PERFORMANCE OF CEMENT-POOR CONCRETE WITH DIFFERENT SUPERPLASTICIZERS

Mohammed Hatem Mohammed[1 & 2], Roland Pusch[1], Sven Knutsson[1] & Jan-Erik Jonasson[1]
[1]Dept. of Civil, Environmental and Natural Resources Engineering,Luleå University of Technology, Luleå 97187, Sweden
[2]Dept. of Civil Engineering, University of Mosul, Mosul 41002, Iraq

ABSTRACT

Concrete can be used for casting plugs in deep boreholes where fracture zones are intersected. They will be exposed to flowing groundwater and be in contact with very tight seals of smectite clay installed where the surrounding rock is tight. The cast concrete must be able to carry the clay segments placed over it after a few days. Its bearing capacity does not have to be very high after that since the clay soon adheres to the rock and carries itself. The concrete must be poor in cement for minimizing the risk of creation of voids caused by dissolution of the cement and it should have "inert" aggregate of quartz-rich material. Inorganic superplasticizers instead of conventional organic ones should be used for eliminating the risk of degradation and loss by formation of colloids that can carry radionuclides to the biosphere from holes bored in repository rock. The two concrete types discussed in the present study had Portland and Merit 5000 low pH cement as binders and crushed quartzite as aggregate. Talc mineral powder and ordinary organic Glenium 51 were used as superplasticizers for comparing their impact on the physical properties. The matrix of the cement-poor talc concrete gave ductile behaviour during initial hardening. The very dense matrix of either of the concretes would not lead to compression of the system even after complete loss of cement, which will happen over a longer period of time. The overall conclusion was that talc as superplasticizer and conditioner of the concrete can make the concrete sufficiently fluid for constructing seals at depth in boreholes, and react with cement to provide high strength with some delay. pH is much lower in Merit than in Portland concrete, which causes less impact on the clay seals. Portland concrete has five times higher strength than Merit concrete after a week but three times lower strength after 28 days.

Keywords:*Concrete, Borehole sealing, Compressive strength, Cement, Superplasticizers, pH, Quartzite.*

1. INTRODUCTION

Sealing of borehole is an important issue for hindering axial transport of Carbone dioxide from deep gas storages to the ground and migration of radioactively contaminated groundwater in deep repositories to the biosphere. In recent time it has become of special interest in conjunction with reconsideration of disposal of HLW waste packages in very deep boreholes (VDH), [1]. Concrete is one of the main materials for sealing and grouting of boreholes by construction of plugs and stabilization of intersected fracture zones (Figure 1), for which the properties in both short and long time perspectives and the technique for placement must be suitable. The role of concrete seals where a VDH intersects fracture zones requires examination of the impact of groundwater erosion and of the chemical interaction with adjacent clay seals. The strong degrading effect on the latter by ordinary concrete with Portland cement as a binder, for which pH of the porewater is 12, suggests use of low-pH cement [1]. Superplasticizers are essential for making concrete fluid, but the conventional organic ones can degrade and cause voids and give off organic colloids that can transport radionuclides. Inorganic material like talc should be considered as discussed in the present paper [2].

