Annual Newsletter informing on the progress of the project

SLOW PROCESSES IN CLOSE-TO-EQUILIBRIUM CONDITIONS FOR RADIONUCLIDES IN WATER/SOLID SYSTEMS OF RELEVANCE TO NUCLEAR WASTE MANGEMENT

SKIN

COLLABORATIVE PROJECT (CP)

Reporting period: 01/01/2011-31/12/2013

Grant agreement N°.: FP7-269688

Submitting organizations: Amphos
Due date of deliverable: 1 Project Months
Actual submission: 1 Project Months

Start date of the project: 01 January 2011
Duration: 36 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 fro partners of the project	

Introduction

Implementation of geological disposal of radioactive waste requires assessment of relevant processes in the near-field (wasteform and engineered barriers) and far-field (host rock and pathways to the biosphere) to allow for development of robust methodologies for performance and safety assessment. Relevant processes are all those affecting the mobility of radionuclides. Questions need to be answered as to whether the engineered and geological barrier systems can isolate and retain the radionuclides in the waste for hundreds of thousands of years. Due to slow groundwater movement in confined deep geological formations, the system of radionuclides, minerals, engineered barrier materials and water will be close to chemical equilibrium. These systems, controlling radionuclide mobility, have been studied for many years, but only a little attention has been given to the fact that, due to the long disposal time, individual very slow processes can have a significant impact on the mobility of radionuclides, despite achievement of local equilibrium states being achieved.

1. Nature and Scope of the project

The project will study slow processes influencing radionuclide mobility in close-to-equilibrium scenarios in a detailed and systematic manner in relation to surface properties, surface site detachment/attachment kinetics, irreversible sorption and surface incorporation, for cases relevant to the assessment of radionuclide mobility in nuclear waste repository sites.
Emphasis is on the temporal evolution of surface detachment and attachment rates on minerals and the coupling of surface equilibrium with slow bulk phase diffusion/ recrystallisation processes of trace element (incorporation or release). This concerns kinetic studies, thermodynamic evaluations of solid solution/aqueous solution equilibrium, trace and principal element relations, structural and morphological observations and molecular modelling.

The project has 10 partners, including national waste management organizations, national research centres, universities/grandes écoles and SMEs, from 5 EU Member States (France, Germany, Sweden, Spain, United Kingdom), one Associated Country (Switzerland) and one Other Country (China) (see figure 1).

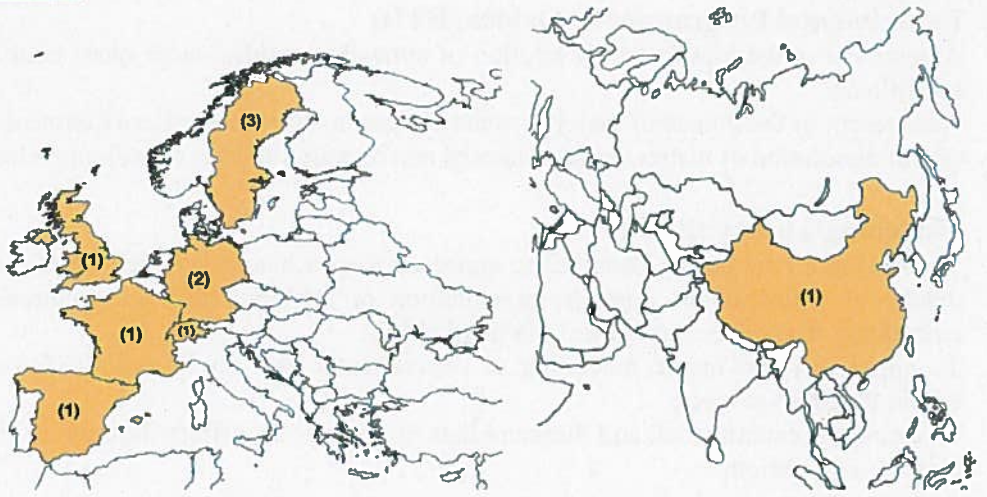

Figure 1. Different partners, including key European research institutes/waste management organisations and universities from 5 EU Member States, one Associated Country and China collaborating in the SKIN project.

