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I. Main tasks scheduled for 2012

The main tasks scheduled for 2012 fall into four different categories. Namely, developing and applying nuclear analytical methods and radiochemical techniques, performing research and development in nuclear security field and to perform surface chemistry and catalytic studies.

The intention on the field of *analysis by nuclear methods* was to improve and apply PGAA, NAA, XRF and Mössbauer techniques for studies in materials sciences, chemistry, archaeometry, geology, biology, collection of nuclear data as well as to perform simultaneous on line studies on various processes by applying neutron-, X-ray and gamma-ray radiography and tomography. Furthermore, a dedicated task for the Nuclear Analysis and Radiography Department is to provide a service for the international users in the framework of various international EU projects (EU FP7 NMI3, EU FP7 CHARISMA and EU FP7 ERINDA) as well as in national consortia (NAP VENEUS08).

In the field of *radiation chemistry* the study of the applicability of ionizing radiation for the treatment of water containing toxic organic impurities, for polymer modification (radiation initiated grafting) and of the radiation resistance of polymers was planned.

Several topics were selected for studies in the fields connected to *nuclear security*. Namely, improvement and application of high-sensitivity gamma spectrometry for analysis of samples containing uranium as well as to determine the extent of the reprocessed uranium in reactor fuels, broadening the fields of applications of luminescence dosimetry by introducing novel detector materials, elaborating methods for determination of the amounts of long life time actinides in biological and environmental samples by LA-ICP-MS technique, extension of applications of Sunna dosimeter films to technological processes by IR detection, studying valence states on uranium oxide surfaces by Auger and ESCA spectrometry, improving neutron coincidence data acquisition software, and the accuracy of the method used for determination of plutonium content in PuBe neutron sources.

Several topics were selected also in the direction of *surface chemistry and catalysis*. Namely, at first, conversions of C1 molecules at dry reforming of methane, second, development of catalysts for removal of N₂O from methane and for preferential oxidation of carbon monoxide in hydrogen (PROX), third, application of environmentally benign processes for removal of organic contaminants from waste waters and for removal of sulphur from gasoline, fourth, application of gold-containing bimetallic catalysts in selective, aerobic oxidation processes, and finally, application of radioactive tracer techniques to study catalytic carboxylation of oleic acid extracted from vegetable oil were proposed for studies.

In addition, the institute provides the expertise as a technical support organisation (TSO) of the Hungarian Atomic Energy Agency in fields related to nuclear security, radiation safety, transport of nuclear and radioactive materials, management of the complete registry of radioactive and nuclear materials for Hungary, and provides possibility to analyse and identify seized nuclear and radioactive materials of unknown origin or from illicit trafficking.

II. Outstanding and other results achieved in 2012

a) Outstanding and other results

Outstanding results have been achieved by **applying nuclear analytical methods** for studying industrial catalytic processes by *in beam & in situ* PGAA technique.

One achievement is related to a process important in synthesis of plastics. Namely, that is the removal of traces of alkynes from ethylene and propylene streams by selective hydrogenation, catalysed usually by palladium. The process was studied by PGAA technique with *in situ & in beam* arrangement. It was revealed that the reaction proceeds in a surface Pd-C layer. The strength of the hydrogen bonding is decreased in the Pd-C, thus the extent of coverage with hydrogen is low. The interpretation of results is also supported by DFT (periodic density functional) calculations and with simultaneous measurements (e.g. *in-situ* XPS). Based on the interpretation of these data novel Al-Fe intermetallic alloys were synthesised which exhibit good activity and selectivity in the process and they can be used for replacing the expensive palladium. The results were published in the Nature Materials journal.

Another process of industrial importance is production of chlorine by oxidation of chloric acid via the Deacon reaction ($2 \text{HCl} + \frac{1}{2} \text{O}_2 \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$). RuO_2 can be used as catalyst. *In situ & in beam* studies performed in dependence of temperature revealed that the reaction rate depends on the temperature via the surface coverage and not via the velocity constant. The results were published in the Nature Chemistry journal. The Deacon reaction was also studied with CeO_2 catalysts, doped with Hf, Zr, La, Y. The Hf and Zr doped catalysts provided outstanding activity in the reaction. The price of the latter catalyst is ca. half of the RuO_2 one, thus perspective industrial application of the new CeO_2 catalyst can be foreseen.