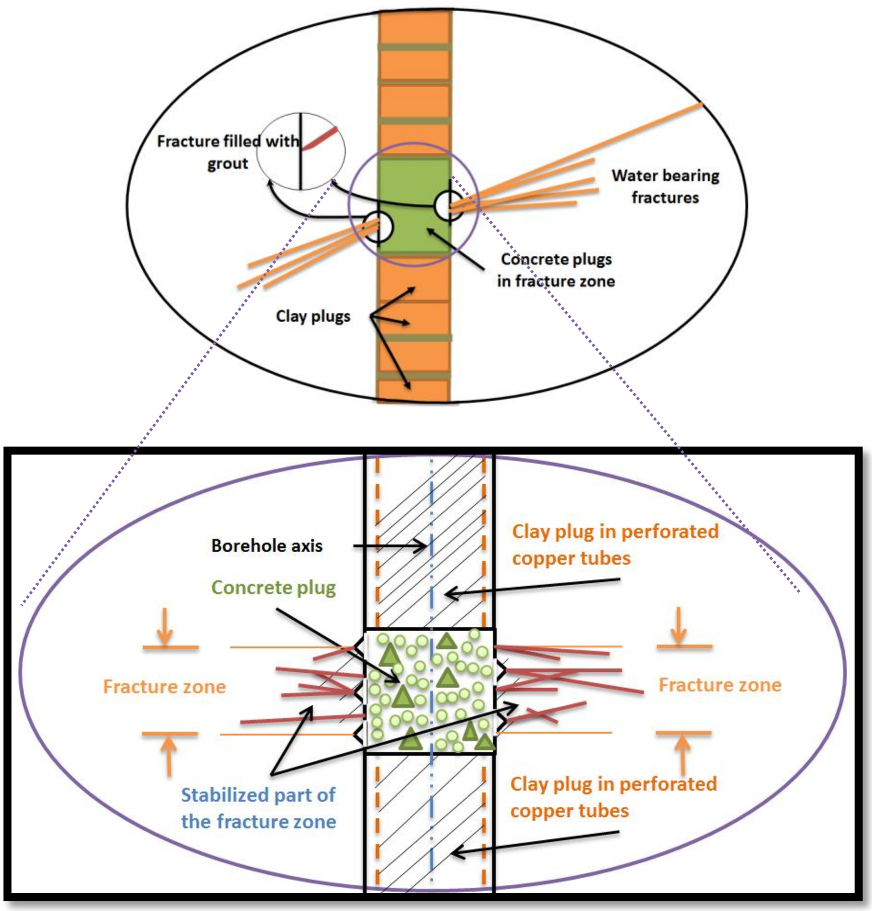


Figure 1. Upper: Principle of borehole sealing. Lower: Detail of concrete cast where the borehole intersects a fracture zone.

1.1. Boreholes

Radionuclides can be moved to the biosphere by water flow in deep boreholes extending from the ground surface to the repository level driven by pressure differences unless they are effectively sealed. Fracture zone system can be short-circuited by the boreholes [3]. Proper construction of the seals requires that they shall perform acceptably for very long periods of time, which, for HLW repositories are on the order of tens to hundreds of thousands of years. This requires that all physical and chemical processes that can endanger their longevity must be considered [4].

1.2. Sealing of ordinary deep boreholes

Borehole sealing can follow the same principles as backfilling of repositories, shafts and tunnels. A fundamental strategy is to tightly seal fracture-poor, rock with highly expandable smectite clay, and to fill the parts that intersect permeable fracture zones with physically stable concrete that does not need to be very tight but be strong enough for supporting the clay segments [3]. Thermally induced stresses, seismic shocks and tectonic strain will generate shear displacements along fracture zones in the repository rock and percolate borehole seals located in them. In these positions clay is not suitable because of the risk of erosion and dispersion [5] and here concrete is proposed as sealing material. It shall have a high density and a low content of cement for minimizing the risk of loosing the bearing capacity that can result from dissolution of this component.

Clay seals consist of highly compacted smectite clay ("bentonite") fitted in perforated copper tubes. After installation the strongly expansive clay migrates through the perforation and forms a dense and tight skin between the tubes and the rock by which the boreholes become effectively sealed [5-7]. Groundwater will hence not flow through the sealed holes but in the rock around them [2, 5]. Portland cement in the concrete is deemed less stable than low-pH cements, which speaks in favour of the latter.

Before clay and concrete seals can be installed the holes must be stabilized so that the risk of failure caused by falling debris from the borehole walls in the construction phase is eliminated. An extra stabilizing act can be to keep the not yet sealed parts of the boreholes filled with smectitic bore mud. Concrete is cast by pumping through tubes reaching down to the desired level in the holes that are initially filled with freshwater or bore mud. The up to 24 m long jointed tubes with clay are moved down through the mud to establish contact with the concrete [3]. After about one day, the expanded clay produces enough wall friction to make each clay segment carry itself [2, 8]. In one week, the concrete gets sufficient bearing capacity to carry subsequently placed clay seals. Both the clay and concrete have an ultimate hydraulic conductivity of less than E-10 m/s and for the clay seals it can be lower than E-11 m/s. Dissolution and loss of the concrete cement component do not change its bearing capacity but the hydraulic conductivity will increase to become as low as for moraine [1]. Sealing of boreholes has been successfully applied in practice of limited length (500 m) but for longer holes full-scale testing and some development are required [7, 9].

1.3. Sealing of VDH

The very high salt content of deep groundwater makes it almost stagnant, which is the main argument for disposal in deep boreholes: possibly contaminated groundwater at more than 2 km depth will not reach higher up than by a hundred meters by convection. Another favourable condition is that the very high rock stresses, 50-110 MPa at 2-4 km depth, that fractures and joints are closed and make the rock tight [10]. A further advantage compared to shallower disposal is that the risk of illegal capturing of the waste is insignificant repository [11]. As to constructability it is obvious that techniques have been developed for boring several thousand meter deep holes. In principle, the concept is hence feasible [1].

