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This is the **Final Publishable Summary Report** of the EURATOM 7<sup>th</sup> EC Framework  
Program Collaborative project **ReCosy** (Contract Number: FP7-212287).

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## EXECUTIVE SUMMARY

The EURATOM 7<sup>th</sup> EC Framework Program Collaborative Project REdox phenomena COntrolling SYstems (ReCosy) started in April 2008 and extended over 4 years. Main objectives of ReCosy were related to the improved understanding of redox phenomena controlling the long-term release or retention of radionuclides in nuclear waste disposal and providing tools to apply the results to Performance Assessment and the Safety Case. The ReCosy consortium has 32 Beneficiaries, 6 Associated Groups to ReCosy and support of an End-User Consultancy Group. The work program had six RTD workpackages (WP1-6) covering near-field and far-field aspects as well as all relevant host-rocks considered in Europe. WPs include “Development of redox determination methods”, “Redox response of defined and near-natural system”, “Redox reactions of radionuclides”, “Redox processes in radionuclide transport” and “Redox reactions affecting the spent fuel source-term”.

The four Annual Project Workshops were key-activities of the project where 67 poster presentations and 129 oral contributions were presented. Workshop Proceedings, published as KIT Scientific Reports, include 71 reviewed S&T papers. The ReCosy Intercomparison Exercise produced a report on “Intercomparison of Redox Determination Methods on Designed and Near-Natural Aqueous Systems”. Work performed within ReCosy has been presented in 144 contributions to 77 conferences, workshops and seminars. More than 46 papers have been published in peer-reviewed journals with 10 more paper submitted or under review as of spring 2012. Another 28 publications to peer-reviewed journals are under preparation and 19 publications contributed to internal reports or PhD thesis. 36 students and 19 Post-Doc researchers were involved in ReCosy, some partially supported by the Mobility Measures tool. Women represented about 40-45% of these young researchers involved in ReCosy. No patent applications have been made and no Exploitable Foreground is reported.

The ReCosy project has provided a significantly improved understanding of Redox Controlling Systems with implications for Performance Assessment and Safety Case. The key issue “Application of redox processes in the Safety Case”, summarizing main S&T results from ReCosy in the view of the French and Swedish Safety Cases, is prepared for publication in a peer-reviewed journal, e.g. the Journal of Nuclear Technology. ReCosy has set up a project webpage at <http://www.recosy.eu> where further information is made available.



## PROJECT CONTEXT AND OBJECTIVES

ReCosy is the acronym for a collaborative project on “Redox Phenomena Controlling Systems” co-funded by the European Commission under the Seventh Euratom Framework Programme for Nuclear Research & Training Activities.

The scientific investigation of redox phenomena controlling systems is not a new geochemical issue. Nevertheless, several topics have been identified where improved understanding can further contribute to acceptance of the Safety Case. These questions are related, amongst others, to redox processes in the long-term, dissolution/chemical transformation of the radioactive waste, waste packages and engineered barriers and migration in the far-field, including which species are formed and their respective various retention mechanisms. Determination and prediction of the redox state is important for establishing the boundary conditions within the disposal Safety Case. Prediction of responses towards various possibly relevant changes in the redox conditions is also required, as well as the system redox response to various changes in the considered conditions.

The objectives of ReCosy were aiming at providing for (i) a better determination of the system redox conditions, (ii) understanding of relevant redox processes, and (iii) impact of these processes on the disposal Safety Case. The scientific and technical objectives cover various relevant topics including the understanding of redox buffer capacities, redox kinetics and the long-term redox evolution and the relevance of the redox impact on the radionuclide transport.

Scientific-technical objectives were:

- Developing advanced methods for determination of redox conditions in the concerned specific systems and performing an intercomparison study on redox determination methods.
- Identification of components that govern the system redox conditions.
- Identification of the equilibrium and deviation from equilibrium of different redox sensitive components.
- Determination of the kinetics/time function response of system components to perturbances related to relevant scenarios within the disposal Safety Case.

- Determination of redox reactions of sensitive radionuclides and the deduction of their transport/retention properties.
- Determination of the impact of microorganisms on the redox conditions of the overall system and individual components.
- Identification of redox processes driving the spent fuel dissolution, including redox coupling with relevant near-field materials.

In addition to the scientific and technical topics, the need of ensuring education, training, documentation, communication and dissemination of knowledge has been addressed. Consequently, the following topics were defined as explicit project objectives:

- Training of young researchers within the project by scientific mobility measures.
- Documentation, communication and dissemination of the results, addressing the directly concerned community involved in the nuclear waste disposal Safety Case and a broader scientific community.

Reflecting these objectives, ReCosy has provided input by mechanistic process understanding, analytical tools, data and information required for geochemical modelling of redox related phenomena.

The ReCosy consortium consisted of 32 beneficiaries from 13 EURATOM signatory states, Russia and one European Joint Research Centre (see [www.recosy.eu](http://www.recosy.eu)). The Coordinator was Karlsruhe Institute of Technology (KIT), Germany. The Coordination Team (CT) consisted of two organizations, namely KIT-INE and AMPHOS. In addition to work program planning and project management, the CT was also implementing activities on training and education, and management and dissemination of knowledge. The Executive Committee (ExCom) consisted of the respective workpackages (WP) leaders, ensuring adequate operation of the project.

The End-User Consultancy Group (EUCG) was established with three representatives from Waste Management Organizations and three organizations with National Regulatory Functions. It advised 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 integration of the End-User Consultancy Group into ReCosy has been very fruitful and ensured a continued feedback from the End-User community. The EUCG member also reviewed the



S&T papers submitted to each of the four Annual Project Workshops, thus contributing to the quality of the reported scientific and technical results within ReCosy.

ReCosy was open for additional organizations entering into formal cooperation and participation via Associated Group agreement. By this cooperation form, different groups have participated at different levels of commitment. There have been six organizations that have entered into formal participation as Associated Groups (*KAIST*, Korea Advanced Institute of Science and Technology, Republic of Korea; *STUK*, Radiation and Nuclear Safety Authority, Finland; *Kyoto University*, Department of Nuclear Engineering, Japan; *IRSN*, Institut de Radioprotection et de Sûreté Nucléaire, France; *BGS*, British Geological Survey, UK; *LANL*, Los Alamos National Laboratory: Actinide Chemistry and Repository Science Program, Earth and Environmental Sciences Division, USA). The Associated Groups to ReCosy have contributed to the successful outcome of ReCosy by attending the Annual Project Workshops and contributing poster, oral talks and S&T paper to the workshop proceedings.

The work program of ReCosy was established so as to reflect all the above-discussed objectives and the need for well defined processes for the R&D, but also training, management and dissemination of knowledge, and project management. The resulting work program consists of eight workpackages (WP), the respective lead organizations active in the several workpackages are indicated. Five workpackages have explicitly dealt with R&D activities related to redox controlling systems.