2. Activities

The proposed strategy combines laboratory experiments and model development with analyses of safety implications. The work consists of combining, for relevant time frames, bottom-up approaches with individual mineral/water systems with top-down analyses of performance assessment needs to describe non-linearly coupled exchange processes in geological disposal environments.
The work programme covers various experimental case studies for solubility and sorption equilibria combined with surface incorporation and associated model development of practical relevance for application within performance assessment.
The R&D work programme is structured along two experimentally oriented RTD work packages and a work package for model development as well as for assessing consequences in safety analyses. In addition, there is one RTD work package for synthesis. The work packages and their objectives are as follows:

WP1 Management (MGT)
To ensure an efficient management of the scientific and technical activities as well as the overall administration.

WP2 Experimental Programme 1: Carbonates, Sulphates, Silicates, Cement (RTD)
In principle four main questions will be addressed: (1) The applicability of $Ra_xBa_{1-x}SO_4$ solid solution - aqueous solution thermodynamics to a specific scenario (Ra exchange with a $BaSO_4$ solid, (2) Identification of the substitution scheme for complex metal ion substitutions, (3) Identification of metal ion binding (precipitation, co-precipitation, surface uptake) in complex cement related systems (4) the questions of reversibility of solid/solution interaction with clays (example Cs on illite frayed edges).

WP3 Experimental Programme 2: Oxides (RTD)

Assessment of the kinetics of dissolution of tetravalent oxides under quasi-equilibrium conditions;
Assessment of the impact of major systems present in the repository environment on the rate of dissolution of matrix-related material and retention/release of radionuclides.

WP4 Modelling/Theory (RTD)

To develop a new partial equilibrium approach to geochemical modelling of the slow uptake of radionuclides upon (re)precipitation of host-mineral solid solutions (SS) embedding the surface entrapment model (SEMO);
To apply thermodynamic modelling to experimental data on Ra-barite SS gathered within the SKIN project;
To assess the experimental and literature data in terms of the affinity law and its validity close-to-equilibrium.

WP5 Synthesis and Safety Analysis (RTD)

To provide an overall synthesis of the project results together with results of previous studies, of literature and field data.

WP6 Dissemination/Mobility/Training (OTHER)

Communication and dissemination of knowledge generated within the project;
The organisation of the annual project workshops and training activities.

The management structure and the decision-making and communication framework are illustrated below in Figure 2.