1.3.1. Concrete seals

Axial support to the clay seals provided by the concrete requires that it remains as mechanical buffer and does not become eroded, a criterion that requires high density and a minimum of cement. A further criterion is that it must not significally degrade the contacting clay seals by chemical interaction. Such impact is caused by concrete containing Portland cement according to earlier field investigations showing that soft parts of the clay coagulated, leading to increased void size and hydraulic conductivity by ion exchange from Na to Ca [12]. They also demonstrated the impact of high pH cement water on the smectite clay, i.e. dissolution and transformation of smectite to non-expanding clay minerals and amorphous silicious compounds, associated with loss in strength of the concrete within a distance of a few centimetres from the clay/concrete contact. The main findings from the about 3 year long borehole plug tests were, 1) the smectite clay had strongly increased calcium content by Ca migration from the concrete, 2) the clay had 2 interlamellar hydrate layers up to 10 mm distance from the concrete and 1 hydrate layer at larger distance, gypsum was found in all parts of the clay, 3) gypsum appeared in all parts of the clay, 4) the concrete was depleted of calcium and the cement phases had undergone significant dissolution.

1.4. Criteria

A number of criteria have been defined concerning concrete seals, in particular with respect to the granular composition and the cement content [13]. They are different for ordinary boreholes and for the concept VDH because of the high temperatures prevailing in its lower part:

- Concrete fluidity at casting has to be sufficient,
- Concrete bearing capacity has to be sufficient and the compressibility sufficiently low for maintaining constant volume conditions under the load of the whole overlying series of supercontainers,
- The concrete must not undergo phase separation when being cast, and it must be physically stable after hardening,
- The hydraulic conductivity of the hardened concrete should be lower than that of the surrounding fracture zone,

2. SCOPE OF STUDY

Clay and concrete seals in boreholes in rock hosting highly radioactive waste shall have high enough physical stability and sufficiently low hydraulic conductivity for at least 100 000 years according to the Swedish Nuclear Fuel and Waste Handling Co (SKB) [11]. The concrete must have a very low content of cement for minimizing the mutual chemical impact on the contacting clay seals and at least 2100 kg/m^3 density to fulfil the requirements respecting tightness. Cement represents about 5-8 weight present of the solids in presently proposed candidate

concretes and it is preferably of low-pH type and very fine-grained. Inorganic substances should be used as supeplasticizers and talc, a hydrophobic easy-slipping mineral, turns out to be a promising candidate material.
Chemical interaction of this mineral and certain cement components give considerable strength despite the very low cement content [14]. Silica-rich aggregate material is being proposed for chemical integrity represented by crushed quartzite with some fine silica silt/sand for obtaining a low porosity and a high internal friction.In this paper comparison is made of the performance of concretes based on two brands of cement (Portland and Merit 5000), two types of superplasticizers (organic Glenium 51, and talc) and two different types of fine materials (FN) added to crushed and ground quartzite. The flow chart in figure 2 illustrates the investigated concrete mixes.