WP	Title	Type	Lead-Org.
1	<i>Harmonization of work program and implications of redox for the Safety Case</i>		AMPHOS
2	<i>Development of redox determination methods</i>	R&D	UPPC
	<i>ReCosy Intercomparison Exercise (ICE)</i>	R&D	KIT-INE
3	<i>Redox response of defined and near-natural systems</i>	R&D	CNRS
4	<i>Redox reactions of radionuclides</i>	R&D	PSI
5	<i>Redox processes in radionuclide transport</i>	R&D	HU
6	<i>Redox reactions affecting the spent fuel source-term</i>	R&D	JRC
7	<i>Knowledge management and dissemination &amp; training</i>		AMPHOS
8	<i>Project management</i>		KIT-INE /AMPHOS

Key activities on a project level have been the Kick-off meeting, four annual project workshops and the Intercomparison Exercise (ICE). The scientific and technical program and results of ReCosy were presented and discussed during the Kick-off meeting and the four Annual Workshop meetings. The workshops were integrating several aspects of ReCosy ranging from detailed presentation and discussion of scientific and technical results to project management related issues. The Annual Workshops are summarized in the Workshop proceedings, the key purpose of which is to document and make available to a broad scientific community the outcome of the ReCosy project. For this purpose, a considerable part of the project activity reporting was done through the proceedings, together with the outcome of a large number of scientific-technical contributions and Topical Sessions on different topics, which could be important for the development of the project, like for instance the integration of redox processes in the Safety Case. Additional purposes of the proceedings were to ensure ongoing documentation of the project outcome, promote systematic scientific-technical development throughout the project, and to allow thorough review of the project progress. The Annual Workshop Proceedings are thus central elements for ensuring the successful progression and dissemination of ReCosy results and have been published as FZKA or KIT-Scientific Reports.

The ReCosy Intercomparison Exercise (ICE) was performed as a joint activity within ReCosy focusing on a detailed comparison of redox measurement techniques including both established approaches and new approaches developed within WP2 of ReCosy. The Intercomparison Exercise (ICE) took place 16-20 November 2009, hosted and organized by KIT-INE, Karlsruhe, Germany. The Consolidated Report on the Intercomparison Exercise has been printed as KIT Scientific Report No 7572 and the outcome of ReCosy ICE presented at international conferences.

## SCIENTIFIC AND TECHNICAL RESULTS

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ReCosy has been a highly successful project with numerous scientific technical results being generated. The following information presented on the scientific and technical results of ReCosy focuses on a detailed summary of published S&T results. A more general overview of issues addressed within the five main ReCosy Workpackages by the respective beneficiaries is also included. The five R&D Workpackages were:

- WP2, Development of redox determination methods
- WP3, Redox response of defined and near-natural system
- WP4, Redox reactions of radionuclides
- WP5, Redox processes in radionuclide transport
- WP6, Redox reactions affecting the spent fuel source-term

The ReCosy Intercomparison Exercise performed within WP2 is separately reported, and the important issue of the “application of redox processes in the Safety Case” is addressed.

The results generated in ReCosy have been published in the Proceedings of the four Annual Workshops, namely as S&T contributions reviewed by EUCG members. A total of 71 S&T contributions to the Annual workshops are available from the respective Workshop Proceedings, published either as publicly available FZKA report (FZKA 7466) by the former Karlsruhe Research Center or as publicly available KIT-Scientific Reports (KIT Scientific Report No. 7557, KIT Scientific Report No. 7603, KIT Scientific Report No. 7626) issued via the Karlsruhe Institute of Technology. In Table I, the list of ReCosy S&T contributions is given.

ReCosy beneficiaries have presented the scientific and technical results obtained within ReCosy at 77 different national and international conferences, workshops and seminars. At the time of reporting by the beneficiaries in spring 2012, 114 contributions related to ReCosy had been given. The knowledge generated by the ReCosy project thus has been successfully disseminated to the international scientific community. 19 publications in

connection to ReCosy were contributed to internal reports or PhD thesis, the number of the latter being expected to increase.

Most importantly, the research performed within ReCosy has led to a significant number of ReCosy-related publications in peer-reviewed journals. More than 46 papers have been published in several peer-reviewed journals with 10 more papers submitted or under review as of spring 2012 (see Table II). Additional 28 manuscripts have been reported as “under preparation”.

No patent applications have been made within ReCosy and no Exploitable Foreground is reported.

**Table I:** List of S&T contributions to the ReCosy Annual Workshop Proceedings. (Publications are listed in alphabetical order of the first-author).

Arcos, D., Duro, L., Richard, L., Rojo, I., Clarens, F., de Pablo, J.; 2 <sup>nd</sup> AWS Proceedings; <i>Kinetics of pyrrhotite oxidation</i>
Banik, N.L., Marquardt, C.M., Schild, D., Rothe, J., Schäfer, T.; 3 <sup>rd</sup> AWS Proceedings; <i>Sorption and redox behavior of radionuclides in natural clay rocks</i>
Behnreds, T.; 4 <sup>th</sup> AWS Proceedings; <i>Reduction of iron oxides by S(-II) and its effect on uranium phase distribution.</i>
Betelu, S., Lerouge, C., Berger, G., Ignatiadis, I.; 4 <sup>th</sup> AWS Proceedings; <i>Mechanistic study of pyrite reduction by hydrogen in NaCl 0.1 M at 90°C using electrochemical techniques.</i>
Carbol, P., Fors, P.; 2 <sup>nd</sup> AWS Proceedings; <i>Corrosion of spent fuel in presence of H<sub>2</sub></i>
Carbol, P., Nicholl, A., Wegen, D., Wiss, T., Janssen, A., Cremer, B., Malmbeck, R., Van Winckel, S., Apostolidis, C., Lavandera, R.A.S., Cui, D.; 4 <sup>th</sup> AWS Proceedings; <i>Reduction of Pu(VI) by Fe.</i>
Charlet, L., Chakraborty, S., Aurelio, G., Mettler, S., Ross, R.G., Bardelli, F., Tisserand, D., Molton, F., Van Gunten, U.; 2 <sup>nd</sup> AWS Proceedings; <i>Reaction of Se(IV) and/or Fe(II) in presence of calcite</i>
Charlet, L., Kang, M., Bardelli, F., Géhin, A., Chen, F.; 4 <sup>th</sup> AWS Proceedings; <i>Nano-sized pyrite/greigite reactivity towards Se(IV) and Se(VI)</i>
Cui, D., Rondinella, V., Kuetahyali, C., Amme, M., Wiss, T., Grolimund, D., Wieland, E., Spahiu, K.; 1 <sup>st</sup> AWS Proceedings;

<i>The reductive immobilization of <math>^{237}\text{Np}</math> on iron canister material under repository conditions</i>
Dobrev, D., Brůha, P., Vokal, A.; 1 <sup>st</sup> AWS Proceedings; <i>The effect of iron corrosion on conditions inside the waste packages</i>
Dobrev, D., Červinka, R., Vokál, A.; 4 <sup>th</sup> AWS Proceedings; <i>The effect of carbon steel corrosion on the evolution of conditions in a deep geological repository.</i>
Dobrev, D., Červinka, R., Vokál, A.; 3 <sup>rd</sup> AWS Proceedings; <i>Redox potential in the near field of a deep geological repository containing carbon steel waste packages.</i>
Domènech, C., Duro, L., Grivé, M., Arcos, D., Rojo, I., Clarens, F., de Pablo, J.; 3 <sup>rd</sup> AWS Proceedings; <i>Quantification of pyrrhotite <math>\text{O}_2</math> consumption by using pyrite oxidation kinetic data.</i>
Druteikienė, R., Lukšienė, B., Pečiulytė, D., Mažeika, K., Gudelis, A., Baltrūnas, D.; 3 <sup>rd</sup> AWS Proceedings; <i>Behaviour of Tc (VII) in aqueous solutions in the presence of iron oxides and microorganisms</i>
Evans, N., Hallam, R., Aldridge, S., Warwick, P., Bryan, N.; 1 <sup>st</sup> AWS Proceedings; <i>The Complexation of Tc(IV) with Gluconic Acid at High pH</i>
Gaona, X., Fellhauer, D., Rothe, J., Altmaier, M.; 4 <sup>th</sup> AWS Proceedings; <i>Investigations on Np(VI) in alkaline NaCl solutions: aqueous chemistry and solid phase characterization</i>
Gaona, X., Tits, J., Dardenne, K., Wieland, E., Altmaier, M.; 3 <sup>rd</sup> AWS Proceedings; <i>XAFS investigations of Np(V/VI) redox speciation in hyperalkaline TMA-OH solutions.</i>
Gimeno, M.J., Auqué, L.F., Acero, P., Gómez, J.B., Asta, M.P.; 2 <sup>nd</sup> AWS Proceedings; <i>Distribution of redox elements and speciation-solubility results as a first approach to the General characterisation of the redox systems in the Swedish candidate sites for deep disposal of nuclear waste.</i>
Gimeno, M.J., Auque, L., Acero, P., Gomez, J., Laaksoharju, M.; 1 <sup>st</sup> AWS Proceedings; <i>General characterisation of the redox systems in the swedish candidate sites for deep disposal of nuclear waste</i>
Gimeno, M.J., Auqué, L.F., Acero, P., Gómez, J.B., Asta, M.P.; 4 <sup>th</sup> AWS Proceedings; <i>Partial equilibrium based redox estimations in groundwaters from crystalline systems.</i>
Grambow, B., Landesman, C., Ribet, S.; 1 <sup>st</sup> AWS Proceedings; <i>Redox state determination in hyperalkaline solutions by speciation of selenium summary of work conducted in 1st year of ReCosy.</i>
Hadi J., Chainet, F., Betelu, S., Tournassat, C., Charlet, L., Ignatiadis, I.; 2 <sup>nd</sup> AWS Proceedings; <i>Modelling the dioctahedral smectites CEC, variation versus structural iron level.</i>
Hadi, J., Ignatiadis, I., Tournassat, C., Charlet, L., Silvester, E.; 4 <sup>th</sup> AWS Proceedings;

