

ReCosy News

Redox Phenomena Controlling Systems



Newsletter, June 2009

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Introducing RECOSY

RECOSY is a four year (2008-2012) Collaborative Project under the Seventh Framework Programme of the European Atomic Energy Community (EURATOM) starting on 1 April 2008. To this aim, the project set up a consortium of 32 Contractors and presently 3 Associated Groups. The consortium includes key European Research Institutes, Universities, National Waste Management Agencies and SMEs from 13 EURATOM signatory states, Russia, Japan, Korea and one European Joint Research Centre.

Main objectives of ReCosy are the sound understanding of redox phenomena controlling the long-term release/retention of radionuclides in nuclear waste disposal and providing tools to apply the result to Performance Assessment/Safety Case.

The ReCosy concept is innovative in the scientific approach to the redox phenomena. It includes i) advanced analytical tools, ii) investigations of processes responsible for redox control (thermodynamically and kinetically controlled processes, surface reactions and microbial processes, ..), iii) provision of required data on redox controlling processes, and iv) response to disturbances in disposal systems.

The work program is structured along six workpackages (WP1-6). They cover near-field and far field aspects as well as all relevant host-rocks considered in Europe. In WP1, the scientific state-of-the-art and its application to Performance Assessment/Safety Case is documented and regularly updated. WP2 focuses on development of redox determination methods. WP3 focuses on redox response of defined and near-natural systems. WP4 studies the redox reactions of radionuclides. WP5 focuses on Redox processes in radionuclide transport and WP6 deals with the redox reactions affecting the spent fuel source-term. Specific workpackages on knowledge management, education and training (WP7) and administrative management issues (WP8) are also included in the project.

2nd Semi-Annual Newsletter

The main purpose of the Semi-Annual Newsletter is to inform the broader community on the progress research carried out by the RECOSY project. The present Newsletter gives a brief overview of the project activities and progress during the project months 7-14 (November 2008- June 2009). It is made available at the public project web page (www.ReCosy.eu). It is also distributed by email to a list of recipients. It is furthermore encouraged to use printouts at different events such as workshops, meetings and conferences in order to inform potentially interested persons.

This Semi-Annual Newsletter is less detailed than the 1st Annual Project Activity and Management Report, used for thorough information of project partners, the Commission and project reviewers

EDITORIAL

Dear Reader,

I have the pleasure to present the second issue of RECOSY Newsletter. With this Newsletter, we would like to inform a wider audience on RECOSY's activities. RECOSY is a four year (2008-2012) Collaborative Project under the Seventh Framework Programme of the European Atomic Energy Community (EURATOM) dealing with research on the geological disposal of radioactive waste including Phenomenology and Performance Assessment studies.

The Coordinator is the Research Centre Karlsruhe (FZK), Germany. The Coordination Team (CT) consists of two organizations, namely FZK-INE and Amphos 21. In addition to work program planning and project management, the CT is also implementing activities on training and education, and management and dissemination of knowledge. The Executive Committee (ExCom) consists of the WP leaders, ensuring adequate operation of the overall project.

The End-User Consultancy Group (EUCG) is established with three representatives from Waste Management Organizations and three organizations with National Regulatory Functions. It advises in view of ensuring usefulness of the project work for application to the disposal Safety Case and review of scientific-technical reporting in this respect.

The project is open for additional organizations entering into formal cooperation and participation via Associated Group agreement.

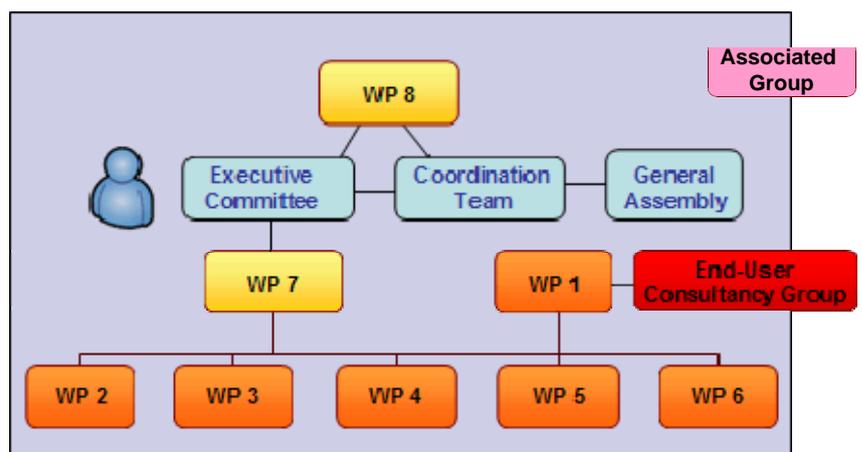
The key objectives of ReCosy are to provide an improved interpretation of redox potential in all relevant host-rock systems to be used within European Safety Cases. In this and the coming issues of the RECOSY Newsletter, we will inform you on major research topics and highlights from the project. I hope you will enjoy reading and welcome your feedback!

