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Detailed WP2 description of scientific work: Compilation of partner descriptions

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PP	Restricted to other programme participants (including the Commission Services)	
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ABSTRACT:

This report gives details of the planned work for each of the participants of work package 2, related to Experiments on Radionuclide retention in high pH concrete. The written descriptions reported here have been provided by the project partners during the project preparation phase during 2014. The information was reviewed and compiled by the WP2 leader, as author of this deliverable. The complimentary overview slides of WP2 work were presented by the partners during the Project's Kick-off meeting held in Brussels on 2nd July 2015.

Keywords: experimental studies, methods, radionuclides, retention, work description

RESPONSIBLE:
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MAIN TEXT:

1 PARTNER WORK DESCRIPTIONS FROM PROJECT PLANNING

All participants in WP2 gave an overview of the expected work scope. This was summarized in written format during the project planning phase, with an emphasis on experimental and modelling work to be performed and cooperative nature between the partners, materials and methodologies. These summaries are presented in Appendix 1.

2 PARTNER WORK DESCRIPTIONS FROM KICK-OFF MEETING PRESENTATIONS

All participants in WP2 gave an overview of the expected work scope, summarized as slides during the Project Kick-off meeting held in Brussels on 2nd July 2015. These summaries are presented in Appendix 2. It has been noted in each set of the partner's slides that there are no deviations from the scientific and technical scope of the work plan compared to the original Project Plan at the time of proposal submission.

APPENDIX 1: Partner Written Summaries

WP 2			KIT

Overall Objectives:

- Work focusses on studying the retention of Be and Ra in cementitious environments. In order to optimize resources, share competence and derive a more comprehensive understanding of the systems studied, the activities are proposed to be performed within a “cluster” set up between KIT-INE, PSI/Empa, BRGM, RATEN-ICN, CTU and Amphos. The partners agree to closely coordinate their studies, cooperate on preparing the cement phases (C-S-H, AFm, AFt) to be studied, use similar experimental protocols for RN retention and solid solution studies, share experimental facilities and RN analytics, and work jointly on data evaluation and modelling. This close cooperation will allow the PhD students involved, to profit maximally from the scientific experience of the cluster partners. By using this approach a systematic and direct comparison of the behavior of different solid phases and different radionuclides will be possible. This will then also contribute to derive a consistent modeling of the systems.
- The activities of KIT-INE will (i) focus upon studies on Be solubility and thermodynamics in aqueous systems relevant in cementitious environments, and (ii) investigate sorption/retention of Be and Ra on relevant cement phases. Work will include (iii) dedicated attempts to derive detailed chemical models as basis for quantitative thermodynamic assessment.
- The main overall objective of all work performed by KIT-INE within WP2 of Cebama is to provide and improve the scientific basis for the Nuclear Waste Disposal Safety Case.

Objectives for different specific steps/periods (if applicable):

- Priority will be given to the evaluation of the aquatic chemistry and thermodynamics of beryllium under alkaline to hyperalkaline conditions, with special focus on solubility phenomena, hydrolysis and carbonate complexation. Although a few studies are already available in the literature, thermodynamic data for species/solid phases prevailing under hyperalkaline conditions is still ill-defined.
- Contribution to sorption/retention studies with Be and Ra. The contribution of INE on this topic will focus both on the quantitative evaluation of sorption processes and the spectroscopic characterization of sorbed radionuclide species on cementitious materials (redox distribution, evaluation of surface speciation) using the large set of advanced radioanalytical and spectroscopic tools available at KIT-INE. The Be sorption/retention studies will be performed only by KIT-INE, Ra will be investigated in cooperation with RATEN and CTU.

WP 2			KIT

Main expected outcome

- Chemical, thermodynamic and activity models will be developed for Be(II) in NaCl, KCl and $CaCl_2$ as background electrolytes in the absence and presence of carbonate. The generated thermodynamic data can be included in thermodynamic databases, and thus contribute to geochemical calculations relevant in performance assessment (PA). A robust understanding on radionuclide solubility control and speciation is essential for analyzing the sorption/retention effects on cement phases.
- The retention of radionuclides Be and Ra on relevant solid phases will be analyzed in a systematic way. Work will include the development of adequate chemical models describing retention mechanism and aims at a comprehensive quantitative description within reliable thermodynamic models.
- The spectroscopic work to be performed at INE is expected to provide key information to develop accurate chemical models for the uptake of the investigated radionuclides by cementitious materials. The spectroscopic tools of KIT-INE are optimized for working with radionuclides in controlled area and include XAS, Raman, SEM-EDS, XPS, XRD, NMR, UV-Vis and hyphenated mass-spectrometry based techniques.

Description of work to be performed:

- Solubility experiments with a well-characterized solid phase ($Be(OH)_2$(s)) will be performed from undersaturation conditions. Independent batch experiments will be prepared at different pH and ionic strength conditions, using separately NaCl, KCl and $CaCl_2$ as background electrolytes. A second series of samples will be also prepared in the presence of carbonate. Chemical, thermodynamic and activity models will be derived based on slope analysis, accurate solid phase characterization and the use of the SIT formulism consistent with the approach of NEA-TDB. Additional samples will be prepared simulating the porewater compositions of the most relevant degradation stages of cement, and will serve to test the thermodynamic model developed, as well as to gain data in "real" system to be considered as upper solubility limits in source term estimations.
- Using the solid phases prepared within the proposed "Cluster" (mainly by PSI/Empa and BRGM) will be used to quantify the sorption/retention of Be and Ra on relevant solid phases. The use of same solid phases, aqueous background electrolyte systems and different radionuclides will allow a systematic evaluation of radionuclide retention and the development of quantitative thermodynamic models. A part of the experiments on Ra interaction with cement phases will be performed in cooperation with RATEN and CTU (PhD students sent to KIT-INE laboratories)
- A selection of sorption/retention samples investigated by KIT-INE and the member organisations of the above mentioned "cluster" will be characterized by spectroscopic means at the INE-facilities, including the INE beamline for actinide research at ANKA. Both XANES and EXAFS data will be compiled during the measuring campaign to constrain redox and derive structural information. Data evaluation will be performed jointly by KIT-INE and cooperation partners.

Cooperations:

- The proposed work of KIT-INE within WP2 will be performed in a close cooperation with PSI/Empa, BRGM, RATEN, CTU and Amphos21. The partners will share competences, dedicated analytical tools and open their laboratories for PhD researchers from the partner institutions. Although this "cluster" is proposed by the institutions mentioned above, it is in no way exclusive and may also include other Cebama partners working within WP2.
- The work performed by KIT-INE within WP2 will be communicated to US, Canadian, and several East Asian research institutions. It will be especially advertised that Cebama will offer the possibility of external partners joining as "Associated Groups", also contributing to the above mentioned topics related to Be and Ra chemistry.

Added value of Cebama:

- The proposed studies will improve the understanding of RN retention processes in relevant cementitious systems and reduce uncertainties in present analyses. Site-independent thermodynamic data will be generated as input for modeling work. Especially:
- development of improved chemical models based upon detailed molecular level information via advanced spectroscopy and radioanalytics
- better quality of model predictions on RN retention processes based upon improved quantitative thermodynamic models and parameter.
- The focus on thermodynamic description and data is closely linked to WP3, where model calculations need these data as input parameter.

Planned training activities (if any):

- Work is planned to be performed by PhD students, including students from other Cebama members having access to KIT-INE labs within specific cooperations with INE. This will contribute to training of young researchers and sharing of expertise.
- Depending on the further decisions of Cebama project regarding training and education, KIT-INE would be willing to host a training event at INE on radionuclide chemistry and analytics in cementitious systems for young researchers.

Plans for dissemination:

- Participation at project meetings, contribution to annual reporting.
- Presentations at international conferences on results generated within Cebama.
- Publication of results generated in Cebama in peer-reviewed scientific journals.

Deliverables and milestones proposed (the information will be integrated for the respective workpackages):

- It will be important to agree on relevant solid phases and background electrolyte systems investigated in the proposed "cluster" at an early stage of the project.
- WP should include a specific deliverable summarizing the chemical models and thermodynamic data generated within WP2 of Cebama as basis for improved geochemical modeling.

WP 2			AMPHOS21

Overall Objectives:

The overall objectives of Amphos 21 participation to the workpackage are to:

- Contribute in the acquisition of data and a sound understanding of the retention mechanisms of Mo in cement/concrete,
- Study the kinetic evolution of the anionic substitution of Mo on pure phases such as AFm and Aft
- Develop a bottom-up development regarding Mo up-take onto the whole cementitious material
- Ensure that the scientific-technical results are further used to increase our understanding of the main retention mechanisms of Mo in the different cement degradation states

Objectives for different specific steps/periods (if applicable):

- Step 1: Establishment of the details of the experimental program (e.g. define type of experimental set up and solid phases to be studied i.e. CEM V type, AFm, Aft, …).
- Step 2: Definition and design of the experimental set up for: a) Batch sorption with cement/pure solid samples and b) Flow-through (kinetic) experiments during anionic substitution
- Step 3: Acquisition of experimental data on retention processes and kinetic evolution, analysis and data treatment. Special focus will be put on the Kd of Mo on the studied solids and on the kinetic evolution of the anionic substitution/retention. The role of Ca on the studied system and the processes governing the retention of Mo in each studied solid will be of special focus.