<i>Investigations on structural iron electrochemical properties in layered silicates using massive mica electrodes.</i>
Hagemann, S., Scharge, T., Bischofer, B.P.; 4 <sup>th</sup> AWS Proceedings; <i>Spectrophotometric and potentiometric investigation on iron (III) hydrolysis in chloride media.</i>
Holgerson, S.; 4 <sup>th</sup> AWS Proceedings; <i>On the use of actinides as redox tracer elements in groundwater samples</i>
Huber, F., Kunze, P., Geckeis, H., Schäfer, T.; 2 <sup>nd</sup> AWS Proceedings; <i>Sorption reversibility studies on the interaction of radionuclides with FEBEX bentonite colloids/nanoparticles under Grimsel groundwater conditions in the presence of fracture filling material.</i>
Icker, M., Walther, C., Geckeis, H.; 2 <sup>nd</sup> AWS Proceedings; <i>The redox potential of Pu containing acidic solutions and the fate of "Pu(IV)-colloids": direct measurement versus optical absorption spectroscopy.</i>
Ivanov, P.I., Griffiths, T., Abrahamsen, L.G., Bryan, N.D., Aksenov, N.V., Bozhikov, G.A., Maslov, O.D., Dmitriev, S.N., Evans, N.D.M., Warwick, P.; 1 <sup>st</sup> AWS Proceedings; <i>Actinide behaviour in humic acid bentonite ternary systems</i>
Kay, R., Abrahamsen, L., Stockdale, A., Smith, K., Bryan, N.D., Warwick, P., Evans, N.; 3 <sup>rd</sup> AWS Proceedings; <i>Actinide partition in humic colloidal ternary systems: experiments and preliminary modelling.</i>
Kay, R., Bryan, N., Evans, N., Warwick, P.; 4 <sup>th</sup> AWS Proceedings; <i>The effect of plutonium oxidation state on sorption and reversibility in humic acid-quartz sand ternary systems.</i>
Kobayashi, T., Gaona, X., Fellhauer, D., Altmaier, M.; 3 <sup>rd</sup> AWS Proceedings; <i>Systematic Evaluation of Tc(VII)/Tc(IV) Redox Processes in 0.1 M NaCl solutions</i>
Krawczyk-Bärsch, E., Arnold, T., Eisbein, E., Brendler, V., Jenk, U., Zimmermann, U.; 3 <sup>rd</sup> AWS Proceedings; <i>The application of microsensors for the determination of redox processes in biofilms from uranium contaminated acidic mine drainage waters.</i>
Krawczyk-Bärsch, E., Lünsdorf, H., Pedersen, K., Arnold, T., Bok, F., Steudtner, R., Lehtinen, A., Brendler, V.; 4 <sup>th</sup> AWS Proceedings; <i>Redox behavior of uranium in biofilms and groundwater seeps, sampled from the granitic rock walls in the Onkalo tunnel (Finland)</i>
Krawczyk-Bärsch, E., Steinbrück, D., Arnold, T., Schmälzlin, E., Kumke, M.; 2 <sup>nd</sup> AWS Proceedings; <i>Comparative study on electrochemical and laser-based fiber-optic oxygen microsensors applied to uranium contaminated biofilms.</i>
Kuczewski, B.; <i>Development of a speciation method for iodine in environmental samples with special focus on the</i>

<i>redox behaviour</i>
Landesman, C., Bailly, C., Baty, V., Vandenborre, J., Grambow, B.; 4 <sup>th</sup> AWS Proceedings; <i>Speciation of reduced selenium species in hyperalkaline solutions: attempt at developing a specific analytical protocol.</i>
Lázár, K., Máthé, Z., Megyeri, J., Széles, É., Mácsik, Z., Suksi, J.; 4 <sup>th</sup> AWS Proceedings; <i>Redox properties of clay minerals and sorption of uranyl ions on Boda Claystone.</i>
Lázár, K., Megyeri, J., Mácsik, Z., Széles, É., Máthé, Z.; 3 <sup>rd</sup> AWS Proceedings; <i>Migration of uranyl ions in Boda Claystone samples.</i>
Lazar, K., Megyeri, J., Mathe, Z.; 2 <sup>nd</sup> AWS Proceedings; <i>Lack of redox responses in certain cases on Boda Claystone samples as reflected in the <math>Fe^{2+}/Fe^{3+}</math> ratios of minerals</i>
Lázár, K.; 1 <sup>st</sup> AWS Proceedings; <i>Redox transitions in Boda Claystone samples under natural conditions as reflected in the change of the <math>Fe^{+2}/Fe^{+3}</math> ratios in clay minerals</i>
Levinskaitė, L., Smirnov, A., Lukšienė, B., Druteikienė, R., Baltrušas, D.; 1 <sup>st</sup> AWS Proceedings; <i>Soil microorganisms tolerance to heavy metals and their accumulation abilities</i>
Loida, A., Bohnert, E., Kienzler, B., Müller, N., Plaschke, M., Schild, D., Soballa, E.; 2 <sup>nd</sup> AWS Proceedings; <i>Release and retention of radionuclides during 10 years corrosion of spent nuclear fuel (SNF) in presence of magnetite.</i>
Loida, A., Metz, V., Bohnert, E., Kienzler, B., Müller, N., Schild, D., Soballa, E.; 3 <sup>rd</sup> AWS Proceedings; <i>Trapping of radionuclides/actinides in canister corrosion products.</i>
Lukšienė, B., Druteikienė, R., Pečiulytė, D., Baltrušas, D., Remeikis, V., Paškevičius, A.; 2 <sup>nd</sup> AWS Proceedings; <i>Effect of microorganisms on plutonium oxidation states.</i>
Marosits, E., Kuczewski, B., Wenzl, K.; 2 <sup>nd</sup> AWS Proceedings; <i>Iodine sorption on kaolinite and humic acid.</i>
Neck, V., Altmair, M., Fellhauer, D., Runke, J., Fanghänel, Th.; 1 <sup>st</sup> AWS Proceedings; <i>Quantification of the redox potential for the reduction of Np (V) in non-complexing aqueous solutions at pH 5-10</i>
Papanicolaou, F., Antoniou, S., Pashalidis, I.; 2 <sup>nd</sup> AWS Proceedings; <i>Redox chemistry of sulphate and uranium in a phosphogypsum stack.</i>
Pashalidis, I., Suksi, J.; 4 <sup>th</sup> AWS Proceedings; <i>Redox reaction of aqueous Se(IV) with pyrite: reaction products and pathway studies.</i>
Pedersen, K., Arlinger, J., Hallbeck, L., Lydmark, S., Johansson, J., Pääjärvi, A.; 3 <sup>rd</sup> AWS Proceedings;



