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Deliverable D1.05

Report on WP1 selected experimental materials to be used, including both new laboratory and aged in-situ samples (M12 - May 2016)

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PU	Public	X
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the partners of the CEBAMA project	
CO	Confidential, only for partners of the CEBAMA project	

ABSTRACT:

CEBAMA Deliverable D1.05 summarizes experimental materials that will be investigated by the 19 partners participating in WP1. Here materials refer to cementitious materials (concrete, paste or cement), to clay based materials (either claystone, or bentonite) and groundwaters that mimic either clay or granitic environments. The report derives from original and updated project plans, follow-up information presented at the Project meeting in London (2015) and from surveys requested from all partners. Details about the materials that will be investigated by the different partners are listed in the appendices.

RESPONSIBLE PERSON(S):

WP1 co-leaders: Erika Holt (VTT), Francis Claret (BRGM), Urs Mäder (UniBern)

MAIN TEXT:

CEBAMA WP1 combines 19 partner projects that all study clay-cement systems by different experimental means that have already been detailed in the Deliverable D1.04. This report D1.05 focuses on the materials (clay or cement based as well as groundwater) that will be used by the different partners. Multi-barrier systems using these types of materials are foreseen in all disposal concepts for high-level radioactive wastes or spent nuclear fuel in Europe and the entire world.

Several European countries have developed or plan to develop disposal programmes which heavily rely on the use of cement-based materials. In order to illustrate this fact, specification about the cementitious materials under investigations in the different countries are given at the end of the appendix by the participant to the End-Users group of Cebama. The cementitious materials used by the different participants of the projects are in line with theses specifications (see Table 1). Portland-based cement materials mixed with among others fly ash, blast furnace slag and superplasticizers will be studied. In addition "low pH" cement formulations that contain additives like pozzolan and blast furnace slag will also be investigated. Advantages of "low pH" cements compared to Ordinary Portland based Cement cements are two-fold: (i) they have a low-heat hydration temperature, which minimizes the micro-cracking that can have negative consequences on cement's long-term durability, and (ii), their alkali content is low, which may reduce changes in clay in contact with this material compared to OPC. After the WP1 meeting in London in November 2015, the WP1 partners have identified the need for a benchmark low-pH concrete/paste for comparative studies. Based on their expertise, VTT and Andra have planned a ternary mix low-pH concrete, similar to the Posiva reference used in the DOPAS EU project but with silica fume and blast furnace slag rather than fly ash. VTT has casted the samples (~25 concrete and ~50 paste) and did quality control testing, including 28 and 91 days strength and pH leachate. This benchmark material is a good opportunity to strengthen collaborative studies between partners.

As also evidenced in Table 1, the studied clay materials are often reflecting the concept under investigation in the partner's country. For a granitic environment, the partners rather focus on bentonite materials, whereas in case of a clay host rock repository concept, natural host-rock formation will be used. The same finding can be applied to the groundwater that will be used in exposure of the cement-based materials.

Table 1: List of WP1 partners and materials

		Materials		Interface
		clay	concrete	
1	KIT	Bentonite	LpH	bentonit groundwater
3	BRGM	COX, Boom Clay	OPC, LPH	aged (URL, Mol)
4	BGS	COX	LPH [CEM I/SF/BFS blend]	aged and fresh
5	CIEMAT	Bentonite (FEBEX)	OPC	OPC/FEBEX
6	TUDelft	Boom clay	Portland fly ash unreinforced cement	fresh, but fully set
10	RWMC	Bentonitic (Kunigel)	OPC, Flyash mixed	5 to 10 years (lab / GTS)
11	SCK	Boom Clay	OPC (high strength/low por, low strength/high por)	aged (URL, Mol) + fresh
13	UJV	Ca-Mg bentonite (CZ)	OPC, LPH (VTT)	fresh + aged (Josef)
15	ULOUGH	COX & BVG	OPC (NRVB), LPH,	Interface with groundwater
16	CTU	bentonite (CZ, Ca-Mg)	OPC, LPH (VTT)	fresh + aged (Josef)
17	USFD	(None)	NRVB, PC - SF, PC - SF - FA	3 groundwater compositions
18	VTT	bentonite (MX80)	LPH	3 groundwaters / fresh samples
19	HZDR	Boom Clay and OPA	like SCK and like UniBE	like SCK and like UniBE
20	LML	COX	LPH	aged
21	UAM	FEBEX bentonite	OPC, LPH	Aged (GTS), Fresh(OPC or LPH)
22	CSIC	FEBEX bentonite	OPC and LPH	aged (GTS) + fresh + groundwater
23	ANDRA	COX	Low pH	fresh
25	UNIBERN	OPA	OPC, LPH	aged (Mont Terri)
26	IRSN	claystone (Tournemire)	LPH, OPC	aged: 1,2, 3 years
		1.2.1 claystone	OPC	aged interface claystone/cem.mat.
		1.2.2 bentonite	LPH	fresh interface claystone/cem.mat.
		no clay material		no interface clay/cem.mat.

APPENDIX: Detailed Answers per Partner, regarding their experimental materials

1. KIT/Bernhard Kienzler, Vanessa Montoya

We are using existing cementitious-material samples, as noted in Table below. We will produce some new samples, with a different superplasticizer compared to the Table results.

		MIX 1	MIX 3-A	MIX 3-B	MIX 3-C	MIX 3-D	MIX 3-E
		SKB R-12-	SKB R-12-	Garcia Calvo ea 2010	Garcia Calvo ea 2010	Garcia Calvo ea 2010	Garcia Calvo ea 2010 modified
Composition							
CEN-Norm sand	**g**	**0**	**1350**	**1350**	**0**	**0**	**0**
Quartz sand K20 (1.40-2.80mm)	**g**	**864.4**	**0**	**0**	**0**	**0**	**0**
Silica fume ELKEM 940U	**g**	**55**	**89.4**	**95.74**	**402.03**	**401.99**	**402**
Limestone filler*[1]	**g**	**0**	**56.999**	**61.02**	**256**	**256.31**	**0**
CEM I 52.5 N/SR3/NA (LAFARGE)	**g**	**82.5**	**133.96**	**143.6**	**603.01**	**603.1**	**603.07**
Water	**ml**	**230**	**187.02**	**137.41**	**502.98**	**503.05**	**402.03**
Superplasticizer (SiOxX, Elkem)	**g**	**2.553**	**4.17**	**2.41**	**10.12**	**0**	**0**
Production date		28.08.2014	3.12.2014	3.12.2014	4.12.2014	4.12.2014	4.12.2014
pH-Measurement							
Date		21.04.2015	23.04.2015	23.04.2015	23.04.2015	23.06.2015	24.06.2015
Messung nach Hydratationszeit (Tage)		236	141	141	140	201	202
Procedure		SKB R-12-	SKB R-12-	SKB R-12-	SKB R-12-	SKB R-12-	SKB R-12-
pH (triple measurement)		**10.87**	**11.45**	**11.68**	**11.64**	**11.71**	**11.71**
Standard deviation		0.02	0.01	0.02	0.01	0.02	0.01
Total mass	**g**	**1234**	**1822**	**1790**	**1774**	**1764**	**1407**

Benchmark samples (Low pH concrete provided by VTT) will be used by KIT-INE to perform diffusion and sorption experiments of different radiotracers (HTO, Cl and I) or toxic elements like Be (in connection with WP2). Diffusion experiments will be performed under non-disturb and disturbed system with bentonite porewater.

The same kind of experiments will be performed with low pH cement pastes prepared in KIT-INE in order to compare the results obtained.

The final aim is to transfer the experimental results obtained in WP1 to WP3 to apply reactive transport models.

3. BRGM/F. Claret

We plan to use existing cementitious-material samples, from both the percolation experiments and the 12 years interface that will be sample in the HADES underground research facility. A meeting has been conducted between SCK-CEN and BRGM in December 2015 in order to defined the best strategy to sample the HADES interface. A successful coring of the concrete-Boom clay interface has been carried out at the end of May 2016. Installation of two anchors (made by resin) during the drilling procedure to reinforce the concrete-clay interface have enabled to preserve both concrete and clay interfaces. Detailed of the material composition can be found in the SCK-CEN workshop contributions/proceedings.

4. NERC-BGS/Rob Cuss

BGS is generating new samples, in agreement with a recipe defined by Andra (Table below). They are not planning to use an existing cementitious-material samples.

Concrete has been defined by Andra; CEM I/SF/BFS blend (Tl).

Kg for 1 m³	**T_{cv}**	**T_L**
%Super plasticizer	1.5	1.5
Binder	375	380
Cement	140.6	76
Silica fume	121.9	123.5
Fly ash	112.5	
Blast furnace slag		180.5
Sand	845	855
Chippings	938	949
Aggregates		
Effective water E_{eff}	150	152
E_{eff}/L	0.4	0.4
G/S	1.1	1.1

Superplasticizer is chryso fluid Optima 175 (mass % compared to the ‘binder’: 1.5%, 5.7 kg for 380 kg of ternary blend TL); binder is ternary blend; cement is the CEM I 52.5 PM ES CP2 from Lafarge facility in Le Teil; Silica fume from Condensil (ref. DM95); Blast Furnace Slag from ECOCEM; Aggregates are limestone >95% (without any reactive silica for the last few % which are not limestone); Sand 0/4 mm; Gravels 4/12 mm

Concrete will be cast directly onto COx or concrete; these will be fully hydrated to ensure that the concrete does not dehydrate the COx.

A total of 24 samples will be prepared. Additional material may be available.

5. CIEMAT/María Jesús Turrero/Elena Torres/Tiziana Missana

Related to interfaces the plan is using existing aged cementitious-material samples whose details are given below. It is not planned to generate new samples.