Main expected outcome:

- The main expected outcome is the acquisition and the understanding of the mobility/retention processes of Mo through the different cementitious barriers. That could lead to a Kd increase in comparison to current data selections, and to establish partially reversible up-take mechanisms ; this will be conducted in agreement with the Andra needs

Description of work to be performed:

- Step 1: Methodological (desk) studies to design the scope of the experimental work.
- Step 2: Detailed definition of the work to be performed with special emphasis on the methodology to be used for the study of retention mechanisms and kinetic experiments, the main experimental techniques needed and the main parameters to measure (i.e., pH, redox potential, Ca concentrations, etc…)
- Step 3: Laboratory experimental work with acquisition of experimental data following the output of Step 1 and Step 2. Evaluation and preliminary modelling of the acquired data for further use in WP 3 modelling exercises

Cooperations

The activities of Amphos 21 within WP2 will be performed within a “cluster” set up between KIT-INE, PSI-LES/Empa, BRGM and Amphos21 with the aim to optimize resources, share competences and deep on the understanding of the studied systems. In particular, the use of the same cement phases or pure AFm or Aft solids used by the other participants of the cluster will be one of the main strengths of the cluster for optimizing resources. In addition, the close cooperation and exchanges with PhD students, experimentalists, post-docs and beneficiaries is foreseen in order to

WP 2			AMPHOS21
take advantage of available techniques in other research centres and laboratories among the beneficiaries of the project and to enrich and improve the acquisition of the knowledge needed by the EUGC. This close cooperation will allow the students to profit from the scientific experience of the four cluster partners. Andra will participate as co-funding partner of the Mo studies undertaken by the Amphos 21 beneficiary.			
Planned training activities (if any): - Participation in the annual project workshops, - Participation in training events /schools in association with the annual project workshops - Participation of the Student in Student Workshops with dedicated training activities, if applicable.			
Plans for dissemination: - Presentation of results at different international conferences series (NUWCEM, CONMOD, MRS, Migration, etc.) - Publishing results in peer reviewed journals - Online resources: IGD-TP website, CEBAMA website, Amphos 21 website, specialized blogs			

WP 2			BRGM

Overall Objectives:

BRGM will combine its efforts into a "cluster" (INE, PSI, Amphos, BRGM) aiming to better understand the sorption properties of relevant RN on cement phases AFm and C-S-H)

Objectives for different specific steps/periods (if applicable):

The project will be divided in four main tasks that will all contribute to a better understanding of the role of the AFm phases on anion retention in cements. Specifically, the three goals are:

- (i) to better constrain the mechanisms of anion exchange in AFm interlayer and to determine the structure of the resulting Afm phases.
- (ii) to provide a realistic description of Afm layer structure, and in particular to provide a range of possible isomorphic substitutions In Afm layers, and to describe the impact of these substitution on anion sorption capacity.
- (iii) to determine the evolution of Afm structure and reactivity during their progressive dissolution in disequilibrium conditions, such as clay/cement interfaces.

Main expected outcome:

- The thermodynamic properties of a given mineral depend on the crystallographic structure. In the specific case of layered structure such as Afm, the position of the interlayer cation will significantly influence thermodynamic properties (Aimoz et al., 2012). **This project will provide refined structures of Afm having interlayer cations of relevance for nuclear waste storage and exchange constants for anions of relevance for nuclear waste storage**.
- Determination of the occurrence from isomorphic layer cation substitutions in solutions representative of in situ condition and their influence on anion retention will also serve as a basis for a **better description of Afm structure**, but will also provide a realistic description of **Afm anion retention capacity**.
- **A realistic kinetic model for Afm degradation** (e.g. is layer dissolution stoichiometric or not, how does in affect anion retention capacities).

Description of work to be performed:

As described here above, the project will consist of four main tasks. The work that will be accomplished during this project is here below described as a function of these four tasks. The preliminary task that would correspond to the synthesis of the samples is not described here because such protocols are well documented in the scientific literature. Still, this task will be described in details if the present project is pre-selected.

This project will focus of AFm, which are lamellar phases, built of layers of Ca and Al polyhedra connected through their edges. These layers, which bear a permanent positive layer charge, are separated by a hydrated space filled with water and anionic species which compensate for the layer charge. As such, AFm (which belong to the family of "layered double hydroxides" phases) are responsible for cement anion retention capacities. A sound understanding of anion migration within cement thus requires a detailed understanding of AFm structure and reactivity as a function of the solution composition.

All here below mentioned experiments will be conducted using anions of relevance for nuclear waste storage. Chlorine, Iodine, sulfates and selenium (this latter being present under anionic form in the physico-chemical conditions of relevance for the present study) are at the moment

WP 2			**BRGM**

considered most relevant, but this list may be re-evaluated during the course of the evaluation process or of the project if proved necessary. It must be empathized that radio-tracers will be employed (at the KIT/INE) in addition to stable elements, which will give access to mechanisms of sorption that proceed at low concentration, and are thus relevant to study potential migration of a minor amount of radioactive waste that could leak from the waste at long time scale.

- **Task 1**: determination of exchange constants for anions of interest and structure of resulting sample

In natural environments, the solution will always contain a variety of anions whose concentration may vary with time. It is thus unlikely that homo-ionic Afm phases will persist during the whole life of the cemented structure. More likely, the interlayer composition will change with time, which will in turn affect the thermodynamic properties of the Afm phase. A first step is thus to understand the mechanisms of anion exchange in Afm and the likehood of such substitution as a function of the competing ions. The exchange constants will be determined using both batch and open-reactor experiments through analysis of solution chemistry. Retrieved data will be compared to solubility constants available in the literature (e.g. Matschei et al., 2007). If useful, the anion used for exchange could be a radioactive isotope, which would allow probing the mechanisms at play in case of low abundance of one of the two anions. The structure of the initial product and of the final products, and in particular the position of the interlayer anion, will be determined using a combination of physical techniques, mainly modelling of XRD patterns and, if needed, spectroscopic methods available in the laboratory such as Raman spectroscopy or EXAFS.

Task 2: influence of layer cations isomorphic substitutions on anion retention capacities Isomorphic substitutions are commonly reported in lamellar structures, such as clays, layer double hydroxides, nanocrystalline calcium silicate hydrates or phyllomanganates. By analogy, it is expected that such substitutions will also occur in Afm. For example, the substitution of Al by Si is likely. Such substitutions will have two main consequences: first, it will increase layer charge, and should thus increase anion sorption capacities. The feasibility of such substitutions will be studied by precipitation from solutions containing cations that are ubiquitous in cement pore water (e.g. Si, Mg, etc.) and then analysis of the solid to get the bulk structural formula (e.g. using microprobe). If likely at this point, the influence of such substitutions on layer structure (e.g. lattice distortion) will be probed by physical methods such as X-ray diffraction on laboratory instruments (e.g. powder XRD) but also high-energy X-ray diffraction available on synchrotron light sources (i.e. pair distribution function). The position of the foreign cation will be determined using spectroscopic methods (e.g. Raman spectroscopy, XANES, EXAFS). The influence of such substitutions on Afm reactivity will be tested through sorption experiments and determination of the anion exchange capacity.

- **Task 3**: kinetics of Afm degradation and influence on anion retention capacities

It has been demonstrated that in a number of environments such as clay-cement interfaces, Afm is unstable and may be (partially) dissolved. In order to be able to understanding and consequently predict the migration of anionic elements such as those contained in radioactive wastes, the mechanisms of Afm dissolution with time and with solution chemistry (i.e. the evolution of layer structure) and its impact on the evolution of anion sorption capacity must be understood. This task will be accomplished by using specifically designed flow-through reactors, with continuous monitoring of most relevant chemical parameters (e.g. eH, pH, Ca, Al, anions, etc.) that will allow determining the kinetics of the dissolution as a function of relevant parameters (e.g. pH). These reactors allow for the sampling of aliquots from the solid being dissolved. This solid will be analysed using methods routinely used in our research group, such as TEM, XRD, Raman or methods taking advantage of synchrotron light sources, and will allow determining the evolution of AFm reactivity towards anions through the course of the dissolution experiment

WP 2			BRGM

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Cooperations:

- *Use of same cement phases in RN retention studies ! (comparability, synergies, systematics)*
- *Partner exchange information on experimental studies and data evaluation.*
- *Partner share technical equipment, like some analytical tools at INE…*
- *Option to have "shared" PhDs which visit different labs (=> training + educ.).*

Added value of Cebama: multi disciplinary co-operation on international level between specialised research teams will result in an efficient increase in understanding of RN retention phenomena on cement phase. The point developed above for the cooperation are all relevant here

Planned training activities (if any):

Plans for dissemination:

- Joint papers, posters/presentations at conferences, open research reports ……

Deliverables and milestones proposed (the information will be integrated for the respective workpackages):

Milestone 1: Synthesis of AFm phase for the "joint cluster"

Deliverable 1: determination of exchange constants for anions of interest and structure of resulting sample

Deliverable 2: influence of layer cations isomorphic substitutions on anion retention capacities

Deliverable 3: kinetics of Afm degradation and influence on anion retention capacities

WP 2			JUELICH

Overall Objectives:
Mechanistic understanding of the structural uptake and retention of safety relevant radionuclides in cementitious systems and the relevance of ageing effects on RN speciation and release derived from the integration of computational and experimental approaches.

Objectives for different specific steps/periods (if applicable):
- Agreement on detailed objectives and experimental programmes with collaborating institutions, set up of experimental programme, fabrication of cementitious sample materials and synthesis of model phases.
- Delivery of the main experimental programme.
- Synthesis of results and implications for process models and safety assessments.

Main expected outcome:
- Enhanced mechanistic process understanding of RN uptake and retention mechanisms and the long-term fate of RN in evolving systems to implement more realistic process descriptions in models used for safety assessments.

Description of work to be performed:
- Experiments on the uptake of selected long-lived long-lived fission and decay products such as Se-79, I-129, Ra-226 and Mo in cementitious systems (HCP and altered concrete) and on single model phases (e.g. CSH, AFm,t, LDH).
- Determination of RN distribution between and within various phases using advanced microanalytical and spectroscopic techniques such as FIB/TEM, ESEM, TOF-SIMS, Atomprobe, Raman/IR-spectroscopy, and XAS.
- Experimental investigation of long-term alteration effects (e.g. by carbonation) on RN-bearing cementitious materials regarding RN release/re-distribution and microstructure development.
- Thermodynamic modelling of phase stabilities and RN bearing solid-solutions employing GEMS.
- Molecular modelling/atomistic modelling of RN incorporation and uptake mechanisms.