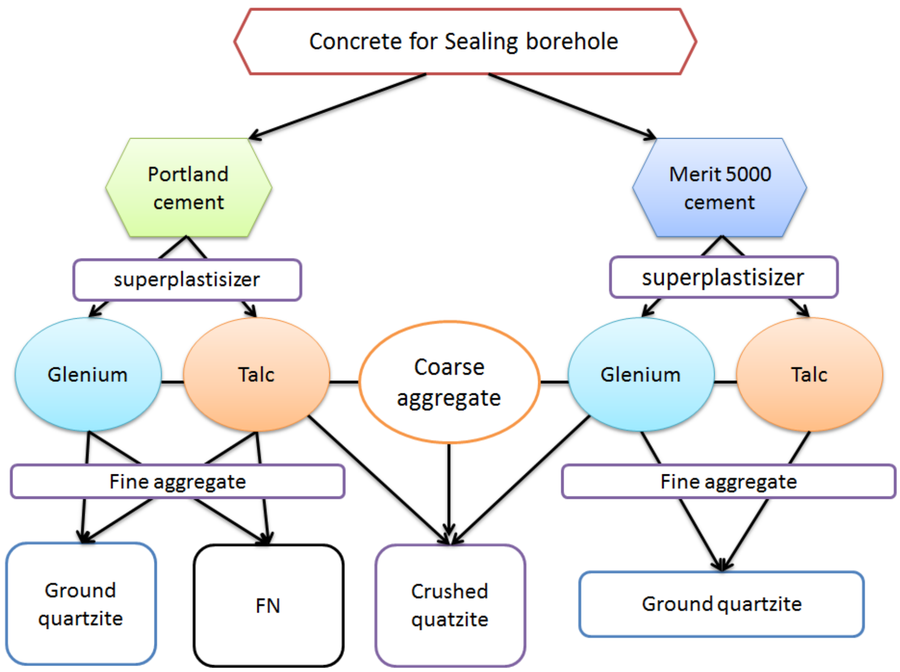


Figure 2. Plot shows the scope of this study

3. EXPERIMENTAL

3.1. Materials

3.1.1. Cement

Portland cement delivered by Cementa AB, Heidelberg cement group, Sweden, and Merit 5000 low-pH cement delivered by the SSAB Merox AB, Oxelösund , were used in the study.Table 1 shows the physical and chemical characteristics of the cements.

3.1.2. Aggregate

Two aggregate components were used, both being quartz-rich for high chemical integrity. A coarse part consisted of crushed quartzite with 2.70 g/cm^3 specific density, and a fine part was represented by milled crushed quartzite with 100 µm maximum aggregate size, to which an extra-fine fine component of very fine quartz particles (75.6 %) manufactured by Forshammar AB mixed with (14%) Na/Ca feldspars was added. The specific density was 2.60 g/cm^3 and pH around 9.6 at water saturation [14]. The grain size distributions of all the aggregate components are shown in figures 3, 4 and 5. The grain size distribution of the aggregate mixture of 70% “coarse” and 30% “fine” quartzite, which shown more suitable than the 50/50 % mixture was used in the experiments.

3.1.3. Superplasticizers

Two types of superplasticizers have been used in the study, one being an organic, brownish liquid termed Glenium 51. This type has been banned by certain organizations responsible for constructing HLW repositories like SKB (Swedish Nuclear Fuel and Waste Managing AB) because of environmental considerations [14]. The second type is the mineral talc in the form of a soft and very fine white mineral powder with the chemical formula

$3MgO.4SiO_2.H_2O$, manufactured by the VWR International Company UK. It is hydrophobic and low-viscous and does not form gels and has no impact on the environment. It is chemically stable in ordinary groundwater, the grain size analysis of Talc as drawn, figure 6.

Table 1. Chemical and Physical characteristics of cements

Analysis		Merit 5000 cement, according to SS-EN 196-1, 2 and 3	Portland cement, according to SS-EN 197-1
MgO		16.6	2.3-2.7
LOI		– 1.23	
LOI compensated for S^{-2} oxidation		1.43	
SO_3		0.085	3.1-3.7
Sulfide		1.33	
cl^-		<0.01	0.03-0.07
Glass content %		99	
Density g/cm^3		2.9	3.08
Specific surface area (m^2/kg)		470	460
Moisture content		0.09	
Initial setting	Water content (%)	27.0	
	Setting time (min)	210	160
Compressive strength (MPa)	7 days	23.3	44
	28 days	50.4	56