- composition (material types, amounts/proportions)

  Bentonite FEBEX: used in both in situ-real scale and laboratory-small scale experiments. The FEBEX bentonite was extracted from the Cortijo de Archidona quarry (Almería, Spain). The physical-chemical properties of the FEBEX bentonite, as well as a summary of its most relevant thermo-hydro-mechanical and geochemical properties can be found in ENRESA (2006)*.

  Shotcrete plug of the real scale FEBEX experiment at GTS: based on ordinary Portland cement (CEM II A-L 32,5 R), with nanosilica, steel and polypropylene fibres (ENRESA, 2006).

  Concrete of the small scale laboratory experiment: based on sulfo-resistant ordinary Portland cement (CEM I 42.5 R/SR).

  **ENRESA (2006). FEBEX Full-scale Engineered Barriers Experiment, Updated Final Report 1994-2004. Publicación Técnica ENRESA 05-0/2006, Madrid, 590 pp.*

- exposure conditions (RH, temperature, groundwater/chemical exposure)

  Both experiments have been subjected to heating (100 ºC) and re-saturation with granitic (real scale experiment - Na^{+}-Ca^{2+}-HCO_3^{-} - natural Grimsel Test Site water – Table 1) or clayey (small scale laboratory experiment - Na^{+}-Ca^{2+}-SO_4^{2-}–type clay water – Table 2) groundwaters. In both cases, the temperature at the concrete-bentonite interface is lower than 40 ºC.

*Table 1. Granite water (molar concentration)**

Na	3.7×10^{-4}
K	2.3×10^{-5}
Ca	1.8×10^{-4}
Mg	1.7×10^{-5}
Cl	2.3×10^{-5}
SO_4	6.1×10^{-5}
F	2.2×10^{-4}
SiO_2	1.9×10^{-4}
HCO_3	4.0×10^{-4}
pH	9.7

**Turrero, M.J., Villar, M.V., Torres, E., et al. 2011. PEBS Project. Deliverable D2.3-3-1.*

*Table 2. Reference clayey water (molar concentration).**

Na	1.3×10^{-1}
K	8.2×10^{-4}
Ca	1.1×10^{-2}
Mg	8.2×10^{-3}
Cl	2.3×10^{-2}
SO_4	7.0×10^{-2}
SiO_2	2.7×10^{-4}
Fe_{tot}	1.1×10^{-5}
HCO_3	1.8×10^{-3}
pH	7.5

**Turrero, M.J., Fernández, A.M., Peña, J., et al. 2006. J. Iber. Geol. 32 (2), 233–258.*

- combined material exposure (adjacent to bentonite, metal, bedrock, etc)

  The studies will be made on the bentonite/shotcrete and bentonite/concrete interfaces.

- <u>age now, age at time of sampling, storage method of samples</u>

  The interface of the real scale in situ experiment has been operating for 13 years and the interface of the laboratory experiment will be in operation for 10 years.

  The samples coming from the in situ experiment are placed into a fridge preserved into vacuum-sealed aluminium bags. The laboratory experiment will be dismantled in an anoxic globe box and samples will be preserved in the same way.

- <u>number (or volume) of samples</u>

  A) Samples coming from overcorings drilled in the FEBEX real scale experiment before dismantling (Urs Mäder team, University of Bern). The preserved samples are 30-cm shotcrete and 35-cm bentonite, being the interface itself a core of 5cm-concrete plus 5cm-bentonite. We have a quarter of these cores shared with UAM to CEBAMA studies.

  B) Aged shotcrete/bentonite core samples obtained by dry drilling with a diamond coring machine in the FEBEX real scale experiment (AITEMIN, CIEMAT and UAM teams).

  C) Therefore, slices will be obtained from the dismantling of the small scale laboratory column experiment (HB). The experiment has 30 mm of concrete and 70 mm of bentonite.

- <u>ability or willingness to share samples with any other partners?</u>

  The samples will be shared with UAM (partner 21) and CSIC (partner 22).

Related to porosity characterization of cement materials under different chemical conditions details are given below:

- <u>composition (material types, amounts/proportions)</u>

  The cement initially used for these tests is CEM V (C3A (10.9 %); C3S (65.5 %); C2S (13.4 %); SO3 (2.9%) and S2- (0.15 %)). The cement powder will be hardened under anoxic conditions with a water/cement relation of 0.4/0.6 during 28 or 90 days, using Milli-Q-water previously boiled to minimize the effects of CO_2. After curing, the hardened cement paste will be grinded and sieved with a size < 63 µm.

- <u>exposure conditions (RH, temperature, groundwater/chemical exposure)</u>

  The cement will be used *fresh* (and a synthetic water representative of the fresh cement will be produced) and degraded to State II. The solid will be degraded by successive washings with deionised water and then equilibrated to a solution representative of the required degradation state. These experiments will be carried out under anoxic atmosphere and at a room temperature. Tests with carbonated materials are also foreseen. They will be carried out in a carbonation chamber with controlled CO2 / temperature / and humidity conditions.

- <u>combined material exposure (adjacent to bentonite, metal, bedrock, etc)</u>

  No

- <u>age now, age at time of sampling, storage method of samples</u>

All the samples are stored in an anoxic glove box under N2 atmosphere

- number (or volume) of samples
- 1 hardened cement paste cured 28 days other cured 3 months
- ability or willingness to share samples with any other partners?

Samples can be shared with the interested partners

6. TUDelft/Denis Bykov

We plan to generate new samples, with details as given below. We do not plan to use any existing cementitious-material samples.

Concrete samples:

Samples from certified concrete supplier
- Real life repository samples
- Mixing cement, water, aggregates, additives

COVRA smallest concrete supplier in the Netherlands
- CEM-III concrete
- Backfill foamed concrete

CEM-I HS (low in tricalciumaluminate content)

CEM-III HS LA

The concrete recipes that are planned to be used in Cebama are given in Tables below:

Waste package

Concrete composition for the disposal of compacted waste in 200 litre drums.

Component	Type		
Cement	CEM III/B 42.5 LH/SR	407-430	kg m^{-3}
Water	-	175-185	kg m^{-3}
Plasticiser	TM OFT-II B84/39 CON. 35% (BT-SPL)	3-5	kg m^{-3}
Fine aggregate	Quartz sand : 0-4 mm	819-972	kg m^{-3}
Coarse aggregate	Quartz gravel : 2-8 mm	891-763	kg m^{-3}

Reference Verhoef et al. Waste families OPERA-PG-COV023, to be published summer 2015.

Backfill

Composition enclosure emplaced waste (backfill – foamed concrete).

Component	Receipt for 1 m^3 of Aercrete FC 1200 to 1600 kg m^{-3}	Type for OPERA	1200 kg m^{-3}	1600 kg m^{-3}	
Cement	360 to 400 kg	CEM I SR 3 <3% C_3A	360	400	kg m^{-3}
Water	140 to 160 kg	-	140	160	kg m^{-3}
Fine aggregate	750 to 1100 kg	Quartz sand: 0-2 mm	750	1100	kg m^{-3}
Foaming agent Synthetic surfactant	0.57 to 0.36 l	Foaming agent TM 80/23 Synthetic	1	1	kg m^{-3}
Water	21.3 to 13.6 l	Water	21.3	13.6	kg m^{-3}
Air	434 to 277 l	Air	0	0	kg m^{-3}

Reference Verhoef et al. Cementitious materials in OPERA disposal concept in Boom Clay OPERA-PG-COV020, 2014

For Cebama also foamed concrete with CEM III.

Component	Receipt for 1 m^3 of Aercrete FC 1200 to 1600 kg m^{-3}	Type for OPERA	1200 kg m^{-3}	1600 kg m^{-3}	
Cement	360 to 400 kg	CEM III/B 42.5 LH/SR	360	400	kg m^{-3}
Water	140 to 160 kg	-	140	160	kg m^{-3}
Fine aggregate	750 to 1100 kg	Quartz sand: 0-4 mm	750	1100	kg m^{-3}
Foaming agent Synthetic surfactant	0.57 to 0.36 l	Foaming agent TM 80/23 Synthetic	1	1	kg m^{-3}
Water	21.3 to 13.6 l	Water	21.3	13.6	kg m^{-3}
Air	434 to 277 l	Air	0	0	kg m^{-3}

Clay samples:

Unoxidized samples from Rupel formation (Boom Clay) excavated from the depth 68–88 m. This formation is a marine deposit with a high saline content. The clay cores are about 50 cm long and about 10 cm in diameter, but for the experiments they are shaped into cylinders with 5 cm in length and 3 cm in diameter. The concrete samples are either cylinders with the same dimensions or cubes with the edge of 5 cm. The samples can be shared with partners, if needed.

10. RWMC/Hitoshi Owada

We plan to use existing cementitious-materials samples, as described below.

Table 1 List of "on going" Coupled Immersion Test

	Bentonite		Cement Paste				
No.	Material	Dry Density	Cement	Water/Cement Ratio	Water	Age (year)	amount
1	Kunigel V1	1.6	OPC	0.6	IEW	11	2
7	MX80	1.6	OPC	0.6	FRHP	11	1
8	MX80	1.6	OPC	0.6	Saline	11	2
9	Kunigel V1	1.6	FAC30	0.6	FRHP	11	1
10	Kunigel V1	1.6	FAC30	0.6	Saline	11	2

(1) Kunigel V1 is the Commercial Bentonitic material distributed by Kunimine Industryies which has 50 to 60% content of Na-Type montmorironite.

(2) MX80 is a Commercial Bentonitic material which has around 80% of Na-Type montmorironite.

(3) OPC has almost the same chemical formulation of CEM I in European Regulation

(4) FAC 30 is the mixture of 30wt% Fly ash and 70wt% OPC which classified into Fly Ash cement type C in Japan.

(5) IEW means Ion Exchanged Water

(6) FRHP is an artificial fresh groundwater which defined Japanese 2000 report.