Cooperations
- FZJ cooperates in WP2 intensively with the Uni Loughborough – based on a shared Postdoc (PDRA) – on RN uptake and RN solid speciation in cementitious systems and long-term aging effects. Information exchange with the Uni Sheffield with respect to the consequences of alteration processes on materials properties.
- External cooperation with respect to cementitious materials exists with other departments in the FZJ (regarding cementitious waste forms) and with COVRA regarding cementitious barrier materials in the OPERA safety case (in collaboration with Brenk Systemplanung and IBR BV).

Plans for dissemination:
- Publications in peer reviewed journals (e.g. Radiochimica Acta, Journal of Materials Research, Cement Concrete Research)
- Presentations at international conferences (e.g. Migration, Goldschmidt, NUWCEM, IGD-TP)

Deliverables and milestones proposed (the information will be integrated for the respective workpackages):
Milestone:
Cementitious sample materials, synthesized model phases, and results of first (batch) uptake experiments available (month 12)
Results of microanalytical and spectroscopic analyses on RN distribution available (month 24)
Annual meetings
Deliverables:
S&T contributions to workshop proceedings and WP summaries

WP2			RATEN-ICN

Overall Objectives: To investigate C-14 and Ra-226 retention and diffusion in high pH concrete and the influence of the concrete ageing on radionuclide retention

Objectives for different specific steps/periods (if applicable):

- Year 1: State of the art review, set-up the experimental program, concrete characterization (mercury intrusion porosimetry, SEM/EDX, DTA/TGA and XRD analysis)
- Year 2 and 3: C-14 and Ra-226 sorption/desorption and diffusion experiments on intact concrete samples and on concrete in different degradation phases; concrete degradation tests
- Year 4: Completing the experimental program and correlation of sorption and diffusion data with concrete composition and structure.

Main expected outcome:

- Understanding the influence of concrete ageing on C-14 and Ra-226 sorption and experimental data for radionuclide transport modeling through the cementitious barrier materials used in geological repository for CANDU spent fuel and long lived radioactive waste

Description of work to be performed:

- *Task 1.1. Current status review on radionuclide sorption in high pH conditions*
  RATEN-ICN will review the current knowledge on radionuclide retention in high pH concrete. The review will cover the open literature and other information provided by the CEBAMA partners.
- ***Task 1.2. C-14 and Ra-226 sorption/desorption experiments***
  - concrete degradation tests (carbonation and sulphate reactions)
  - C-14 and Ra-226 sorption/desorption experiments on concrete in different degradation stages
  - correlation of the sorption experimental data with concrete composition
- *Task 1.3.C-14 and Ra-226 diffusion experiments*
  - C-14 and Ra-226 diffusion experiments on concrete in different degradation stages
  - correlation of the diffusion experimental data with concrete structure and composition

  Long-lived radionuclides presented both in long-lived radioactive waste and CANDU spent fuel are selected: C-14 and Ra-226.

  Mercury intrusion porosimetry, SEM/EDX, DTA/TGA and XRD analysis will be used to investigate the changes in porosity structure and composition of the concrete in different degradation stages.

Cooperations

- *For the C-14 experimental program RATEN-ICN team will collaborate with more experienced partners of WP2 in selecting the adequate experimental protocol. C-14 sorption and diffusion experiments will be performed on concrete samples degraded in RATEN-ICN laboratory, but also on concrete samples provided by SUBATECH.*
- *For Ra-226 experiments, the KIT-ITU experience with this radionuclide will be used, especially in Ra measurement at* very low concentration.

WP2			RATEN-ICN

Planned training activities (if any):

- A PhD student will be involved in the experimental program developed by RATEN-ICN.

Plans for dissemination:

- The main experimental results will be published in international journals and conferences. Experimental data will be used to support AN&DR (Romanian agency responsible for radioactive waste management) in developing and implementing the geological disposal program in Romania

WP 2			ARMINES

Overall Objectives:

Armines (Subatech) will contribute to a better understand²ing of the retention and transport properties of inorganic carbon-14, both in aqueous and volatile species, under unsaturated and saturated conditions and for different materials (stage of water degradation)

Objectives for different specific steps/periods (if applicable):

Context: Cemented wastes in disposal cells in clayrock formations may remain partially unsaturated for many thousands of years and carbon-14 species (aqueous and volatile, organic and inorganic) released from waste may react with the unsaturated cement materials. The carbonation process, describing the reactivity of inorganic carbon (CO_2) from porewater or atmosphere with cement materials, occurs at the outer surface of cement under saturated conditions (clogging), but under unsaturated conditions, this process may occur in the whole gas saturated pore volume and modify not only the mechanical properties of the cement material but carbonation may as well lead to entrapment of C-14 species and it may impact the transfer properties for volatile radionuclides through cementitious barriers

Armines (Subatech) contribution will be divided into four tasks:

- **Task 2.1:** Development of a specific experimental set-up in order to acquire data on the retention and diffusive transport properties under unsaturated and saturated conditions
- **Task 2.2:** Determination of transport parameter (De) of aqueous inorganic carbon-14 (and HTO, as water tracer) under unsaturated and saturated conditions: Influence of specific conditions (cement degradation)
- **Task 2.3:** Determination of transport parameter of gaseous species (CO_2)
- **Task 2.4:** Geochemical modelling of the experimental data in order to describe the different chemical processes (precipitation, isotopic exchange, coprecipitation,…) which could take place into the cement material

Main expected outcome:

- **Task 2.1:** Qualification of the osmotic technique to cement material (hardened cement paste (HCP)) using HTO as a water tracer: Evolution of D_e(HTO) *vs* saturation degrees ; Comparison with literature data
- **Task 2.2:** Acquisition of transport parameters (De) for inorganic aqueous carbon-14 species (as carbonate ions)
- **Task 2.3:** Acquisition of transport parameters for gaseous carbon-14 species (CO_2)
- **Task 2.4:** Modelling the chemical processes involved in the reactive transport of C-14

Description of work to be performed:

Cement samples used in this project originated from cylindrical samples of CEM I Hardened Cement Paste (HCP), cured for 7 years under water with a W/C ratio of 0.4.

Task 2.1: ***Application of the osmotic technique to a cement paste***
The experimental development will be based on the use of a specific osmotic technique in order to reach different degrees of saturation (RH) of a cement paste. This technique has been already

WP 2			ARMINES

applied for the study of the diffusion of species through unsaturated core sample of Callovo-Oxfordian argillite [SAV,10]). The diffusion parameters in such conditions are determined using modified through-diffusion cells in which the suction is generated by the osmosis process between the pore water (present in the pores of the sample) and a highly concentrated solution with large-sized molecules of polyethylene glycol (PEG).

In the modified diffusion cell, the sample is separated from the PEG-solution by a semi-permeable membrane (which is permeable to all except PEG). The exclusion of the PEG from the sample results in a chemical-potential imbalance between the pore water and the water in the reservoir chambers. This osmotic suction potential has the effect of keeping the sample unsaturated. We proposed to apply this technique to cement paste samples in order to acquire the diffusive parameters of radionuclides for different degrees of saturation.

Additional diffusion experiments with tritiated water (HTO) will be performed for each degree of saturation, effective diffusion coefficients (D_e(HTO)) will be measured and compared to literature data under saturated and unsaturated conditions [BEJ06].

Task 2.2: ***Acquisition of effective diffusive coefficients data for inorganic aqueous carbon-14 species (carbonates ions) under saturated and unsaturated conditions***

Influence of degradation of cement by interaction with water: The interaction of water with a cement paste leads to the decrease of the pH value (from 13.4 for young cement to 10.5 for an aged cement) and to the decalcification of the material (dissolution of portlandite and progressive decalcification of the C-S-H phases). These processes have a strong influence on the reactivity of carbonate ions with cement paste. Diffusion experiments will be performed for three different (young, fresh (alkaline free) and aged) cement samples. For this task, diffusion experiments with HTO will also be performed for comparison with literature data

For the two tasks 2.1 and 2.2, radionuclide (HTO and C-14) activities are measured by direct liquid scintillation. ICP-MS and ion chromatography will be used for measurements of all the other aqueous compounds. Solids samples will be analysed by beta-autoradiography and Scanning Electron Microscopy (SEM) in order to obtain a more precise localization of C-14 in the solid (precipitated as $CaCO_3$ or secondary phase such as monocarboaluminate). Some micro tomography (µCT) analysis will also be performed for imaging the pore network.

Task 2.3: ***Acquisition of transport parameter for volatile carbon-14 species ($C0_2$)***

In this task, the experimental program is based on the use of percolation set-ups. Centimetric cement samples, inserted in flow-through reactors, are stored in dessicators where RH is controlled by the use of oversaturated saline solutions. After a defined period of time, the reactors are put on a percolation set-up (see scheme below). A mixture of inert gas and CO_2 labelled with C- 14 is then injected at very low flowrates through the flow-through reactor. The temporal evolution of pressure and flowrate during the experiment will give information on the impact of carbonation by clogging the porosity. The non reacting fraction of CO_2 will be trapped by a highly alkaline solution (NaOH) and the C-14 activity will be measured by liquid scintillation. At test termination, samples will be cut into thin slices which will be analysed in order to determine the percolation profile of the CO_2 into the cement sample. This will be done for each degree of saturation.

For all the experimental tasks, some experiments would be performed with enriched C-13 compound instead of C-14 labelled compounds, in order to use other techniques for solid characterization such as nanoSIMS cartography.

Task 2.4: ***Geochemical modelling***

The aim of the task is to model the different chemical processes (degradation of cement samples, precipitation, gas/liquid distribution, isotopic exchange, coprecipitation, formation of secondary phase,…) which can occur during the percolation experiments under saturated and unsaturated conditions. PhreeqC code will be used for modeling the C-14 profile in the cement sample.

