Development and Performance of Various low-pH Cementitious Materials for Tunnel End Plugs in Geological Disposal Demonstrations

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Tunnel end plugs and shaft seals of nuclear repositories may use low-pH cementitious materials to maintain the safety functions of the engineered barrier systems. Low-pH materials can be used for concrete containment walls of the plug, tunnel shotcrete and rock/bolt injection grouts used for mechanical stability and hydraulical isolation in the repository. The need for using low-pH materials (pH typically under 11 in leached water) rather than traditional concrete (pH about 13) is governed by the impact of leachate on long-term performance of bentonite clay within the engineered barrier systems (EBS) or plug seal. Within the DOPAS full-scale demonstration experiments of Finland (POPLU), Sweden (DOMPLU), Czech Republic (EPSP) and France (FSS), various low-pH materials formulations were used and lessons learned regarding their implementation. Example recipes are presented together with their performance characteristics and lessons learned during emplacement and monitoring. Detailed analysis about the total plug concrete performance is outside the scope of this paper, yet may be shared in other papers within the same DOPAS Seminar (i.e. by Posiva, SKB, SURAO, Andra and others).

1 Introduction

Concrete plugs, containment walls, shotcrete and injection grouts may need to be made of cementitious materials that produce a low-pH plume in the order of 11or less, in order to maintain the swelling capacity of the bentonite clay used within engineered barrier systems (EBS) of a nuclear waste repository. Such products made of cement alone will have a pH on the order of 13, which can create leachate endangering the bentonite, thus alternative binders of silica fume, fly ash and/or blast furnace slag are used as cement replacements. The low-pH concrete will also have low heat-of-hydration and possibly a delayed setting time, yet all other performance characteristics can be engineered to be comparable to traditional materials. Much work has been done in past years on the development of low-pH cementitious materials [Martino 2011, Vogt 2009], yet these recipes and performance must always be validated for the local conditions based on available suitable materials, environmental exposure classes and performance requirements. Such work was undertaken in DOPAS, to provide a wider range of low-pH materials that can be adapted to other programs and applications in the future.

2 Objectives

Four of the five full-scale plugs and seals demonstrated in DOPAS have utilized low-pH materials. The performance requirements of the concretes have differed slightly, but there are also many similarities between the mixtures used. The targets for the mixture are to have low pH, low heat, low shrinkage, high workability and in many cases also good durability especially with regard to watertightness. Applying traditional concrete design methods and durability requirements according to international standards, these properties are challenging to simultaneously achieve.

All of the experiments undertook laboratory development programs to establish the suitable mixture proportions, for instance the suitable binder content (kg/m^3), gradation of aggregate, water-to-binder (w/b) ratio and dosage of admixtures. Properties under evaluation have included early age or fresh mixture properties of workability and flowability, open or workable time until setting, segregation risk and heat of hydration. Once a suitable mixture has been found, samples were made for assessing longer-term properties. These tests have included compressive and tensile strength, watertightness (permeability), drying and autogenous shrinkage, and leachate for pH assessment at various ages from 7 days to 1 year or more.

After suitable laboratory mixtures were found for the specific experimental application, larger-scale trials were done at ready-mix supplier companies to evaluate consistency when upscaling. In some cases, such as POPLU, method tests were done above or underground to further demonstrate the suitable mixture and construction techniques. This was also beneficial for practicing the delivery sequence and quality control methods that would be used for the actual plug construction.

Finally low-pH concrete and shotcrete was used in the full-scale demonstrations of DOPAS. Quality control samples were made to show conformance with the specifications, laboratory trials and design basis. The results from the demonstrations are used to validate the safety of the plugs, especially with regard to watertightness and the durability for the intended service life.

3 Materials & Methods

All of the low-pH concrete mixes applied a common approach in mix designs by substitution of cement used in high-pH concretes with silica fume, blast furnace slag, and/or fly ash, with the addition of fine aggregate filler. Some recipes were a binary blend (cement plus one substitute), while others were ternary blends (cement plus two substitutes). Aggregates and binders were locally sourced. and had to be tailored to the boundary conditions of the experiments (e.g., dimensions and positioning of other structures such as reinforcement and monitoring systems influenced maximum aggregate size or emplacement techniques). It should be noted that in some cases, such as POPLU, extra precautions about foreign materials acceptance were done so as not to harm the site [Posiva 2014], which posed limitations on the use of materials such polycarboxylate-based superplasticizers. Table 1 shows the comparison of mixture designs used in the four experiments.