Mireia Grivé (info@recosy.eu)

Knowledge Management and Training RECOSY- Officer

Recosy's main areas of research

The scientific-technical work program is structured along six Research Technological Development workpackages (WP1-6). They cover near-field and far-field aspects as well as relevant host-rocks considered in Europe.



RECOSY organisation

*The project is OPEN for additional organizations entering into formal cooperation and participation via **Associated Group agreement**.*

RESEARCH

Research on Development of redox determination methods (WP2)

The objective of WP2 is the development and testing of redox determination methods. Electrochemical, optical and thermodynamic methods are used, and in many cases developed. The redox state of different nuclear waste repository relevant systems are calculated/modelled from chemical analysis and thermodynamic data. The overall goals are (i) to develop redox determination methods specifically designed for environmental applications, and (ii) a broader information base for interpretation of system conditions.

The first point reflects the limitations of existing determination methods and models (and new developments) due to poisoning of electrode material, diffusion potentials in electrode bridges, drift through catalytic reactions on electrode material, drift through changes in electrolytes via diffusion, analytical difficulties in determining concentrations of redox sensitive system components or state of involved solids/minerals, and insufficient/inadequate thermodynamic data for calculation of the redox state.

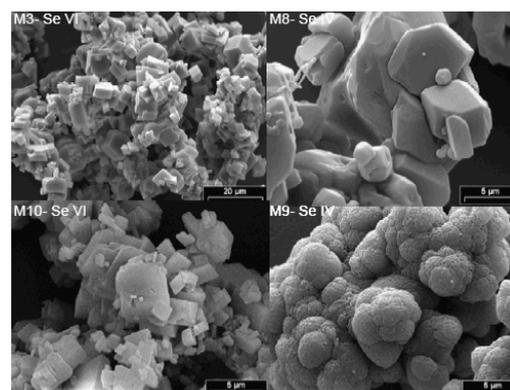
WP leader: Dr. Michael Kumke (University of Postdam, Physical Chemistry)

Research on Redox response of defined and near-natural systems (WP3)

The objective of WP3 is to quantify and develop process understanding for redox buffer capacity and kinetics of response to redox perturbations of defined and near-natural systems. This includes, determination of key electrochemical parameters of electrodes as well as redox response of defined and near-natural systems to redox disturbance (i) finely ground Callovo Oxfordian materials, ii) ions naturally present in the porewater (e.g. H^+ , SO_4^{2-} , HS^- , Fe^{2+}), iii) redox sensitive radionuclides analogues (e.g. Se(VI), Se(IV), I⁻, CH_4 for ^{14}C) and iv) gases (O_2 , CO_2 , H_2 , H_2S), in different situations, both similar to the expected natural situations and to very perturbed conditions.

In the first year of the project, the characterizations of the redox determining minerals which will be used in the investigations have been performed. This minerals includes natural, synthetic, commercial, minerals and metallic samples

WP leader: Dr. Laurent Charlet (Centre National de la Recherche Scientifique)



SEM pictures of calcite precipitated in presence of either Se(VI) (left) or Se(IV) (Aurello et al., in prep.)

Research on redox reactions of radionuclides (WP4)

The goal of the activities within this work package is to provide fundamental process understanding of the redox behaviour of radionuclides, including the question of equilibrium / disequilibrium with the system redox conditions. The objectives of this work package result from gaps in the knowledge identified from previous projects dealing with redox processes involving radionuclides

The activities within can broadly be divided in three main topics: 1) Interactions of radionuclides with pyrite 2) Interactions of radionuclides with far-field solids 3) Redox processes under hyperalkaline conditions.

