without Scram
BEXUS –	Balloon Experiment for University Students
BME NTI	Budapest University of Technology and Economics, Institute of Nuclear Techniques
BNC	Budapest Neutron Center
BRR	Budapest Research Reactor
CERTA	Centre for Emergency Response, Training and Analysis
CFD	computational fluid dynamics
CHF	critical heat flux
CMC	carboxymethyl-cellulose
CNESTEN	Centre National de Énergie, des Sciences et des Techniques Nucléaires, Marokkó
CoCoRAD –	Combined TriTel/Pille Cosmic RADIation and dosimetric measurements
CP-ECR	Cathcart-Pawel Equivalent Cladding Reacted
CCS	carbon capture and storage
CSTP	Council for Science and Technology Policy
DBA	Design Basis Accident
DIM	Dust Impact Monitor
DLR	National Aeronautics and Space Research Centre of Germany
DNBR	Departure from Nucleate Boiling Ratio
DNR	Dinamic radiography
DÖME	Damn heavy measuring equipment
DPU	Digital Processing Unit
EC	European Commission
ECR	Equivalent Cladding Reacted
EIA	environmental impact assessment
EPR	European pressurized water reactor
ESA	European Space Agency
EU	European Union
EVA	Extra-vehicular Activity
FGR	Fission Gas Release
FP	Framework Programmes
FRM-II	Forschungs-Neutronenquelle Heinz Maier-Leibnitz, Technische Universität München (TUM) in Garching
FSS	First Scientific Sequence
FTIR	Fourier transform infrared spectroscopy
GFR	gas-cooled fast reactor
GIF	The Generation IV International Forum
GRM	Ground Reference Model
GSE	Ground Support Equipment
HAEA	Hungarian Atomic Energy Authority
HBS	High-Burnup Structure
HEU	Highly enriched uranium
HPLC	High Performance Liquid Chromatography
IBMP	Institute for Biomedical Problems
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
ICP-MS	Inductively coupled plasma mass spectrometry

ISS	International Space Station
JSPS	Japan Society for the Promotion of Science
LB	Large Break
LBLOCA	large break LOCA
LeGe	Low-energy germanium detector
LET	Linear Energy Transfer
LOCA	Loss-of-Coolant Accident
LOWG	Lander Operation Working Group
LTS	Long Term Science
MCP	Main Coolant Pump
MFGI	Geological and Geophysical Institute of Hungary
MORABA	Mobile Rocket Base
MPS	Max Planck Institute für Sonnensystemforschung (for Solar System Research)
MS	Mass spectrometry
MSIV	Main Steam Isolation Valve
MTA EK	Hungarian Academy of Sciences Centre for Energy Research
MTC	Moderator Temperature Coefficient of reactivity
NAA	Instrumental Neutron Activation Analysis
NCP	Network Control Program
NIPS	Neutron Induced Prompt-gamma spectrometry
NMS	New Member State
NORMA	Neutron Tomography
NPP	Nuclear Power Plant
NT	Neutron Tomography
OCA	Orbiter Communications Adapter
OMS	Old Member State
PAZAR	Hungarian acronym of the Paks Autonomous Noise Data Acquisition System
PAZAR-K	Evaluation system for the data measured by PAZAR
PCI	Pellet Cladding Interaction.
PCI-SCC	Pellet Cladding Interaction - fission products assisted Stress Corrosion Cracking.
PCMI	Pellet Cladding Mechanical Interaction.
PDCS	Pre-Delivery Calibration and Science
PDP	Passive Detector Package
PECS	Plan for European Cooperating States
PGAA	Prompt-Gamma Activation Analysis
PGAI	Prompt Gamma Activation Imaging
PHC	Post Hibernation Commissioning
PRISE	primary to secondary leakage
R&D	Research and Development
REM-RED	GM Sounding Rocket Experiment to Measure the Cosmic Radiation and Estimate its Dose Contribution
REXUS	Rocket Experiment for University Students
RIA	Reactivity Initiated Accident
ROMAP	Rosetta Lander Magnetometer and Plasma Monitor
SAA	South Atlantic Anomaly
SCWR	Super Critical Water-cooled Reactor
SCWR-FQT	Supercritical Water Reactor-Fuel Qualification Test
SDL	Separation, Descent and Landing
SEI	Software Engineering Institute
SEM	scanning electron microscopy
SEM-EDX	Scanning electron microscope - Energy dispersive X-ray analysis
SESAME	Surface Electrical, Seismic and Acoustic Monitoring Experiments
SIP	Small Instrument Package
SNSB	Swedish National Space Board
SPM	Simple Plasma Monitor
SRL	Space Robotics Laboratory

SSA	specific surface area
SSC	Swedish Space Corporation
SSNTD	Solid state nuclear track detectors
SURE	International Space Station: a Unique Research Infrastructure
SW	Software
TANDEM	Trans-uranium Actinide Nuclear Data - Evaluation and Measurement
TECHDOSE	Development of a Complex Balloon Technology Platform for Advanced Cosmic Radiation and Dosimetric Measurements
TEM	Transmission electron microscopy
TL	thermoluminescent
TLD	thermoluminescent dosimeter
TPR-TG	temperature-programmed reduction - thermogravimetry
VOF	volume of fluid
VVER	well known Russian reactor type, Russian acronym
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence