Consolidated report on outcome of the inter-laboratory comparison exercise

Deliverable No. D2.3

REDOX PHENOMENA CONTROLLING SYSTEMS
ReCosy

COLLABORATIVE PROJECT (CP)

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PU	Public	X
RE	Restricted to a group specified by the partners of the project	
CO	Confidential, only for partners of the project	


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Within Deliverable No. D2.3, the “Consolidated report on outcome of the inter-laboratory comparison exercise” is reported. Due to the additional time and work effort the participating ReCosy ICE partners have put into the data evaluation and the joined preparation of the final Consolidated Report entitled “Intercomparison of Redox Determination Methods on Designed and Near-Natural Aqueous Systems”, it was necessary to shift the Deliverable D2.3 from PM 24 to PM 36.

ReCosy ICE was conducted within the EURATOM FP7 Collaborative Project “Redox phenomena controlling systems” (CP ReCosy). The experimental work was performed on 16th-20th November 2009, hosted by the “Institut für Nukleare Entsorgung” (“Institute for Nuclear Waste Disposal”) of the Karlsruhe Institute of Technology (KIT-INE), followed by a second meeting at KIT-INE focussing on the joint final discussion of ReCosy ICE on 19th and 20th October 2010. The writing and proof reading of the Consolidated Report lasted until January 2011, the subsequent printing as KIT-Scientific report was finished in March 2011. The Consolidated Report “Intercomparison of Redox Determination Methods on Designed and Near-Natural Aqueous Systems” is published as KIT-Scientific Report No. 7572, edited by M. Altmaier, X. Gaona, D. Fellhauer and G. Buckau (KIT-INE and JRC-ITU). The Consolidated Report was presented and distributed to the participants at the 3rd Annual ReCosy Project Workshop, 21st-24th March 2011, in Balaruc-les-Baines, France.

More than 40 scientists working on different topics related to redox chemistry from 20 ReCosy partner organisations and associated groups contributed to ReCosy ICE, thus providing a broad scientific basis for ICE. The objectives of the ReCosy ICE were to compare different redox determination methods in order to (i) identify critical redox determination issues, (ii) provide the basis for more confidence in redox determinations for the individual groups, and (iii) identify future activities that could contribute to further progress in the confidence in determination of the redox state of nuclear waste disposal Safety Case relevant systems and conditions.
The intercomparison was based upon different redox determination methods, i.e. static electrodes (platinum, gold glassy carbon, single/combined electrodes), dynamic electrochemical measurements, amperometric measurements, optodes (optical fibres with oxygen sensitive tips) and thermodynamic calculations based on chemical composition and physicochemical properties (such as pH, ionic strength and temperature). For this purpose, a wide set of samples was used with three different types of origin and properties, namely (i) simple samples with well defined composition, (ii) natural samples kept under near-natural conditions, and (iii) samples with microbial cultures.

The main conclusion of ReCosy ICE is that the redox state of an aqueous system can be determined by the existing experimental techniques, although the degree of confidence strongly depends of the kind of aqueous system investigated and the degree of optimisation of the experimental equipment and handling protocols. In how far the available experimental accuracy and precision is sufficient to adequately characterise the sample must be assessed in each single case and cannot be generalised. As observed in the ReCosy ICE, some samples show clusters of readings from different groups and electrodes used. These samples are artificial, with high redox buffer content, with pH buffered and in the pH neutral to acidic range. Natural samples show very large differences between the different groups, electrodes and handling protocols. A predictive capability based on any of such measurements alone is considered rather uncertain. The ReCosy ICE has not yet provided

the basis for identification of different processes responsible for the large drift and large differences in redox readings.

Based upon the outcome of ReCosy ICE and the joint data evaluation and interpretation, the partners of ReCosy ICE have agreed on several recommendations. ReCosy ICE was using the presently available experimental and conceptual approaches to compare and evaluate various aspects related to redox measurement and redox data interpretation, aiming at defining the current state-of-the-art. In this respect, ReCosy ICE has compiled a list of recommendations regarding redox measurements. Important outcomes are:

- It is strongly recommended *to use a combination of several experimental approaches to identify and assess systematic errors as there is no single "best method" to determine the redox state of a given system*. This is especially true for the analysis of (intrinsically highly complex) real systems. Ideally, it is recommended to use different sensor materials and complement potentiometric measurements with thermodynamic model calculations based upon the distribution of redox couples.

- The use of a "quality assurance" protocol for Eh measurements is advisable.

- The use of non-conventional approaches (optodes, amperomentry, …) can help to clarify the redox state and could also be used to complement conventional measurements whenever possible.

- The problems arising from electronics of the instrumentation are generally minor compared to "chemical" interferences affecting redox measurements.

- It is recommended to consider that dilution experiments with redox buffers indicate that there is a "critical minimum concentration" of redox active species to allow measurement of meaningful pe values with combined electrodes.

Further recommendations concerning sampling and handling, better equilibration of samples, stirring or non-stirring during measurements, drift and surface effects on the sensor, pe-pH measurements and thermodynamic modelling of redox processes have been derived and reported in the final ReCosy ICE report.

In addition, several topics have been identified within ReCosy ICE beyond the present state-of-the-art that may provide significant input for future research activities related to redox state determination. The main arguments again concern the central question of how the redox state of a system is defined, and what consequences result for redox state determinations? Individual questions related to this overall complex are concerning:

- New approaches to identify and quantify the reasons for the observed long-term drift on measurements in a comprehensive multi-step approach.

- Better understand the alteration processes at the electrode surface, caused by sorption of ions, colloids or organics on the sensor material, or partial oxidation (e.g. PtO formation) and consecutive surface coating of the sensor.

- Work towards the further optimisation of cleaning protocols for electrode surfaces.

- Improve alternative techniques to complement conventional potentiometric measurements. None of the non-conventional techniques used in ReCosy ICE at present can be used for routine analysis under reducing conditions.

- Systematic assessment of temperature effects on redox related processes and redox measurements.

- Development of advanced tools for long-term monitoring, relevant for the robust (experimental) assessment of main performance indicators in post-closure scenarios.

The Consolidated Report on ReCosy ICE "Intercomparison of Redox Determination Methods on Designed and Near-Natural Aqueous Systems" consist of a printed report complemented by a CD-ROM distributed together with the printed report. While the printed report is focused on presenting the main outcome, conclusions and recommendations from ReCosy ICE in a compact and readable manner, the CD-ROM offers plenty additional information for further in-depths reading. In addition to a pdf version of the printed report, several reports by individual groups are made available, for example highlighting specific scientific perspectives reflecting certain experimental techniques, characteristics of specific aqueous reference systems or evaluation methods. In as much as the entire printed report, including the outcome, overall findings and recommendations represent the joint opinion of all ICE participants, the individual reports represent the view of individual groups reflecting their specific expertise and opinion. On the CD-ROM, several Excel files containing all measured data and plots for the respective reference samples are available for documentation and possible input for future studies.

The Consolidated Report "Intercomparison of Redox Determination Methods on Designed and Near-Natural Aqueous Systems" has been distributed to the ReCosy partners at the 3rd Annual ReCosy Project Workshop and is available:

(i) directly from the authors and editors,
(ii) by download via the ReCosy project webpage www.recosy.eu,
(iii) from KIT: http://www.ksp.kit.edu/shop/index.php/manufacturers_id/2634