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Oxfordian, Environmental and Science Technology, **2010,** *44,* 3698–3704

[BEJ06] Bejaoui S., Bary B., Nitsche S., Chaudanson D. & Blanc C. (2006) Experimental and modelling studies of the link between microstructure and effective diffusivity of cement pastes. Revue Européenne de Génie Civil, 10, 1073-1106.-

Cooperations

- *explain your cooperations with Cebama partners in this Workpackage*

It is planned to cooperate with RATEN-ICN on C14 retention. Cooperation involves the exchange of samples to allow at least to a certain degree to work on common materials. In fact the works of the two organizations are entirely complementary.

Some discussion is ongoing with UDC on potential interaction on modeling , in case modeling goes beyond simple modelling of experimental results.

- *Cebama external partners: None*

- **Planned training activities (if any):**

Participation in overall training activities in coordinating special sessions on radionuclide behavior

- **Plans for dissemination:**

Publications, participation in international conferences

WP 2			ULOUGH

Overall Objectives:

Mechanistic understanding of the uptake of safety relevant radionuclides in selected cementitious systems. The impact of environmental parameters (e.g. temperature, salinity), ageing and carbonation on radionuclide retention will be assessed using archive and freshly prepared specimens.

Objectives for different specific steps/periods (if applicable):

- Phase 1 (6 months) – collaboration with partner laboratories to agree objectives, access archive materials and plan programme;
- Phase 2 (36 months) – delivery of main experimental programme;
- Phase 3 (12 months) – characterisation, synthesis and final reporting. Part concurrent with Phase 2

Main expected outcome:

- Enhanced understanding of the processes governing radionuclide uptake by backfill and structural cements in Fe-dominated redox systems. Derivation of parameters for mechanistic speciation-solubility modelling and evaluation of simplifying assumptions for implementation in safety assessment.

Description of work to be performed:

- Solubility and washout experiments on selected radionuclides (Cl-36, Se-79, Tc-99, I-129, Ca-45) in cementitious systems (low strength backfill (NRVB) and low pH cement). Washout experiments will be performed on archive samples containing the radionuclides of interest;
- Solution analysis by gamma spectrometry, LSC, ICP-MS. Solids by (µ)XRD, ESEM and digital autoradiography;
- Synthesis and characterisation of single mineral phases capable of incorporating the above radionuclides (e.g. Friedel's Salt - Cl-36) using advanced nano/microanalytical and spectroscopic techniques, including µXRD, EXAFS, TEM, ESEM, NMR, Raman/IR-spectroscopy and AFM;
- Determination of uptake and release kinetics for target radionuclides in each phase and assessment of their prospective contribution to multiphase cement assemblages;
- Investigation of the impact of changing redox and pH conditions on radionuclide speciation and solubility and their effect on cement phase stability. Experiments will be carried out in air, under N_2, CO_2 and in the presence of metallic Fe, respectively;
- Provision of data to assist thermodynamic and molecular/atomistic modelling by partners under WP3.

Cooperation:

Uni Loughborough will cooperate closely with FZJ in WP2 based on a shared PDRA. The study will draw on extensive experience with cementitious materials at Uni Loughborough across the Chemistry, Materials and Civil Engineering departments. Access will be provided to state of the art phase characterisation facilities at the Diamond Light Source.

Added value of Cebama: Cebama will benefit from access to archive samples and experience gained in national (e.g. NDA) and international (e.g. CEC SKIN) projects.

WP 2			ULOUGH

Planned training activities (if any): Uni Loughborough is a partner in the CEC CINCHII programme developing a pan-European Masters course in Radiochemistry. The PDRA will actively contribute to this programme.

Plans for dissemination:

- Publication in peer-reviewed journals
- Presentations at international (e.g. Migration), IGD-TP and national (NDA) conferences.

Deliverables and milestones proposed (the information will be integrated for the respective workpackages):

Milestones

- Finalisation of joint PDRA programme. Collation of archive cement materials (month 6)
- Synthesis/ characterisation of selected discrete phases for radionuclide incorporation (month 18)
- Completion of solubility and washout experiments (month 24)
- Completion of kinetic experiments on uptake and release for target radionuclides/phases (month 36)
- Synthesis of results and assessed contribution to multiphase assemblage behaviour, including comparison with bulk solubility and empirical washout data (month 42)
- Final reporting (month 48)

Deliverables

- Report on re-mobilisation of radionuclides encapsulated in archive cement
- Report on radionuclide uptake/release with synthesised pure phases
- Report on phase stability as a function of environmental parameters (redox, pH, CO_2) and impact on radionuclide mobility together with assessed relative contribution of target phases for each radionuclide under investigation
- Provision of data for modelling groups under WP3
- Two publications on scientific/technical programme and contribution to a further paper on implications for safety assessment

WP 2			CTU

Overall Objectives:)
Czech Technical University in Prague (CTU), Department of Nuclear Chemistry (DNS) will contribute to experimental program focusing on study of ^{226}Ra interaction with cementitious materials. The planned experimental study will render data for the development of models of interaction of Ra with cementitious barrier materials and to the preparation of methodology necessary for a case study of LLW-ILW repository Bratrstvi (CZ) that is of SURAO interest. The laboratory of CTU-CEG will help with the preparation of cementitious samples of composition consulted with SURAO.

Objectives for different specific steps/periods (if applicable):

- Project year 1 - state-of-the-art, planning, preparation and characterisation of selected cementitious materials including basic description of their sorption qualities.
- Project years 2-3 - laboratory sorption, leaching and diffusion experiments.
- Project year 4 – completing of set of experiments necessary for the working out of a mathematical model of Ra interaction and transport in cementitious barrier materials, aiming mainly the description of Ra behaviour in the of LLW-ILW repositories in tze Czech Republic.

Main expected outcome:

- Characterization of Ra interaction with cementitious barrier materials used in repositories and application of them for the model description of Ra transport.

Description of work to be performed:
Both sorption/retention and leaching from cement matrix containing modelled radioactive waste will be studied using batch and diffusion techniques. The experimental program will be held in close cooperation with UJV Rez, where interaction of cement with other critical radionuclides will be studied. Selection of appropriate cementitious materials, testing their physical (in cooperation with CEG) and chemical qualities; execution of laboratory sorption, leaching and diffusion experiments with ^{226}Ra; preparation of data for the formulation of models.

Cooperations
CTU-DNS will closely cooperate with UJV Rez in laboratory experiments and with CTU-CEG in physical characterization of selected cements. The programme is fully supported by SURAO, the responsible implementor for Bratrstvi LLW/ILW repository. The experimental plan, practical problems and model formulation will be also consulted with RATEN and KIT.

Planned training activities (if any): involvement of 1-2 Ph.D. students and 1-2 pre-graduates

Plans for dissemination: International conferences, articles in journals; transfer of data and experience with experimental work within the project and to SURAO as an end-user.

WP 2			PSI

Overall Objectives:
PSI/Empa will jointly study the mechanisms controlling the retention of redox-sensitive anions (Se, I) by AFm-phases at high pH under well-defined redox conditions and their competition with sulfide. The ion-exchange behavior of Se and I onto relevant AFm phases will be investigated and thermodynamic solid solution models will be developed.

Objectives for different specific steps/periods (if applicable):
- Quantitative determination of Se and I uptake by relevant AFm phases and their competition with sulphide.
- Structural description of Se(IV), Se(-II), S(-II) and I^- containing AFm solid-solutions and their end-members
- Thermodynamic modelling of the retention processes on AFm phases and hydrated cement using the Gibbs free energy minimization selector (GEMS) approach

Main expected outcome:
- A macroscopic (wet chemistry) and structural description of Se(IV), Se(-II), S(-II) and I^- containing AFm solid-solutions and their end-members
- A thermodynamic model describing Se(IV), Se(-II), S(-II) and I^- containing AFm solid-solutions and their end-members
- Predictions of anion uptake by hydrated cement based on the solid solution modelling

Description of work to be performed:
- Synthesis of Se(IV), Se(-II), S(-II) and I^- containing AFm solid-solutions
- Characterization of Se(IV), Se(-II), S(-II) and I^- containing AFm solid-solutions with XAS, XRD-Rietveld, TG, IR
- Construction of a thermodynamic model describing the formation of Se(IV), Se(-II), S(-II) and I^- containing AFm solid-solutions
- Calculation of anion uptake by hydrated cement based on this solid solution model

Cooperations

- *Close collaboration with Empa, KIT-INE, BRGM and Amphos21 on experimental sorption work*

Planned training activities (if any):
PhD student should receive training in XRD/Rietveld, EXAFS data analysis and thermodynamic modelling

Plans for dissemination:
- Presentations at international conferences (e.g., Goldschmidt Conference, Migration conference)
- Publication of experimental results in well-known peer-reviewed scientific journals (e.g., Environmental Science & Technology, Applied geochemistry,…).

WP 2			EMPA

Overall Objectives:

Empa/PSI will study the mechanisms controlling the retention of redox-sensitive anions (S, Se, I) by AFm-phases at high pH under well-defined redox conditions and their competition with sulfide**.** **Empa** will focus on the Se and S anion exchange behavior at high loadings and the development of thermodynamic solid solution models. This work will be carried out in close collaboration (a shared PhD student) with PSI.

Objectives for different specific steps/periods (if applicable):

- Quantitative determination of S and Se uptake by relevant AFm phases at high S and Se loadings.
- Structural description of S(-II), Se(IV), Se(-II) containing AFm solid-solutions and their end- members.
- Thermodynamic modelling of the retention processes on AFm phases and hydrated cement using the Gibbs free energy minimization selector (GEMS) approach

Main expected outcome (in close collaboration with PSI):

- A macroscopic (wet chemistry) description of Se(IV), Se(-II) and S(-II) containing AFm solid- solutions and their end-members
- A thermodynamic model describing Se(IV), Se(-II) and S(-II) containing AFm solid-solutions and their end-members

Description of work to be performed:

- Synthesis of S(-II), Se(IV) and Se(-II) containing AFm solid-solutions.
- Characterization of S(-II), Se(IV) and Se(-II) containing AFm solid-solutions with XRD-Rietveld, TG, IR.
- Construction of a thermodynamic model describing the formation of Se(IV), Se(-II) and S(-II) containing AFm solid-solutions based upon experimental data obtained by PSI and our own experimental data.