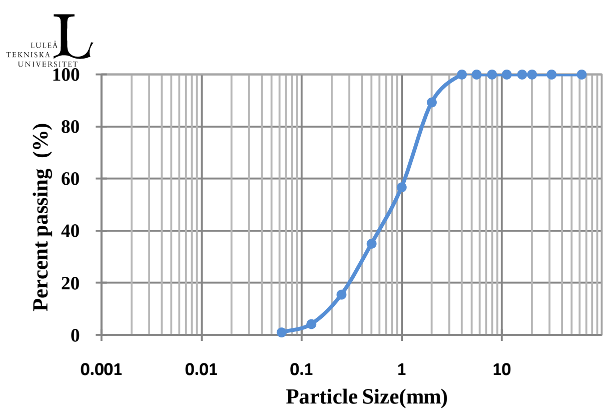


Figure 3. Grain size analysis of crushed quartzite

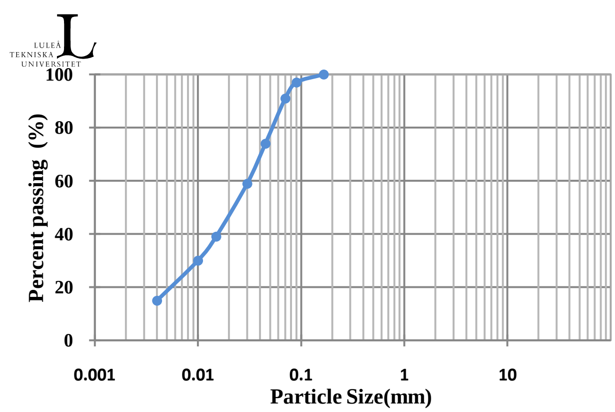


Figure 4. Grain size analysis of fine aggregate component

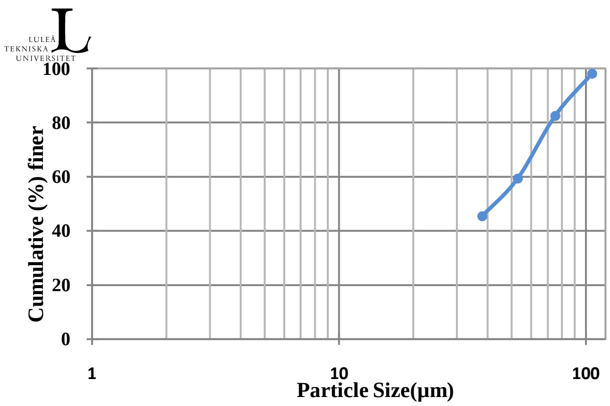


Figure 5. Grain size analysis of ground crushed quartzite

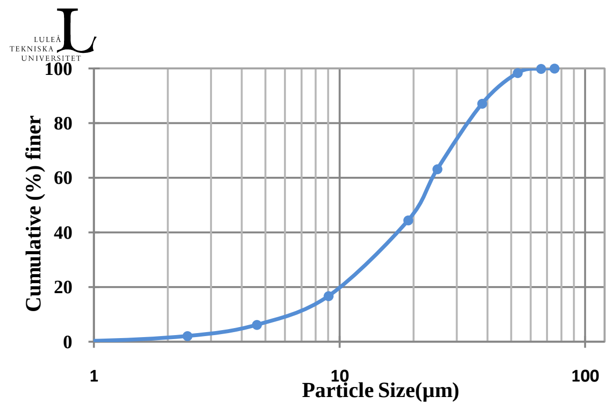


Figure 6. Grain size analysis of Talc

3.2. Sample preparation and mix proportions

The solid components cement, aggregates, additives and water were mixed and agitated using a mixer to reach homogeneity, left in figure 7. Plastic tubes (L=100 mm, D=50 mm) were used as moulds for casting the semi-fluid concrete pastes, which were densified by use of a vibrator, right in figure 7. An aquarium was used for storing the tubes in freshwater until testing took place. Portland and Merit 5000 concrete recipes were as shown in tables 2 and 3. The concrete unit weight was evaluated as reported in tables 2&3.The amount of water was selected so as to make them semifluid.

Figure 7. Left: Concrete mixture preparation demonstrating fluidity, Right: Molded samples

Table 2. Investigated Portland concrete recipes; the amounts of the components are expressed in weight percent of the total weight.

Concrete 1		PO/Gl. 1	PO/Gl. 2	PO/T. 1	PO/T. 2
Component (%)	Portland cement, (PO)	3.50	4.75	4.22	4.35
	Glenium 51, (Gl)	0.14	0.15	-	-
	Talc, (T)	-	-	9.3	9.56
	Crushed quartzite, (Q)	53.0	71.3	47.25	65.22
	Ground Q, (GQ)	32.1	-	20.25	-
	Fine material, (FN)	-	14.26	-	4.35
	Water, (W)	11.2	9.5	19.0	16.52
Density, kg/m^3		2255	2222	2140	2116
Component ratios	W/PO cement	3.2	2.0	4.5	3.8
	PO cement/ Total agg.	0.041	0.055	0.062	0.062
	GL/Total agg.	1.65E-3	1.75E-3	-	-
	T/Total agg.	-	-	0.137	0.137
	Fine agg./Total agg.	0.377	0.166	0.3	0.0625

Table 3. Investigated Merit 5000 low-pH concrete recipes; the amounts of the components are expressed in weight percent of the total weight.

<table>
<tr><td>Concrete 2</td><td></td><td>M/Gl</td><td>M/T. 1</td><td>M/T. 2</td></tr>
<tr><td rowspan="6">Component (%)</td><td>Merit 5000 cement, (M)</td><td>5.68</td><td>5.3</td><td>10</td></tr>
<tr><td>Glenium 51, (Gl)</td><td>0.136</td><td>-</td><td>-</td></tr>
<tr><td>Talc, (T)</td><td>-</td><td>7.6</td><td>7.25</td></tr>
<tr><td>Crushed quartzite, (Q)</td><td>51.0</td><td>47.5</td><td>45.1</td></tr>
<tr><td>Ground Q, (GQ)</td><td>30.9</td><td>20.4</td><td>19.3</td></tr>
<tr><td>Water, (W)</td><td>12.28</td><td>19.1</td><td>18.14</td></tr>
<tr><td>Density, kg/m^3</td><td></td><td>2154</td><td>2125</td><td>2160</td></tr>
<tr><td rowspan="5">Component ratios</td><td>W/M cement</td><td>2.16</td><td>3.6</td><td>1.8</td></tr>
<tr><td>M cement/Total agg.</td><td>0.069</td><td>0.078</td><td>0.156</td></tr>
<tr><td>Gl/Total agg.</td><td>1.6E-3</td><td>-</td><td>-</td></tr>
<tr><td>T/Total agg.</td><td>-</td><td>0.112</td><td>0.112</td></tr>
<tr><td>Fine agg./Total agg</td><td>0.377</td><td>0.3</td><td>0.3</td></tr>
</table>

One can see that the concrete with ground crushed quartzite gave a higher density (2255 and 2222) than the one based on fine materials (2140 and 2116) (Table 2). This might be due to an increasing of solid mixture density when using finer and with sharp edges particles. Glenium gave higher density than talc for the same fluidity (tables 2 and 3).

4. RESULTS AND DISCUSSION

4.1. Compressive strength

Determination of the unconfined compressive strength after 2, 7 and 28 days was made by means of a hydraulic compression machine, figure 8. The rate of compression was 1.5% per minute until failure took place as manifested by the appearance of fractures in hardened brittle concrete and by 10 % compression in ductile concrete. Tables 4 and 5 summarize the results from all the experiments.

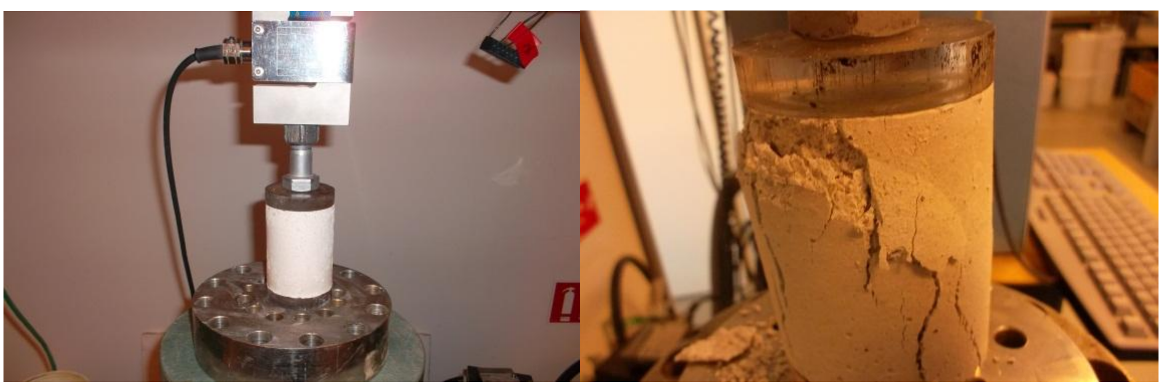


Figure 8. Uniaxial compression test

Table 4. Compressive strength, pH and fluidity of Portland concrete with different superplasticizers according to table 2

Concrete 1	Age of sample (days)	PO/Gl. 1	PO/Gl. 2	PO/T. 1	PO/T. 2
Compressive strength (MPa)	2	1.57	1.26	0.54	0.27
	7	2.88	2.25	0.66	0.99
	28	5.11	5.39	0.82	0.9
pH		11	12	13	13
Slump (mm)		35	45	20	35

Table 5. Compressive strength, pH and fluidity of Merit 5000 concrete with different superplasticizer according to table 3

Concrete 2	Age of sample (days)	M/Gl	M/T. 1	M/T. 2
Compressive strength (MPa)	2	-	0.017	0.015
	7	-	0.11	0.335
	28	0.057	2.63	2.22
pH		9	10	10
Slump (mm)		35	30	30

The Portland concrete gave quick strengthening increasing insignificantly after a week, while the Merit concrete gave initially slow but steadily increased strength. This is explained by neoformation of silicious cementing compounds in chemical reactions between this type of cement and the talc material [15].