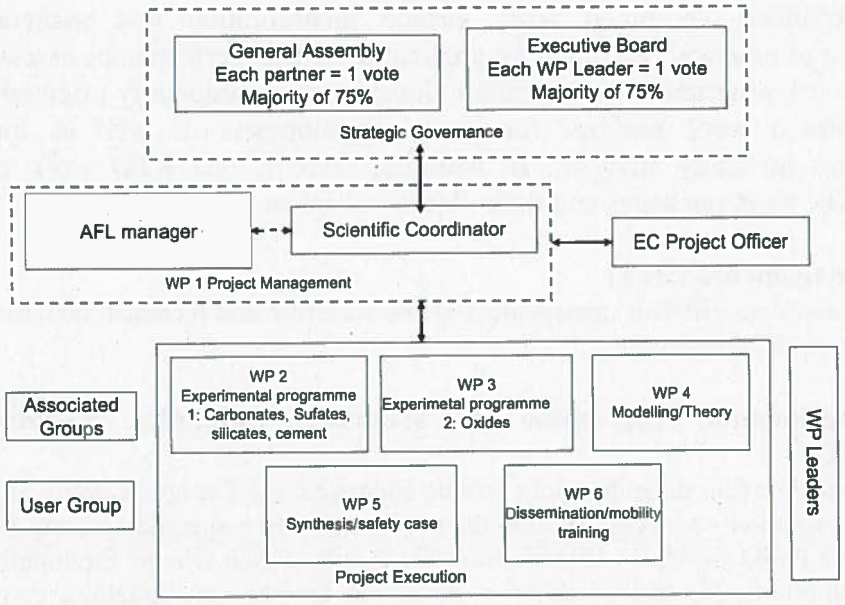

Figure 2. Scheme of the management structure, decision-making and communication structure providing the basis for adequate project implementation

3. Expected results

The project results are expected to impact strongly on; (1) the use/misuse of solubility data for thermodynamics; (2) the understanding of affinity/rate relations close-to-equilibrium; (3) the inclusion of irreversibility in models on the long-term mobility of radionuclides in geological disposal systems; and (4) the coupling of radionuclide chemistry with main element chemistry in the repository environment. The results of the project will probably show that safety margins in geological disposal concepts are larger than anticipated.

The study of **SKIN** will have a strong impact on the development of scientific methodology in assessing the long-term aspects of radionuclide migration in geological disposal.

A number of questions of general relevance will be addressed in the project which are as well of relevance of performance assessment and with different responses expected for the different solids/water systems studied.

4. Societal Impact

The research results expected from the SKIN project have a direct impact on the European nuclear power community, including authorities representing public safety concerns. This impact is related to the environmental, economic and political advantages of continued use of the clean and economic nuclear power, as well as its contribution to political stability through lowered dependency of energy import. This is directly related to long term improvement in European competitiveness, employment, environmental quality and quality of life.

5. Information about important public events

Persons with interest in the project may participate in annual workshops, announced at the project website.

6. Project website address & contact person

Project Website: http://www.emn.fr/z-subatech/skin/index.php/Main_Page

Contact person: Tomo Suzuki-Muresan suzuki@subatech.in2p3.fr

SLOW PROCESSES IN CLOSE-TO-EQUILIBRIUM CONDITIONS FOR RADIONUCLIDES IN WATER/SOLID SYSTEMS OF RELEVANCE TO NUCLEAR WASTE MANGEMENT

LIST OF PARTNERS

No	Partner	Beneficiary name	Country
1	**ARMINES** www.armines.net	Association pour la Recherche et le Dévelop-pement des Méthodes et Processus Industriels	FR
2	**KIT** http://www.kit.edu/	Karlsruher institut fuer Technologie	DE
3	**FZJ** http://www.fz-juelich.de/portal/DE/Home/home_node.html	Forschungszentrum Juelich GMBH	DE
4	**SKB** www.skb.se	Svensk Kärnbränslehantering AB	SE
5	**AMPHOS** www.amphos21.com	AMPHOS 21 Consulting, S.L.	ES
6	**CTH** www.chalmers.se	Chalmers University of Technology	SE
7	**SU** http://www.su.se/english/	Stockholms Universitet	SE
8	**PSI** www.psi.ch	Paul Scherrer Institut	CH
9	**LU** http://www.lboro.ac.uk/	Loughborough University	UK
10	**PKU** http://english.pku.edu.cn/	Peking University	

Coordination

Prof. Bernd Grambow, ARMINES/SUBATECH, 4 rue Alfred Kastler, 44307 Nantes

EC Project Officer

Christophe Davies, European Commission, DG RTD, CDMA 0/55, BE-1049 Brussels, Belgium

Period: 04.2008-2011

Budget: Total project cost (€): 2,004,728

EC contribution (€): 1,171,470

2nd Annual Newsletter informing on the progress of the project

SLOW PROCESSES IN CLOSE-TO-EQUILIBRIUM CONDITIONS FOR RADIONUCLIDES IN WATER/SOLID SYSTEMS OF RELEVANCE TO NUCLEAR WASTE MANGEMENT

