JRC Scientific and Technical Reports

Deliverable D6.1 (45 months) - RECOSY WP6 -

Contract No. FP7-212287
ReCosy

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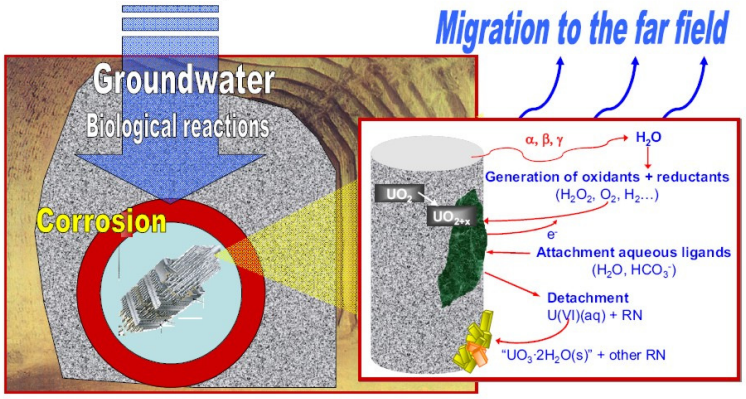
Objectives

- Sound understanding of redox phenomena controlling the long-term release/retention of radionuclides in nuclear waste disposal.
- Providing tools to apply the results to Performance Assessment/Safety Case.



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Reosy

Deliverable No. D6.1

NAME OF DELIVERABLE:
REPORT ON REDOX DRIVEN SPENT FUEL DISSOLUTION AND RADIONUCLIDE TRAPPING BY STEEL CANISTER CORROSION PRODUCTS AND OTHER FE MINERALS.

REDOX PHENOMENA CONTROLLING SYSTEMS
ReCosy

COLLABORATIVE PROJECT (CP)

Submitting organizations: ITU, INE, NRI, Studsvik
Due date of deliverable: 45 Project Months
Actual submission: 47 Project Months

Grant agreement N°.: FP7-212287

Start date of the project: 01 April 2008
Duration: 48 months

Project co-funded by the European Commission under the Seventh Framework Programme of the European Atomic Energy Community (Euratom) for nuclear research and training activities (2007 to 2011)		
Dissemination Level		
PU	Public	PU
RE	Restricted to a group specified by the partners of the project	
CO	Confidential, only for partners of the project	

Objectives

The objectives for project months 37-45 of the ReCosy project related to redox driven spent fuel corrosion and radionuclide trapping by steel/iron corrosion products were the following.
At ITU it was foreseen to re-sample leachates from the high burn-up UO_2 fuel in presence of 50 bar H_2 and H_2/0.03% CO_2 to verify experimental deviations and to determine the Fe^{2+}/Fe^{3+} ratio.

INE planned studies to determine the oxidation state of U retained upon the magnetite present during 10 years spent fuel corrosion experiment in NaCl solution by means of TTA extraction and to complete studies upon the 10 y in the same solution altered magnetite by means of light and electron optical microscopy, Raman spectroscopy and XRD.

In collaboration with ITU, STUDSVIK planned investigations on the kinetics and mechanisms of redox sensitive radionuclides (RSRN) immobilization processes under simulated near-far field conditions in contact with canister components (Fe(0), Fe(II) corrosion products) with emphasis on the behaviour of Pu.

STUDSVIK will also evaluate the hydrogen catalytic effects of UO_2, SIMFUEL and fission product alloy particles (extracted from spent fuel) by monitoring the formation of DH, H2, HDO and D_2O in a system containing D_2, O_2 and H_2O.

Continuation and finalisation of the experimental determination of the effect of corroding iron on conditions inside waste packages in various corrosion systems in an anaerobic glove box at NRI.

Status and results

ITU has carried out a study to determine the Fe^{2+}/Fe^{3+} ratio. The outcome was negative, since there are no analytical methods for the Fe concentration range of 10^{-6}-10^{-7} M, as present in ITU's experiment. The corrosion data obtained in the high burn-up UO_2 fuel corrosion experiment in presence of H_2 are sufficient to draw the main conclusions: the coupling of the measured redox values and the measured redox sensitive elements as well as confirming the absence of oxidising species at steady state, such as H_2O_2 and O_2 in the studied system, and finally to make the mass balance of oxidising and reducing species [1-4,13].