Some of the participating institutes are focusing their work on the study of the microbial impact (IPL) and on the O₂ concentration and uranium redox state in-situ in biofilms with emphasis on biologically mediated redox processes. The studies are carried out on isolated microorganisms as well as on biofilms. Biofilms are composed of bacteria, fungi, algae, protozoa, exopolymeric substances (EPS), corrosion products and 50–95% water. They are ubiquitous and have to be considered as an important factor in natural biogeochemical processes influencing the redox state of radionuclides. They show a multiplicity of interactions with metals and contribute to metal mobility or immobilization. Once on the surface, the organisms secrete a slimy or glue-like substance (EPS) that allows them to securely anchor themselves on the surface and form connections with other organisms. After attachment, the organisms divide and expand into multicellular communities or microcolonies and create a protective barrier commonly known as a biofilm.

At the detachment stage, single mobile cells and cell communities are released from the biofilm. They are transported away with the bulk solution and will attach themselves on other surfaces. Since microbial processes emerge whenever suitable conditions are found, biofilms are influencing the transport behaviour of heavy metals and radionuclides by changing the geochemical parameters (e.g. dissolved oxygen, pH, redox potential), increasing the metabolic and respiratory activity, inducing redox reactions in anoxic zones within the biofilms and finally immobilising toxic heavy metals and radionuclides.

WP leader: Dr. Jan Tits (Paul Scherrer Institut)



Autoclave used as a batch reactor to perform the solubility experiments and connected to TRLFS.

*Impact of
Microorganisms from
clay and groundwater
samples will be studied*

Research on Redox processes in radionuclide transport (WP5)

The goal of the activities within this work package is to understand the transport/retention properties of redox sensitive radionuclides through crystalline rocks, clay rocks and contaminated systems.

Due to extreme hydraulic and retention properties, indurate clay rocks are considered worldwide as potential host rocks for radioactive waste disposal. Numerous studies have shown that migration of radionuclides in argillaceous rocks is mainly controlled by molecular diffusion. This is the case for the Callovo-Oxfordian argillite (France) and the Boda clay (Hungary).

In the case of contaminated systems, different objectives have been achieved during this year: 1) Sampling of bottom sediments and surface waters from different Lakes of cascade of industrial basins at the Mayak site. A number of samples of surface lake water and bottom sediments have been obtained. 2) Characterization of organic colloids from the surface groundwater of the Lakes using DOC analysis, ICP-MS, ICP-AES, SEM, AsFFFF. 3) Extraction of HA and FA, was performed from the bottom sediments of the Mayak site and Siberian Chemical Combine.

WP leader: Dr. Juhani Suksi (University of Helsinki).

Research on Redox reactions affecting the spent fuel source-term (WP6)

The source term from spent fuel dissolution is subject to considerable uncertainties, both with respect to the presence and extent of oxidative dissolution processes of the spent fuel itself and the coupling with processes associated with the iron canister. Related problems to be examined in this work package are the representativeness and reliability of laboratory data with respect to the impact of unavoidable minor concentrations of oxygen also in inert-gas boxes used, the potential reactivity and its outcome of hydrogen from container corrosion in combination with high burn-up spent fuel, possible galvanic coupling of spent fuel and container material and the retention of redox sensitive radionuclides by relevant minerals, especially by steel container corrosion products.

A set of investigations has been conducted with the aim of getting better insight into redox processes determining spent fuel and iron canister corrosion. The investigations include galvanic coupling of spent fuel and waste canister components as well as spent high burn-up fuel corrosion/dissolution under high temperatures and hydrogen pressures. A specific aspect is the use of uranium thin films allowing coupling with the high-end analytical methods available through the project in order to gain the desired process understanding for uranium dissolution and the relation to redox processes.

Another field of investigation is the corrosion and redox response behaviour of Fe with different pre-treatments and different conditions, including high radiation fields. In particular, redox-based retention properties of corroded iron phases with respect to dissolved radionuclides are investigated.

WP leader: Dr. Detlef Wegen (Joint Research Centre- Institute for Transuranium elements)



Core material of the Callovo-Oxfordian (EST30471) observed in anoxic glove box prior conditioning

Kinetic data on Np(V), Tc(VII) and Pu(IV) sorption/sorptive reduction in presence of fracture filling material with long term pH/Eh monitoring have been obtained.