<i>The response in redox from additions of hydrogen and oxygen to natural deep groundwater/rock systems with active microorganisms</i>
Pedersen, K.; 1 <sup>st</sup> AWS Proceedings; <i>The effect from microorganisms on the redox state of laboratory and natural systems</i>
Pehrman, R., Trummer, M., Lousada, C., Jonsson, M.; 3 <sup>rd</sup> AWS Proceedings; <i>Redox reactivity of doped UO<sub>2</sub> - Effects on the reactivity towards H<sub>2</sub>O<sub>2</sub></i>
Perdicakis, M., Chebil, A., Etienne, M., Cheikh-Ibrahim, A.; 4 <sup>th</sup> AWS Proceedings; <i>An attempt for fabricating ultramicroelectrodes compatible with sodium chloride brines</i>
Perdicakis, M., Thomahowski, R., Malhomme, C.; 4 <sup>th</sup> AWS Proceedings; <i>Dielectric monitoring of pyrite during its exposure to air or pure oxygen</i>
Petersmann, T., Seibert, A., Wegen, D. H., Gouder, T., Stumpf, S., Fanghänel, Th.; 3 <sup>rd</sup> AWS Proceedings; <i>Electrochemical investigations on doped and undoped UO<sub>2</sub> spent fuel model surfaces.</i>
Pidchenko, I., Salminen-Paatero, S., Suksi, J.; 4 <sup>th</sup> AWS Proceedings; <i>Study of U oxidation states in natural geological material.</i>
Pourtier, E., Nguyen-Trung, C., Perdicakis, M., Baros, F., Bordg, D., Richard, L.; 4 <sup>th</sup> AWS Proceedings; <i>Synthesis of fulvic acid-like compounds in alkaline media and their interactions with iodide ion.</i>
Reed, D., Borkowski, M., Swanson, J., Richmann, M., Khaing, H., Lucchini, J.F., Ams, D.; 3 <sup>rd</sup> AWS Proceedings; <i>Redox-controlling processes for multivalent metals and actinides in the WIPP.</i>
Riba, O., Montoya, V., Grivé, M., Duro, L.; 4 <sup>th</sup> AWS Proceedings; <i>Uranium solubility under alkaline conditions using different reducing agents.</i>
Savoye, S., Frasca, B., Fayette, A., Grenut, B., Radwan, J.; 3 <sup>rd</sup> AWS Proceedings; <i>Study of the diffusive behavior of selenite and selenate through the Callovo-Oxfordian claystones (France): Effect of the initial selenite concentration.</i>
Savoye, S., Schlegel, M., Frasca, B., Fayette, A., Grenut, B.; 4 <sup>th</sup> AWS Proceedings; <i>How mobile is selenite diffusing through the Callovo-Oxfordian Claystones? Insights given by radiochemistry and X-ray absorption spectroscopy.</i>
Scharge, T., Bischofer, B.P., Hagemann, S., Schönwiese, D.; 2 <sup>nd</sup> AWS Proceedings; <i>Spectrophotometric and potentiometric determination of the redox potential in solutions of high ionic strength</i>
Shcherbina, N.S., Perminova, I.V., Novikov, A.P., Kalmykov, S.N., Marquardt, C.M., Walther, C., Buckau, G., Kumke, M., Eidner, S.; 2 <sup>nd</sup> AWS Proceedings; <i>Redox properties of Humic Substances: Identification of Redox Functional Groups by TRLFS.</i>
Steinbrück, D., Geißler, F., Kumke, M.U.; 4 <sup>th</sup> AWS Proceedings;



<i>Advances in multiplexed fiber-optical sensing for environmental applications</i>
Steinbrück, D., Schmäzlin, E., Kumke, M. U.; 3 <sup>rd</sup> AWS Proceedings; <i>Progress in the development of a fibre optical chemical sensor (FOCS) for the simultaneous determination of proton, oxygen and chloride concentrations.</i>
Steinbrück, D., Schmäzlin, E., Kumke, M.U.; 2 <sup>nd</sup> AWS Proceedings; <i>Development of an fibre optical chemical sensor (FOCS) for the determination of low dissolved oxygen concentrations.</i>
Steinbrück, D., Schmäzlin, E., Kumke, M.; 1 <sup>st</sup> AWS Proceedings; <i>Development of multiparametric optical sensing for environmental applications</i>
Stumpf, S., Seibert, A., Gouder, T., Huber, F., Petersmann, T., Denecke, M.A., Fanghänel, Th.; 2 <sup>nd</sup> AWS Proceedings; <i>UO<sub>2</sub> fuel corrosion - studies on the H<sub>2</sub> Activation at a UO<sub>2</sub>-Pd spent fuel model surface</i>
Stumpf, S., Seibert, A., Gouder, T., Wegen, D., Wiss, T., Bosbach, D., Römer, J., Soballa, E.; 1 <sup>st</sup> AWS Proceedings; <i>Thin films as Spent fuel models</i>
Suksi, J., Salminen, S.; 2 <sup>nd</sup> AWS Proceedings; <i>Study of redox state of U deposited on fracture lining rock.</i>
Tits, J., Gaona, X., Laube, A., Wieland, E.; 3 <sup>rd</sup> AWS Proceedings; <i>Influence of the redox state on the neptunium sorption by cementitious materials.</i>
Vester, B.; 1 <sup>st</sup> AWS Proceedings; <i>Effect of Chloride Brines on determination of the Fe Redox potential and of the UV-Spectrometry of Fe species</i>

**Table II:** List of publications in peer-reviewed journals related to ReCosy. (Publications are listed in alphabetical order of the first-author).

<p>Arnold, T., Baumann, N., Krawczyk-Bärsch, E., Brockmann, S., Zimmermann, U., Jenk, U., Weiß, S.</p> <p><i>Identification of the uranium speciation in an underground acid mine drainage environment. Geochimica et Cosmochimica Acta 75, (2011) 2200-2212.</i></p>
<p>Aurelio, G., Fernandez-Martinez, A., Cuello, G.J., Roman-Ross, G., Alliot, I., Charlet, L.</p> <p><i>Structural study of selenium(IV) substitutions in calcite. Chemical Geology 270, (2009) 249-256.</i></p>
<p>Birj Kumar, K.H., Bryan, N. D., Kaltsoyannis, N.</p> <p><i>Computational investigation of the speciation of uranyl gluconate complexes in aqueous solution, Dalton Transactions 40, (2011) 11248-11257.</i></p>
<p>Bouby, M., Geckeis, H., Lützenkirchen, J., Mihai, Schäfer, T.</p> <p><i>Interaction of bentonite colloids with Cs, Eu, Th and U in presence of humic acid: A flow field-flow fractionation study. Geochim. Cosmochim. Acta, 75, (2011) 3866.</i></p>
<p>Bruggeman, Maes, Christiansen, Stipp, Breynaert, Maes, Regenspurg, Malmström, Liu, Grambow, Schäfer</p> <p><i>Redox-active phases and radionuclide equilibrium valence state in subsurface environments. Appl. Geochem. 27, (2012) 404-413.</i></p>
<p>Chakraborty, S., Bardelli, F., Charlet, L.</p> <p><i>Reactivity of Fe(II) on calcite : Selenium reduction. Environmental Science &amp; Technology 44, (2010) 1288– 1294.</i></p>
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<p>Cui, D., Low, J., Spahiu, K.</p> <p><i>Environmental behaviors of spent nuclear fuel and canister material. Energy &amp; Environmental Science 4, (2011) 2537 – 2545.</i></p>
<p>Cui, D., Rondinella, V.V., Borca, C., Kütahyalı, C., Amme, M., Wiss, T., Grolimund, D., Wieland, E., Spahiu, K.</p> <p><i>Reductive immobilization of neptunium(V) on iron surface under anaerobic conditions. <u>Accepted by Radiochimica Acta (2011).</u></i></p>

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Evans, N.D.M., Hallam, R.J., <i>The Complexation of Tc(IV) with EDTA and Picolinic Acid at High pH, Accepted by Mineralogical Magazine</i>
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In the following sections, the results of the scientific and technical research performed within ReCosy are summarized on a Workpackage level. It is further reported which beneficiaries have contributed to the respective Workpackages.