SKIN

COLLABORATIVE PROJECT (CP)

Grant agreement N°.: FP7-269688

Submitting organizations: Amphos and ARMINES
Due date of deliverable: 13 Project Months
Actual submission: 18 Project Months

Start date of the project: 01 January 2011
Duration: 36 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		
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Introducing SKIN

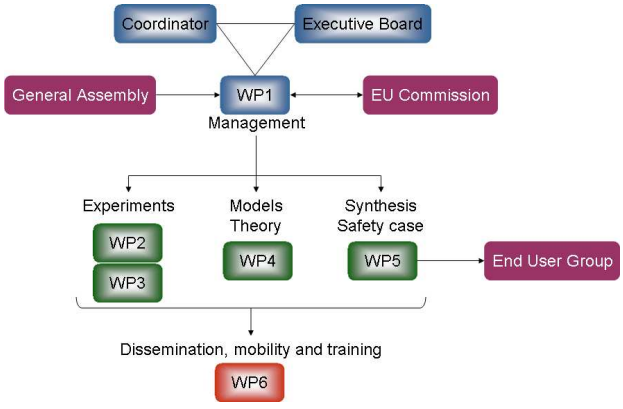
Implementation of geological disposal of radioactive waste requires assessment of relevant processes in the near-field (wasteform and engineered barriers) and far-field (host rock and pathways to the biosphere) to allow for development of robust methodologies for performance and safety assessment. Relevant processes are all those affecting the mobility of radionuclides. Questions need to be answered as to whether the engineered and geological barrier systems can isolate and retain the radionuclides in the waste for hundreds of thousands of years. Due to slow groundwater movement in confined deep geological formations, the system of radionuclides, minerals, engineered barrier materials and water will be close to chemical equilibrium. These systems, controlling radionuclide mobility, have been studied for many years, but only a little attention has been given to the fact that, due to the long disposal time, individual very slow processes can have a significant impact on the mobility of radionuclides, despite achievement of local equilibrium states being achieved.

2nd Annual Newsletter

The main objective of the Annual Newsletters is to inform the community on the progresses achieved in the SKIN project. The present newsletter gives a brief overview of the activities carried out during the first year of the project (January 2011 – January 2012).

SKIN organization

SKIN is structured along four Research Technological Development work packages (WP2 to WP5). Two of them are oriented to experimental research and another for model development as well as for assessing consequences in safety analyses. In addition, there is one RTD work package for synthesis. Specific work packages on administrative management (WP1) and dissemination, mobility and training issues (WP6) are also included in the project.



The project is divided into the following work packages:

WP1 Management (MGT)

WP2 Experimental Programme 1: Carbonates, Sulphates, Silicates, Cement (RTD)

WP3 Experimental Programme 2: Oxides (RTD)

WP4 Modelling/Theory (RTD)

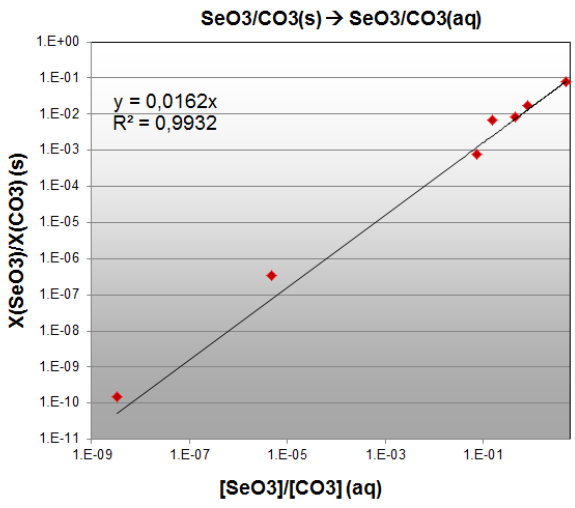
WP5 Synthesis and Safety Analysis (RTD)

WP6 Dissemination/Mobility/Training (OTHER)

Tasks Overview.
Short summary of first year of activities.