Other important results achieved in the field of **nuclear analysis**:

Improvement of the PGAA analytical method and the spectroscopy database

The trace detector method was applied to determine the content and distribution of boron in Co-Re alloys in cooperation with TU Braunschweig. It was shown with combination of PGAA and complementary solid state trace detector method (SSNTD) that the amount of boron changes its spatial distribution in the Co-Re alloy, and in particular, it prefers to segregate at grain boundaries, providing a mean to improve the mechanical properties of the alloy.

A new technique was elaborated to improve the detection limit of uranium in comparison to the direct PGAA method. The new method is based on the coincidence counting of gamma radiation generated by cold neutrons. This technique allows the detection of ^{235}U in amounts of micrograms, which limit is lower with several orders of magnitude in comparison to recent standard safeguards techniques.

The evaluation of spectroscopic data of W was carried out in cooperation with Lawrence Berkeley Laboratory. In connection with the catalytic measurements, the spectroscopic data of Hf, Zr, La, Y were verified, and their accuracies were improved from new measurements.

Analysis of nuclear materials

PGAA measurements were carried out on $^{237}\text{NpO}_2$ and $^{242}\text{PuO}_2$ samples in the framework of EU FP7 ERINDA project in order to obtain data which can be used to identify components of nuclear wastes.

Hydrogen contents of E110 and E110G claddings of reactor fuels were measured by PGAA following a high temperature (1200 °C) treatment with water/steam. The measurements showed that the amount of zirconium hydride formed during the treatment is significantly less in the E110G than in E110 cladding. This observation may provide strong support of licensing the use of the former one as well.

(n, γ) and (γ,γ') measurements were carried out on enriched ^{77}Se and ^{78}Se as well as on ^{195}Pt and ^{196}Pt pairs of nuclei on the PGAA and ELBE (Dresden) facilities in the framework of EFNUDAT in order to determine Gamma Strength Function (GSF) which can be used for simultaneous description of both processes.

Three day long series of measurements was performed with the EXOGAM appliance equipped with 46 HPGe detectors on the PFB1 beam of the Institute Laue-Langevin to measure (n, $\gamma\gamma\gamma$) triple coincidences in order to collect information on the Pigmy (neutron skin) resonance, as well as on related spins and parities. The evaluation of collected data, amounting to 1.5 Tbyte, has been in progress.

Studies connected to geology

Boron content of several deep seabed serpentinite rock samples were determined. It was established that enrichment of Cl, B, Sr, U, Sb, Rb, Cs elements in the samples is connected to the process of the transformation to serpentinite.

Calibration of a special geological tool, the REGARD muon-tomograph was also carried out in cooperation with teams of MTA Wigner FK, MTA-ELTE research group of geology and BME. The equipment enables mapping of geological rock inhomogeneities as well as unknown galleries in caves. The principle of operation is based on the detection of muons, the count rate of which depends on their mass absorption. In the procedure variable thicknesses were used (0 – 460 g/cm²) to obtain the calibration curve, which may help to evaluate the muon-radiography images.

The information related to disposal of high level nuclear waste in clay rock formations are summarised in a chapter of a textbook, as well as the results of related isotope migration experiments with long half life time radionuclides ($^{99}\text{TcO}_4^-$, $\text{H}^{14}\text{CO}_3^-$) and sorption measurement with uranyl (UO_2^{2+}) cations carried out on borecore samples originated from Boda claystone (Mecsek Mountains, Hungary) performed in the framework of EU FP6 FUNMIG and EU FP7 RECOZY projects.

Archaeometry:

Provenance research of chipped and polished stone tools has been continued. The main types of raw material for chipped stone tools were obsidian, silex, Szeletian porphyry, while for polished stone tools greenschist and high pressure metamorphite rocks. The range of the investigated obsidians has been extended by objects of Polish and Romanian origin. The Polish origin samples proved to be Carpathian 1 (i.e. Slovakian) type, while the Romanian samples turned out to be either Carpathian 1 (Slovakian) or Carpathian 2 (Hungarian) types. In the latter case, based on PGAA, Melosian origin can be excluded with high confidence.

This research was funded by the OTKA K 100385 and by the EU FP7 CHARISMA projects. Funded by CHARISMA, too, provenance of „Ljubljana type” shaft-hole axes found in Caput Adriæ, Italy have been investigated. Based on PGAA investigations, it was confirmed that the raw material of these objects originate from the nearby Slovenian regions.