## **WP2. Development of redox determination methods**

Existing redox determination methods are known to be limited due to: a) poisoning of electrode material, b) diffusion potentials in electrode bridges, c) drift through catalytic reactions on electrode material, d) drift through changes in electrolytes via diffusion, and e) analytical difficulties in determining concentrations of redox sensitive system components or state of involved solids/minerals. The redox state of complex systems can therefore only be properly assessed based on a sound combination of chemical analysis and associated thermodynamic modelling. WP2 has improved the necessary scientific-technical basis for redox determination in environments relevant for nuclear waste disposal. The application and modification of existing methods as well as the development of advanced methods for the determination of the redox state of relevant systems were pursued.

In order to provide trust in the outcome of the studies performed within ReCosy related to redox measurement an inter-laboratory comparison exercise (ICE) on samples selected from the relevant host rocks in the project where the different methods are foreseen to be applied was performed which is reported in a separate section.

In the context of developing redox determination methods, the different participants of this workpackage were working on different issues:

### ***Redox speciation using selected redox pairs as probes***

*KIT-INE* studied the kinetics and thermodynamics of Np and Tc in homogenous and heterogeneous systems. In order to investigate whether there is a well-defined redox potential or pe value for the reduction of  $\text{NpO}_2^+(\text{aq})$  or  $\text{TcO}_4^-$ , the redox behaviour of  $3.5 \cdot 10^{-5}$  M Np(V) solutions and analog Tc(VII) systems in 0.1 M NaCl was studied in the pH range of  $5 < \text{pH} < 10$  under Ar atmosphere.

The sorption behaviour of iodine species from  $\text{NaClO}_4$  solution by kaolinite (KGa-1b) and humic acid (HS, Sigma Aldrich) was examined by *TUG*.

The speciation of Se was evaluated as a probe for redox state determination in hyperalkaline solution by *ARMINES*.

*GRS* studied the speciation of Fe including extremely high ionic strength conditions.

### ***Advanced redox measurements in natural systems***

Within ReCosy, *UPPC* developed optodes for fiber-based chemical sensing of redox-relevant parameters and compared electrochemical and fiber-optic oxygen sensor measurements in uranium contaminated biofilms.

### ***Development of amperometric and potentiometric tools for redox measurements***

During this work, *CNRS* made use of the higher sensitivity of ultramicroelectrodes to measure very low concentrations of redox indicators in order to determine redox potentials by monitoring voltammetrically the concentrations of the reduced and oxidized forms of a redox indicator. The compounds investigated were soluble species of selenium and iodide as well as oxygen/oxygen peroxide mixtures, minor electroactive constituents of Callovo-Oxfordian argillite porewater (Fe) or NaCl brines (I, Fe) and potential potentiometric indicators to be added in the system (hydroquinone, quinhydrone).

## **WP3. Redox response of defined and near-natural system**

In WP3 process understanding for redox buffer capacity and kinetics of response to redox perturbations of defined and near-natural systems were developed and quantified. Amongst



others, WP3 work have been especially focused on (i) field data, (ii) field samples, (iii) microbiology, (iv) sorption experiments, (v) redox experiments and (vi) conceptual modelling.

Different ReCosy participants have worked on:

### ***Response of crystalline environment to redox perturbation***

UNIZAR performed redox  $E_h$  - pH pair field measurements and modelling. The work carried out on this topic is based on the observations and interpretations done in the two sites proposed in Sweden for hosting a deep repository for spent nuclear fuel: Forsmark and Laxemar. The control of the measured  $E_h$  values has been evaluated by means of redox pairs distribution calculations. These calculations have shown that potentiometrically measured clearly reducing  $E_h$  values are consistent with the calculated redox potentials from the  $Fe^{2+}/Fe(OH)_3$  redox couple, with most of the feasible sulphur redox pairs and the  $CO_2/CH_4$  couple.

The redox buffer capacity of pyrrhotite and pyrite and two fracture filling materials (one from Grimsel and another from Äspö) has been studied by CTM. The conditions imposed by the host-rock may perturb the redox state of uranium, leading to the immobilization of uranium under its tetravalent form.

### ***Response of clay environment to redox perturbation***

A large part of the activities in WP3 were devoted to the electrochemical characterization of clays using three techniques: voltammetry of microparticles, voltammetry of microparticles in thin layer and clay matrix voltammetry. In this sense, CNRS has performed voltammetric characterization of Boda claystone, Boda Albitic Claystone and Callovo-Oxfordian argillite.

Redox responses of Boda Claystone were also investigated by ILL-HAS. The changes in the redox state of Boda Claystone were followed by monitoring the  $Fe^{2+}/Fe^{3+}$  ratios in clay minerals (predominantly in chlorite) and comparing their portions to the amount of hematite present in the sample.

Particular equipment has been used and methodology developed and/or adapted for the investigation performed by BRGM, including the design of various specific electrodes and the use of diverse electrochemical techniques, in order to explore the electrochemical kinetics of the Callovo-Oxfordian argillite system in contact with different plausible redox perturbations (e.g. nitrate plume, contact with atmosphere before closure of the system,  $H_2$  perturbation...).

Studies on natural claystone organic matter have been done by *KIT-INE* and work focused on (i) the characterization of the organic matter carbon functionality and its radiation sensitivity as well as (ii) the isolation of the kerogen and the characterization of redox sensitive groups.

Studies performed by *CNRS* are related to (i) the interaction of soluble I and Se species with Callovo Oxfordian claystone under anaerobic conditions, (ii) the sorption and catalytic oxidation of Fe(II) at the calcite surface, and (iii) the sorption and Fe(II)-induced reduction of selenite at the calcite surface.

### ***Role of Fe/S system in buffering redox***

*BRGM* studied the interaction of FeS<sub>2</sub> alone with H<sub>2</sub>, using electrochemical techniques and the analysis of solutions and interfaces. Moreover, *BRGM* investigated the abiotic pyrite reactivity versus nitrate, selenate and selenite using chemical and electrochemical methods. *CNRS* studied by spectroscopic techniques the reduction of selenite by natural pyrite and synthetic nano-sized pyrite/greigite.

*AMPHOS* studied the oxidation kinetics of pyrrhotite and pyrite by oxygen and *UCYPRUS* studied the reduction of uranium as a function of sulphate in phosphogypsum.

### ***Role of microbes***

Sulphate Reducing Bacteria (SRB) in the deep groundwater Äspö hard rock laboratory was investigated by *MICANS*. The effect of hydrogen on microbial sulphate reduction was also studied.

*UNIUTR* characterized the products of microbial U(VI) reduction and studied the mobility of U(VI) adsorbed onto iron oxides.

Uranium interaction with magnetite surface was studied by *KIT-INE*. Studies on sorption and/or reduction of U(VI) in presence of magnetite are mostly motivated by the importance of elucidating effective immobilization processes of (i.e. U(VI)-U(IV) redox transformations) and the role of aqueous, surface sorbed or structural bound Fe(II).