Cooperations

- Close collaboration with KIT-INE, BRGM and Amphos21 on experimental sorption work

Planned training activities (if any):

PhD student should receive training in XRD/Rietveld and thermodynamic modelling

Plans for dissemination:

- Presentations at international conferences (e.g., Goldschmidt Conference, Migration conference)
- Publication of experimental results in well-known peer-reviewed scientific journals (e.g., Environmental Science & Technology, Applied Geochemistry,…).

APPENDIX 2

PARTNER WORK DESCRIPTIONS FROM KICK-OFF MEETING PRESENTATIONS

Partner Summary slides

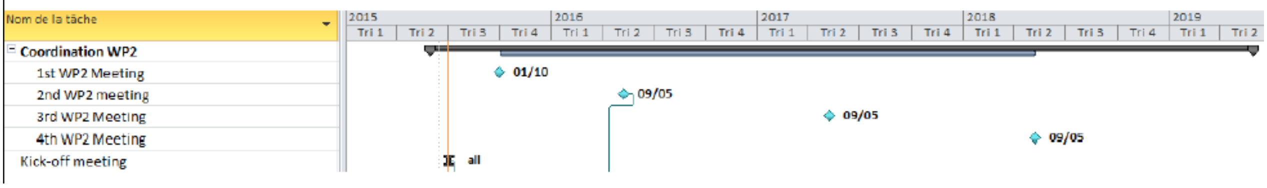
Cebama **KICK OFF MEETING/ WP2** HORIZON 2020

Work plan:
Radionuclide retention in high pH concrete

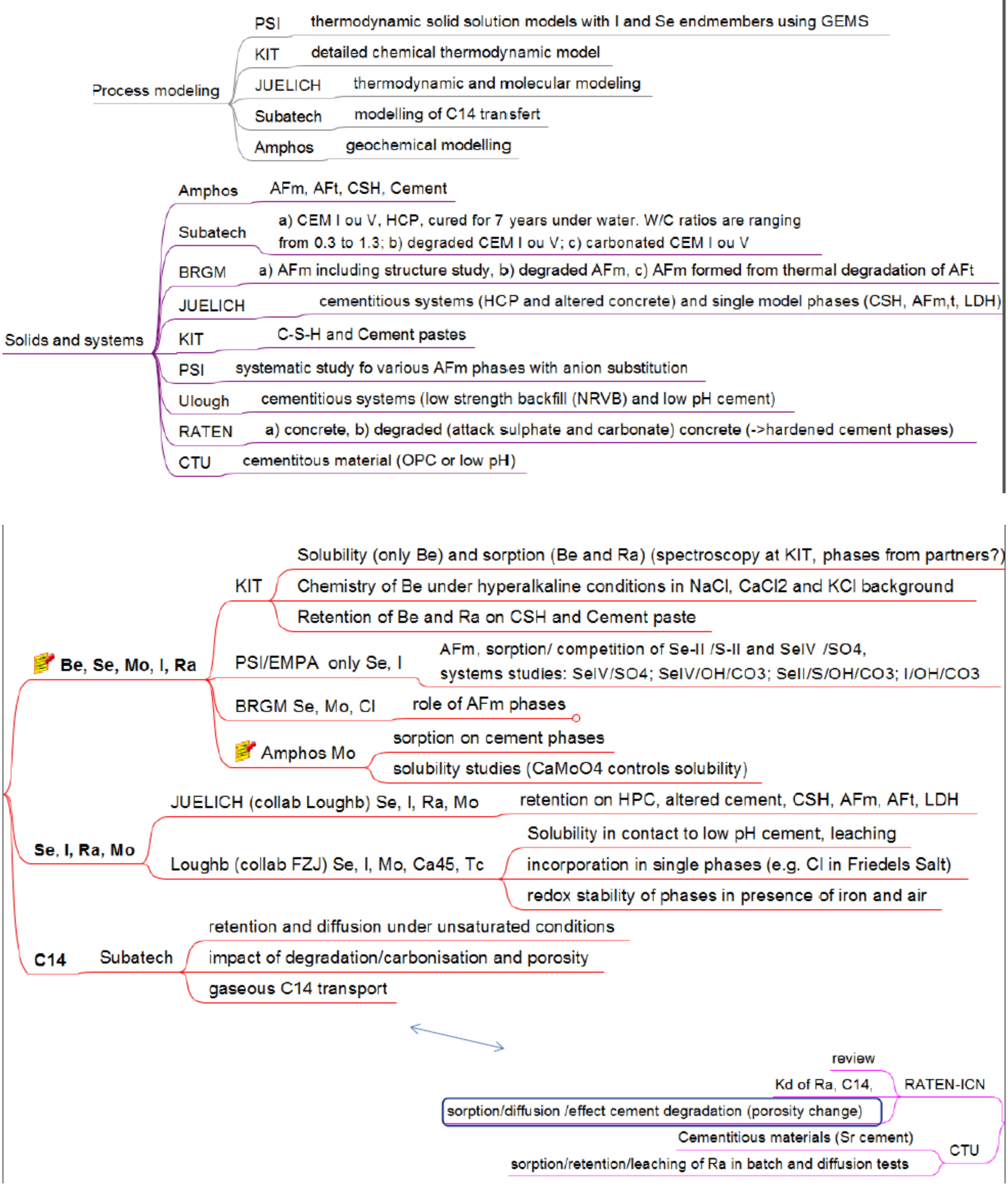
WP leader: B. Grambow, SUBATECH

10 partners
In total about 200 person month:

Amphos	20
BRGM	10,5
FZJ	15
RATEN-ICN	20
SUBATECH	34
ULOUGH	30
CTU	12
KIT	24
PSI	24,25
EMPA	13,75



Cebama /WP2 Overall view:



Cebama /WP2 PSI+Empa

- **Description of scientific work:**

  Se^{IV}, Se^{-II}, S^{-II} and I^{-I} binding by AFm phases under reducing conditions

  - Sorption studies with Se^{IV}, Se^{-II}, I^{-I} onto AFm phases
  - Reversibility studies
  - Synthesis and characterization of AFm solid solutions containing various ratios of Se^{IV}, Se^{-II},$S^{-II,}$ I^{-I} and X^{n} (X^{n-}=SO_4^{2-}, CO_3^{2-} or OH^{-}; **choice to be discussed with WP2 partners**)
    Characterization methods: ESEM, TG, IR, XRD+Rietveld refinement, XAS
  - Construction of thermodynamic models for binary Se^{IV}-X^{n-}, Se^{-II}-X^{n-}, S^{-II}-X^{n-} and I^{-I}-X^{n-} AFm solid solutions using the in-house GEMS Gibbs Energy Minimization software
  - 1 PhD planned if financing assured

- **Initial state of the art:**
  - Structure and thermodynamics of AFm-$X_{1/n}$ well known (X^{n-}=SO_4^{2-}, CO_3^{2-} and OH^{-})
    (E.g., Matschei et al., 2007. Cem. Concr. Res., 37, 1379; Renaudin et al., 1999. Cem. Concr. Res. 29, 63; Pöllmann et al., 1997. Neues Jahrb. Mineral. Monatsh. 423;…)
  - Uptake of Se^{IV} by AFm phases is strong
    (E.g., Baur et al., 2003, Environ. Sci. Technol., 37, 3442; Bonhoure et al. 2006. Cem. Concr. Res., 36, 91;…)
  - Sorption of Se^{IV} and Se^{-II} onto AFm phases strongly depends on the type of interlayer anion (X^{n-}).
    ⇒ Indication for Se^{IV} and Se^{-II} intercalation in some AFm phases
    (Rojo et al., 2015. In prep.)

- **Interactions with partners**

  Collaboration with: Amphos21, BRGM, KIT/INE, others?

  Fields of collaboration under discussion:

  – Use of the same cement phases – same synthesis procedures

  – Application of similar experimental protocols for sorption / co-precipitation experiments

  – Use of each others research facilities / equipment

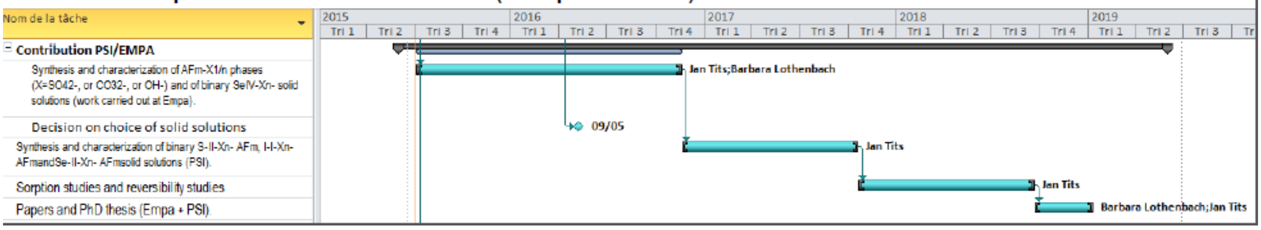
- **Detailed planning (internal milestones and deliverables)**

  – Synthesis and characterization of AFm-$X_{1/n}$ phases ($X=SO_4^{2-}$, or CO_3^{2-}, or OH^-) and of binary Se^{IV}-X^{n-} solid solutions (work carried out at Empa). M 18

  – Synthesis and characterization of binary S^{-II}-X^{n-} AFm, I^{-I}-X^{n-} AFm and Se^{-II}-X^{n-} AFm solid solutions (PSI). M 30

  – Sorption studies and reversibility studies with Se^{IV}, Se^{-II}, I^{-I} onto AFm phases (PSI). M 42