(7) Saline water is the artificial sea water

Both of bentonitic and cementitious material are molded into 20 mm diameter and 20 mm thickness and coupled in the call just like a diffusion test. That cell have been being immersed in IEW, FRHP or saline water for 11 years under the condition of room temperature and Ar atmosphere.

Table 2 List of samples of "determination test"

<table>
<tr><th></th><th colspan="3">Bentonite</th><th colspan="2">Cement Paste</th><th></th></tr>
<tr><th>No.</th><th>Material</th><th>Dry Density g/cm^3</th><th>thickness</th><th>Cement</th><th>Water/Cement Ratio</th><th>Age (year)</th></tr>
<tr><td>1</td><td rowspan="4">Kunigel V1</td><td rowspan="3">1.6</td><td>10</td><td rowspan="6">OPC</td><td>0.45</td><td rowspan="10">7</td></tr>
<tr><td>2</td><td>5</td><td rowspan="9">0.6</td></tr>
<tr><td>4</td><td rowspan="8">10</td></tr>
<tr><td>3</td><td>1.2</td></tr>
<tr><td>5</td><td rowspan="2">MX80</td><td>1.2</td></tr>
<tr><td>6</td><td>1.6</td></tr>
<tr><td>7</td><td rowspan="4">Kunigel V1</td><td>1.2</td><td rowspan="2">FAC30</td></tr>
<tr><td>8</td><td>1.6</td></tr>
<tr><td>9</td><td>1.2</td><td rowspan="2">BFSC70</td></tr>
<tr><td>10</td><td>1.6</td></tr>
</table>

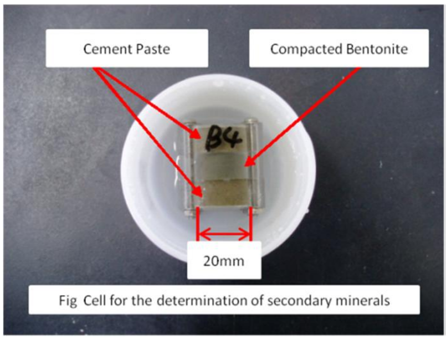

Fig Cell for the determination of secondary minerals

BFSC70 is the mixture of 70wt% blast furnace slag and 30wt% OPC which is classified into Slag cement type C in Japan.

Immersed in IEW for 7 years.

Few samples of the “determination of secondary minerals” are available to share with other partners.

Few number of “Bulky (20 mm X 20 mm X 20 mm) cement paste” samples of OPC, FAC and silica mixed cement are immersed in IEW, FRHP and saline water for 10years or longer. RWMC might be able to share those samples.

We do not plan to generate any new samples within CEBAMA. Yet , the generation of new samples depends on the plan of the Japanese national project. If we, RWMC, generate new samples in near future, then it may be possible to share samples as well.

11. SCK CEN/Norbert Maes; Quoc Tri Phung (with input from F. Claret, BRGM)

We plan to use existing cementitious-material samples, as described here.

- composition (material types, amounts/proportions): High strength concretes (Wedge Blocks) used as lining material in HADES URL – Connecting Gallery. Age of interface concrete/Boom Clay host rock ~13 years.

For 1 m^3 concrete	Cement kg	Fly ash kg	Coarse agg. kg	Fine agg. kg	Admixture, l		Water l
					SP	µsilica	
Connecting gallery	335 (CEM I)	115	1252	540	4.5	90	135
Praclay gallery	400 (CEM II – PFA)	-	1152	690	5	80	132

- exposure conditions (RH, temperature, groundwater/chemical exposure): saturated, clay pore water (main composition is ~0.014 mol/l $NaHCO_3^-$)
- combined material exposure (adjacent to bentonite, metal, bedrock, etc): Boom clay
- age now, age at time of sampling, storage method of samples: 13 years
- number (or volume) of samples: We are limited in taking samples from the interface Concrete lining/Boom Clay. But for our purposes, at least 2 drilled samples will be needed. More is possible but needs to be discussed with manager of URL. Besides interface samples, there are a few "witness" wedge blocks available from which cores can be taken for use.
- ability or willingness to share samples with any other partners? Yes, but keep in mind the previous remark.

We also plan to generate new samples, as described below.

- composition (material types, amounts/proportions): **High porosity cement pastes:**

Cement	Limestone filler/cement	Admixture	Water/cement
CEM I 52.5 N	3/1	SP = 1% cement	1.3

- exposure conditions (RH, temperature, groundwater/chemical exposure): **saturated; 22 °C; Boom clay pore water[1] (main composition is ~0.014 mol/l $NaHCO_3^-$)**,

Na	359 mg/l
K	7.2 mg/l
Ca	2.0 mg/l
Mg	1.6 mg/l
Fe	0.2 mg/l
Cl	26 mg/l
SO4	2.2 mg/l
HCO3	879 mg/l
DOC	115 mg/l
Eh (mV)	-274 mV vs SHE
pCO2 (atm)	$10^{-2.62}$ atm
pH	8.5

- combined material exposure (adjacent to bentonite, metal, bedrock, etc):
  - batch experiments in which a cement sample is immersed in Boom Clay suspensions
  - column experiments:
    - Boom Clay plug in contact with cement plug and Boom Clay pore water is forced under pressure to flow through the samples ("percolation type of experiments similar to set-ups used to study radionuclide migration through Boom Clay cores used at SCK•CEN)
    - Cement plug only, percolated with Boom Clay pore water
- number (or volume) of samples: For each test condition, tests will be set up for dismantling/further treatment after different periods of interaction time (~3–4 sampling periods). Tests will be done in double.
- ability or willingness to share samples with any other partners? Yes (we collaborate with BRGM, part of the samples will be transferred to them for post analysis). Samples can also be prepared for other users, but depends on availability of "percolation cells" & peripheral equipment.

[1] De Craen M., Wang L., Van Geet M., Moors H. (2004) Geochemistry of Boom Clay pore water at the Mol site – status 2004. SCK•CEN report BLG-990, Mol, Belgium.

13. UJV/Petr Večerník, Radek Červinka, Václava Havlová

We plan to use existing cementitious-material samples, as follows.

Cement CEM II /A-S 42,5 R, product of Lafarge Cement, a.s., Czech Republic was used for preparation of cylindrical samples. These samples were inserted into perforated tubes and placed into boreholes in URL Josef together with compacted bentonite samples. Samples are still located in the borehole under natural environment and conditions of underground gallery. These samples are 5 years old (2010) and will be used by ÚJV and CTU; detailed characterisation of samples preparation, the experiment conditions, storage and sampling will be described by CEG CTU, operating the URL Josef where this "in-situ experimental system" is placed.

The overall volume of cement samples is very small, so there is a limit to share samples among the other partners. We will try to share some, but we can't promise it.

We also plan to generate new samples.

Ordinary and low pH cement materials /will be used for preparation of experimental samples, that will be used in "laboratory experimental system". For preparation of the samples is responsible CEG CTU, which is responsible also on their physical and mechanical testing. UJV Rez is responsible for mineralogical characterisation, porosity, CEC, tracer studies etc. Testing samples of cement materials will be placed into experimental reactor and surrounded by bentonite suspension or groundwater obtained from Josef gallery. Some of the experiments will be heated up to 95 °C and some others will be stored in the underground in Josef gallery conditions.

Due to the new procedures of sample preparation, we are able to share samples prepared for experiments (fresh ones); amount of the samples after experiments (aged samples) will be limited.

15. ULough/Matthew Isaacs, Monica Felipe-Sotelo, David Read

The cementitious-material samples to be used in our experimental work will be prepared at USFD for deployment in experiments at both partner institutions. The formulation for the low pH cement blend will be provided by VTT.

16. CTU/Lucie Hausmannova

We plan to use existing cementitious-material samples. Samples from previous interaction experiments bentonite/cement will be used. One of the experimental procedures was carried as in-situ test in Josef gallery. For this purpose perforated tubes with tested materials (see Figure 1) were placed in borehole in 2010. One of this tubes was kept in the underground and will be dismantled during CEBAMA project (interaction time 60 months).

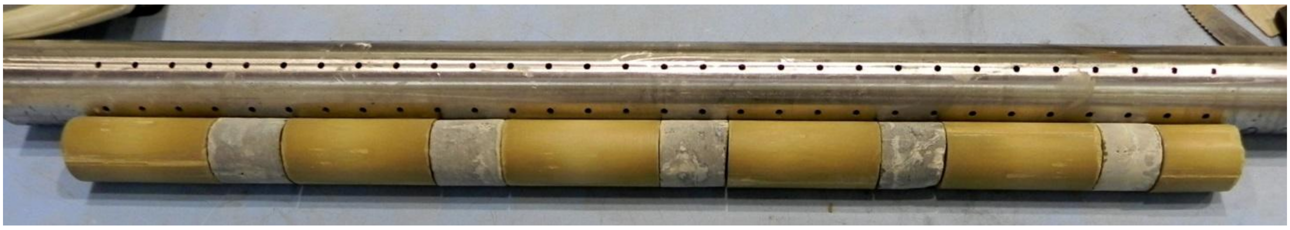

Figure 1 – Bentonite and cementitious prepared for placing into perforated tube (Vasicek et al. 2013).

Portland cement CEM II 42,5 R was used (chemical composition in Table 1); five cylindrical samples (diameter: 30 mm and height: 35–40 mm) were compacted to dry density of 1.8 Mg/m^3 and placed between bentonite samples from Czech Ca-Mg bentonite (Bentonite 75) as it is shown in Figure 1.

Conditions: Stable temperature ~9 °C. Natural saturation of samples (chemical composition of underground water is showed in Table 2).

CTU-CEG will study only bentonite from these cartridges, cement will be analysed by CTU-DNS and UJV.

Potential to share samples is very limited since there is only five samples which will be analysed by CTU-DNS and UJV.

Table 1 – Chemical composition of used cement (Vasicek et al. 2013).

