Deliverable No D2.4

Report on further work on determination of redox state of systems and system components

Redox Phenomena controlling Systems
ReCosy

Collaborative Project (CP)

Submitting organizations:	UPPC
Due date of deliverable:	36 Project Months
Actual submission:	36 Project Months
Dissemination level:	PU
Grant agreement N°.:	FP7-212287
Start date of the project:	01 April 2008
Duration:	48 Months

The research leading to these results has received funding from the European Union's European Atomic Energy Community's (Euratom) Seventh Framework Programme FP7/2007-2011.

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 partners of WP2 and of the ReCosy Interlaboratory Comparison Exercise (ICE) have worked out a list of recommendations for further improvements of redox determinations. Based on the ICE a list of future activities beyond the ReCosy project was generated to address further address the scientific-technical challenges that were identified as an outcome of the ICE. The recommendations and suggestions are summarized on the following page and the detailed report is found in chapter 7 of the ReCosy ICE report *"Intercomparison of Redox Determination Methods on Designed and Near-Natural Aqueous Systems"; M. Altmaier, X. Gaona, D. Fellhauer, G. Buckau (eds); KIT Scientific Reports 7572 (2010), ISSN 1869-9669.*

The main arguments are concerned with the central question of how the redox state of a system is defined, and the consequences resulting for redox state determinations. A general concept was developed based on the available state-of-the-art experimental and conceptual approaches and address recommendations towards improvements of experimental data acquisition as well as future research activities.

First action steps with respect to electrode design, improvements in electrode preparation and in minimization of contributions from instrumental artefacts were taken by the partners of the ReCosy CP and are described in detail in the 3rd annual report of ReCosy.

A summary of the recommendations for future work as a result of the ICE in the scientific field of redox determinations is given below.

Recommendation for future redox determination

General aspects

- In order to minimize systematic errors (i.e., investigation of complex samples) a combination of different methods is recommended
- Implementation of a “quality assurance” protocol
- Integration of complentary experimental techniques such as optical measurements and amperometry
- awareness of influence from electronic components
- proper consideration of limit of detection of the experimental technique used and/or redox couples investigated

Sampling and handling

- In-situ measurements or transportation and measurement conditions as close as possible to the real system
- Strict control of temperature and atmosphere during measurement and sample handling
- Exact control and documentation of reference electrodes, bridging as well as junction solutions
- Storage condition of (reference) electrodes should be controlled and documented to minimize influence of surface effects

Equilibration and stirring

- Stirring of the samples improves homogenisation by minimizing possible mass transfer gradients, but during measurements the performance of the methods should be strictly controlled to avoid any contributions from tangential flow velocity related effects on the measured values
- The establishment of protocol for stirring conditions of homogeneous as well as heterogeneous samples is suggested. Documentation of stirring conditions is considered of utmost importance

Drift and surface effects on sensor

- Strict cleaning protocol of electrode surfaces in order to control/minimize influence of possible surface coatings
- Control and documentation of (possible) drift of experimentally observed readings is strongly recommended to define the criteria used for the selection of the “correct” reading
- “History” of electrode in use has to be taken in to account, e.g., to avoid contamination of the sample

pH-pe measurements

- pe measurements should be complemented by pH measurements
- pH and pe data must be corrected to give thermodynamically meaningful values

Thermodynamic modelling

- modelling for high ionic strength conditions is limited because conditions are not covered by thermodynamic databases

- the determination of all redox species involved is ultimately needed for proper modelling. In addition, possible kinetic effects should be included (non equilibrium conditions)

Recommendation for future research activities

Investigation of electrode surface effects

- investigation of physical and chemical gradients on or close to electrode surfaces
- generation of mixed electrode surfaces due to sorption processes
- influence of colloids as well as materials present in suspensions and solid phases present in the sample
- development of improved electrode cleaning protocols

Improvement of fundamental redox process understanding

- improved identification of redox couples dominating the redox state of a system
- determination of method-specific as well as redox-couple-specific critical concentration needed for unambiguous detection
- interplay of solid phase, aqueous phase, and gas phase for the redox properties of a system (mechanistic understanding)

Investigation, integration, and improvement of non-convential techniques such as

- “membrane-protected” electrodes
- Spectrophotometric indicators
- optodes

Assessment of temperature effects on redox processes

- investigation of redox processes at elevated temperatures
- improve thermodynamic databases for such conditions
- impact of temperature on performance of experimental methods
- consideration of kinetic effects

Development of advanced tools for long-time monitoring

- development of advanced strategies for long-term monitoring of redox conditions
- fundamental understanding of electrode surface processes (aging of electrode)
- proper consideration of aging effects for improved long-term performance of monitoring tools
- tailoring long-term stable redox set-ups