### ***Modelling and application***

An important work performed by *BRGM* was devoted to model the di-octahedral smectites CEC variation versus structural iron level.

UNIZAR has performed macroscopic modelling on distribution of redox elements (Fe, S, Mn and N) and speciation-solubility calculations.

#### **WP4. Redox reactions of radionuclides**

Redox reactions of radionuclides have manifold and often specific chemical characteristics. The different investigations presented below are summarized along relevant key aspects investigated within ReCosy.

##### ***Use of redox-sensitive radionuclides as redox indicators***

Depending on their redox state, redox-sensitive radionuclides behave very differently with regard to their reactivity and mobility. Consequently, a reliable characterization of the redox conditions prevailing in the repository environment is essential. Determination of the redox conditions in environmental samples is usually carried out with the help of electrochemical measurements of redox potentials. Such measurements may provide a direct measure of redox conditions in the system under investigation. However, redox potential measurements have a number of practical and theoretical weaknesses as investigated within WP2 and alternative methodologies for the determination of the redox conditions in a repository environment are therefore of interest.

One possible alternative methodology has been investigated by CTH. The CTH methodology is based upon the addition of trace amounts of redox-sensitive actinides, such as uranium and neptunium to repository-relevant groundwater followed by the determination of their redox speciation by solvent extraction. The total system redox potential is calculated based upon the measured redox speciation of the two actinide species.

##### ***Influence of complexing ligands on radionuclide redox speciation***

Complexing ligands in repository pore waters can strongly influence the redox state of radionuclides by stabilizing one of the redox states through complex formation. In a study carried out by Loughborough University ULOUGH, the effect of the presence of organic ligands on the redox state of technetium has been investigated.

### ***Influence of the redox conditions on the solubility of radionuclides***

The influence of the uranium redox state on the solubility of uranium has been investigated by *AMPHOS*. This study has been performed under alkaline conditions ( $10.0 \leq \text{pH} \leq 13.3$ ) reflecting the situation in the near-field of a cement-based low and intermediate level nuclear waste repository and the redox transformation U(VI)-U(IV) considered.

### ***Effect of the redox state on radionuclides sorption processes***

The sorption of americium and plutonium on Fe(II/III) oxides, natural clays and soils was investigated. The applicability of the chemical analogy approach was tested in a study of the sorption of Pu, Np, Am and U on different iron oxides, triassic clay and a meadow soil by *FMTc*. To assess the sorption behaviour of Pu(III) on Fe(II/III) oxides (wustite/magnetite and hematite) as well as by soil, Am (III) was used as a chemical analogue for Pu(III).

### ***Influence of changing redox conditions on the sorption of radionuclides***

*KIT-INE* has investigated the sorption of neptunium, plutonium and technetium on two natural clay rocks, Opalinus clay (OPA) and Callovo-Oxfordian argillite (COx, Bure, France) as well as the influence of a disturbance of the existing redox conditions on the sorption behaviour of these three radionuclides. A disturbance of the redox state was obtained by the addition of either magnetite or hydroquinone.

Validation of the chemical analogy approach for the actinides was one goal of the studies carried out by *PSI* in the framework of ReCosy. The influence of the redox state of neptunium on its uptake by cementitious materials under hyperalkaline conditions was investigated

### ***Interaction of redox-sensitive radionuclides with pyrite***

*CNRS/LCPME* investigated the interaction of long-lived fission products with pyrite by means of electrochemical methods. The interactions of pyrite with elemental iodine as well as with iodate, iodide, selenate and selenite ions were investigated in acidic, neutral, and alkaline solutions.

*CNRS/LCPME* activities essentially addressed (i) electrochemical measurements performed in acidic, neutral and alkaline media using massive pyrite electrodes in the presence of iodine and iodate, selenite and selenate ions, (ii) the chemical conditioning at different pH values of pyrite microparticles with solutions of iodine, iodide, iodate, selenite and selenate

ions (solution aliquots were sampled during the conditioning and analyzed by ICP-OES, ion chromatography and UV-visible spectroscopy), (iii) the characterization of the reacted pyrite microparticles by SEM, XPS, voltammetric and dielectric measurements, (iv) the dielectric monitoring of dry pyrite during its exposure to air or pure oxygen.

### ***Chemical and redox behaviour of radionuclides in different systems through microbial mediated processes***

The uranium redox speciation in biofilms and the effect of microorganisms on the redox behaviour and sorption of plutonium and technetium was investigated. The studies performed by *HZDR* clearly demonstrated that biological systems can significantly influence radionuclide behaviour. The results of *HZDR* improve the understanding of the mechanisms of biofilm response to radionuclides.

The studies performed by *FTMC* were focused on (i) effects of microorganisms on redox behaviour of plutonium, (ii) evaluation of Fe(III) biogenic transformations by the ferrozine method and UV-vis spectrophotometry, (iii) combined effect of microorganisms and iron-bearing mineral hematite on Tc(VII) sorption.

### **WP5. Redox processes in radionuclide transport**

WP 5 has increased process understanding of the transport of redox-sensitive nuclear waste radionuclides through clayrocks and crystalline rocks also in view of uncertainties still existing in disposal concepts. To answer or at least to discuss these questions information was collected from (i) laboratory diffusion experiments with samples from potential host clayrock formations (Collovo-Oxfordian in France and Boda Claystone in Hungary), (ii) studies on the behaviour of actinides in natural crystalline environment (natural uranium at Olkiluoto), (iii) for near natural conditions in laboratory investigations with samples from Äspö Hard Rock Laboratory, and (iv) from studies on behaviour radionuclides in contaminated areas in Cyprus and Russia. Major attention was paid to radionuclide immobilisation processes because redox transformations into lower valence states are known to immobilise radionuclides. Required reducing redox potential is provided by Fe(II)-containing mineral phases abundantly found in clay and crystalline rocks. However, redox-reactions can also

potentially transform radionuclides into higher valence states thus promoting their mobility. This is possible e.g. under natural redox-disturbances such as glacial melt water intrusion which is expected at the repository sites in Finland and Sweden.

### **Diffusion studies**

CEA studied diffusion of U(VI), Se(IV,VI) and I(-I,V) in Callovo-Oxfordian (CO<sub>x</sub>) argillite samples. Investigations were performed using through-diffusion and batch experiments with physico-chemical conditions as close as possible to those prevailing *in situ*.

II-HAS studied U(VI) diffusion in Boda Claystone samples. The aim was to see whether migration of U(VI) through Boda Claystone borecore samples can be coupled with simultaneous Fe<sup>2+</sup> => Fe<sup>3+</sup> oxidation taking place in the layered clay minerals of the rock.

### **Radionuclide mobility under the influence of glacial melt water intrusion**

KIT-INE studied simulated glacial melt water intrusion on the mobility of redox sensitive radionuclides in crystalline rock. In the simulation glacial groundwater from the Grimsel Test Site (GTS, Switzerland) and granodiorite from Äspö were used in batch-experiments.

### **Study of radionuclide behaviour in contaminated areas**

UCYPRUS studied the behaviour of uranium within a phosphogypsum (PG) disposal site in a coastal area in front of a former fertilizer plant in Cyprus.

MSU has studied the behaviour of radionuclides in contaminated soil and lake environments in industrial reservoirs at PA “Mayak” (Russia) in collaboration with KIT-INE.

## **WP6. Redox reactions affecting the spent fuel source-term**

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 examined within WP6 are (i) the representativeness and reliability of laboratory data with respect to the impact of unavoidable minor concentrations of oxygen also in inert-gas boxes used, (ii) the potential reactivity and its outcome of hydrogen from container corrosion in

combination with high burn-up spent fuel, (iii) possible galvanic coupling of spent fuel and container material and (iv) the retention of redox sensitive radionuclides by relevant minerals, especially by steel container corrosion products. In this context, a set of investigations has been conducted with the aim of getting better insight into redox processes determining spent fuel and iron canister corrosion.

