Experimental scheme for the inter-laboratory comparison exercise

Deliverable No. D2.2

REDOX PHENOMENA CONTROLLING SYSTEMS
ReCosy

COLLABORATIVE PROJECT (CP)

Submitting organizations: FZK-INE
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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	

1) The Intercomparison Exercise (ICE) will take place from 16-20 Nov. 2009 (PM20) at FZK-INE (Karlsruhe, Germany).

2) During the first Annual ReCosy Workshop (9th to 12th Feb. 2009, Barcelona) a session was focused entirely upon the Organisation of the Intercomparison Exercise. Furthermore, the "request for information" documents distributed to all ReCosy partners by M. Altmaier in December 2008 were evaluated and summarized at the Topical Session. Based upon the lively discussions and input from several ReCosy partners, the Experimental Scheme for the Intercomparison Exercise has been fixed.

3) The ReCosy partners have agreed that samples for the Intercomparison Exercise will be prepared in accordance with the following general principles:

- Samples are prepared in duplicates (backup option!) and stored in two separate Ar-gloveboxes at FZK-INE.
- The amount of samples must be sufficient to allow several independent measurements. The total volume of solution is minimum 500 ml each.
- Equilibration/storage of solutions is done in large reaction vessels. The solution is distributed to smaller vials (10-20 ml each) prior to measurement at ICE.
- PE vessels are used whenever possible. For the handling of samples outside inert gas atmosphere (=> transport to FZK-INE or shipment of samples to partners with immobile equipment) gastight container are used.
- Whenever a background electrolyte concentration is fixed in a sample, this is done at 0.1 M NaCl.

4) ICE uses samples covering different types of redox systems and reflecting typical geochemical boundary conditions. Four well defined reference systems (samples **REF 1–4**) are expected to have very stable redox conditions. They are of major importance for evaluating the different techniques and handling protocols and assessing the trueness of the redox reading. A set of samples more relevant to the key question, i.e. near-natural groundwater samples with varying redox stability (samples **NAT 1-4**) is also prepared. Samples with microbial activity (samples **MIC**) are used to assess redox measurement in aqueous systems with microbes present. Some systems will have sub-samples with varying pH or spiked trace components.

The tables on the following pages summarise the samples available for ICE. Some basic information on the main chemical sample characteristics is included. The scientists and partner institutions involved in the sample preparation are mentioned.

Sample: REF 1

Fe-system at low ionic strength	**FZK-INE**	**M. Altmaier**
• Fe solid phases are used to equilibrate redox conditions. • Samples with varying pH conditions prepared (if necessary by organic buffers). • Background electrolyte fixed at 0.1 M NaCl.		

Sample: REF 2

Fe-system at high salinity / brine conditions	**GRS** **FZK-INE**	**B. Vester, T. Scharge** **M. Altmaier**
• Samples prepared in 5 M NaCl, 4.5 M $MgCl_2$ and 2 M $CaCl_2$. • pH conditions not fixed from beginning. Fe concentration should be above 10^{-7} M for analysis of Fe redox distribution. • Fe(II)/Fe(III) solution is added to brines. No Fe-solids used to equilibrate samples.		

Sample: REF 3

System with simple organics	**FZK-INE**	**M. Altmaier**
• Hydroquinone or substituted Hydroquinone (anthrahydroquinone (2,6)-disulfonate) used to define redox system. • Variation of pH conditions (using organic buffers if necessary). • Preparation of parallel samples spiked with Se, I or Fe solution. • Background electrolyte fixed at 0.1 M NaCl.		

Sample: REF 4

Systems under hyperalkaline conditions	**PSI** **ARMINES** **FZK-INE**	**J. Tits, J. Gaona** **B. Grambow** **M. Altmaier**
• Na-dithionite solution used to prepare strongly reducing hyperalkaline solutions (no organic redox buffers used as proposed at the 1st ReCosy Workshop) • Background electrolyte not fixed at 0.1 M NaCl. • Variation of pH conditions still under discussion. • Discussion on how to prepare suitable Se samples under way.		

Sample: NAT 1

Groundwater with humic substances (Gorleben)	**FZK-INE**	**G. Buckau, M. Altmaier**
• Natural Gorleben groundwater equilibrated several years with corresponding sediment under Ar supplied by FZK-INE. • One system with high and one with low HA concentration provided.		

Sample: NAT 2

Clay-rock system (COX)	**BRGM** **FZK-INE**	**E. Gaucher** **Th. Schäfer, M. Altmaier**
• Appropriate COX material supplied to FZK-INE. • Protocol for preparation of artificial COX porewater available from BRGM. • Samples are prepared at FZK-INE by equilibrating crushed COX rock and artificial porewater in Ar glove box.		

Sample: NAT 3

Granitic groundwater (Grimsel)	**FZK-INE**	**Th. Schäfer, M. Altmaier**
• Grimsel groundwater sampled shortly before ICE supplied by INE.		

Sample: NAT 4

High salinity / brine conditions (Asse salt mine)	**GRS** **FZK-INE**	**B. Vester, T. Scharge** **M. Altmaier**
• Sample either obtained by dissolving rock salt or by preparing synthetic brine. • pH conditions not fixed. • Possibility to spike sample with Fe(II)/(III) under discussion.		

Sample: MIC

Homogenous systems with microbiological activity	**MICANS**	**K. Pedersen**
• Two different Samples prepared by MICANS and transferred to FZK-INE shortly before ICE. • Several “ready to use” samples in closed vials (~20 ml each) supplied so that further treatment/cultivation of microbial samples at INE before measurement is not required. • Microbes used: a) *Desulfovibrio aespoeensis* and b) *Acetobacterium carbonolicum*.		

Further information on media, cultivation etc. is available.

5) Additional activities at ICE will include presentations of advanced experimental techniques by ReCosy partners, a critical evaluation of different redox electrodes, information and practical advice on how to avoid artefacts from the measurement setup, a test of different pre-treatment protocols for conventional Pt-combination electrodes and efforts to understand the often large and systematic differences between short time and long time redox measurements. Significant time is reserved for a detailed presentation and discussion of results, thus providing a unique platform for scientific exchange and an improved understanding of redox determination methods.

6) It is expected that most members of WP2 attend ICE in Karlsruhe. Several groups involved in other work packages of ReCosy and Associated Groups have expressed interest to participate at ICE. Therefore, a letter of invitation to ICE at Karlsruhe will be distributed to all ReCosy partners and Associated Groups by the end of June. In this letter, detailed information on measurement equipment or specific experimental requirements of the participants will be requested. Based upon this, a detailed timeframe for experimental work within ICE is prepared and the technical hardware for ICE adapted at INE. Groups with immobile equipment request samples that can be expected to remain sufficiently stable during transport.

7) The outcome of the ICE will be presented and discussed during the Second Annual Project Meeting in March 2010 (PM24). Following a joint discussion, a consolidated report on the outcome of the ICE (Deliverable D2.3) is prepared by FZK-INE / M. Altmaier.

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

Project Month	Activity and documentation
12 (→13)	(Deliverable D2.2): “Experimental scheme for the ICE”
>12	Generation of samples for the ICE, followed by regular monitoring until ICE
20	ICE held at FZK-INE (16-20 Nov. 2009)
24	Outcome of ICE presented and discussed during the 2nd Annual Project Meeting.
>24	Consolidated report on the outcome of the Intercomparison exercise (Deliverable D2.3) is prepared by FZK-INE / M. Altmaier