Component	CEM II /A-S 42,5 R	Units
Lost by drying	1.95	%
SiO2	21.87	%
Al2O3	6.63	%
Fe2O3	2.04	%
TiO2	0.41	%
CaO total	59.94	%
MgO	2.55	%
Na2O	0.16	%
K2O	1.02	%
P2O5	0.23	%
MnO	0.067	%
SO3 total	2.40	%

Table 2 – Chemical composition of underground water in Josef gallery where samples were installed (Čelina P3) (Vasicek et al. 2013).

	Čelina, P3 20.5.2010	units
pH	7.70	
T	10.3	°C
Na	26.0	mg/l
K	1.8	mg/l
Mg	54.0	mg/l
Ca	125.5	mg/l
F	0.12	mg/l
Cl	10.48	mg/l
SO_4	174.7	mg/l
NO_3	15.56	mg/l
HCO_3	482	mg/l

We also plan to create new samples for our experimental work._ For this testing CTU will use OPC CEM II /A-S 42,5 R (composition will be published later), Low-PH cementitious powder blend (with fly ash and silica fume) (from VTT) and Czech bentonite (see Table 3). Exposure conditions are summarized in Table 1 of the previous page.

Table 3 – Chemical composition of Czech bentonite B75 (Vasicek et al. 2013)

	B75	**Units**
Loss in 1000 °C	10.65	%
SiO2	51.91	%
Al2O3	15.52	%
Fe2O3	8.89	%
TiO2	2.28	%
CaO	4.60	%
MgO	2.22	%
Na2O	1.21	%
K2O	1.27	%
P2O5	0.40	%
MnO	0.108	%
SO3 síran.	0.09	%
CO2	5.15	%
FeO	2.95	%
CaCO3	11.71	%

CTU can share samples from these ageing procedures, but request has to be made before preparation of materials for procedures (11/2015).

17. USFD/Claire Corkhill

We plan to use existing cementitious material samples. We have a number of relevant cement samples that will be 1.5 years old at the start of the CEBAMA project. These cements are being analysed for a 2 year period at the Diamond Light Source, where they are undergoing in situ XRD analysis of cement hydration. Thus, these samples will be extremely well characterised at the time of investigation, ca. 4 years old.

The cement compositions include:

- 1:1, 3:1 and 9:1 GGBFS/PC blends. The PC is CEM I 42.5N, Sellafield specification (low calcite, no organic grinding agents). w/s ratio 0.4
- CEM 1 42.5N and CEM 1 52.5R, w/s ratio 0.4
- Nirex Reference Vault Backfill (UK cement backfill candidate), w/s ratio 0.6

All cements are cured in ambient conditions (20 ± 2 °C, no humidity control).

We also plan to generate new samples for our work. We intend to produce large batches of cement-based materials (in 50 mL tubes & 5 cm^3 cubes) to share with UK partners at ULough. We are happy to extend this to other partners if requested. Cement synthesis will occur in Nov/Dec 2015. We intend to prepare the following:

Table 1. Paste samples, curing time and conditions, and interface for analysis, prepared at USFD.

Cement	Composition	Curing time	Interface to be examined	Exposure conditions
Nirex Reference Vault Backfill (NRVB)	PC (40 wt%), CaCO3 (45 wt%), Ca(OH)2 (15 wt%) Water added to a w/s ratio of 0.55	28, 90, 180 days 1, 2, 3 years	1. Granitic GW 2. COx GW 3. High ionic strength GW 4. with/without added bicarbonate	1. 20 °C 2. 20 °C controlled CO2 3. 20 °C anoxic atmosphere
CEM III/B (analogous to UK BFS/PC cement)	3:1 GGBFS/PC w/s ratio of 0.35			
CEM I silica fume blend	As per NAGRA formulation			

In addition the University of Sheffield is conducting groundwater exposure tests on their cement compositions. For this purpose, three different types of groundwater will be used:

- *Granitic groundwater* simulates groundwater in granitic terrain (Allard water), after [1]. The composition represents groundwater between 100 - 500 m in Swedish bedrock [2].

- *Saline groundwater* simulates deep saline groundwater (NASK water), after [1]. The composition represents groundwater found at 500 m depth below Aspo [2].

- *Clay groundwater* simulates groundwater in Callovo-Oxfordian formation, after [3]. The composition represents groundwater between 460-505 m in the Meuse/Haute-Marne URL.

	Granitic Groundwater (mmol/L) [1]	Saline Groundwater (mmol/L) [1]	Clay Groundwater (mmol/L) [3]
Na	2.8	140	55
K	0.1	2.1	1.1
Ca	0.5	19.9	7.5
Mg	0.2	0.4	5.7
Cl	2.0	180	50
HCO_3	2.0	2.0	-
SO_4	0.1	4.0	15
SiO_2	0.2	-	-
pH	8.2	7.7	7.4

Bibliography

[1] M. Gascoyne, *Influence of grout and cement on groundwater composition. Posiva Working Report 2002-07*, no. February. 2002.

[2] B. Lagerblad and J. Trägårdh, “Conceptual model for concrete long time degradation in a deep nuclear waste repository,” *SKB, Tech. Rep.*, no. February, 1994.

[3] A. Vinsot, S. Mettler, and S. Wechner, “In situ characterization of the Callovo-Oxfordian pore water composition,” *Phys. Chem. Earth*, vol. 33, no. SUPPL. 1, 2008.

18. VTT/Tapio Vehmas

We plan to generate new samples for our experimental work. The low-pH concrete has two studied mix designs developed in EU-DOPAS –project (2012-16). The first mix has a ternary binder composition (CEM I, silica fume and fly ash) and the second reference recipe has a binary binder composition (CEM I, silica fume). Both mix designs utilize locally available aggregates, quartz filler and naphthalene based plasticizer. The plasticizer content of both mix designs is relatively high 4.5–7.5%, from the binder content. More detailed information is in Table 1. Bolt mortar mix design consist CEM I, grout aid, aggregates and naphthalene based plasticizer. Injection grout composition is not yet defined but is expected to be provided by Posiva Oy in the near future. Paste and mortar mixtures may be created following the powder proportions as noted in Table 1.

Cebama reference concrete with CEM I, silica fume and blast furnace slag was casted. Reference samples were distributed among the Cebama research partners. The reference concrete will serve as internal reference between the project partners.

Table 1. Mix designs of the studied low-pH concretes.

	Ternary mix design	Binary mix design	Cebama reference mix design
CEM I 42,5 MH/SR/LA	105 kg/m^3	120 kg/m^3	105 kg/m^3
Silica fume	91 kg/m^3	80 kg/m^3	110 kg/m^3
Fly ash	84 kg/m^3	-	-
Quartz filler	114 kg/m^3	256 kg/m^3	116 kg/m^3
Blast furnace slag	-	-	65 kg/m^3
Local aggregate	1840 kg/m^3	1805 kg/m^3	1866 kg/m^3
Plasticizer content (from binder content)	4.5–7.5%	4.5–7.5%	6.0 %
Effective water content	126 kg/m^3	125 kg/m^3	120 kg/m^3
Water/binder -ratio	0.45	0.60	0.43

Samples are stored in RH100 in temperatures 20 °C and 40 °C. Samples are further exposed to leaching. Leaching solutions will be ion exchanged water, simulated groundwater or simulated bentonite water. Approximately 20–40 concrete samples will be casted (150*150*150mm). Number of mortar samples is approximately 10.

Paste samples to study kinetics of pozzolanic reaction and leaching process more detailed will be also casted. Paste samples consists $Ca(OH)_2$, CEM I, granulated silica, nanosized silica and grout aid. Paste samples are also exposed to leaching solutions. Paste samples are leached to determine the equilibrium pH and composition in various leachates, whereas the concrete and mortar samples are leached to define physical parameters affecting to the leaching process.

Samples are available for research partners, pending Posiva Oy permission.

In addition the leaching experiments performed on CEBAMA materials will be conducted using saline reference groundwater as described by Posiva. Saline groundwater which has been equilibrated with bentonite backfill materials will be also studied. These represents waters at the repository depth of approximately 450 metres at Olkiluoto. The waters are described by Hellä 2014[2], with composition shown in Table 1.

Table 1. Posiva saline groundwater and saline bentonite porewater.

Saline groundwater				Saline bentonite porewater		
Na+	208,84	mmol/l		Na+	499,02	mmol/l
Cl-	412,91	mmol/l		Cl-	340,10	mmol/l
K+	0,54	mmol/l		K+	2,55	mmol/l
Ca2+	99,78	mmol/l		Ca2+	11,08	mmol/l
Mg2+	2,30	mmol/l		Mg2+	10,49	mmol/l
Sr2+	0,40	mmol/l		Sr2+	0,40	mmol/l
SO42-	0,04	mmol/l		SO42-	102,01	mmol/l
Br-	1,31	mmol/l		Br-	1,31	mmol/l

[2] Hellä, P., Pitkänen, P., Löfman, J., Partamies, Wersin, P., & Vuorinen, U. Safety Case for the Disposal of Spent Nuclear Fuel at Olkiluoto - Definition of Reference and Bounding Groundwaters, Buffer and Backfill Porewaters. Posiva Report 2014-4. Posiva Oy. 2014. 164 p.

19. HZDR/Johannes Kulenkampff

1.2 We are using **existing** cementitious-material samples? YES

We are using existing cementitious-material samples which are provided and jointly-characterized by UNIBE. Experimental work is also done on newly generated samples, as provided and then jointly-characterized by SCK CEN and UNIBE.

20. LML/Jianfu Shao

We will be generating new samples for our experimental studies._The half cylinder of concrete will be fabricated directly in a mould, beside the half-cylinder of Cox claystone.