WP2: Research on Carbonates, Sulphates, Silicates and Cement

Radionuclide incorporation into calcite and barite



The study of the incorporation of Selenium (IV) into calcite is the aim of this activity. The equilibrium recrystallization of calcite is extremely slow, therefore research is focused on coprecipitation experiments under supersaturated conditions to study radionuclide incorporation into calcite.

A partition coefficient (D) for selenium(IV) into calciteof 0.02 ±0.01 has been obtained.

Recrystallization of Barite in the presence of Radium

The possible solubility control of Ra by coprecipitation of a $Ra_xBa_{1-x}SO_4$ solid solution has been demonstrated in many cases. However, an open question is whether a Ra containing solution will equilibrate with solid $BaSO_4$ under repository relevant

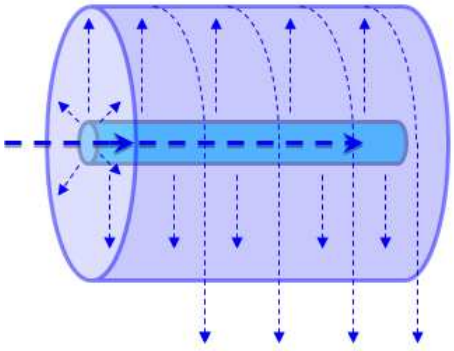
conditions. Here, Radium enters a system in which Barite is in equilibrium with the aqueous solution.

Different models describing the mechanism of Ra incorporation into barite have been calculated. Crystallization rates calculated are in a similar range of 10^{-5} to 10^{-7} mol/($m^2 \cdot d^1$) for all experiments (normalized to the barite surface area).

Methods to assess radioisotope migration in cementitious media by using radial diffusion and advection tests

It has been generally assumed that the safety functions of the cement within the near field of a Geological Disposal Facility (GDF) will include reduction of the solubility of many radionuclides and retardation of migration by sorption and incorporation in the solid phases.

The work undertaken involves the development of experimental methods that use radial flow through intact cylinders to evaluate the potential for diffusion and advection of relevant isotopes through the Nirex reference vault backfill (NRVB).



Sorption of Cs on the Callovo-Oxfordian claystone (COX)

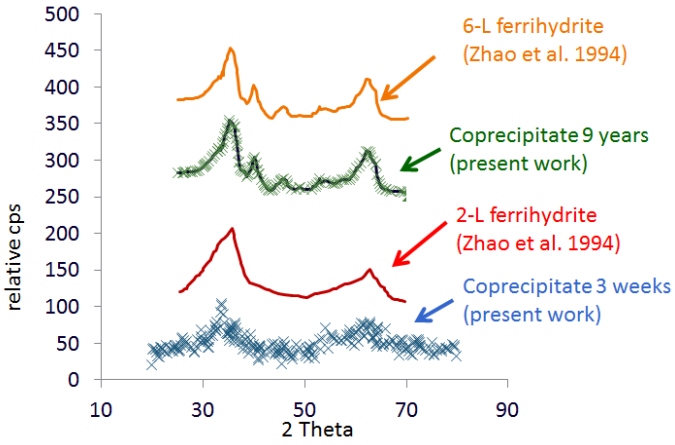
Experiments with COX have been performed to study the irreversibility of the sorption of caesium into illite. Although a partial irreversibility was expected, the results show a complete reversibility of the sorption. Perhaps explained by the low content of “pure” illite in the sample.

WP3: Research on Oxides

Interaction between Uranium and Iron (III) oxides

The objectives of this activity is the study of the nature and long term kinetics of the interaction between uranium and iron oxides, linking short-term sorption and long-term coprecipitation processes.