*ITU* reported on studies with spent fuel in presence of corroding Fe, on corrosion of spent fuel in presence of  $H_2$  and on fuel corrosion studies based upon thin film model systems. The experimental investigations were supported by the use of newly developed electrochemical cell especially designed for thin film applications.

The redox reactivity of doped  $UO_2$ , in view of effects related to the reactivity towards  $H_2O_2$ , has been studied at *KTH*. Experiments showed that the oxidative dissolution yield, i.e. the amount of dissolved uranium per consumed  $H_2O_2$  varies dramatically between different  $UO_2$ -based materials. The redox reactivity of  $UO_2$  pellets decreases significantly upon rare earth oxide doping, the effect being more pronounced for weaker oxidants than for strong oxidants. The reductive trapping of actinides in container corrosion products during spent fuel corrosion was investigated by *KIT-INE*. An experiment running for about 10 years was analysed to study the effect of magnetite on the overall corrosion behaviour of SNF in NaCl solution. Experimental studies were carried out by means of optical microscopy, SEMEDS, XPS and Raman spectroscopy.

*STUDSVIK* investigated the redox chemistry at the near field of repository and the influences of iron canister material and hydrogen. Reductive plutonium immobilization processes by iron canister material was investigated in collaboration with *JRC-ITU*. The stability of Pu(VI) in a synthetic groundwater solution of pH 10 was investigated in presence of carbonates. The possibility of a redox reaction between Pu(VI) and iron canister surface, i.e. Fe(0) surface or  $Fe_3O_4$  (magnetite) coated Fe(0) surface was also studied.

Redox conditions near waste packages were studied by *NRI*. The investigation performed have clarified uncertainties concerning the effect of iron and carbon steel on redox conditions developed in or around spent fuel canisters. The firmly adhering corrosion product layers formed on the carbon steel surface, containing a high amount of oxygen and carbon, have an important impact on the development of geochemical conditions in a repository. The impact of solid bentonite on the corrosion rate of iron was investigated.

## **ReCosy Intercomparison Exercise**

The ReCosy Intercomparison Exercise has been an important activity performed within ReCosy. A total of 19 organizations from 12 countries were participating ReCosy ICE with about 40 scientist contributing to ICE and ICE evaluation and reporting. Based upon the experimental work and detailed evaluation of results, ReCosy ICE has resulted in a better understanding of redox measurements. ReCosy ICE has derived a list of specific recommendations for improved redox measurements, also including ideas for future research activities. A publication on the “Intercomparison of Redox Determination Methods on Designed and Near-Natural Aqueous Systems” is publicly available via KIT Scientific publishing (KIT Scientific Report No 7572). ReCosy ICE has been successfully communicated to the interested scientific community at several international workshops and conferences.

## **Application of redox processes in the Safety Case**

An important aspect of ReCosy was to relate the scientific results within the project to the application in Performance Assessment and the Safety Case. The ReCosy project included an End User Consultancy Group (EUCG) established with three representatives from Waste Management Organizations and three organizations with National Regulatory Functions, which advised the consortium 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 key issue of “application of redox processes in the Safety Case”, summarizing main S&T results from ReCosy mainly in the view of the French and Swedish Safety Cases, is prepared for publication in a peer-reviewed journal, e.g. the Journal of Nuclear Technology.



## POTENTIAL IMPACT, DISSEMINATION

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ReCosy project offers a significant contribution to the European Research Area by strengthening the knowledge and the research activities in support of implementation of geological disposal. It has increased the scientific knowledge on redox related processes and contributed to fundamental scientific progress and increased knowledge. Within the context of re-emerging discussion of the European energy needs, the present project contributes to acceptance of nuclear waste disposal and thus to the continued use of nuclear power as part of a possible energy mix.

### **Potential impacts from the project**

The expected impact specified in the call was that “improved understanding of the processes investigated in ReCosy at one-to-one scale and the relation with long-term safety will assist in the practical demonstration of geological disposal of high-level and long-lived radioactive waste and facilitate its implementation”. The outcome of the project provides the expected impact by improving required process understanding.

The key impact from the project is the application and implementation of the knowledge generated during the 4 years of ReCosy in the Safety Case. Throughout Europe, only few Safety Cases are presently under preparation, with countries like France, Sweden, Belgium or Switzerland being most advanced. The impact of the project outcome on a specific disposal Safety Cases is depending on the level of use and the specific significance of redox related processes within the envisaged disposal concept. The integration of an End-User Consultancy Group (EUCG) within the ReCosy project, established with three representatives from Waste Management Organizations (from France, Sweden, Spain) and three organizations with National Regulatory Functions (from Germany, Switzerland and USA), was a decisive factor of ensuring usefulness of the ReCosy project work for application to the disposal Safety Case. The impact of an improved understanding of redox on a Safety case can generally be expected to be high.

In addition to the general impact that ReCosy has on existing and future European Safety Cases, additional more specific impact arising from the work program need to be taken into consideration. These are related to specific questions and key achievements obtained in the different ReCosy workpackages:

- a. Development of new complementary methods for determining the redox state of a given system, including optical fiber based optode technology and ultramicro-electrodes.

*Impact: improved redox measurement techniques will enhance the trust in the quality and reliability of predictions on redox state dependent chemical processes and thus finally contributes to acceptance of the Safety Case.*

- b. Intercomparison exercise of new and existing methods for determining the redox state of different systems, including comparison of different protocols used by different groups.

*Impact: trust is provided in the capability to adequately determine the system redox state as a prerequisite for adequate regard of redox within the Safety Case.*

- c. Identification of redox determining processes in natural systems

*Impact: improved long-term predictions are possible with respect to the system redox response towards impact of perturbations issuing from specific disposal cell concepts on the near-field and far-field environments. For crystalline rock concepts, an important impact is the improved predictability of the effects on near and far-field redox conditions induced by changes in the recharge conditions induced by changes in land-use and climatic conditions. This also contributes to the understanding of general geochemistry for other environmental issues.*

- d. Determination of redox state of radionuclides under different systems, especially considering whether or not the radionuclides are in redox equilibrium or disequilibrium with the overall system.

*Impact: the redox state of relevant radionuclides can be predicted with respect to future system changes. As a consequence, trust is provided in the capability to predict the radionuclide mobility.*

- e. Determination of key redox processes in the very near-field, i.e. the spent fuel and the container, including process identification, especially with respect to the potential impact of hydrogen and potential galvanic coupling between the spent fuel and the container.

*Impact: the actual dissolution rate of spent fuel and trapping of redox sensitive radionuclides in the near-field can be determined under relevant conditions. This allows a considerable lowering of the release rate used as the spent fuel dissolution source term. In addition, trust is provided with respect to the probability of galvanic coupling influencing the source term, and thus the uncertainty of the source term is lowered.*

The broad European representation in the Consortium partly reflects that different individual key questions are related specific host-rock types under investigation in different European countries. Solving the underlying problems, however, namely providing an adequate process understanding for interpretation of processes in different host rock types, as well as developing new redox determination methods, were done by bringing together different European players and combining the available competence.

The project objectives of ReCosy were met by the joint effort of a broad European Consortium. The ReCosy Consortium composed by 32 beneficiaries from 13 EURATOM signatory states, Russia and one European Joint Research Centre and provided a dedicated work group for information exchange, transfer of knowledge and technology and dissemination in this respect. The ReCosy Consortium has facilitated the cooperation between experts in advanced research and developed programmes and less developed repository implementation. ReCosy thus has the impact of increasing the level of competence in nuclear waste management among countries needing to dispose of spent fuel and highly radioactive waste.