  – Papers and PhD thesis (Empa + PSI). M 48



Ce ba ma WP2

KIT Karlsruhe Institute of Technology

HORIZON 2020

KIT-INE

i. Aquatic chemistry and thermodynamics of Be under alkaline to hyperalkaline conditions

- Undersaturation solubility experiments with $Be(OH)_2(s)$
- Anoxic atmosphere: Ar-gloveboxes
- $7 \leq pH_m \leq 14$
- Background electrolytes: NaCl, KCl and $CaCl_2$ ($I \leq 3.0$ M)
- Complementary experiments in the presence of carbonate
- Accurate solid phase characterization by XRD, SEM–EDS, XPS and quantitative chemical analysis

Main goals:

- Derive chemical, thermodynamic and (SIT) activity models for Be under conditions relevant for cementitious systems (and beyond)
- Provide robust solubility upper limits for source term estimations

=> No deviation from the original workplan

ii. Interaction of Be and Ra with C-S-H phases and cement

- Uptake of Be and Ra by C-S-H phases ($0.7 \leq Ca:Si \leq 1.5$) and cement
- Sorption isotherms with increasing [Be]
- Anoxic atmosphere: Ar-gloveboxes
- $10 \leq pH_m \leq 13.3$ (as buffered by C-S-H phases and cement)
- Accurate solid phase characterization by XRD, SEM–EDS, XPS and quantitative chemical analysis
- Assessment of the retention mechanism: adsorption vs. solid solution formation

Main goals:

- Development of improved chemical models based upon detailed molecular level information via advanced spectroscopy and radioanalytics.
- Quantification of retention processes, input for source term estimations.

=> No deviation from the original workplan

Detailed planning (internal milestones and deliverables)

Year 1

- Literature review
- Synthesis and characterization of Be solid phase
- Start of solubility experiments with $Be(OH)_2(s)$ (absence of carbonate)
- Selection of cement phases for Be/Ra uptake studies (coop. PSI, EMPA, AMPHOS21, BRGM)

Year 2

- Completion of Be solubility studies in absence of carbonate
- Start of Be solubility studies in presence of carbonate
- Start of uptake experiments with Be and Ra

Year 3

- Completion of Be solubility studies in presence of carbonate
- Peer reviewed publication on Be aquatic chemistry **(D2.1 KIT)**
- Completion of Be uptake experiments

Year 4

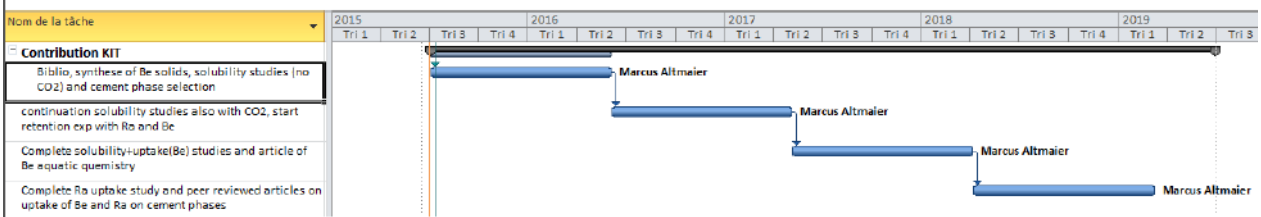
- Completion of Ra uptake experiments
- Peer reviewed publications on Be and Ra uptake by cement phases **(D2.2 and D2.3 KIT)**

Cooperation with other partners:

PSI/EMPA/BRGM/AMPHOS/KIT

- use of the same cement phases and same synthesis procedures
  => KIT focusing on C-S-H phases and cement (fresh)
- use similar experimental protocols for sorption experiments, co-precipitation experiments
- use of codes for thermodynamic modelling of the radionuclide uptake
- use each other's facilities/equipment for specific types of analysis
  => KIT facilities open to other partners of the consortium

Cooperation of KIT on Ra retention with RATEN and CTU under discussion



Cebama /WP2 BRGM

- AFm are layered double hydroxides found in cementitious environments. They are foreseen to play a pivotal role on the fate of anion, through sorption/incorporation mechanisms.
- Retention and incorporation capacities are certainly driven by AFm crystallographic structure, including crystal size, and nature of the layer charge (e.g., isomorphic substitutions, vacancies).
- This study will focus on the:
  - determination of exchange constants for a set of anions of interest, and structure of the resulting phase.
  - influence of the nature and density of the layer charge on anion retention capacities
  - kinetics and mechanisms of AFm degradation, and their influence on anion retention capacities.

- Previous publications by Aimoz and coworkers have demonstrated that understanding the nature of the product formed after interaction (including the position of the interlayer anion), is a fundamental prerequisite to a better capacity to understand and model its reactivity and thermodynamic properties.

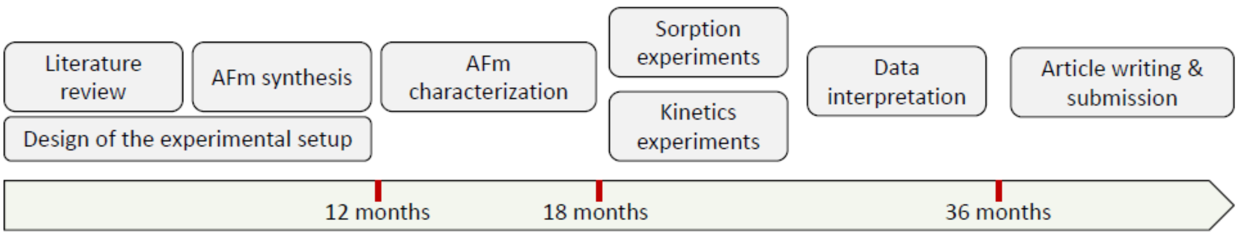
- This work will use AFm samples having varying reactivity (e.g., several samples having different nature and density of layer charge).

- Different anion of interest will be studied, in the Se/Mo/Cl competition system.

- BRGM will synthesis its own samples and could, if needed, provide some to partners. BRGM laboratories are opened to partners. The choice of samples should be discussed with partners.

- The first step will be the synthesis of AFm samples. A second step will consist in the determination of their properties (including nature and density of the layer charge). Then, several tests will be performed to determine the best experimental conditions required for experiments focusing on (i) anion retention and (ii) kinetics of AFm degradation. Although (i) is foreseen to be the first series of experiments, (i) and (ii) may be reversed if (ii) is found to experimentally easier.

- BRGM does not plan to deviate from its initial proposition.



Cebama /WP2 AMPHOS 21

• Description of scientific work

i. **Solubility studies.** A set of batch solubility studies of sodium molybdate under cementitious conditions. The composition and pH of such waters will be selected as a function of the equilibrium with target cementitious phases.

ii. **Synthesis and characterization of cementitious phases.** AFm, AFt and/or CSH gels (with two different Ca/Si ratios) will be synthesized and characterized.

iii. **Sorption/desorption (reversibility) tests.** MoO_4^{2-} sorption/desorption onto synthesized solid AFm, AFt and CSH phases will be analyzed by batch sorption experiments under air-tight conditions.

Sorption behavior of MoO_4^{2-} in ternary systems including competing anions such as **CO_3^{2-}, SO_4^{2-}** or **SeO_4^{2-}** will be also studied.

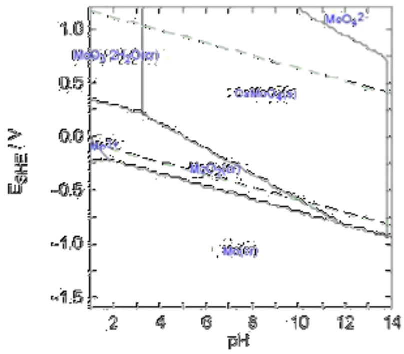
Kinetics of adsorption will be monitorised in terms of master parameters:

- Two solid-to-liquid ratios (i.e. 50 and 200 g/L)
- Two redox conditions (i.e. -230 < Eh(mV) < +300)

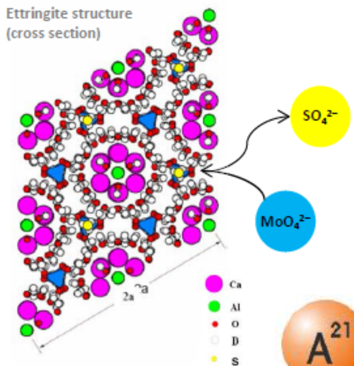
iv. **Modelling exercises.** Implementation and validation

Main techniques proposed for analysis and characterization of both solid and liquid phase: **XRD, XRF, TG-ATD, FT-IR, ICP-AES, XPS…**

• Initial state of the art



- Mo-93: activation product from the steel with a **half-life of 3500 years.**
- Mo is a redox-sensitive element with an aqueous **speciation dominated by molybdate** (MoO_4^{2-}) even at reducing conditions in a wide pH range.
- **Powellite** ($CaMoO_4$) is likely to control the solubility of Mo in the hyperalkaline waters resulting from cement degradation
- **In the presence of cement, AFt and AFm** phases are reported(*) to be the main phases for **molybdate immobilization** by means of two identified mechanisms:
  i. **Adsorption** onto the surfaces
  ii. Direct partial/complete **substitution for SO_4^{2-} or** OH^- in the interlayer regions.



(*) Chrysochoou, M., & Dermatas, D. (2006). Evaluation of ettringite and hydrocalumite formation for heavy metal immobilization: Literature review and experimental study. Journal of Hazardous Materials, 136(1), 20-33.