Within the frame of CHARISMA FP7 project, methodological studies on 16-13 c. BC Mycenaean glass beads have been performed. Corrosion process as well as provenance of glass has been investigated. Bulk PGAA, near-surface PIXE and microscopic SEM-EDS results have been compared, in order to determine the chemical components most affected by corrosion.

In another case study, corroded iron beads from 3200 B.C. Egypt have been studied by TOF-ND, PIXE, PGAA and neutron radiography. The raw material of the objects that supposed to be the earliest man made iron objects, proved to be meteoritic iron.

12-15. c. A.D. Inca pottery fragments excavated in Bolivia, have been analysed by PGAA, INAA and XRF. Following the changes in composition for various periods, it was possible to

demonstrate the changes in the utilized raw materials and also in the applied manufacturing technologies from the Late Intermediate (from 1000/1200 A.D. to 1438) till the Classic Inca Period (1438-1535).

Dynamic Neutron Radiography (DNR) studies:

Special equipment was constructed in which cooling of a fuel assembly by supercritical water can be modelled. The warm side can be heated with electric current whereas the other, cold branch can be cooled, enabling this way the natural circulation of water. Simultaneous recording of data from 16 thermometers, from 4 absolute and 2 differential pressure gauges, and from a mass flow meter with 5 Hertz frequency allows determining the thermodynamic conditions of the system. The transition of water to supercritical state and eventual formation of bubbles can be monitored. The equipment may contribute to the better understanding of the process of supercritical cooling.

Mössbauer spectroscopy

was applied to study the initial stages of the formation of Metal-Organic Frameworks (MOF-s). Small changes in the synthesis conditions may result in structural changes of MOF-s. Namely, MIL-100(Fe) can be formed from 1,3,5-tricarboxy-benzoic acid and aqueous solution of FeCl₃ in hydrothermal synthesis. In contrast, MIL-45(Fe) forms if 1:1 acetone-water mixture is used as a solvent. Double-layered Mg/Al/Fe hydroxide catalysts used for removal of N₂O by decomposition or by reduction with ammonia were also studied by this in situ technique. The primary role of Fe-O-Fe-O-Fe chains is confirmed in both catalytic processes. Co-ferrite catalysts, supported on MCM-41 and SBA-15 were compared in total oxidation of toluene. Better catalytic activity was found for CoFe-MCM-41 where higher dispersion for the ferrite component was found by in situ measurements.

Results achieved in the field of radiation chemistry

One of them is related to study of the radiation induced degradation of toxic organic compounds in aqueous solutions. The purpose of this work was to study the radiation induced degradation of pharmaceutical compounds and their metabolites in dilute aqueous solutions. The compounds investigated were: 2,6-dichloroaniline, acetovanillone, ketoprofen and chloramphenicol. Based on their results it was proved that the hydroxyl radical formed during the radiolysis of water attacks the benzene ring. The intermediate formed is hydroxycyclohexadienyl radical which will be converted to anilino radical (in 2,6 dichloroaniline solution), or phenoxyl radical (in acetovanillone solution). In solutions saturated with oxygen the hydroxycyclohexadienyl radical will be converted first to peroxy radical, and this step initiates a chain reaction leading to the mineralization of the solution. The toxicity of the products formed at lower doses is mostly higher than those of the original compounds, however, with increasing dose the products decompose and the toxicity decreases.

The other research field is the radiation resistance and radiation modification of polymers. Cotton-cellulose was functionalized by glycidyl methacrylate (GMA) grafting in order to change the hydrophilic properties of cellulose surface. Both pre-irradiation (PIG) and simultaneous grafting (SG) methods were used for functionalization. The samples prepared by PIG had more homogenous surfaces and low grafting yield, while those prepared by SG had much higher grafting yields, however, some homopolymer formation was also observed. The effect of changing the reaction parameters (grafting method, dose, monomer concentration, solvent composition) was followed by scanning electron microscope, gravimetry and FTIR spectroscopy. The water uptake of the samples decreased while the absorption of pesticide molecules from aqueous solutions increased with increasing grafting yield. Improved

pesticide absorption was observed when cyclodextrin was added to the grafting solution in SG. An advanced version of this method will be applicable for producing adsorbents for wastewater treatment in the agriculture.

The model which was developed earlier for the description of the *electron-ion recombination*, has been successfully applied recently for supercritical ammonia, and the model has also been enabled to describe properties of charge carrying pairs.