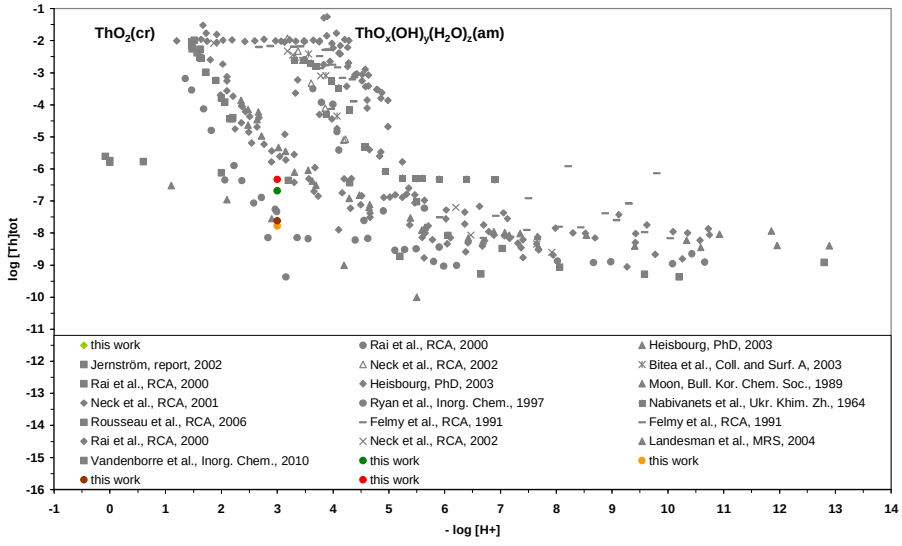
The preliminary conclusion obtained until now indicates that the U(VI)-Fe(III) coprecipitate has a ferrihydrite-like structure which evolves with time, as the ageing process proceeds, as shown in the plot. New EXAFS experiments are on going.



Discrepancies in thorium oxide solubility values: ThO_2 synthesis and characterization

The aim of this task is to study the solubility of ThO_2(s) in the pH range 3 to 7. ^{232}Th and ^{229}Th are used as tracers of the thorium behaviour.

Solubility measurements have been conducted in the acidic pH range and the results compared with available data in the literature, as shown in the picture.

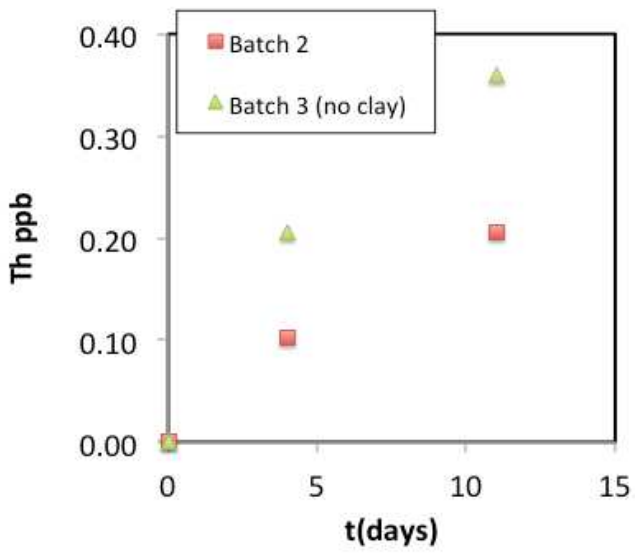


Kinetics of TcO_2(s) dissolution under hyperalkaline conditions

The investigation of the dissolution behaviour or technetium(IV) oxide as a function of pH (10.5, 12.5 and 13.3), ageing of solid phase (1 hour to 1 year) and ionic strength (I=1 and I=3) is the objective of this activity.

At the time of the annual workshop, Tc-95m had been purchased, received and was being extracted from the target, although its short (60day) half life may mean that more ^{95m}Tc will be needed before experiments can be completed.