4.2. pH

Litmus strip papers were used for determining the pH of the all freshly prepared concretes recipes since glass electrodes, also tried, gave varying data. Tables 4 and 5 show that Merit concrete gave lower pH results than Portland concrete at repeated testing. However, for Portland cement one finds that the Glenium concrete had pH-values of 11 and 12 while talc gave pH 13 for different fine aggregate brands. In contrast, Merit 5000 cement with talc had pH 10 (cf. table 5) [2, 14]. For sealing of boreholes and stabilization of tunnel backfills in repositories for radioactive waste where they are intersected by fracture zones concrete with Merit 5000 cement is preferable.

4.3. Workability

For determining the fluidity of the differently composed concretes slump tests were made immediately after preparation. The results shown in tables 4 and 5 demonstrate that Glenium gave higher fluidity than talc but that the difference is not significant [13].

4.4. Impact of concrete components on the mechanical strength

4.4.1. Effect of fine aggregate

Figure 9 shows the impact of two fine aggregate types on the compressive strength for the same type of cement and superplasticizer. For Glenium-Portland concrete, use of ground crushed quartzite as fine aggregate gave the highest strength early after casting (2 and 7 days) but lower strength after 28 days than when FN was used. This is in contrast with the behaviour of Talc-Portland cement and FN, which had higher strength after 7 and 28 days (figure 9, right). This can be explained by the higher surface area of FN than of ground crushed quartzite (cf. figures 4 and 5) as indicated by the higher water content needed for complete hydration.

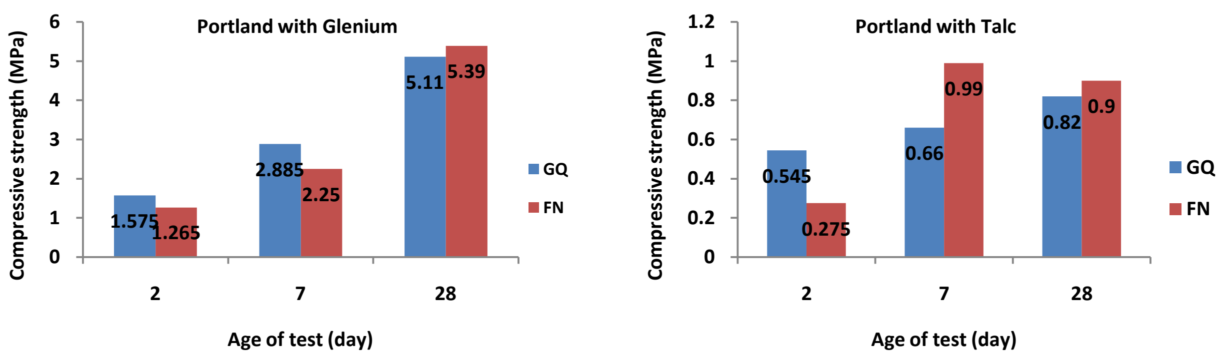
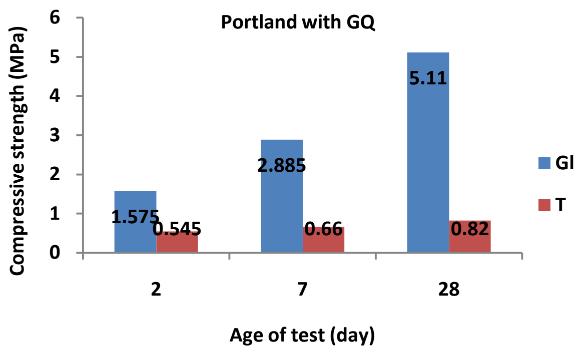


Figure 9. Compressive strengths of concretes based on Portland cement and different fine aggregate types with superplasisizer, Left: Glenium, Right: Talc

4.4.2. Effect of superplastisizer

Figure 10 summarizes the effect of different superplasticizers on the compressive strength. Portland concrete with Glenium showed higher strength than with talc for all aggregate types. In contrast, low-pH, Merit 5000 cement with talc gave the highest compressive strength (figure 11), indicating that the chemical reactions of cement and talc were particularly important for the strengthening.