The composition of the low pH concrete is based on those used in the low pH concretes previously investigated by Andra. The cement CEM I will be used. Two different typical compositions will be considered, respectively using flying ashes (TCV) and dairy (TL) as the principal component to obtain low pH:

%SP	Binder	Cement	Silica fume	Flying ashes	Dairy	Sand	Gravels	Effective water
TCV	365	136.9	118.6	109		829	1014	164
TL	380	76	123.5		180.5	807	986	146

The first group of about 20 samples will be conserved at room temperature (20 °C) and under different RH, say 50%, 70%, 90%, 98% to study effects of saturation.

The second group of about 20 samples will be conserved under saturated condition (98%RH) but with different temperature, say 40 °C, 60 °C and 80 °C to investigate effects of temperature.

A total of about 40 samples will be fabricated, and we did not plan on sharing samples with other partners.

21. UAM/Raúl Fernández Martín; Ana Isabel Ruiz; Jaime Cuevas

Our work is based mainly in existing cementitious-material samples for our experimental work. In addition, new small cell experiments are being carried out with FEBEX bentonite and cement paste/quartz mortars. The Table 1 is an actualization of the systems described in Cebama deliverable D1.02 (Agreement and documentation of systems to be studied (M06 - Nov 2015)).

Table 1. EXPERIMENTAL SYSTEMS AND OBJECTIVES

#System	Cement material **(C)**	Bentonite **(B)**	Aqueous phase	Bulk scale (thickness) ºC	Focus scale	Time scale	Objective
#1 Interface	CEM I/quartz mortar CEM I+ silica fume/ quartz mortar	FEBEX 0.5mm grain size	Grimsel type GW	~5-10 mm **C**/ ~5-10 mm **B** **25ºC (ambient)**	μm/nm	2-12 months	First mineral phases formation High pH-low pH comparison **where/when**
#2 Interface	CEM II* /quartz mortar	FEBEX 0.5mm grain size	Grimsel type GW	~5-10 mm **C**/ ~5-10 mm **B** **25 ºC (ambient)**	μm/nm	2-12 months	First mineral phases formation **where/when**
#3 Bulk interface cell experiment	CEM-I-SR-45 /quartzite concrete	FEBEX 5 mm grain size	RAF clay formation saline water **	30 mm **C** 70 mm **B** **40 ºC**	mm/μm	10 years	Mineral phases in a cell constrained experiment **Is there any relationship to #1 short-term? ageing**
#4 In Situ GTS shotcrete/ bentonite interface	CEM II A-L 32,5 R), with nanosilica, steel and polypropylene fibres	FEBEX 5 mm grain size	**AGED** Grimsel type GW	1000 mm **C** / > 1000 mm **B**	cm/μm	13 years	Mineral phases in unconstrained conditions **Is there any relationship to #2 short-term? ageing**

C: concrete; B: bentonite; GW: groundwater
*: CEM-II A/L 42.5 R: similar to FEBEX in situ shotcrete plug
**: Concrete-bentonite system was expected to be significant in a clay formation context in Spain. It is a Na-Mg sulfate water and can be useful to consider sulfate and Mg interactions in the concrete system affected by the bentonite.

- **Composition (material types, amounts/proportions):** We will work with two existing cementitious materials: the CEM-I_SR-45 in use in the 10 years cell to be dismantled (reference #3 in , and the CEM-II + (variety of agregates and materials: marl quartz, steel and propylen fibers) and additives, already used in the FEBEX experiment (#4, D1.02)]. In addition, for the small scale interface experiments to be performed (#1 and #2, D1.02), the use of a CEM-I OPC mortar, a LPH type (CEM-I+silica fume(60+40%)); and a CEM II/A-L 42,5 R, resembling the cementitious material used in the *in situ* FEBEX experiment, are foreseen. The mortars have been manufactured with 3 parts of siliceous sand and 1 part of the corresponding cement paste.

- **Exposure conditions (RH, temperature, groundwater/chemical exposure):** The concrete-bentonite laboratory experiment to be dismantled after 10 years of reaction (#3) is exposed to hydration with a saline water (RAF, see below) from the concrete face and heat (100 ºC) from the bentonite face. Temperature at the concrete-bentonite interface is lower than 40 ºC. The conditions in the samples from the FEBEX experiment (#4) are those inherent from the exposure at the Grimsel Test Site. Hydration is produced with the aged Grimsel type groundwater (GW). The small scale experiments (#1 and #2) will be controlled under laboratory conditions at ambient controlled temperature (25^0C±5) and using the Grimsel test site type groundwater.

- **Combined material exposure (adjacent to bentonite, metal, bedrock, etc.):** For the three types of experiments, the cementitious materials are adjacent to a compacted FEBEX bentonite as our interest is to characterize the interface reactions.

- **Age now, age at time of sampling, storage method of samples:** The samples from the FEBEX experiment are 13 years and they are wrapped and vacuum-sealed into plastic bags until time of laboratory sampling, the concrete-bentonite cell with CEM-I-SR-45 OPC type will be dismantled and examined after 10 years. The small scale interface experiments will be prepared within this project with a maximum duration of 12 years.

- **Number (or volume) of samples:** One cylindrical column of concrete (30 mm in height x 70 mm in diameter) will be obtained from the #3 experiment. Preserved large samples from the #4 experiment (UniBe Overcoring bentonite/concrete segments) are ready to be examined. Experiments of short duration #1 and #2 will produce at least 12 small samples (< 10 cm^3 each) to be characterised. As far as the production of suitable volumes for leachate analisys have been obtained in 2-3 months, six cells containing mortar-bentonite interfaces are being launched for a 3 month experiment and other six have been launched for a 6-12 months experiment (the extension from 6 to 12 will be decided as a function of the leachate production rate). Each interface will be linked to several liquid effluents to be taken and analyzed. In any case, all solid samples are subjected to segmentation to be examined at different length scales. These cement mortar samples are fabricated in cooperation with IETcc-CSIC.

- **Ability or willingness to share samples with any other partners?** Our characterisation scheme for the cementitious-bentonite interface materials includes collaboration with CIEMAT and IETcc-CSIC. CSIC will study aging of concrete through experiments and the in-situ samples in a wider scale than our interface study. CIEMAT will study geochemical parameters characterizing bentonite in the cm to m scale in relation to the bentonite thickness around medium scale 10 years cells or the in situ experiment. In addition, CIEMAT group will share the study of interfaces in order to complete porosity and FTIR studies in this zone. The samples from the FEBEX experiment (#4) withdrawn through the overcoring technique will be studied in agreement with the characterization methodology used by other groups that study equivalent samples. The latter characterization may be complementary with the examination of samples performed by the group at the University of Bern. Some collaboration in this respect is foreseen.

- **Water composition for interface (systems #1 and #2) and long-term cell (system #3) experiments.**

  UAM will use the same water composition as CIEMAT and CSIC teams:

  Artificial clay water (Na+-Ca2+- Mg2+- SO42-−type) obtained in the laboratory after the analysis and synthesis of the water of a Spanish reference clayey formation (RAF), with composition in Table 2[1].

Water from the BO-ADUS borehole (Na+-Ca2+-HCO3- -F-−type) located in the Grimsel Test Site, which is representative of the granite deep groundwater (GTS-GW) of the site with composition shown in Table 2[2].

Table 2. Reference clayey water (RAF) and Reference granite water (GTS-GW)

Component	RAF	Component	GTS-GW
	mol/L		mol/L
Na	1.3 x 10-1	Na	3.7 x 10-4
K	8.2 x 10-4	K	2.3 x 10-5
Ca	1.1 x 10-2	Ca	1.8 x 10-4
Mg	8.2 x 10-3	Mg	1.7 x 10-5
Cl	2.3 x 10-2	Cl	2.3 x 10-5
SO4	7.0 x 10-2	SO4	6.1 x 10-5
SiO2	2.7 x 10-4	F	2.2 x 10-4
Fetot	1.1 x 10-5	SiO2	1.9 x 10-4
HCO3	1.8 x 10-3	HCO3	4.0 x 10-4
pH	7.5	pH	9.7

[1]Turrero, M.J., Fernández, A.M., Peña, J., et al. 2006. J. Iber. Geol. 32 (2), 233–258.
[2]Turrero, M.J., Villar, M.V., Torres, E., et al. 2011. PEBS Project. Deliverable D2.3-3-1.

22. CSIC/Maria Cruz Alonso/Jose Luis Garcia Calvo

We plan to use both existing and new materials for our experimental studies, as described below. Table 1 shows the different materials and type of groundwaters interactions to be evaluated by CSIC.

Table 1: *Concretes and groundwater systems to be evaluated by CSIC within CEBAMA project*

Exposure conditions	Ground water	1)Febex concrete plug	2) HB6 concrete	3) Febex concrete plug Not altered	4)Low-pH concrete Äspö plug	5) HB6 concrete new	6)low-pH concrete VTT
In-situ	Granitic	X					
	Clayey		X				
Lab Percolation test	Granitic			X	X		X
	Clayey				X	X	X

<u>Existing aged concrete:</u>

1) **<u>Febex plug:</u>**

- **Composition (material types, amounts/proportions)**: Concrete cores (cement type CEM II A-L+6.5% nanosilica+11% steel fibers (SF)+0.17%Polypropilen fibers (PPF) by weight of binder) from Febex shotcrete plug near bentonite site of Grimsel. Cores extracted from the last 10 cm of the shotcrete plug in nearest contact with bentonite.
- **Exposure conditions (RH, temperature, groundwater/chemical exposure):** real exposure conditions from the Grimsel site, Aging of concrete with the Grimsel groundwater and the saturated bentonite waters
- **Combined material** exposure (adjacent to bentonite, metal, bedrock, etc): concrete near to bentonite (up to 10 cm).
- **Age now, age at time of sampling, storage method of samples**: 13 years aging in Grimsel site, samples wrapped and placed into vacuum-sealed plastic bags. The samples coming from the in situ experiment are placed into a fridge preserved into vacuum-sealed aluminium bags.
- **Number (o.r volume) of samples**: those received from dismantling of Febex plug cores. Samples coming from overcorings made in the real scale experiment before dismantling, each sample has 10 cm of concrete and 10 cm of bentonite.
- **Ability or willingness to share samples with any other partners?** The samples will be shared with UAM (partner 21) and CIEMAT (partner 5).