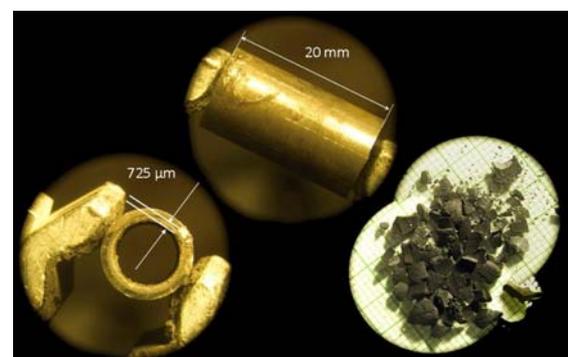


Photo of the fuel (top: cut segment, left: core drilled fuel, right: rim structure containing fuel fragments)

KNOWLEDGE MANAGEMENT AND TRAINING

The WP 7 addresses the internal and external training as well as knowledge management for the RECOSY project.

A public web site has been established within the project (www.recosy.eu). At this site, information about the project and the project activities are made available to the broad community. A project internal Intranet site has been established where non-public documents and reports are kept.

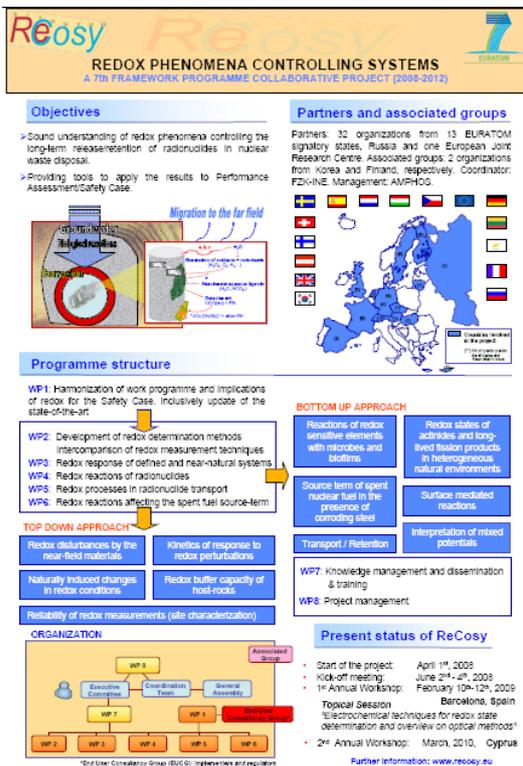
The generic poster has been presented at different occasions, including Euradwaste'08, 20-23 October 2008 in Luxembourg, and is submitted and accepted for amongst others Migration'09 and ICEM 2009.

The Annual Project Workshops are important elements in the documentation and dissemination of the project outcome. The Annual Project Workshop Proceedings are comprehensive public reports with the key scientific-technical outcome. Proceedings with the scientific-technical outcome of the first project year are in preparation. They will be published as report FZKA 7466, presumably before the summer break 2009.

Dissemination of more detailed results are done through scientific journal papers, PhD thesis, etc. Presentations at different occasions of detailed project work and results or the overall project is also a key contributor to dissemination. Despite the only recent full start of the technical WP program, the dissemination of the project is impressive (17 scientific journal papers, 2 technical reports, oral presentations and posters at 18 international occasions in Europe, Japan, USA, Canada and Russia)

There are many aspects of TRAINING and different training actions can be used. Training resources will be used for training-on-the-job of young researchers by project internal mobility measures. The measures are aiming for a maximum period of about three months where travel costs for the stay at another organization (or organizations) are covered. Partners or Associated groups need to apply through the Coordination Team for such training measures. The application contains a justification for the use of project resources, i.e. it needs to be shown that the measure (i) is a training on the job for a young researcher, (ii) includes application of material, methods and/or analytical approaches that are not available at the home institution, (iii) will help the young researcher in his/her future carrier, and (iv) has an added value for the young researcher if staying in the EURATOM field of activities. The first example of such a training measure is Natalia Shcherbina, MSU, who is staying for a 3 months training measure at INE, UPPC and Brookhaven SLS, starting 15 April 2009.

WP leader: Dr. Mireia Grivé (Amphos 21)



RECOsy Generic poster

Partners are requested to make use of different other sources for financing training activities. One such source is the new project ACTINET B, a follow-up project to the FP6 NoE ACTINET. The new ACTINET B started 1 February 2009 and the first call for training mobility proposals is expected at the summer.