Examples of the methods used for assessing early age performance of the low-pH materials include: workability (Slump EN 12350-2, Slump flow with t500 by EN 12350-8 or EN206-9, Flow table EN 12350-5, Rheology using a Contec 5 –viscometer); air content (pressure method EN 12350-7); density (EN12350-7); setting time (penetration resistance Finnish SFS 5289); segregation (visual inspection, microscopy of hardened cubes); heat of hydration (semi-adiabatic for concrete RILEM

TC119-TCE1, isothermal for paste by TAM-air). These tests were performed on multiple batch tests in order to establish suitable proportions.

Examples of the methods used for assessing long-term performance of the low-pH materials include: compressive strength (EN12390-3); density (EN12390-9); flexural strength (EN 14488-3); splitting tensile strength (EN12390-6); elastic modulus (Finnish method SFS 5450); watertightness (pressure test EN12390-8); water permeability (EN17892-11); shrinkage (autogenous and drying shrinkage from 1 day onwards) and creep; chloride diffusivity (non-steady state chloride migration by NT Build 490); sulphate resistance (scaling and loss of strength after exposure to Na_2SO_4 ; $MgSO_4$); pH leachate (in deionized water and simulated groundwater according to [Alonso 2012]. These tests were performed on select mixtures for validation of design basis and performance requirements.

Table 1. Low-pH mix proportions used in the DOPAS Project full-scale demonstrators. Some aspects of the concrete recipes are confidential and are not, therefore, reproduced here.

	FSS SCC	FSS Shotcrete	EPSP Shotcrete*	DOMPLU SCC	POPLU SCC**
Cement	CEM III/A 52.5 130 kg	CEM I 52.5 190 kg	CEM II / B – M (S-LL) 42,5 N	120 kg/m^3	106 kg/m^3
Silica Fume	130 kg	190 kg	Yes (approx. 1:1 to cement)	80 kg/m^3 ***	89 kg/m^3
Fly Ash	-	-	-	-	85 kg/m^3
Slag	-	-	-	-	0
Water	204.1 kg	200 kg	Yes	165 kg/m^3	128 kg/m^3
Limestone or Quartz Filler	408.4 kg	-	-	369 kg/m^3 (limestone)	115 kg/m^3 (quartz)
Sand	698.7 kg	1 347 kg	Yes	1037 kg/m^3 (natural sand 0-8 mm)	929 kg/m^3
Gravel	682.1 kg	408 kg	Yes	558 kg/m^3 (8-16 mm crushed granite)	911 kg/m^3
Super-plasticiser	2.2%	3.4%	SIKA 1035CZ	6,38 kg/m^3	18,6 kg/m^3
Retardant	0.1%	0.7%	SIKA VZ1	0	0
Glass fibres			crack HP (Sklocement Beneš)		
Water-cement ratio				1,375	1.20
Water-binder ratio				0,825	0.46
Water-powder ratio***				0,290	0.28

Notes:
** EPSP Shotcrete - exact proportions are proprietary information of supplier*
*** POPLU SCC recipe provided for mass used in plug section #2 with 32 mm maximum aggregate size mixture*
**** DOMPLU Silica fume: in powder form in laboratory, as slurry in large-scale in-situ castings*

4 Results & Discussion

Each of the full-scale experiments of Finland (POPLU), Sweden (DOMPLU), Czech Republic (EPSP) and France (FSS) were successful in emplacing the various low-pH materials formulations in-situ. The volume of materials and key results from field demonstration quality control are given in Table 2. It should be reminded that the results cannot be directly compared between mixtures, because each experiment had a different set of requirements for the low-pH material. An example of the appearance of fresh self-compacting concrete and quality control blocks from POPLU are given in Figure 1 and Figure 2 respectively. Examples of DOMPLU and EPSP casting are shown in Figures 3 and 4 respectively.

Full details of results for each experiment can be found in the DOPAS summary reports [Grahm 2015, Holt 2016, SÚRAO 2016, Andra 2016].