Results achieved in radiation security studies

High sensitivity gamma spectrometry was used

- To qualify uranium samples with ^{232}U measurements whether they contain reprocessed uranium. Some seized as well as etalon samples were found to contain reprocessed U. The results were confirmed by ^{236}U mass spectrometric data, too. No indications for presence of reprocessed U were found in the Paks NPP fuel investigated.

- Verification of the of enrichment degree in the Paks NPP fuel assemblies went on. The enrichment of the outer and inner fuel rods of the assemblies of freshly arrived transport batches was determined by gamma spectrometry combined with MCNP simulations.

- An outstanding result is the development of a gamma spectrometric method for determining burnup of spent fuel assemblies at the Paks NPP. The results can be compared with those of reactor physical depletion calculations. The contribution from different fuel rods at different depths was also calculated by MCNP simulation. The assumed uncertainty of the depletion code (13 %) can significantly be decreased by utilizing the 3-4 % (1 STD) uncertainty of the measurements. Thus, safety margin can be lessened enabling higher burnup and longer fuel cycles for better fuel economy.

- Calibration of the Canberra devices (with blood and urine samples) has been performed in the framework of BOOSTER (EU FP7 project), as well as the test of CdZnTe gamma-chamber developed by CEA with various radiation sources.

- A pilot station is assembled for testing NaI and plastic detectors of SYMETRICA Co. and tests were performed in the framework of SCINTILLA (EU FP7) project. The guidelines for establishing a test and practice laboratory for developing detectors for assaying nuclear materials have been elaborated.

- Surface layers of uranium oxide samples were analysed by X-ray photoelectron and Auger spectroscopy. The peaks of uranium, oxygen and carbon can clearly be identified and distinguished. The number of analysed samples should be increased for elaboration a method applicable for nuclear security purposes.

In the field related to *neutron-coincidence measurements* the PTR-32 pulse train recorder, developed earlier in the framework of a national support program for IAEA, has been improved. The control and data acquisition routines have been improved, in order to promote the international spreading of the instrument. The Passive Scrap Multiplicity Counter (PSMC) used regularly at the Nuclear Safeguards and Forensics Department of the ITU was also tested with the PTR-32 device. Furthermore, certified high-enriched nuclear samples and metallic plutonium were also measured.

The accuracy of the method used for determination of plutonium content of Pu-Be sources has been increased by improving the calculation and measurements of specific neutron yields, and by using radiography of the charges combined with density measurements.

In the topic of *development of methods and materials for dosimetry* the possibilities of applications of surface mounted (SM) resistances for *retrospective dosimetry* were evaluated with the method of optically stimulated luminescence (OSL). The OSL technique has been

proven to provide estimation for a wider range of the dose than the thermoluminescence (TL) does. On the other side, the fading of the signals was faster with OSL detection than with TL. The assembly of an instrument which can be used for in-field measurements with OSL detection has been commenced.

New materials usable for dosimetry were also investigated. In particular, double doped calcium-phosphate, $\text{CaSO}_4:\text{Tm,Cu}$ and $\text{CaSO}_4:\text{Dy,Cu}$ samples were evaluated. These copper containing substances show broader range of response for dose, glow curve of simpler structure than the copper-free ($\text{CaSO}_4:\text{Tm}$, $\text{CaSO}_4:\text{Dy}$) substances, however they have smaller sensitivity. The effect of copper was interpreted by decreasing the probability of trapping of charge traps. Optimal compositions were also determined with a series of measurements. Study of TL emission of another potential raw-material, doped $\text{Li}_2\text{B}_4\text{O}_7$, showed that the wavelength of the emission is characteristic for the dopants (Cu^+ , Mn^{2+} , Ag^+), i.e. they are the centres of luminescence.

Improvement of dosimeters for technical applications was also carried out with LiF-based („Sunna”) type. The sensitivity range of these devices is 1-200 kGy. The lower limit of the range was extended to smaller doses by applying infrared detection of the emitted light. Close to linear calibration curve was recorded for LiF in the 50 – 1000 Gy range at 1040 nm wavelength emission.

In connection with applications of high sensitivity mass spectrometric methods samples of biological origins were analysed. Fast and accurate determination of radionuclides in small amounts is an important point for determination of the extent of internal contaminations of involved persons following eventual terrorist acts or nuclear failures. A method was elaborated for determination of the amount of actinides (primarily uranium) in blood and urine samples with LA-ICP-MS technique. The lower detection limit for uranium in blood was 4 picogram, in urine 8.5 picogram. An even more sensitive method was also developed; which uses chemical separation steps with liquids.