The influence of clay slurry on the dissolution of spent nuclear fuel under reductive repository environments



The aim of this task is to evaluate the potential enhancing of SNF dissolution during a deglaciation period due to the effect of the erosion of the bentonite clay.

Results obtained so far indicate lower Th dissolved in the presence of clay. A quantitative analyses is currently being conducted in order to quantify whether the differerence can be attributed to the effect of clay.

WP4: Developments on modelling slow processes in close-to-equilibrium conditions

Approaches to model the kinetics of trace element uptake in host minerals

The present task is focused on the modeling of non-equilibrium trace element partitioning between a host mineral and aqueous solution that occurs during co-precipitation or recrystallization.

Experimental data indicate a time-dependent trace element partitioning during recrystallization, showing hysteresis between sorption and desorption of the trace element as a function on the ageing time. These deviations from equilibrium cannot be explained by using a simple aqueous solid-solution thermodynamic model. For this reason, three existing models of time-dependent trace element uptake in host minerals are being tested.

- *Surface Entrapment (SE) Model*
- *Surface Reaction (SR) Kinetics Model*
- *Adsorption- Desorption- In-Diffusion (AD) Model*

Theory on the Affinity Law

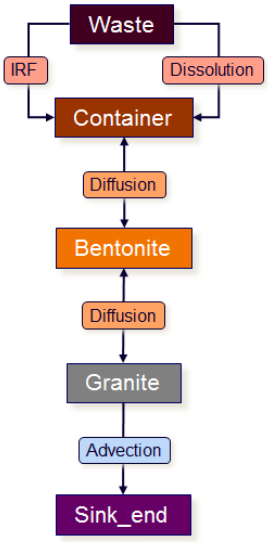
The present task concerns the application of the chemical affinity law. Numerous experimental observations note that the dissolution rate decreases when the solution reach esa composition close to the saturation of the mineral. Investigators have attempted to extrapolate far-from-equilibrium data to near-equilibrium conditions, sometimes with poor results because of the lack of understanding of the dependence of dissolution rate on the Gibbs free energy of the reaction.

The models aimed at describing the variations of the rate when approaching saturation are mostly based upon the transition state theory (TST), which predict a linear decrease of the rate close to equilibrium. This behaviour appears valid for some minerals but others experiments in literature present a non-linear behaviour.

WP5: Progresses on Synthesis and Safety Assessment

The main objective of WP5 is to show to which extent some of the experimental results gathered within the SKIN project can reduce these uncertainties.

The assessment of the impact of SKIN on the conservatism will be done through a compartmental modelling approach. A performance assessment reference case has been defined based on SR-Site system considered by SKB.



WP6: Dissemination, mobility and training

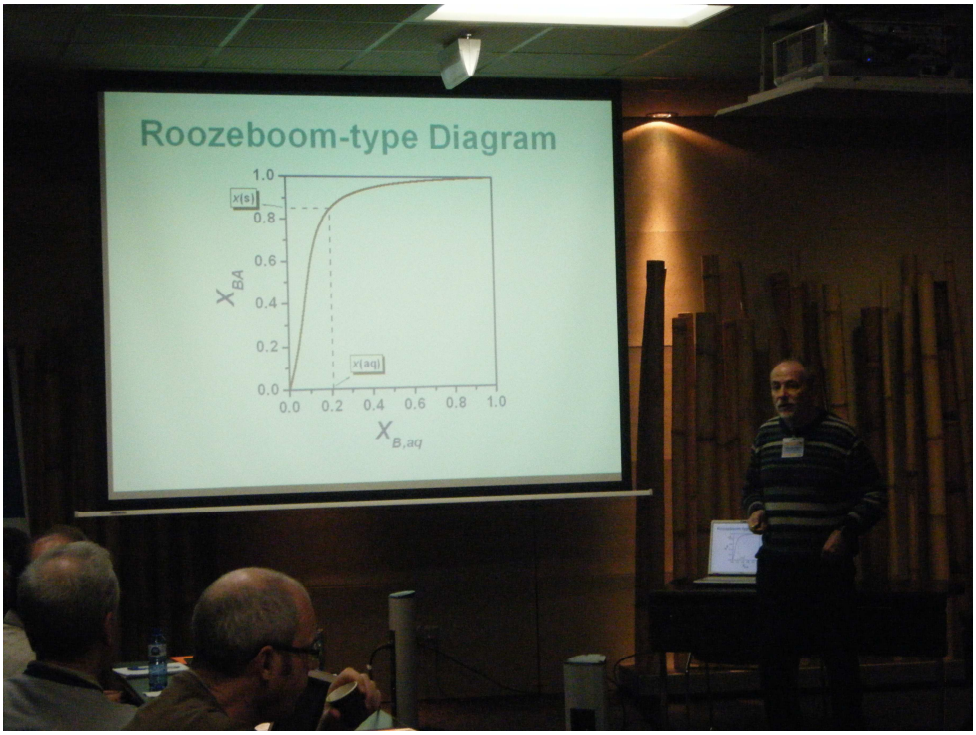
WP 6 addresses the internal and external training as well as knowledge management for the SKIN project.