KIT-INE has completed the characterisation of the magnetite, present during 10 years corrosion together with high burn-up spent fuel in a 5 M NaCl solution using XRD and Raman spectroscopy. It is shown that a slight impurity of carbon in the magnetite lead to an increase of CO_2 in the gas phase and consequently to an accelerated release of radionuclides. Considerable amounts of released radionuclides were re-immobilized upon the magnetite surface. A hematite layer is present on the surface of this material, therefore, the retention cannot be attributed to reductive processes alone, but sorption processes have also to be considered [1-6,14].

STUDSVIK has published Np retention results. In collaboration between ITU, STUDSVIK and SKB a nitrate free Pu(VI) solution was used to perform experiments on immobilization of Pu in contact with iron and iron oxide phases. The results show a much less immobilization of Pu compared to Np.

The evaluation of the hydrogen catalytic effect of potential catalysts at near field repository by the D/H isotope exchange method was performed. It was found that UO_2 powder and Simfuel have, if any, only a very little hydrogen catalytic effect, while Epsilon alloy particles show clearly a hydrogen catalytic effect under near field conditions [1-4,7-10,15].

NRI has measured E_h and pH in various corrosion systems in an anaerobic glove box. The evolution of pH is different depending on whether carbon steel or iron powder was used in the experiments. This could be explained by the presence of impurities, particularly carbon in carbon steel, which migrates to the surface and can be released to the water. The measured E_h increases over time due to the oxidation of ferrous ions and the precipitation of iron-bearing minerals. It was found that firmly adhering corrosion product layers containing a high amount of oxygen and carbon were formed in bentonite water under anaerobic conditions. These layers passivate the steel but under strongly reducing conditions this protective effect of the corrosion layers could disappear, leading to an increase of hydrogen generation rates and consequently corrosion rates [1-4,11,12,16].

Dissemination

Reports or contributions in reports, proceedings:

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[2] G. Buckau, B. Kienzler, L. Duro, M. Grivé, V. Montoya (eds.) (2010): 2nd Annual Workshop Proceedings of the Collaborative Project "Redox Phenomena Controlling Systems" (EC 7th FP CP RECOSY), Karlsruhe Institute of Technology, KIT Scientific Reports 7557, Germany.

[3] M. Altmaier, B. Kienzler, L. Duro, M. Grivé, V. Montoya (eds.) (2011): 3rd Annual Workshop Proceedings of the Collaborative Project "Redox Phenomena Controlling Systems" (EC 7th FP CP RECOSY), Karlsruhe Institute of Technology, KIT Scientific Reports 7603, Germany.

[4] D.H. Wegen, P. Carbol, A. Seibert, T. Gouder, T. Petersmann, M. Jonsson, M. Trummer, R.Pehrman, C. Lousada, A. Loida, B. Kienzler, D. Cui, K. Spahiu, D. Dobrev, A. Vokál, R. Červinka (2012): REDOX PROCESSES AFFECTING THE SPENT FUEL SOURCE-TERM. Summary report WP6 in: Proc. RECOSY 4th ANNUAL MEETING, 23rd – 26th January 2012, Karlsruhe, Germany.

[5] A. Loida, V. Metz, E. Bohnert, B. Kienzler, N. Müller, D. Schild, E. Soballa (2011): TRAPPING OF RADIONUCLIDES/ACTINIDES IN THE CANISTER CORROSION PRODUCT MAGNETITE. 3rd Annual Workshop Proceedings of the Collaborative Project "Redox Phenomena Controlling Systems" (EC 7th FP CP RECOSY), Karlsruhe Institute of Technology, KIT Scientific Reports 7603, Germany, pp. 265 – 271.

[6] A Loida, V. Metz, E. Bohnert, B. Kienzler, N. Müller, D. Schild, E. Soballa (2011): TRAPPING OF RADIONUCLIDES/ ACTINIDES ONTO CANISTER CORROSION PRODUCTS. 3rd Annual Workshop Proceedings of the Collaborative Project "Redox Phenomena Controlling Systems" (EC 7th FP CP RECOSY), Karlsruhe Institute of Technology, KIT Scientific Reports 7603, Germany, p. 287.