A method based on Laser Induced Breakdown Spectrometry (LIBS) technique was also developed and adapted for analysis of biological liquids. Specifically, the amount of caesium can exactly be determined from a drop of blood or urine. Portable LIBS equipment was also acquired. The equipment will be tuned up in order to allow field measurements in correspondence with expectations of the IAEA and HAEA providing a tool for identification of nuclear substances, for determination of the extent of enrichment of uranium, etc.

Main results achieved in surface chemistry and catalysis

Hydrogen production and purification

Catalytic methane dry reforming ($\text{CO}_2 + \text{CH}_4 = 2 \text{CO} + 2 \text{H}_2$) is one of the possibilities of the exploitation of biogas and Hungarian natural gas wells containing CO_2 in large concentration. During the research connecting with development of catalysts of high activity and tolerance against carbon deposition in this process, it was revealed that the catalytic properties of the monometallic $\text{Ni/MgAl}_2\text{O}_4$ samples were independent of the preparation method if Ni content and particle size were the same, and that NiAu phase produced with sol preparation method underwent structural changes during the high temperature pretreatments and the catalytic reactions. The addition of Au had a negative effect in terms of catalyst stability and the easiness of carbon removal.

Investigations on N_2O decomposition and N_2O reduction by methane carried out with different M/Ga/H-ZSM-5 (M: Fe, Co, Ni, Mo, Ru, Pd, Ag, Ir, Pt, Au) catalysts arranged the samples into two groups: the presence of CH_4 increased N_2O conversion in the case of Pt and Pd, while there was no effect observed in the case of all other metals. Since the N_2O removal

can be necessary in the purification of biogas containing also CO, the N_2O+CH_4+CO reaction was investigated on the above samples. It was observed that 0.5% CO causes a reversible deactivation only for Pt sample while it is detrimental for Fe, which can be explained by the differences of active centres of catalytic turnover for the competitive N_2O+CH_4 and $CO+CH_4$ reactions on Pt.

For removal of small amount of electrocatalyst poison CO from the H_2 feed for fuel cell applications the catalytic preferential CO oxidation (PROX) is the most promising method. It was revealed that PtSn sample after O_2 and H_2 treatment resulted better CO oxidation activity in PROX process than after only H_2 treatment, moreover, in situ XPS detected more Pt in the near surface region (Pt_3Sn) and some Sn-oxides and the enrichment of water and surface hydroxides.

Noble metal free oxide catalysts were also studied in PROX reaction. Mn-, Co-oxides and manganese promoted cobalt-oxides (Mn/Co=5/95 and 12/88 atomic ratio) of high surface area ($>50\text{ m}^2/\text{g}$, $MnO_x > Mn_mCoO_x > CoO_x$) were prepared by deposition as oxalates followed by temperature programmed oxidation. MnO_x was mostly amorphous beside about 25% Mn_3O_4 , CoO_x was crystalline Co_3O_4 , the mixed oxide contained Mn substituted Co_3O_4 according to XRD investigations. The mixed oxide is much more stable against sintering than Co_3O_4 . TPR-TPO studies indicated the Mn substitution induced modification of redox properties of Co_3O_4 . The PROX properties (activity, CO oxidation selectivity) changed in the $MnO_x < Co_3O_4 < Mn_mCo_{3-m}O_4$ order. During the reaction the catalysts were reduced in different extent decreasing the CO oxidation activity. By reoxidation the catalysts could be more or less regenerated. On the effect of reduction of Co_3O_4 in repeated PROX cycles, the less favourable methanation reaction appeared and strengthened. Methanation was not detected on the other samples. Taking into account also the specific surface area, synergetic effect of the combination of Mn- and Co-oxide was observed likely as a result of the advantageous modification of the oxygen binding energy in the mixed oxide.

Research in relation with alternative energy

The conversion of oleic acid has been studied applying oleic acid labelled with radioactive carbon (oleic acid-1- ^{14}C) to follow the hydro-treating process of this compound over sulphided alumina-supported NiMo(containing P) and NiW catalysts. A unique catalytic reactor equipped with a special unit for microanalysis was applied for the study of the mechanism of decarboxilation, decarbonilation and hydrodeoxidation reactions and the degradation of the surface sulphur by radiotracer method using ^{14}C and ^{35}S . The radioactive micro analytic method based on the application of oleic acid-1- ^{14}C is suitable well for the testing and evaluation of new catalyst samples in hydro-treating process of vegetable oils relating to the biodiesel production.