2) **<u>HB6 Cell:</u>**

- **Composition (material types, amounts/proportions)**: sample small pieces of concrete from the cell (cement type CEM I 45 SR).
- **Exposure conditions (RH, temperature, groundwater/chemical exposure**): heating 100 ºC from bentonite site and resaturation with clayey groundwaters
- **Combined material exposure (adjacent to bentonite, metal, bedrock, etc):** 30mm concrete/70mm bentonite. When the laboratory experiment is dismantled samples will be preserved in placed into a fridge preserved into vacuum-sealed aluminium bags
- **Age now, age at time of sampling, storage method of samples**: 10 years

- **Number (or volume) of samples**: small samples for characterisation of microstructure concrete alteration. Slabs coming from the dismantling of the small scale laboratory column experiment
- **Ability or willingness to share samples with any other partners?:** YES, The samples will be shared with UAM (partner 21) and CIEMAT (partner 5).

3) <u>Febex plug: non-altered zone</u>:

- **Composition (material types, amounts/proportions)**: Concrete cores (cement type CEM II A-L+6.5% nanosilica+11% steel fibers (SF)+0.17%Polypropilen fibers (PPF) by weight of binder) from Febex shotcrete plug far form bentonite barrier.
- **Exposure conditions (RH, temperature, groundwater/chemical exposure):** concretes will be exposed to simulated clayey groundwater.
- **Combined material** exposure (adjacent to bentonite, metal, bedrock, etc): non-altered front of Febex plug.
- **Age now, age at time of sampling, storage method of samples**: 13 years aging in Grimsel site, samples wrapped and placed into vacuum-sealed plastic bags. The samples coming from the in situ experiment are placed into a fridge preserved into vacuum-sealed aluminium bags.
- **Number (o.r volume) of samples**: 3 samples for percolation tests in contact with simulated clayey groundwater.
- **Ability or willingness to share samples with any other partners?** The samples will be shared with UAM (partner 21) and CIEMAT (partner 5).

4) <u>Low-pH concrete:</u>

- **Composition (material types, amounts/proportions):** cores from low-pH concrete of Äspö site. Binder based on 60%PC + 40% SF. This concrete was designed by CSIC within ESDRED project.
- **Exposure conditions (RH, temperature, groundwater/chemical exposure):** concretes will be exposed to simulated granite groundwater and simulated clayey groundwater.
- **Combined material exposure (adjacent to bentonite, metal, bedrock, etc**): nothing to add.
- **Age now, age at time of sampling, storage method of samples**: 9 years aging. Cores were extracted 9 years ago and have been cured in humidity chamber at 98%RH and 20ºC.
- **Number (or volume) of samples**: At least 3 per condition.
- **Ability or willingness to share samples with any other partners**? Limited number of samples.

<u>New samples</u>:

1) **<u>High-pH concrete</u>**:

- **Composition (material types, amounts/proportions):**
  1) Design and production of concrete samples, using CEM I 45 SR type (low alkaline and aluminates content). Concrete composition will be similar to that used in HB6 cell
  2) Extra concrete cores from Febex plug (aged concrete), not affected by Grimsel underground site waters will be used
- **Exposure conditions (RH, temperature, groundwater/chemical exposure):**

- 1) New CEM I 45 SR will be exposed to percolation clayey waters contact at 20 ºC to study the initial stages of young concrete interaction with simulated clayey waters. .
- **Combined material exposure (adjacent to bentonite, metal, bedrock, etc):** New and aged (13 years) high pH concretes exposed to clayey and granitic waters to identify initial degradation stages
- **Number (or volume) of samples**: At least 3 samples per test condition

2) **Ability or willingness to share samples with any other partners?** Some samples will be shared with CIEMAT and UAM. Some additional samples can be fabricated if required by other/s CEBAMA partner/s.**Low-pH concrete**:

- **Composition (material types, amounts/proportions):** CEBAMA benchmark mix fabricated by VTT, CEM I+ SF+BFS
- **Exposure conditions (RH, temperature, groundwater/chemical exposure):** concretes will be exposed to simulated granite groundwater and clayey water.
- **Combined material exposure (adjacent to bentonite, metal, bedrock, etc**): .
- **Number (or volume) of samples**: At least 3 per condition.
- **Ability or willingness to share samples with any other partners**? Samples pH concrete will be received from VTT

Water composition for percolation tests to be made by CSIC.

CSIC will conduct percolation leaching experiments on CEBAMA materials using two type of ground waters, similar to those used by CIEMAT and UAM:

1) Artificial clay water (Na^{+}-Ca^{2+}-SO_4^{2-}–type) obtained in the laboratory after the analysis and synthesis of the water of a Spanish reference clayey formation, with composition in Table 2[1].
2) Water from the BO-ADUS borehole (Na^{+}-Ca^{2+}-HCO_3^{-} -F^{-}–type) located in the Grimsel Test Site, which is representative of the granite deep groundwater of the site with composition shown in Table 2[2].

Table 2. *Reference clayey water (molar concentration) Left. Reference granite water (molar concentration)*

Component	Clayey water	Component	Grimsel Granitic BOADUS water
Na	1.3 x 10-1	Na	3.7 x 10-4
K	8.2 x 10-4	K	2.3 x 10-5
Ca	1.1 x 10-2	Ca	1.8 x 10-4
Mg	8.2 x 10-3	Mg	1.7 x 10-5
Cl	2.3 x 10-2	Cl	2.3 x 10-5
SO4	7.0 x 10-2	SO4	6.1 x 10-5
SiO2	2.7 x 10-4	F	2.2 x 10-4
Fetot	1.1 x 10-5	SiO2	1.9 x 10-4
HCO3	1.8 x 10-3	HCO3	4.0 x 10-4
pH	7.5	pH	9.7

23. ANDRA/Xavier Bourbon

We still have few (small) samples of low pH concretes from previous studies, in a room at 100%RH in a laboratory we work with (TL and TCV formulations aged 5 to 8 years). These samples are possible to use and to study. It is mainly 4x4x16 prisms.

There is also the possibility to use existing low-pH materials from Andra's FSS dismantling (Full-Shaft Seal demonstration, within the EU-DOPAS project 2012-16). We have a few kilograms (cylinders 8 cm of diameter) of both Self Compacting Concrete and Shotcrete, based on a binary mix CEM III (= CEM I+BFS)/SF poured two years and a half ago. Some physical and chemical characterizations are ongoing. As this formulation is close to TL, it could be possible to compare the properties and the characteristics of these two materials. All FSS samples are in sealed bags to prevent from drying.

All these samples could be shared if needed. It is possible too, but this needs to be organized, to prepare concrete (large) samples to drill or to slice. Cement paste is more complicated to cast due to the physical behaviour of such a material (mainly shrinkage and cracks).

25. UNIBERN/Urs Mäder

We plan to use existing cementitious-material samples for our experimental work, as described here. More details about the materials can be found in the report Mont Terri TN 2012-56 (to be released for CEBAMA). Note that not all sample materials will be used; decision expected in month 8–12 of CEBAMA.

Composition (material types, amounts/proportions)

1) OPC-based mortar: CEM I 42.5 N Holcim 899 kg/m^3, w/c 0.47, qz-sand 0.1/0.3
2) OPC-based paste: CEM I 42.5 N Holcim 1260 kg/m^3, w/c 0.47
3) ESDRED mortar: CEM I 42.5 N Holcim 495 kg/m^3, SF 332 kg/m^3, qz-sand 0.1/0.3, SP, AC
4) ESDRED paste: CEM I 42.5 N Holcim 653 kg/m^3, SF 438 kg/m^3, qz-sand 0.1/0.3, SP, AC

Saturated conditions; T ≈ 14 °C, claystone pore water (ca. 13.19 g/l NaCl)

Aged in-situ: 3 years; storage: 1 year; vacuum-sealed; cold storage

(Parts of) drill cores of 101 mm diameter across interfaces

At discretion of CI Experiment, Mont Terri: limited sample material may be available for sharing

We do not plan to generate any new samples for experimental studies.

Artificial pre waters used for experiments

Depending on mode of infiltration, either from claystone side or from mortar side, different artificial pore water compositions will be used:

- Claystone pore water based on Phreeqc equilibrium modelling as detailed in Mäder (2009). A recipe already used in the context of the CI Experiment is listed below, taken from a Mont Terri internal technical report. It may be updated according to results from pore water sampling carried out presently at the CI Experiment location.

Salt	mfw	APW
	g/mol	g/l
NaCl	58.44	10.553
KCl	74.56	0.087
MgCl2 6H2O	203.301	2.911
CaCl2 2H2O	147.016	1.859
SrCl2	neglected	0.000
Na2SO4	142.036	1.670
Na2CO3	0	0.0384

	meq/L	mmol/l	mg/l
Na+	204.8	204.8	4709.1
K+	2.33	2.33	91.26
Mg+2	28.66	14.33	344.35
Ca+2	25.30	12.65	507.00
SO4-2	23.52	11.76	1129.25
CO3-2	0.717	0.359	21.510
Cl-	236.9	236.9	8397.7

- Cement pore waters will be matched to the state of maturation of either OPC morter or ESDRED mortar. The exact composition has not yet been detailed.

References

Mäder, U. (2009). Reference pore water for the Opalinus Clay and "Brown Dogger" for the provisional safety-analysis in the framework of sectoral plan - interim results (SGT-ZE). Nagra Working Report NAB 09-14, Nagra, Wettingen, Switzerland. (download from www.nagra.ch)

26. IRSN/Alexandre Dauzeres

We plan to use both existing and new samples for our experimental work. These plans are described below.