EVENTS

RECOSY 1st Annual Workshop (10-12 February 2009, Barcelona)

The 1st Annual Project Workshop was held in Barcelona, Spain (10-12 February 2009). In association with this event, meetings of the different project consortium bodies (Executive Committee, General Assembly, End-User Consultancy Group) took also place.

In total 72 persons attended, including: beneficiaries partners (30 out of 32 partners involved in the project), associated groups (KAIST) and associated Groups in process (BGS, NDA and IRSN), EUCG's members, external participants (University of Hokkaido), and the European Commission project officer, Gaetano di Bartolo.

The main purpose of the Workshop was to communicate and discuss the scientific-technical outcome of the first project year in the form of oral presentations around the project, a poster session, a topical session and additional talks. The respective workpackage leaders presented a summary of the work conducted. Next to an overview of the achievements within the respective WP, scientific highlights were also presented (27).

During the workshop a specific Topical Session focused on the scientific state-of-the-art and the present status of electrochemical techniques for Redox state determination was held. A lesser part of the Topical Session was also used to introduce the participants to optical/optode methods for redox determination.

Additional presentations were given on topics of general interest, especially the context of the present project within the Euratom FP7 program on geologic disposal.

The scientific-technical outcome of the first project year is documented, reviewed by the EUCG and disseminated in the form of workshop proceedings (FZKA 7466, in print).

RECOSY 2nd Annual Workshop (16-19 March 2010, Larnaca)

The 2nd Annual Project Workshop (AWS) is under preparation. It will be held in Larnaca, Cyprus 16th to 19th March 2010 hosted by University of Cyprus.

This second annual workshop, like the first one, gives the project internal and external participants an insight into the project, its activities, status and achievements. It also provides decisions and communication of the planning for the third project year, and beyond. Meetings of the Executive Committee, the General Assembly and the End-User Consultancy Group are held within the context of the Workshop. Compared to the first annual project workshop, this second one will have more panel presentations and discussions across the different project workpackages. This reflects that the administrative, agreement and planning issues that are very important at the first annual workshop, now is giving way for more in-depth R&D work and developments. The topical session is entitled "Redox determination by thermodynamic methods and associated Thermodynamic Databases. Application to Performance Assessment/Safety Case." It is jointly organized by AMPHOS and FZK-INE. Poster sessions are held where the progress in work and joint project activities should be reflected in multi-partner presentations. The flyer with the main information about the meeting is distributed among the project partners and uploaded to the internet website, accessible for any interested party ([www. ReCosy.eu](http://www.ReCosy.eu)).



RECOSY 1st Annual Workshop (10-12 February 2009, Barcelona)



*Electronic brochure
informing on the 2nd
Annual Workshop is
available in the RECOSY
WEB page*

InterComparison Exercise on determination of system redox state (16-20 November 2009, Karlsruhe)

The InterComparison Exercise (ICE) will take place 16-20 November 2009, at FZK-INE, Karlsruhe, Germany. FZK-INE is hosting and organizing the exercise.

The aim of this Exercise is the Assessment of inter-laboratory comparison with the different existing and the new developed methods for redox determination, including comparison of different protocols used by different research groups. The impact is that trust is provided in the capability to adequately determine the system redox state as a prerequisite for adequate regard of redox within the SafetyCase. The ICE uses samples covering different types of redox systems and reflecting typical geochemical boundary conditions including, among others, systems with organics, or with high ionic strength, under hyperalkaline conditions, or with microbial activity..

A multiple step process has been taken in order to agree upon details around the ICE. The first step was gathering of information through questionnaire for presentation, discussion and agreement at the kick-off meeting of RECOY project. The next step was a second more detailed questionnaire, reflecting conclusions from the discussions at the kick-off meeting. The outcome of the second questionnaire was presented and discussed at the Topical Session of the 1st Annual Project Workshop. Partners as well as external groups are strongly encouraged to participate in this Intercomparison exercise.

Key event schedule

Below are given key events of RECOY project that are open to external participation.

2nd Annual Project Workshop

16-19 March 2010, Larnaca, Cyprus

3rd Annual Project Workshop

February/March 2011, France

Final Annual Project Workshop

February/March 2012, Karlsruhe, Germany

InterComparison Exercise on determination of system redox state

16-20 November 2009, at FZK-INE, Karlsruhe, Germany

NOVEMBER 2009						
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MARCH 2010						
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RECOSY PARTNERS