Research in relation with environment protecting catalytic technologies

The necessary and sufficient degree of catalytic wet oxidation of wastewaters has been determined, which ensured the biodegradability of the treated wastewater without complete mineralization of the carbon content. The temperature of catalytic wet oxidation could be decreased from $180^\circ C$ to ambient temperature with high energy irradiation. The monolith catalysts were characterized in the wet oxidation of real wastewaters.

It has been demonstrated by radioisotope tracer technique using ^{35}S that over alumina supported Ni, Mo and NiMo catalysts with thiophene HDS process simultaneously thiophene recyclization is taking place too. The appearance of thiophene with significant ratio of products radioactivity indicates the reaction between catalyst sulfur and butadiene as by-product of thiophene HDS. The sequence of the rates of thiophene production on these catalysts in a circulation system was the same as that of thiophene hydrodesulphurization

observed before. It follows that the overcompensation between the constants of the Arrhenius equation, indicating that the effect of the increasing number of the active sites at the growing energy barrier of the reaction compensates over the rate decreasing effect of this growth.

Highly selective catalytic processes

In the frame of exploration of applicability of gold based bimetallic catalysts in selective oxidation processes using glucose and benzyl alcohol model substrates and O₂ reactant, the study of AuAg system was continued. According to UV-vis, HRTEM and XPS measurements alloyed AuAg bimetallic particles were formed by HAuCl₄ reduction in aqueous Ag sol prepared by Ag-nitrate reduction in presence of stabilizing agent. Bimetallic sols of different Ag/Au atomic ratio were adsorbed on SiO₂ support. For removal of organic residues calcination was applied, which caused the formation of Au-Ag₂O structure, as evidenced by XPS results. Under optimized conditions both the bimetallic samples and also the monometallic analogous provided 100% gluconic acid selectivity in the oxidation of glucose. Synergetic effect was observed in activity of bimetallic samples of Ag/Au ≤ 0.5. Their activity inversely correlated with the Ag/Au surface atomic ratio determined by XPS. The presence of Ag₂O on or beside the Au surface possibly enhances the O₂ adsorption ability; however decreasing the extended Au surfaces necessary for glucose adsorption, lowers the activity.

For the study of the supported AuCu catalyst in selective oxidation bimetallic nanoparticles of different structure (alloyed, core/shell type) stabilized in sols were prepared and characterized by UV-vis spectroscopy and TEM, HRTEM. The nanoparticles were successfully adsorbed on Al₂O₃ and SiO₂ support. The catalytic tests and further characterization are in progress.

The catalytic and molecular conditions of asymmetric induction have been studied in heterogeneous catalytic hydrogenations. The kinetic resolution of 2- and 3-methylcyclohexanone was studied with reductive alkylation by (*S*)-proline. Significant enantioselectivity could be detected at 2-methyl derivative, but its value is far less than with 3,3,5-trimethylcyclohexanone. The hydrogenation of racemic 3,5-dimethyl cyclohex-2-enone resulted in one stereoisomer, in the meso compound.

Corrosion research in relation with reactor safety

Reaction of zirconium and water above normal operation temperature (> 900 °C) can result in the accelerated degradation of cladding of nuclear heating elements. During an ATWS type accident also the pressure can be highly increased (e.g. 150 bar for half an hour). A special autoclave was created for the study of the temperature and pressure dependence of oxidation reaction rate of different Zr-based cladding samples up to 1000 °C and 150 bar water pressure. Preliminary results on Zircaloy-4 and Zr-1%Nb (E110) samples showed exponential pressure dependence in the average oxidation rate during 30 minutes reaction time. Results on E110 gave very high scattering in the oxidation ratio in parallel experiments. Presumably the oxidation process had an incubation period and its time had a probability distribution.

b) Science and society

To disseminate the results achieved at the institute summarizing presentations were held on the analytical applications of the PGAA technique on the „80 years of neutron” and on the „Celebration of Science at the Hungarian Academy of Science” programs.

The anchor person of a radio series „The place” Erika Farkas visited the laboratories of the former Central Research Institute of Physics. She devoted also interest to introduce the nuclear analytics at the Budapest Neutron Centre. The broadcast and the related video is archived at the

http://www.youtube.com/watch?feature=player_embedded&v=SQYa6HL7KcA site.

The directors responsible for the research and development of the Downstream portfolio at the MOL Company visited the institute. Presentations were held to demonstrate the available perspective methods and procedures which may merit common interest in the future. The session was closed with a consultation.