A public web site was established within the project (http://www.emn.fr/z-subatech/skin/index.php/Main_Page). Information about the project and the project activities are made available to the broad community on this site.

The Annual Project Workshop is an important element in the documentation and dissemination of the project outcome. The Annual Project Workshop Proceedings are comprehensive public reports with the key scientific-technical outcome.

Dissemination of more detailed results will be also done through scientific journal papers, books, reports, proceedings of various conferences and workshops, PhD thesis, etc.

The training activity organized within the context of the first workshop (Barcelona, November 2011) was given by Manolo Prieto, from the Oviedo University (Spain) who was invited to give a talk about the Interfacial tension, metastability and solubility of solid solutions.



Events

SKIN 1st Annual Workshop (17th-18th November 2011, Barcelona, Spain)

The 1st Annual Project Workshop was held in Barcelona, Spain (17th -18th November 2011) hosted by Amphos 21. In total 24 persons attended the workshop including partners (9 out of 10 partners involved in the project), EUCG's members and external participants.

The Workshop combined different activities and meetings with the following objectives:

- Informing about the scientific progress
- Informing about the administrative status
- Discussing various topics of interest
- Informing/agreeing upon forthcoming reporting
- Agreeing upon the forthcoming work program

Emphasis was on scientific-technical topics with administrative issues kept to the minimum necessary.

During the workshop an Invited talk was focused on the interfacial tension, metastability and solubility of solid solutions given by Manolo Prieto from the Oviedo University.

Further extended information regarding the activities carried out during the first year of SKIN is compiled in the proceedings of that workshop.

SKIN 2nd Annual Workshop (21th-22th November 2012, Villigen, Switzerland)

The 2nd Annual Project Workshop is under preparation. It will be held in Switzerland on 21th to 22th November 2011, organized by Dmitrii Kulik and Bruno Thien from Paul Scherrer Institut (PSI).

This second annual workshop, like the first one, will give the participants an overview of the project, its activities, status and achievements. It will also provide decisions and communication of the planning for the third and final project year. Meetings of the Executive Committee, the General Assembly and the End-User Consultancy Group will be held within the context of the Workshop.

A training course on the use of GEM is planned the day after the workshop.

News

The University of Oviedo has been accepted by the general assembly as an *associated group*. There was an absolute majority and there were no counter-votes. This allows Professor Manolo Prieto, from Oviedo University, specialist on crystal growth, to join the SKIN project and be in close contact with the WP2 on the experimental aspects on calcite and barite.

Register on the training course to be held after the 2nd annual workshop! In Switzerland, PSI, on the Gibbs Energy Minimisation software, and given by Dr. Dimitri Kulik.

SKIN partners

SKIN contact

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