An impact from the implemented ReCosy work program is that Consortium members became aware of the respective complementary competencies. This led to improved networking between research institutions on a European level and contributes to joint tackling follow-up problems in the future.

## **Strengthening ties with the international community: Associated Groups to ReCosy**

The ReCosy project has offered the possibility to other groups to participate in the Project at their own costs with specific RTD contributions or particular information exchange functions. This tool has drawn significant interest and formalized cooperation with EU and non-EU research centers and organizations. Different groups have joined the CP ReCosy as Associated Groups:

British Geological Survey (BGS). Their main interest has been in the impact of microorganisms in the far-field. BGS has been developing a research project complementary to the work performed within ReCosy.

Los Alamos National Laboratory (LANL). Their main interest has been focused on the solubility and redox processes of actinides in brine systems and microbial processes.

Institut de Radioprotection et de Sûreté Nucléaire (IRSN). IRSN was mainly interested in information exchange and contributing to discussion concerning generation and application of knowledge.

Kyoto University (UKYO), Department of Nuclear Engineering. Their main interest has been the study of actinide chemistry for nuclear waste disposal safety assessment. Their expertise is related with aqueous actinide and fission product chemistry.

Radiation and Nuclear Safety Authority (STUK). Their main goal within ReCosy was to obtain a quantitative description of the chemical and transport processes, focused for example on the uranium system.

Korea Advanced Institute of Science and Technology (KAIST). The main interest of KAIST is the understanding of radionuclide redox phenomena in aquifers. They are particularly interested in the determination of redox states and redox processes in radionuclide transport.

## Dissemination activities and exploitation of project results

The highly successful communication activities of ReCosy have enhanced the impact of the results generated in ReCosy on the international scientific and technical community interested in redox processes and phenomena related to nuclear waste disposal.

All results generated by the ReCosy project are open to use by any interested party. The results generated have been communicated within the project but also to a broader interested community outside ReCosy. For this purpose, a large number of activities have been included in ReCosy to promote knowledge management, dissemination and communication:

- Establishing of a WEB portal of the project ([www.recosy.eu](http://www.recosy.eu)). The project web-page allows all those interested in ReCosy results to access to information and the public deliverables from the project. The ReCosy web-page highlights main achievements and events organized within the project. A reference list of reviewed journal publications with acknowledgement to the project available at this site. The web portal will be operative for several years after the closure of the project, so that everyone will be able to retrieve public information from there.
- The Intranet (project internal workspace) is accessible only for the partners of the consortium and the project officer. It is used by the ReCosy Consortium to communicate and document results, and exchange information in an easy and effective way.
- Annual Workshops. The Annual Project Workshops have been used to discuss results among the beneficiaries as well as to communicate the results to the attendants. The Annual Project Workshops were the main platform of communication with the Associated Groups to ReCosy and the End-User Consultancy Group. Specific Topical Sessions to the Workshops by invited international experts supported knowledge transfer and dissemination. The Annual Workshops were also used to discuss and document the outcome of the different activities through the generation of Annual Project Workshop proceedings.
- The Proceedings of the Annual Project Workshop with scientific results in pre-publication form (workshop proceedings) and high-level descriptions of technical issues have been a key tool for documenting the results of the project. This was an

essential element in ensuring dissemination of knowledge and creating the required awareness of the project achievements. The Annual Workshop Proceedings were distributed in hard-copy format, but are also available to the broader international community as pdf-download from FZKA or KIT-Scientific Publishing.

- Participation of project participants at international conferences, workshops have been very successful and partly been supported by ReCosy. Work performed within ReCosy has been presented in 144 contributions to 77 conferences, workshops and seminars.
- Communicating the outcome of the project to a broader community. Apart from the presentation at international conferences and workshops, there have a broad spectrum of events, conferences and meetings where the project was presented. Brochures and information about the possibility to request information on the S&T outcome of ReCosy, e.g. the Annual Workshop Proceedings or public project reports, were distributed. Representatives of the consortium have represented the project and actively created awareness of the project activities and achievements.
- The scientific and technical results generated in ReCosy have been disseminated in the form of peer-reviewed publications in publicly accessible international journals. More than 46 papers have been published in peer-reviewed journals with 10 more paper submitted or under review as of spring 2012. Another 28 publications to peer-reviewed journals were under preparation and 19 publications contributed to internal reports or PhD thesis.
- The training and education of students and young Post-Doc researchers was an essential aspect of ReCosy related to knowledge transfer and especially knowledge maintenance. This contributes to ensuring a sufficiently high level of competence for future of nuclear waste disposal activities on a European level. A total of 36 students and 19 Post-Doc researchers were involved in ReCosy, some partially supported by the ReCosy Mobility Measures tool. Applications for ReCosy Mobility Measures were accepted for the following applicants (sending organisation given in brackets): N. Shcherbina (MSU), R. Verbickas (IPL), M. Kang (GIGCAS & SCK-CEN), J. Hadi (BRGM), C. Sabater (AMPHOS).



Contrary to the highly successful scientific and technical results generated by ReCosy and the similarly positive dissemination activities, (i) no patent applications have been made and (ii) no Exploitable Foreground is reported by the ReCosy Consortium.





## ADDRESS OF PUBLIC WEBSITE

ReCosy has established a project website at [www.recosy.eu](http://www.recosy.eu) disseminating detailed information about the project and also serving as project intranet.

The ReCosy webpage was set up and maintained by AMPHOS Contact: Dr. Mireia Grive [mireia.grive@amphos21.com](mailto:mireia.grive@amphos21.com).

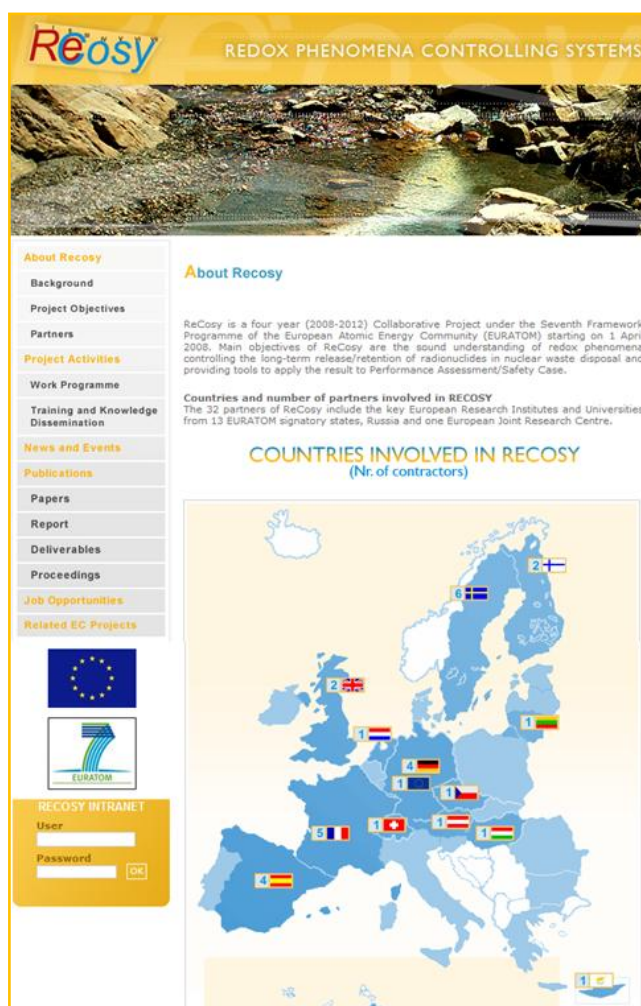


Figure I: ReCosy project webpage ([www.recosy.eu](http://www.recosy.eu))