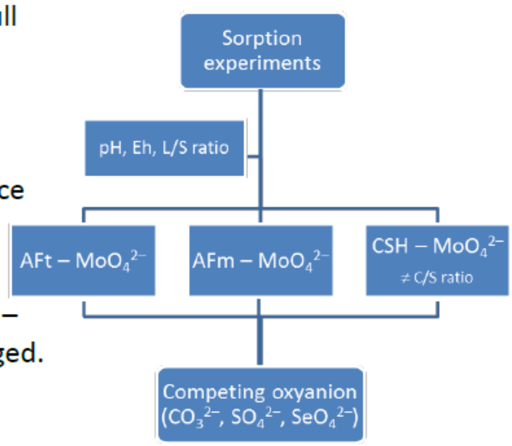
Kindness, A., Lachowski, E. E., Minocha, A. K., & Glasser, F. P. (1994). Immobilisation and fixation of molybdenum (VI) by Portland cement. Waste management, 14(2), 97-102.

Zhang, M. (2000) Incorporations of oxyanionic B, Cr, Mo and Se into hydrocalumite and ettringite: Application to cementitious systems. PhD thesis, Canada.

• Systems to be studied

Molybdate sorption/desorption onto different cementitious phases will be analyzed by batch tests at different porewater conditions (pH, Eh, L/S ratio):

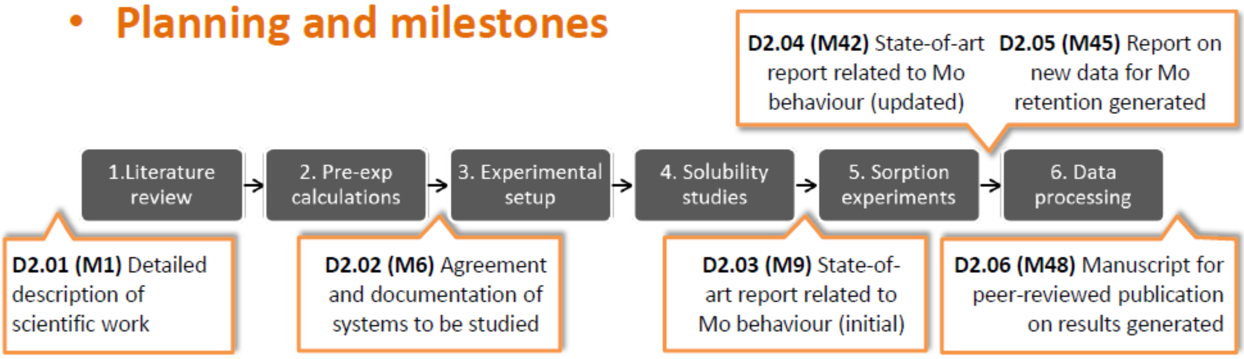
- **AFt – MoO_4^{2-}:** Solid solution through partial or full replacement of SO_4^{2-} by MoO_4^{2-} ?
- **AFm – MoO_4^{2-}:** Solid solution (also) formed between molybdate and these structures?
- **CSH – MoO_4^{2-}:** No specific studies done. Relevance of CSH vs Mo immobilization? Importance of different C/S ratios?
- **Anionic competitive effect?** Systems **CEM phase – MoO_4^{2-} – (CO_3^{2-}, SO_4^{2-}or SeO_4^{2-})** are also envisaged. to acknowledge the side effects of **competing oxyanions** present in the system over the reversibility and kinetics of Mo uptake.



• Interaction with partners

- Collaboration among the different participants will be stablished. KIT, PSI, EMPA, AMPHOS 21, BRGM
  - Agreement on the same synthesis procedures of the studied cement phases
  - Agreement on the use of same experimental protocols for equivalent experiments
  - Agreement on performing modelling exercises of RN uptake by using different codes **(link to WP3)**
  - Agreement to use facilities for both, experimental and modelling exercises
- AMPHOS 21 will develop this scientific work with close collaboration and support from **ANDRA.**

• Planning and milestones



Cebama /WP2 CTU in Prague

- **Description of scientific work**

Both sorption/retention and leaching from cement (portland or low pH) matrix containing modelled radioactive waste will be studied using batch and diffusion techniques.

Preparation of data for the formulation of advanced models (ion-exchange, surface complexation, diffusion).

- **Initial state of the art**

Laboratory is experienced in standard techniques necessary for interaction and diffusion studies.

The laboratory equipment available enables to work with a broad set of radionuclides.

The methodology of ^{223}Ra generation is being developed:

$$^{226}Ra(n,\gamma)\,^{227}Ra \rightarrow {}^{227}Ac \rightarrow {}^{227}Th \rightarrow {}^{223}Ra$$

(~1 MBq quantities available every two weeks)

Helena Filipská,
Dušan Vopálka
Department of Nuclear Chemistry
(DNC)

- **Systems to be studied**

Ra interaction with cementitious materials, the system Sr – cement will be studied for methodological reasons.

- **Interactions with partners**

The focusing on system Ra – cement was initialized by SURAO interest about a case study of LLW-ILW repository Bratrstvi (CZ).

The laboratories in CTU and UJV will collaborate in the preparation of samples of selected cement and by characterization of them.

- **Internal milestones**

Experimental study would give data for the development of models of interaction of Ra with cementitious barrier materials.

Methodological contributions to the application of models based on laboratory results in transport models necessary for near-field region description (GoldSim, PHREEQC – realization in WP3).

Cebama /WP2 RATEN ICN

- Description of scientific work: To investigate C-14 and Ra-226 retention and diffusion in high pH concrete and the influence of the concrete ageing on radionuclide retention

- Initial state of the art:
  - C-14 sorption/desorption and diffusion experiments on intact concrete samples
  - Experience on DTA/TGA investigation on concrete in different degradation stage
  - No previous experience on Ra-226 sorption and diffusion on concrete samples

- **Systems to be studied**: high pH concrete system
  - fresh concrete samples
  - concrete samples accelerated degraded in RATEN-ICN laboratory
  - ~~concrete~~ hardened cement paste samples provided by SUBATECH (fresh and degraded?)
- **Interactions with partners**:
  - SUBATECH to provide degraded ~~concrete~~ hardened cement paste samples (also fresh)
  - For Ra-226 experiments, the KIT-ITU experience with this radionuclide will be used, especially in Ra measurement at very low concentration

- **Detailed planning** (internal milestones and deliverables):

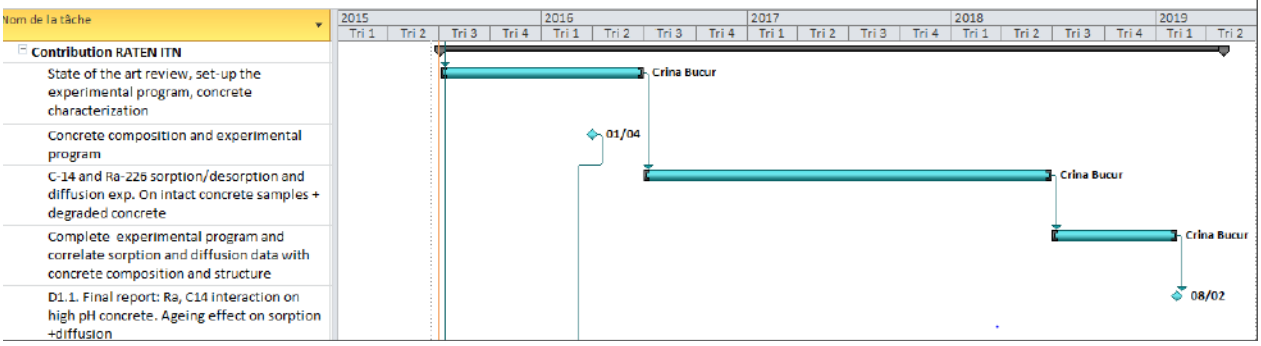
✓ Year 1: State of the art review, set-up the experimental program, concrete characterization (mercury intrusion porosimetry, SEM/EDX, DTA/TGA and XRD analysis)

✓ Year 2 and 3: C-14 and Ra-226 sorption/desorption and diffusion experiments on intact concrete samples and on concrete in different degradation phases; concrete degradation tests

✓ Year 4: Completing the experimental program and correlation of sorption and diffusion data with concrete composition and structure.

  – M1.1. Concrete composition and experimental program – M8

  – D1.1. Final report: RN interaction with high pH concrete. Ageing effect on radionuclide (C-14 and Ra-226) sorption and diffusion – M40



Cebama /WP2 Armines

- **Description of scientific work:**

Determination of the transport parameters of inorganic ^{14}C species (aqueous and gas) through unsaturated hardened cement pastes (HCP) –(CEMI and V available). Influence of RH and water degradation.

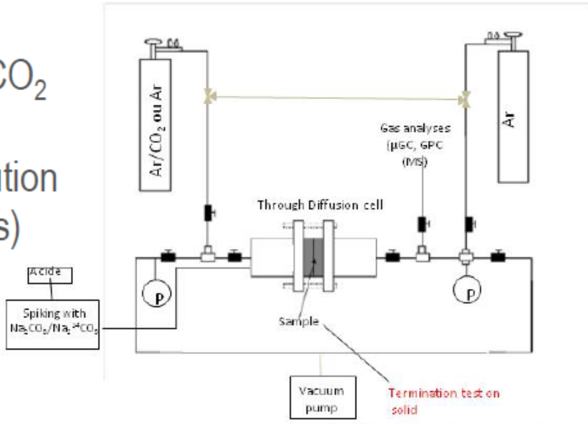
Experimental approach based on Through Diffusion experiments

- *Application of the osmotic technique to the diffusion of aqueous species (carbonate ions) under high saturation conditions (85% < RH < 100%)*

  Principle : suction generated by the osmosis process between the pore water and a highly concentrated solution of macromolecule separated by a semi-permeable membrane (difference of chemical potentials) → partial insaturation

- *"Classical" gas Through-Diffusion experiments → Determination of diffusion coefficient under unsaturated conditions (65% < RH < 85%)*

Generation *in situ* of radiolabelled $^{14}CO_2$
→ mixture of $^{14}CO_2/CO_2$
RH imposed by the use of saline solution
Carbonation level controlled (samples)



Adapted from Sercombe *et al*, CCR 37, (2007) 579-588

Experimental approach

Change to appendix B: replace percolation tests by osmotic diffusion tests

- *Geochemical modelling (PhreeqC) taking into account different chemical processes (sorption, incorporation, coprecipitation, isotopic exchange,…)*

- **Initial state of the art**

  - ○ ^{14}C highly sorbed on (non carbonated) cement paste ($10^3 < Rd < 10^4$ L/kg) depending in pH (*ie* : water cement degradation)
    Complex retention behaviour (isotopic exchange, sorption and/or incorporation)
    (E.g., Pointeau et al., 2008. Radiochem. Acta, 96, 367-374;...)