A part of the CEMTEX project, existing samples will be used in the CEBAMA project. Each of these ones, i.e. Low-pH and OPC, were placed in contact during 1 and 2 years at 70 °C with the CLS. Currently, two other experiments are in progress: OPC/CLS and Low-pH/CLS during 5 years. These last two experiments will be sampled in 2017 (OPC: January; Low-pH: June). These samples will be studied as part of the CEBAMA project.

Existing Materials:
The cements used for elaborating pure OPC and low-pH cement pastes were two sulphate-resistant Portland cements (SRPC) from the Lafarge Corporation (Val d'Azergues (Val DZ) and Le Teil, respectively). The first cement was very poor in C3A and rich in C4AF, while the latter was chosen for its very low alkaline content. Their bulk chemical compositions and mineralogy were provided by Lafarge (Table 1).

Table 1 – Cements compositions in CEMTEX in situ tests.

	Chemical phase analysis [g/100g]			Components and composition [mass]	
	Val DZ	Le Teil		Val DZ	Le Teil
CaO	64.6	66.8	C3S	68	66.5
SiO_2	20.7	22.2	C2S	17	16.8
Al_2O_3	3.2	2.9	C3A	0.9	<5
Fe_2O_3	4.6	2.6	C4AF	14	8.1
CaO (free)	1.8	0.0	Clinker	97	97
MgO	0.6	0.9	Gypsum	4	2.7
K_2O	0.6	0.2	Filler	3	3
Na_2O	0.1	0.2			
CO_2	1.1	1.3			
SO_3	2.8	2.2			

The low-pH cement was prepared with a water-to-binder ratio (w/b ratio) of 0.42. The binder consisted of 37% OPC cement, 30% fly ashes and 33% silica fume (mass percentages with respect to cement weight) [Codina, 2008]. 1% superplasticiser (*CHRYSO Fluid Optima 175)* was added to the mixture during preparation.

The OPC cement pastes were made with a water/cement (w/c) ratio of 0.42.

Experimental conditions:
In order to have interface as perfect as possible to optimize the post-mortem characterizations, downward vertical boreholes of 1 m depth and 25 cm of diameter were (or "will be") drilled into the CLS in the Tournemire tunnel. This depth was chosen to ensure that devices were located out of the excavation disturbed zone (EDZ) created while the gallery was excavated. The bottom of each borehole was polished with a specific tool and all the dust was carefully vacuum cleaned, in order to obtain an as perfect as possible contact surface between the CLS and the cementitious material.

After the drilling and the polishing, 3 cups filled with water and humidity probes were placed into the borehole, which was then tightly closed to resaturate the rock in vapour phase. The rock was considered saturated when the measured relative humidity within the borehole reached a value of 99.5%. In each borehole, the relative humidity reached 97.5% and 99.5% after 7 and 45 days, respectively. To force a one-dimension mass transport (vertical) across the interface and to protect the borehole sides from hyperalkaline solution, a PVC tube (25 cm outer diameter, 0.5 cm thick, 125 cm height) was placed within the borehole. A rubber seal was placed at the bottom of the PVC tubing to seal the bottom of the tube from the wall of the borehole.

At the same time, heater devices were built outside the boreholes. Four temperature sensors (PT 100) were attached to a single support in order to monitor the temperature during the experiment. Two sensors were close to the centre of the coil, one at 1 cm height from the future interface (M1) and the other at 20 cm (M0). The two other sensors were placed just inside the coil, again at 1 cm (M2) and 20 cm (M3). The coil top and the temperature sensor support were fixed to a PVC shell of 20 cm diameter. A rubber seal provided sealing between the argillite borehole bottom and this latter PVC shell. After the argillite saturation, the entire device was placed into the borehole and then connected to a boiler via 6 mm diameter PFA pipes (perfluoroalkoxy) and to the temperature acquisition system (ALMEMO). Once all these steps were achieved, the cement paste was poured onto the heater device and the temperature sensors to fill the full inner PVC volume constituting a 30 cm height OPC paste plug.

One month after the beginning of the cement hydration, heating was started while the device was being maintained under the hyperalkaline solution in order to ensure water saturation throughout the test. The solution level was frequently checked and when it decreased, hyperalkaline solution was added. Above the cement paste block, bubble wrap and a polystyrene cap were placed, to try to prevent water and heat losses. The system was closed at the top by a tight PVC cover. A schematic view of the experimental system is displayed in figure 1.

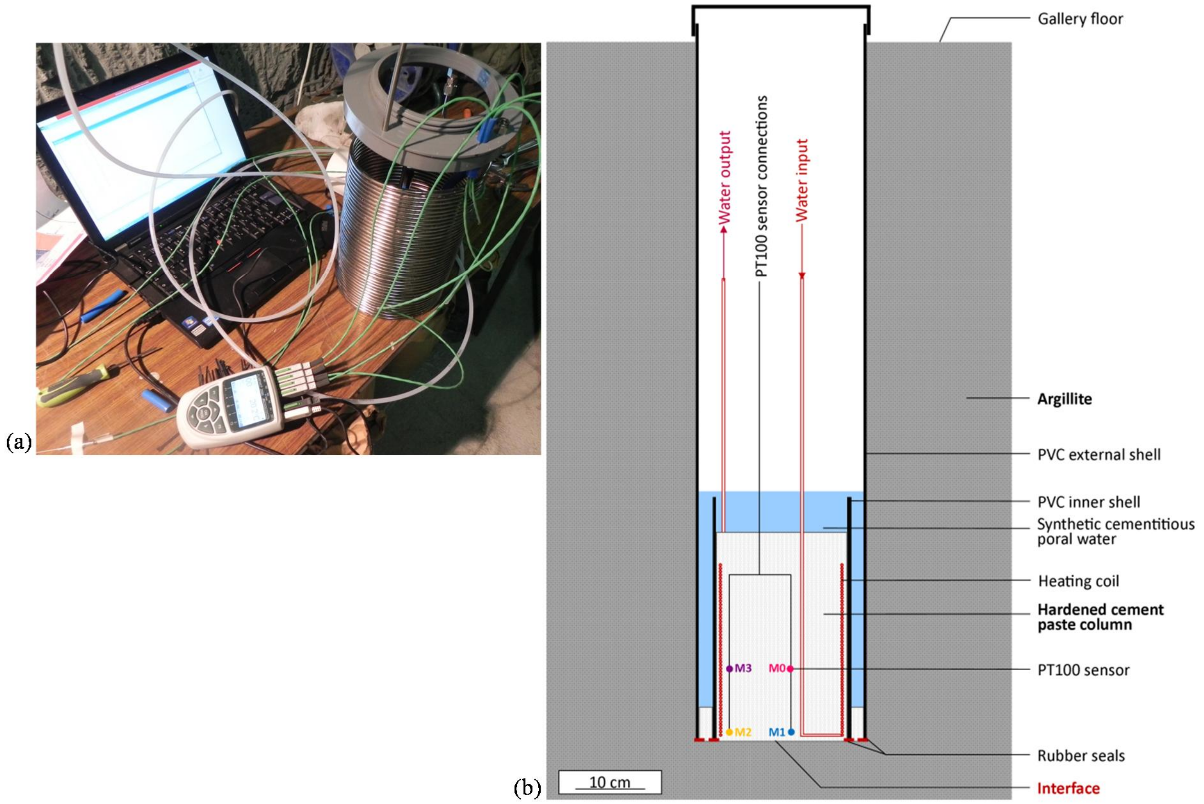

Figure 1 – View of the heating coil device connected to the temperature monitoring system (a) and outline of the CEMTEX in situ device (b).

Based on a modelling work, a coil heating device was the best option to prescribed temperature at the interface between both materials.

The selected heating design (coil device) was optimized to resist to in situ conditions and duration (up to 5 years) of the test: the inner and outer sides of the coil tubing are respectively in contact with water around 70 °C and a hyperalkaline environment. The choice of the coil material was thus a critical issue. Aluminium and copper have high thermal conductivity, but they are very sensitive to hyperalkaline pH, whereas stainless steel resists to alkaline medium but is a poor thermal conductor. The compromise was thus to coat the copper coil with nickel, using electrochemical plating. Practically, a 10 µm thick nickel plating was deposited on the coil surface. Each spin of the coil was butt-jointed to its neighbours to finally form a pseudo cylinder of 18 cm. After installation, the coil was connected to an electric boiler providing hot water.

The temperature reaches in the 6 experiments carried out or in progress varies between 65 °C and 73 °C, near the interface.

Sampling, cutting and conditioning
The main concern for experiment dismantling was to protect the rock/cement paste interface throughout the process. Hence in order to lift the sample up, a specific extractor was designed to take advantage of the almost horizontal layering and induce its rupture along this orientation at about 20 centimetres below the rock/cement paste interface. It enabled sampling of both side of the interface.

The next steps were then followed. (i) Once the heating system was stopped and the alkaline water was pumped out from the top of the cement paste column, a 40 cm diameter overcoring was initiated on 60 cm depth. (ii) The hot water circuit and the temperature sensors connectors were then cut and three boreholes of 76 mm diameter and 1.55 m depth were drilled at periphery of the 40 cm diameter overcoring, with aim of later inserting the extractors. (iii) The external PVC shell and the argillite ring (40 cm external diameter, 25 cm inner diameter) were cut at 60 cm depth and removed, two stainless threaded steel rods were screwed into argillite within the 40 cm overcore and epoxy resin was poured over the cement paste column to strengthen the entire system. (iv) 24h later, after resin polymerization, the extractors were inserted into the peripheral boreholes. A hammer blow was put on the top of the extractor metal rod to free the sample from the rock. Then a metal support plate was slid and fixed with nuts to the two stainless threaded steel rods in order to lift the sample out of the borehole thanks to a chain hoist. Immediately, the sample (40 cm diameter and 65 cm height) was packaged in insulating paper to keep it safe from the atmosphere. Successive cuttings were performed first by a circular saw of wide diameter and then, by a diamond wire saw to obtain samples of the interface about few centimetres in size.