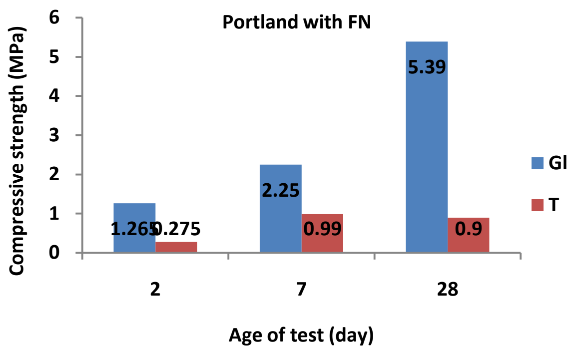


Figure 10. Compressive strengths of Portland concrete with different superplastisizers and fine aggregate, Left: Ground quartzite, Right: FN

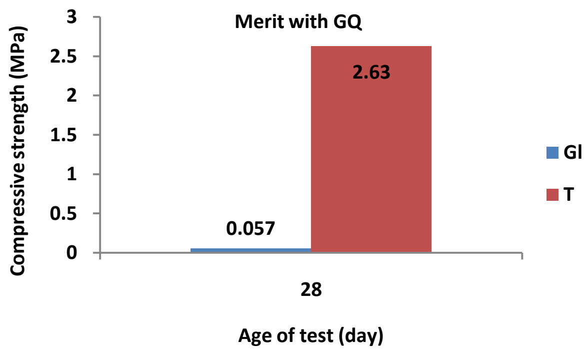
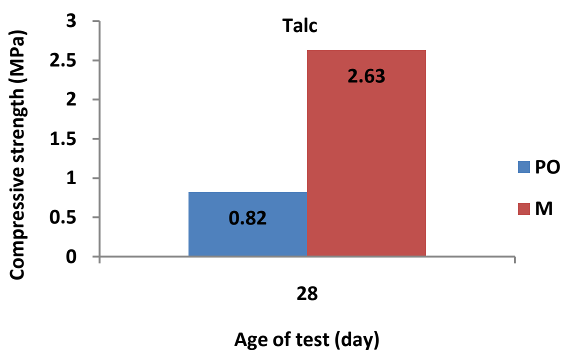


Figure 11. Comparison between compressive strengths of concrete with Merit cement and different superplasticizers

4.4.3. Effect of cement type

The left histogram in figure 12 demonstrates that Merit 5000 concrete with talc gave higher compressive strength than Portland concrete after 28 days of maturation. This can be explained by a delayed chemical interacting between talc and Merit cement causing dissolution of the first mentioned and formation of new cementing agents [15]. Such interaction between cement and superplasticizer did not take place in Merit 5000 concrete with Glenium as shown by the right histogram in figure 12.



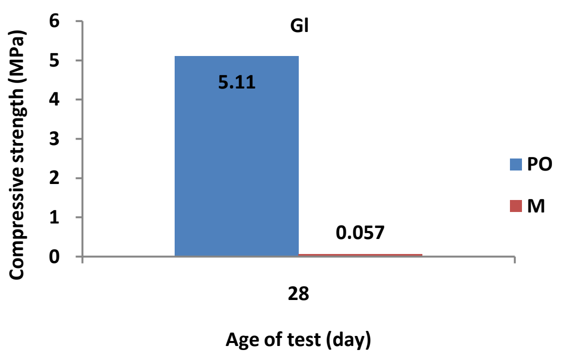


Figure 12. Comparison between compressive strengths of concrete based on different types of cement and superplasticizer, Left: Talc, Right: Glenium

5. CONCLUSSIONS

Concretes with crushed quartzite as coarse aggregate, and milled crushed quartzite or FN consisting of very fine quartz particles and Na/Ca feldspars as fine aggregate material, and with talc as superplasticizer were prepared and investigated in this study for possible use in sealing deep boreholes. The cement content was lower than 10 percent by weight and less than 6 percent for most of the samples. The major conclusions from the study were:

Concrete with Portland cement gave quick strengthening but very little additional strength after a week, while the "Merit concrete" gave slow but steady increase in strength that was ultimately higher than for Portland concrete,

pH was lower for Merit concrete than for Portland concrete. For the firstmentioned it was around 10,

The density of concrete with crushed and ground was higher than when fine materials in the aggregate,

6. ACKNOLEDMENTS

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