[7] D. Cui, J. Low, and K. Spahiu (2011): ENVIRONMENTAL BEHAVIORS OF SPENT NUCLEAR FUEL AND CANISTER MATERIALS, Energy & Environmental Science 2011, 4, 2537 – 2545

[8] D. Cui, V.V. Rondinella, C. Borca, C. Kütahyali, M. Amme, T. Wiss, D. Grolimund, E. Wieland and K. Spahiu (2011): REDUCTIVE IMMOBILIZATION OF NEPTUNIUM(V) ON IRON SURFACE UNDER ANAEROBIC CONDITIONS, accepted by Radiochimica Acta

[9] D. Cui, P. Carbol, K. Spahiu (2011): ON THE REDOX CHEMISTRY AT THE NEAR FIELD OF REPOSITORY, THE INFLUENCES OF IRON CANISTER MATERIAL AND HYDROGEN, 3rd Annual Workshop Proceedings of the Collaborative Project "Redox Phenomena Controlling Systems" (EC 7th FP CP RECOSY), Karlsruhe Institute of Technology, KIT Scientific Reports 7603, Germany, p. 278.

[10] P. Carbol, A. Nicholl1, D.H. Wegen, T. Wiss, A. Janssen, B. Cremer, R. Malmbeck, S. Van Winckel, C. Apostolidis, R. Alvarez Sarandes Lavandera, J. Himbert, D. Cui (2012): REDUCTION OF PU(VI) BY FE, S&T contribution in: Proc. RECOSY4th ANNUAL MEETING, 23rd – 26th January 2012, Karlsruhe, Germany.

[11] D. Dobrev, R. Cervinka, A. Vokal (2011): REDOX POTENTIAL IN NEAR FIELD OF DEEP GEOLOGICAL REPOSITORY CONTAINING CARBON STEEL WASTE PACKAGES, 3rd Annual Workshop Proceedings of the Collaborative Project "Redox Phenomena Controlling Systems" (EC 7th FP CP RECOSY), Karlsruhe Institute of Technology, KIT Scientific Reports 7603, Germany, pp.99 – 116.

[12] D. Dobrev, R. Cervinka, A. Vokal (2012): THE EFFECT OF CARBON STEEL CORROSION ON THE EVOLUTION OF CONDITIONS IN A DEEP GEOLOGICAL REPOSITORY, S&T contribution in: Proc. RECOSY4th ANNUAL MEETING, 23rd – 26th January 2012, Karlsruhe, Germany.

Presentations:

[13] P. Carbol, P. Fors, S. Van Winckel, K. Spahiu (2012): CORROSION OF SPENT FUEL IN PRESENCE OF H_2, RECOSY 4th Annual Workshop, 23-26.01.2012, Karlsruhe, Germany.

[14] A. Loida, N. Müller, V. Metz, E. Bohnert, B. Kienzler, D. Schild, E. Soballa (2012): TRAPPING OF RADIONUCLIDES / ACTINIDES ONTO CANISTER (FE) CORROSION PRODUCTS, RECOSY 4th Annual Workshop, 23-26.01.2012, Karlsruhe, Germany.

[15] D. Cui, P. Carbol, V.V. Rondinella, C. Borca, C. Kütahyali, M. Amme, T. Wiss, D. Grolimund, M. Granfors and K. Spahiu (2012): THE REDUCTIVE IMMOBILIZATION OF REDOX SENSITIVE NUCLIDES ON IRON CANISTER UNDER REPOSITORY CONDITIONS. RECOSY 4th Annual Workshop, 23-26.01.2012, Karlsruhe, Germany.

[16] D. Dobrev, R. Červinka, A. Vokál (2012): THE EFFECT OF CARBON STEEL CORROSION ON THE EVOLUTION OF CONDITIONS IN A DEEP GEOLOGICAL REPOSITORY. RECOSY 4th Annual Workshop, 23-26.01.2012, Karlsruhe, Germany.

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Abstract

This report summarises the activities planned and performed in project months 37 - 45 in work package (WP) 6 of the ReCosy project. The main achievements in the fourth project year are given.

The mission of the JRC is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of EU policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Union. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.