III. National and international connections and co-operations

In the field of *applications of nuclear analytical* methods the connections established with the researchers of the Hungarian National Museum, and with the member institutions of the Budapest Neutron Centre (Wigner FK RMI and SzFI) as well as with MTA CsFK, ATOMKI and with the department of Petrology and Geochemistry are of great importance. Connections built up with the colleagues from the Mecsekérc Co. are importance for aspects related to the studies for establishing high level nuclear waste depository in Hungary.

Several international cooperation have been established with researchers e.g. of DG JRC IRMM, (Belgium), FZ (Jülich), HZ (Dresden), LBNL, (USA), Charles University (Prague), Department of Nuclear Data and Physics IAEA (Wien), Fritz-Haber Institute (Berlin), FRM-II, TU Munich, and Kemijski Institut (Ljubljana).

TANDEM agreement of cooperation has recently been constructed targeting joint studies for characterisation of nuclear wastes with participation of TU Munich, FZ Jülich, LBNL and EK.

Researchers working on the field of *radiation chemistry* are also lecturers at the Chemical and Biological Engineering Faculty of BMGE, at University of Szeged, at Óbuda University and at Pannon University, in disciplines of materials chemistry, environmental protection and water treatment. National cooperations have also been established with Bay Zoltán ATI, PEMŰ and Corvinus University. International cooperations are mostly based on joint projects (EUREKA, Indian-Hungarian TeT, and with IAEA).

In the field of *nuclear security* connections are primarily established to International Atomic Energy Agency (IAEA). The institute participates in the national support project of Hungarian Atomic Energy Authority (HAEA) in nuclear analytical methods with aims of the improvement of PTR-32 neutron coincidence detector („A1667: Development and Evaluation of a Multiplicity Spectrometer Prototype”), and with enabling the method of laser induced breakdown spectroscopy by developing a portable equipment for nuclear safety analyses („A1597: Support for Novel Technologies”).

They also have cooperations with two Joint Research Centres of the EU. On the commission of the ITU (Institute for Transuranium Elements) they held a two-week course on nuclear forensics, and also tested the ITU’s Passive Scrap Multiplicity Counter (PSMC) neutron detector with the PTR-32. At the Ispra JRC similar calibration measurements were carried out.

On topics related to *dosimetry* cooperations were established with the Pacific Northwest National Laboratories, with „Ruder Boskovic” institute of Croatian Academy, with the Vinca Nuclear Research Centre in Serbia and with the Institute of Surface Chemistry in Ukraine. The group of *mass spectrometry* cooperates with the French Triskem International company on development of methods for analysis of nuclear materials.

Researchers working on the field of *surface chemistry and catalysis* regularly participate also in the education of students at the BMGE University, they are delivering seminars, instruct

laboratory courses and are consultants of MSc theses. Further cooperations, both formal and informal ones are also established with the Pannon University, as well as with the MTA TTK MFA, and MTA Wigner SzFI institutes. International bilateral cooperations are also established with researchers of Swiss (École polytechnique fédérale de Lausanne, EPFL), Austrian (Institute of Materials Chemistry, Vienna University of Technology), Belgian (Université Libre de Bruxelles, ULB) and Italian (CNR, Istituto per lo Studio dei Materiali Nanostrutturati, CNR, Palermo) institutes.

IV. Short description of national and international projects obtained in 2012

OTKA K 100385, „Non-destructive study of the origin of the raw materials of ancient stone tools find in the Carpathian Basin”. The main aim of the project is the identification of the provenance of chipped and polished stone tool (obsidian and quartz stones) findings. The intended research is based on in-field collection of samples for comparison as well as on applying non-destructive techniques (primarily PGAA, completed with optical microscopy, SEM-EDS, XRF, INAA). Proposed locations for collection of samples are in Hungary, in the neighbour countries, and in Poland and in Italy, utilizing earlier cooperations (CHARISMA, TeT). Construction of a new open database for raw materials of the ancient stone tools is also intended which contains the data obtained in the project.

Moroccan-Hungarian TeT, The researchers of the institute are supposed to share their experience and support the construction of a PGAA laboratory in the new Research Reactor Complex in Maroc. Further on, joint projects are also considered in the future.