Surface interface sample available for each test ≈ 400 cm^2.

As written in the proposal of the CEBAMA project, we are ready to share the samples to the community of the CEBAMA project.

<u>We also plan to generate new samples.</u>

The first part of the CEMTEX project was carried out with OPC and Low-pH to compare the physical-chemical behaviour of the both samples. The formulation of the Low-pH binder was determined with the data existing in the literature. We know today that the formulation of Low-pH chosen by Andra for the disposal has strongly evolved. For this reason, we would like to start a new set of three experiments 1, 2 and 3 years with the updated low-pH formulation. **To do that, we**

need data from Andra about the new formulations and their corresponding pore solution in equilibrium.

The hydric, thermal, chemical and physical conditions will be absolutely the same as in the previous tests (cf. part 1.2.).

The drilling and the resaturation step of the rock surface (cf. part 1.2.) in each test will be carried out in December 2015. The low-pH material will be emplaced at the end of January 2016. The heating phase will be launched at the end of February 2016 (after one month of hydration).

As for the existing samples, the new samples will be at the disposal of the CEBAMA community.

27. END USERS GROUP: Specifications of the used materials in the EU repository designs (provided summer 2015)

The following describes materials to be used in the repository facilities. For most countries involved in the CEBAMA project, the WMO and the corresponding CEBAMA participant already have an established partnership and those materials are well-known. These specifications aims at:

- Giving a relatively accurate list of the cements and concretes to be used so that the work projects focus as strictly as possible on those materials,
- Having a general view of the used materials in the other countries designs for a better cooperation between the participants/WMOs.

ANDRA (France):

For cements, ANDRA is mostly using blended cements (CEM-V and low pH), but other formulations are also used/expected. Concrete recipes will be provided for WP1 from ANDRA participants.

- Holcim Heming CEM V/A 32.5N and Rombas CEM V/A 42.5N (CEM V)
- For low pH cements, ANDRA is using a single formulation for experiments in deep lab and industrial trials.

COVRA (Netherlands):

The COVRA design mainly focuses on two categories of cements:

- CEM I HS
- CEM III/B 42.5 LH/SR

The following gives three concrete recipes: one for the compacted waste package and two foamed concretes (Aercrete) to be used in the backfill composition.
Waste package

Concrete composition for the disposal of compacted waste in 200 litre drums

Component	Type		
Cement	CEM III/B 42.5 LH/SR	407-430	kg m^{-3}
Water	-	175-185	kg m^{-3}
Plasticiser	TM OFT-II B84/39 CON. 35% (BT-SPL)	3-5	kg m^{-3}
Fine aggregate	Quartz sand : 0-4 mm	819-972	kg m^{-3}
Coarse aggregate	Quartz gravel : 2-8 mm	891-763	kg m^{-3}

Reference Verhoef et al. Waste families OPERA-PG-COV023, to be published summer 2015.

Backfill

Composition enclosure emplaced waste (backfill – foamed concrete)

Component	Receipt for 1 m^3 of Aercrete FC 1200 to 1600 kg m^{-3}	Type for OPERA		1600 kg m^{-3}	
Cement	360 to 400 kg	CEM I SR 3 <3% C_3A		417	kg m^{-3}
Water	140 to 160 kg	-		165	kg m^{-3}
Fine aggregate	750 to 1100 kg	Sand: 0-2 mm		1018	kg m^{-3}
Foaming agent Synthetic surfactant	0.57 to 0.36 l	Foaming agent TM 80/23 Synthetic		1	kg m^{-3}
Water	21.3 to 13.6 l	Water			kg m^{-3}
Air	434 to 277 l	Air		0	kg m^{-3}

Reference Verhoef et al. Cementitious materials in OPERA disposal concept in Boom Clay OPERA-PG-COV020, 2014

For Cebama also foamed concrete with CEM III

Component	Receipt for 1 m^3 of Aercrete FC 1200 to 1600 kg m^{-3}	Type for OPERA		1500 kg m^{-3}	
Cement	360 to 400 kg	CEM III/B 42.5 LH/SR		391	kg m^{-3}
Water	140 to 160 kg	-		154	kg m^{-3}
Fine aggregate	750 to 1100 kg	Sand: 0-2 mm		955	kg m^{-3}
Foaming agent Synthetic surfactant	0.57 to 0.36 l	Foaming agent TM 80/23 Synthetic			kg m^{-3}
Water	21.3 to 13.6 l	Water			kg m^{-3}
Air	434 to 277 l	Air		0	kg m^{-3}

NAGRA (Switzerland)

As for the Swiss repository design, two concrete preliminary recipes were agreed on: the first is for the backfilling mortar in the L/ILW repository, the second is a low-pH shotcrete used for the tunnel support in the HLW repository.

However, these recipes will most likely be adjusted for better performances (for example, the use of quartz or calcite aggregates is still under discussion).

Component	Portion [wt%]	Mix content [kg.m^{-3}]
Sulfacem, Portland Cement CEM I 42.5 HS	1	285
Potable water	0.4	113
Unit grain, quartz sand rounded, grain size 2/3 mm	5.33	1519
Additives	-	-
Fresh mortar density	-	1917

Component	Mix content
Water [kg.m^{-3}]	200
Cement CEM I 42.5N [kg.m^{-3}]	210
Silica fume (EN 13263) [kg.m^{-3}]	140
Sand 0/1 [kg.m^{-3}]	162
Sand 1/4. [kg.m^{-3}]	1022
Gravel 4/8 [kg.m^{-3}]	659
Total aggregates [kg.m^{-3}]	1843
Superplasticizer Glenium 51 [kg.m^{-3}]	4.2 (2% CEM)
Set accelerator Sigunit-L53 AF [kg.m^{-3}]	10.5 (5% CEM)
Water/binder ratio [-]	0.57
Water/cement ratio [-]	0.95
Flow table (0 min) [mm]	380
Air content [%]	2.5
Density [kg.m^{-3}]	2285

ONDRAF/NIRAS (Belgium):

Concrete recipes used in the Belgian repository are mainly based on CEM I and CEM II types. The formulations may still be adjusted to fit the desired performances.

SCC buffer concrete (Waste package)

Component	Proportion
Cement CEM I 42.5N HSR LA LH	350 $kg.m^{-3}$
Limestone filler	100 $kg.m^{-3}$
Limestone 0/4	840 $kg.m^{-3}$
Limestone 2/6	327 $kg.m^{-3}$
Limestone 6/14	559 $kg.m^{-3}$
Limestone 14/20	0 $kg.m^{-3}$
Polycarbonxylate based superplasticizer	10-14 $kg.m^{-3}$
Water	175 $kg.m^{-3}$

Backfill

The backfill mortar composition is yet to be confirmed and adjusted for better performance properties. The grout mixture would use a cement based on 25% CEM I 52.5 N HSR LA and 75% limestone flour. Polycarboxylate superplasticizer may be added to improve the fluidity of the material and the water to cement ratio would be around W/C = 1.3.

Moreover, alternative recipes are investigated based on CEM II/A-LL, CEM II/B-LL or CEM II/A-D and silica fumes.

POSIVA (Finland)

The exact concrete recipes for all of Posiva's mixtures are partially confidential and cannot be freely communicated. Formulations have been made available directly to VTT so that they adequate test samples can be batched. More particularly, VTT is studying a plug recipe (EU-DOPAS project for POPLU plug recipe), a rock bolt grout recipe (CEM I) and a grout recipe (CEM I), all of them being low-pH mixes.

Radioactive Waste Management (United-Kingdom):

For the Intermediate-Level Waste disposal concept in a higher strength rock in the UK, a specific backfill recipe was developed about twenty years for a Portland cement/lime/limestone flour mix. This is the Nirex Reference Vault Backfill as described in the Nirex Safety Assessment Research Programme report S/97/014, which is openly available.

More recent work, yet to be published, shows a need for a slightly increased water content (676.5 instead of 615 $kg.m^{-3}$) using some currently available powders.

Component	Proportion
Portland Cement	450 $kg.m^{-3}$
Limestone Flour	495 $kg.m^{-3}$
Lime	170 $kg.m^{-3}$
Water	615 $kg.m^{-3}$
Water/Cement	1.37 by weight
Water/Solids	0.55 by weight

Nirex Safety Assessment Research Programme. Development of the Nirex Reference Vault Backfill; Report on Current Status in 1994, Report n° S/97/014.

SURAO (Czech Republic):

There are no special cements to be used in the Czech repository design. Most of them are based on Portland cement (CEM I). All concrete mixtures are related to the required properties of solidification matrices, backfill or sealing, for example strength.

SKB (Sweden):

The following information is related to the cement and concrete to be used in the Silo and the Rock vault structures. Table 3-1 gives the used cement chemical composition (CEM I 42.5 N SR3/MH/LA) and Table 3-3 lists the two corresponding concrete recipes.

Table 3-1. Chemical composition of Swedish CEM I 42.5N SR3/MH/LA.

Chemical formulation	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	Cl
Percentage	64	22.2	3.6	4.4	0.94	0.07	0.72	2.2	0.01

Table 3-3. Properties of concrete used in SFR repository located in Forsmark, Sweden.

Properties	**Silo**[1]	**BMA**[2]
Cement type	Swedish structural cement	Swedish structural cement
W/C	0.48	0.62
Cement content (kg/m^3)	350	300
Aggregate volume fraction[3]	0.7	0.7

[1] Based on Emborg et al. [33], however with a symmetrical deviation of 48±5 MPa in compressive strength instead of 43-58 MPa with a mean 48 MPa.

[2] BMA: rock vault for intermediate level radioactive waste. The data has been estimated based on the previous Swedish concrete class K30.

[3] Estimated based on the general mix design of concrete mix proportion, which is in line with Höglund [78] for the concrete in silo.