



Agreement on details for the inter-laboratory comparison exercise

Deliverable No. D2.1

REDOX PHENOMENA CONTROLLING SYSTEMS ReCosy

COLLABORATIVE PROJECT (CP)

Submitting organizations: FZK-INE
Due date of deliverable: 3 PM
Actual submission: 4 PM

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



The Intercomparison Exercise (ICE) is a key element in the project, tackling the question of how the redox state is determined, what different redox determination methods register and if differences in the protocols between different groups/ organizations is the reason for considerable differences in results reported between different groups apparently applying the same redox determination methods. It also allows a first critical evaluation of the experimental techniques being newly developed within WP2.

As scheduled, in conjunction with the Kick-Off meeting, 2-4 June 2008, Sitges, Catalunya, Spain, (PM2), the ICE was discussed and the following remarks were made and the following decisions were taken:

- 1) There was a general support for the ICE and the overall concept for the ICE as presented by M. Altmaier.
- 2) The ICE will take place from 16-20 Nov 2009 (PM20) at FZK-INE (Karlsruhe, Germany).
- 3) The questionnaire on “Systems, samples, conditions and studies” that has been distributed within WP1 as preparatory work for D.1.1 is not yielding the detailed information regarding redox measurement techniques needed for discussions within the context of the ICE. Therefore, a similar but more detailed “request for information” document will be prepared and distributed to all ReCosy partners in September 2008 (PM6). It is mandatory for WP2 participants to return the completed document, however, it is considered reasonable and is strongly encouraged that all ReCosy partners contribute to this activity. Deadline for the return of the documents to M. Altmaier is November 2008 (PM8).
- 4) The “request for information” documents are evaluated and the main results presented and discussed at the First Annual Project Workshop in February 2008 (PM11). This summarizes the present state of knowledge of redox measurements and as basis for a detailed agreement on the ICE also scheduled for the First Annual Project Workshop.
- 5) All groups taking part in WP2 will also take part in the ICE. However, it is strived for that all methods for redox measurements to be used in ReCosy are included in the ICE. Therefore, additional participation from groups outside of WP2 and also from associated groups is explicitly strongly encouraged. Thus, the ICE will not be restricted to the new experimental techniques being developed within WP2 but also include a test of the well established conventional electrochemical electrode systems currently being used by the majority of groups.
- 6) There is a general consent, that about 6-8 samples covering different types of redox systems and geochemical boundary conditions will be used at the ICE. All samples are to be prepared and stored at FZK-INE unless noted otherwise (see comments *in italics* below).



Four reference samples will be well defined and expected to have very stable redox conditions. They are of major importance for evaluating the different techniques and assessing the trueness of the redox reading. They will also cover different pH conditions and include:

- Fe-system at low ionic strength.
- Fe-system at high salinity/brine conditions.
- System with “simple” organics (Hydrochinone ?) including Se, I, Fe as potential redox indicators.
- System under hyperalkaline conditions including Se.
(Preparation of hyperalkaline samples with support by J. Tits / PSI)

Another set of samples will be more relevant to the key question, i.e. near-natural groundwater samples with varying redox stability. First suggestions are given below:

- Groundwater with humic substances (Gorleben).
(Sample is supplied by FZK-INE)
- Clay-rock system (COX).
(Sample possibly supplied or prepared with support by E. Gaucher / BRGM)
- Granitic groundwater (Äspö, Grimsel).
*(Äspö groundwater possibly supplied by SKB ?
Grimsel groundwater supplied in cooperation with NAGRA?)*

Further systems with direct relevance to nuclear waste disposal may include:

- Systems with redox-sensitive radionuclides.
- Highly active (spend fuel) samples.
- Systems with microbiological activity.

In order to facilitate the ICE on the practical side, no work will be performed in a controlled area, that is to say, no systems with radioactive nuclides will be prepared or analysed. As this also excludes spend fuel samples, the possibility of at least investigating the effect of dissolved hydrogen gas on redox measurements, using a reference system with simulated fuel is being discussed.

The plan of having biofilm samples included in the ICE has not been further regarded as there are only very few groups and methods that could be applied and thus the basis for an ICE is not given. However, the investigation of homogeneous systems with microbiological activity is still under consideration. For the forthcoming decision on this topic, K. Pedersen (MICANS, partner No.24, Sweden) will be contacted concerning information on protocols for the preparation of samples including appropriate micro-organisms.

The question of exactly which specific features the different samples for the ICE should exhibit and exactly which protocols are used to prepare them accordingly is still under discussion. During the First Annual Project Meeting (PM11), a final decision on ICE will be taken by the partners and subsequently documented in Deliverable D2.2 “Experimental scheme for the ICE” accordingly.

7) Samples within the ICE that can be expected to remain sufficiently stable during transport will be sent to groups with “immobile equipment”. The samples are sent in



due time for these partners to conduct the necessary experimental work. At least one participant from each group will then join the ICE at Karlsruhe at least for the last day where assessment and documentation the outcome of the exercise is started.

8) Within the First Annual Project Workshop (PM11) a special “topical session” will focus attention on different key aspects concerning electrochemical methods for redox determination. The use of optical methods will also be briefly presented. Together, this will be a significant contribution to the ICE, offering both a critical review on established conventional electrochemical techniques as well as presenting promising new developments in redox measurement.

9) A critical evaluation of the ICE is presented and discussed during the Second Annual Project Meeting in March 2010 (PM24). Following this joint discussion, a consolidated report on the outcome of the ICE (Deliverable D2.3) is prepared.

10) During the ReCosy Kick-Off meeting, the possibility of initiating a special training workshop at FZK-INE related to the use of redox measurement techniques has been proposed. Pending the positive outcome of the ICE this option can be further discussed.

11) The time-schedule around the Intercomparison Exercise is:

Project Month	Activity and documentation
2	General agreement around the ICE in conjunction with the Kick-Off meeting
3	Documentation of general agreement through the present Deliverable D2.1
6	Distribution of “request for information” document to the ReCosy partners, focusing on various fundamental aspects of redox measurement
8	Deadline for return of “request for information” document to M. Altmaier
11	Detailed agreement on ICE in association with the First Annual Project Workshop. Evaluation of “request for information” document to be presented and discussed at the First Annual Project Workshop.
12	Documentation of “Experimental scheme for the ICE” (Deliverable D2.2)
>12	Generation of samples for the ICE, followed by regular monitoring until ICE
20	The ICE held at FZK-INE (16-20 Nov. 2009)
24	A critical evaluation of the ICE to be presented and discussed during the Second Annual Project Meeting.
>24	Consolidated report on the outcome of the ICE (Deliverable D2.3)