OTKA NK 105802, „Degradation of pharmaceuticals with hydroxy radicals produced by irradiation of aqueous solutions”. The aim of the project is to describe the mechanism of the decomposition organic pollutants dissolved in water induced by ionising radiation. One sort of the advanced oxidation processes (AOP) is the technique applying ionising radiation, providing a mean to follow the reactions with radicals (by measuring the concentration of radicals in dependence of the elapsed time), to determine the kinetic constants, and to reveal the mechanism. The results obtained can be generalized to other AOP processes, too.

TET_09_IN_DST - PIEZOFIB, „Development, characterisation and modelling of flexible fibre based nanogenerators”. The aim of this project to develop piezoelectric structures which are composed of non-woven (vlies) fibres, the surface of which is covered by ZnO nanofibres. Seeds are generated by radiation on the non-woven fibres then ZnO nanofibres are grown on this seeds in electrochemical processes in the cooperating BAY ATI Institute.

OTKA 101854, (2012-2016), „Aerobic selective oxidation on bimetallic catalysts containing gold”. Bimetallic Au-M (M: Ag, Cu, Ru, Ir) supported catalysts are prepared, characterised and compared in selective oxidation of hydroxy aldehydes, alcohols and hydrocarbons by using glucose, benzyl alcohol, and toluene. The influence of preparation procedure and the atomic ratio of the two metals on the structure, activity, selectivity and stability of the catalysts are to be studied. The acid-base properties are also evaluated providing basis for potential development of novel multifunctional catalysts in the future.

ERACHEMISTRY, OTKA NN 107170, 2012-2015, „Dry reforming: path from the elementary steps to the active catalyst”. The aim of the project is to develop novel, efficient and stable Pt, Ni catalysts for the process of dry reforming ($\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2 \text{CO} + 2 \text{H}_2$). The emphasis is laid on studying the side process, the formation of carbon black resulting deactivation. The

studies are performed in cooperation with the Technical Universities of Munich and Wien (Prof. J. Lercher, and Prof. Rupprechter, respectively).

Six projects were obtained in the frame of „*Technical Support Activity*” assigned for the Hungarian Atomic Energy Authority.

Foundation of Austro-Hungarian Scientific and Education Action of Cooperation, 84öu, 2012-2013, „Induction effect of oxides in oxidation of CO on noble metal catalysts”. The aim of the project is to reveal the connections between the catalytic activity and the structure of the gold-oxide phase boundary.

EU FP-7 Scintilla, „Scintillation detectors and new techniques for nuclear security” project consortium is also obtained support with the participation of researchers from the institute.

V. Significant scientific publications in 2012

1. Teschner, D., Novell-Leruth, G., Farra, R., Knop-Gericke, A., Schlögl, R., Szentmiklósi, L., et al. (11), In situ surface coverage analysis of RuO₂-catalysed HCl oxidation reveals the entropic origin of compensation in heterogeneous catalysis, *Nature Chemistry*, 4: pp. 739-745. (2012)
2. Armbrüster M., Kovnir K., Friedrich M., Teschner D., Wowsnick G., Hahne M., Gille P., Szentmiklósi L., et al. (14), Al₁₃Fe₄ as a low-cost alternative for palladium in heterogeneous hydrogenation, *Nature Materials*, 11: pp. 690-693. (2012)
3. Birsa Celic T., Rangus M., Lázár K., Kaucic V., Zabukovec Logar N., Spectroscopic evidence for the structure directing role of the solvent in the synthesis of two iron carboxylates, *Angewandte Chemie International Edition*, 51: pp. 12490-12494. (2012)
4. Guczi L., Erdőhelyi A. (szerk.) *Catalysis for Alternative Energy Generation*, New York, Springer, 536 pp.
5. Hosseini A.M., Tungler A., Schay Z., Szabó S., Kristóf J., Széles É., Szentmiklósi L., Comparison of precious metal oxide/titanium monolith catalysts in wet oxidation of wastewaters, *Applied Catalysis B: Environmental*: 127, pp. 99-104. (2012)
6. Illés E., Takács E., Dombi A., Gajda-Schranz K., Gonter K., Wojnárovits L., Radiation induced degradation of ketoprofen in dilute aqueous solution. *Radiation Physics and Chemistry* 81: pp. 1479-1483. (2012)
7. Almási I., Nguyen C.T., Zsigrai J., Lakosi L., Hlavathy Z., P. Nagy P., Buglyó N., Verification of ²³⁵U enrichment of fresh VVER-440 fuel assemblies. *Appl. Radiat. Isot.* 70: pp. 2403-2408. (2012)