  - ○ Very few data under insaturated condtions (only for ^{3}HTO)
    (E.g. Bejaoui et al, 2006, Revue européenne de Génie Civil, 10, 1073-1106)

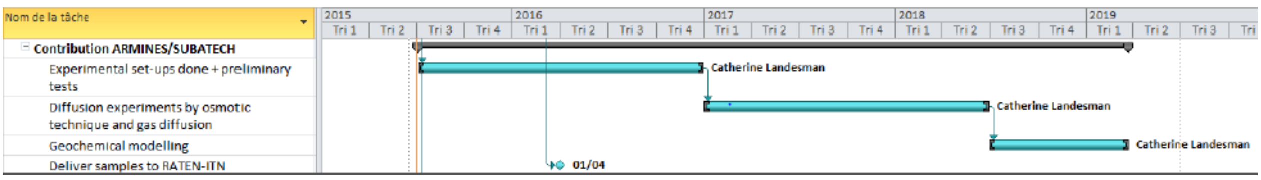
  - ○ To our knowledge, no application of the osmotic technique to cement materials (except currently experiment on HTO/^{3}H system at CEA/Saclay)

- **Interaction with partner**

  - ○ RATEN-ICN : work on common materials (HCP)

- **Detailed planning (internal milestones and deliverables)**

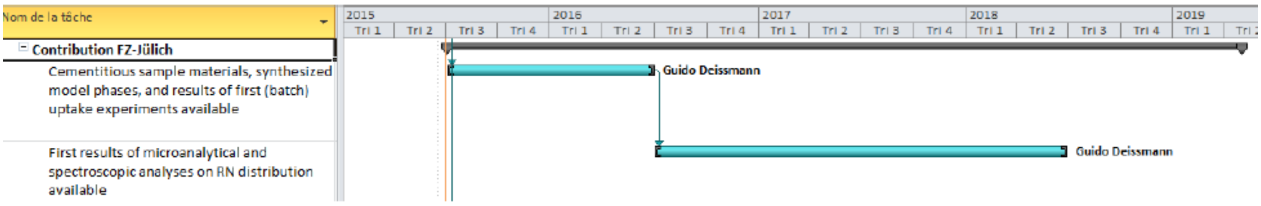
○ Experimental set-ups done + preliminary tests	M 18
○ Diffusion experiments by osmotic technique	M 36
○ Gas Diffusion experiments	M 36
○ Geochemical modelling	M 45



Cebama /WP2 JUELICH

- Description of scientific work:
  - Experiments on the uptake of selected long-lived long-lived fission and decay products in cementitious systems and on single model phases
  - Determination of RN distribution between and within various phases using advanced microanalytical and spectroscopic techniques
  - Experimental investigation of long-term alteration effects regarding RN release/re-distribution and microstructure development
  - Thermodynamic modelling of phase stabilities and RN bearing solid-solutions
  - Molecular modelling/atomistic modelling of RN incorporation and uptake
- Initial state of the art:
  - Long-standing experience with phase synthesis and experiments on RN-uptake by secondary phases, micro-/nano-scale characterisation of reaction products, and interpretation of RN-uptake experiments using thermodynamic and molecular modelling
- Systems to be studied:
  - Bulk cementitious systems (fresh and carbonated HCP/concrete) and model phases (CSH, $AF_{m,t}$, LDH)
  - RN: Se-79, I-129, Ra-226 and Mo
- Interactions with partners:
  - Cooperation with ULOUGH on RN uptake and RN solid speciation in cementitious systems (shared PDRA)
  - Information exchange with USFD regarding consequences of alteration processes on materials properties
- Detailed planning:
  - Preparatory phase (agreement on detailed objectives/programmes with collaborating institutions, set up of experiments, start of fabrication/synthesis of cementitious sample materials/ model phases (6 month)
  - Delivery of the main experimental programme (36 month)
  - Synthesis of results and implications for process models and safety assessments (6 month)

- Detailed planning (internal milestones and deliverables):
  - Cementitious sample materials, synthesized model phases, and results of first (batch) uptake experiments available (month 12)
  - First results of microanalytical and spectroscopic analyses on RN distribution available (month 24)
  - Deliverables:
    Contributions to D2.1 … D2.5
    S&T contributions to workshop proceedings and WP summaries



Cebama /WP2 Loughborough University

- **Description of scientific work:**

▪ Objective: Improved description of the transport of radioactive elements and the impact of chemical alterations (e.g. carbonation, redox) on radionuclide retention and transport.

▪ Loughborough's contribution;

- **Solubility and washout experiments** on selected radionuclides (^{36}Cl, ^{79}Se, ^{99}Tc, ^{129}I, ^{45}Ca) in cementitious systems (low strength backfill (NRVB) and low pH cement). Washout experiments will be performed on archive samples containing the radionuclides of interest.

- Solution analysis by gamma spectrometry, LSC, ICP-MS.

- Solids by (μ)XRD, ESEM and digital autoradiography.

- **Synthesis and characterisation of single mineral phases** capable of incorporating the above radionuclides (e.g. Friedel's Salt - ^{36}Cl) using advanced nano/microanalytical and spectroscopic techniques, including μXRD, EXAFS, TEM, ESEM, NMR, Raman/IR-spectroscopy and AFM.

- Determination of **uptake and release kinetics** for target radionuclides in each phase and assessment of their prospective contribution to multiphase cement assemblages.

- Investigation of the **impact of changing redox and pH conditions** on radionuclide speciation and solubility and their effect on cement phase stability. Experiments will be carried out in air, under N2, CO2 and in the presence of metallic Fe, respectively;

- **Initial state of the art/Previous work**

Related publications

- E. van Es, J. Hinchliff, M. Felipe-Sotelo, A.E. Milodowski, L.P. Field, N.D.M. Evans, D. Read. Retention of chlorine-36 by a cementitious backfill. Mineralogical Magazine (2015) in press.

- M. Felipe-Sotelo, J. Hinchliff, D. Drury, N.D.M. Evans, S. Williams, D. Read. Radial diffusion of radiocaesium and radioiodide through cementitious backfill. Physics and Chemistry of the Earth (2014) 70-71 60-70.

- M. Felipe-Sotelo, J. Hinchliff, N. Evans, P. Warwick, D. Read. Sorption of radionuclides to a cementitious backfill material under near-field conditions. Mineralogical Magazine (2012) 76(8), 3401-3410.

Related projects

- Experiments to Demonstrate Chemical Containment in the near field. Principal investigator: Prof David Read. Funding: NDA (National Decommissioning Authority). From October 2008 to March 2015.

- SKIN, Slow processes in close-to-equilibrium conditions for radionuclides in water/solid systems of relevance to nuclear waste management , Collaborative Project under the Seventh Framework Programme of the European Atomic Energy Community (EURATOM).

- **Interactions with partners**

Uni Loughborough will cooperate closely with **JUELICH in WP2** based on a shared PDRA. The study will draw on extensive experience with cementitious materials at Uni Loughborough across the **Chemistry, Materials and Civil Engineering departments**. Access will be provided to state of the art phase characterisation facilities at the **Diamond Light Source**.

- **Detailed planning (internal milestones and deliverables)**

Milestones

- Finalisation of joint PDRA programme. Collation of archive cement materials (month 6)

- Synthesis/ characterisation of selected discrete phases for radionuclide incorporation (month 18)

- Completion of solubility and washout experiments (month 24)

- Completion of kinetic experiments on uptake and release for target radionuclides/phases (month 36)

- Synthesis of results and assessed contribution to multiphase assemblage behaviour, including comparison with bulk solubility and empirical washout data (month 42)

- Final reporting (month 48)

Deliverables

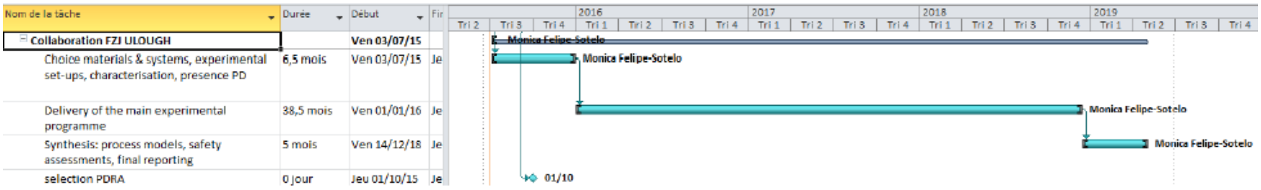
- Report on re-mobilisation of radionuclides encapsulated in archive cement

- Report on radionuclide uptake/release with synthesised pure phases

- Report on phase stability as a function of environmental parameters (redox, pH, CO_2) and impact on radionuclide mobility together with assessed relative contribution of target phases for each radionuclide under investigation

- Provision of data for modelling groups under WP3

- Two publications on scientific/technical programme and contribution to a further paper on implications for safety assessment



Cebama /WP2 JUELICH - ULOUGH

- Collaboration JUELICH – ULOUGH
  - Shared PDRA investigating the structural uptake of safety relevant radionuclides by cementitious materials and single cement phases
- Detailed planning
  - Selection of PDRA (month 3)
  - Finalization of detailed roadmap regarding materials & systems, experimental set-ups, characterization methods, presence of the PDRA at ULOUGH/JUELICH, facilities, internal deliverables (month 6)
  - Delivery of the main experimental programme (month 7 to 42)
  - Synthesis of results and implications for process models and safety assessments, final reporting (month 43 to 48)