Amongst the key properties of concrete used in plugs and seals are compressive strength, pH of leachate and curing temperature. High compressive strengths of ~40-60 MPa could be achieved for concrete mixes applied in all of the experiments. In FSS, the shotcrete used had a relatively low compressive strength of ~24 MPa, whereas the concrete used in EPSP, which incorporated glass fibres for additional strength, had a compressive strength of ~55 MPa. The compressive strength and tensile capacity of the concrete used in POPLU was provided by a combination of the concrete and the reinforcement, whereas DOMPLU was built without steel reinforcement bars.

Table 2. Low-pH material amounts used in full-scale experiment and some of the quality control key parameters (average values).

	FSS SCC	FSS Shotcrete	EPSP Shotcrete	DOMPLU SCC	POPLU SCC
Material amount emplaced (m^3)	250	250	80	94	178
Slump (mm)	-	±20	180-260	-	-
Slump flow (mm)	>80	-	350-590	643	605
Density (kg/m^3)	2253	-	2200	2210	2356
Air content (%)	-	-	-	7,2	1,7
Maximum temperature in-situ (°C)	48	67	53	9,3	43
Compressive strength (MPa), at 91 days	> 43	41.5 (28d)	> 50	82,2 *	83 **
Flexural strength (MPa)	-	-	>5	-	-
Watertightness (mm), at 91 days	-	-	-	-	2,1
Water permeability (m/s)	-	-	$<10^{-11}$	-	-
pH leachate, 91 days in groundwater	10.3	10.4	11.3	-	10,8
t_{500}				3,2	

Notes:

** DOMPLU: Tested on cylinders drilled from the 1m^3 monolite casted at the same time and with same material as the plug.*

*** POPLU: Tested on quality control 15cm cubes cast at the same time as the plug, stored underground.*

Figure 1. Appearance of POPLU ternary mixture, during field quality control testing.

Figure 2. Example of 1m³ quality control blocks produced with POPLU experiment.

Figure 3. Checking t500 during DOMPLU slump flow test, field quality control.

Figure 4. Shotcrete of EPSP plug.

Challenges encountered during the emplacement of the concrete mixes have been overcome:

- The approaches used in DOMPLU allowed for addition of superplasticiser to the mixture following acceptance testing in order to ensure the appropriate rheological characteristics for the concrete.
- In FSS, the preparation of concrete mixes at the concrete plant had to be scrutinised and monitored to ensure compliance with the mix specification, for example to check the homogeneity of the dry material mixture.
- Posiva was able to tailor their new ternary mix design of the low-pH concrete mix used in POPLU to the specific conditions of the experiment, especially the nature of the congested reinforcement used in the concrete wedge and the type of superplasticiser.
- For EPSP the logistics (transport of concrete in the underground) has been the main issue limiting the speed of emplacement. Further work also needs to be done on lowering of the concrete pH.

However, there is further work to be undertaken on low-pH concrete mixes. Additional work should be done to evaluate the sensitivity of the concrete performances to marginal variations in component percentages and infer, by so doing, how robust a given mix can be. The role of certain additives e.g., plasticisers should also be further explored to see how dependant on the ratio between organic and mineral components a concrete mix composition can be. This is necessary to better assess the robustness of the safety demonstration (i.e. determine the role of complexing products in long-term safety). All of the concrete mixes used in the DOPAS Project experiments are novel materials, and, therefore, are not yet compliant with existing standards.

Testing of the B200 mix used by SKB and the ternary mix by Posiva has indicated that the shrinkage of the concrete may be less than expected. For SKB's case, this may mean that it will not be necessary for the concrete to fully release from the rock for curing to occur without significant crack formation. The monitoring of the DOMPLU experiment concrete dome will contribute to further understanding phenomena related to concrete shrinkage and performance and also help to determine whether further work is needed on the shrinkage characteristics and release requirements.

The DOPAS Project experiments have demonstrated that reinforced and non-reinforced low-pH SCC can be emplaced successfully in repository-like conditions. The POPLU project has shown that self-compacting concrete can be achieved where no vibration is needed to emplace the material in the mould, thus a longer plug section could be envisioned as feedback to the design basis.

5 Conclusions

A range of low-pH cementitious mixes has been developed from lab through full-scale for application in repository plugs and seals. The recipes were tailored to meet early age and long-term performance, considering the construction methods for material emplacement and structural design basis. All the experiments were successful in up-scaling mixtures and emplacing the demonstrations in-situ. Monitoring and quality control testing provided verification of performance and yielded valuable lessons that can be integrated in the future and by other waste management programs utilizing low-pH cementitious materials.

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