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LONG-TERM DURABILITY ASSESSMENT OF CONCRETE IN LOW AND INTERMEDIATE LEVEL WASTE REPOSITORIES

Abobaker Ba Ragaa[1], Fahim Al-Neshawy[2], Ester M. Jolis[3], Jukka Kuva[4] and Jouni Punkki[5]

[1] Researcher, Aalto University School of Engineering, Finland (abobaker.baragaa@aalto.fi)
[2] Staff Scientist, Aalto University School of Engineering, Finland
[3] Research Scientist, Geological Survey of Finland GTK, Finland
[4] Senior Scientist, Geological Survey of Finland GTK, Finland
[5] Professor, Aalto University School of Engineering, Finland

ABSTRACT

In Low and Intermediate Level Waste (LILW) repositories, concrete barriers must be able to resist their environments for hundreds of years. The concrete structures can be subjected to various degradation mechanisms, such as chloride induced corrosion, sulfate attacks, portlandite leaching and alkali-silica reaction.

The purpose of this research was to evaluate the environmental effects on different types of concrete mixtures stored in an environment that simulates the LILW repositories for 25 years and assess their performance for the intended service life. Concrete specimens cast 25 years ago were tested in this study, and their mechanical capabilities, as well as their durability to various environmental conditions. The tested concrete specimens were stored in various salt solutions and had different mix compositions.

The concrete specimens showed high strength properties, with a slight increase compared to their previous results after casting. The petrographic analysis of the specimens only showed very minor instances of degradation, mostly being local, and no significant damage was observed. The chloride content increased slightly in aggressive solutions, but it is still below the determined threshold for submerged specimens. The sulfate and magnesium results were sporadic, but they were mostly low.

This research proves that long term studies are important in studying the behavior of concrete structures in LILW environments. Therefore, it is essential to analyze and investigate these structures effectively, to ensure that such critical concrete structures serve their purpose.

INTRODUCTION

Reinforced concrete structures are used in Nuclear Power Plants (NPPs) in an engineered barrier system, to shield the nuclear waste in the repositories. The concrete structure is required to withstand the chemical and atmospheric environment that surrounds it during both the operation and post-closure phases of the structures. Generally, the reinforced concrete must have high capabilities to resist this long-term degradation.

Concrete structures can be subjected to various modes of degradation in LILW repositories. These can be due to the atmospheric conditions that surrounds the structure, leading to its interaction with chemicals and water, which could result in changes to the concrete's microstructure and chemical composition. These changes influence the long-term capabilities of the reinforced concrete.

The degradation of concrete in LILW repositories occur via various mechanisms. The degradation in the repository is influenced by the exposure conditions surrounding the reinforced concrete. Repository structures are used for a long duration. The duration can be divided into two phases: **i) the operation phase** and **ii) the post-closure phase**. During the operation phase, which can last for 100 years, the concrete is exposed to atmospheric conditions of the caverns, and the main ‘degradation driver’ is the carbonation of concrete and subsequent corrosion of reinforcement. During the post-closure phase, the facilities are decommissioned, and the caverns are gradually filled with groundwater. The chemistry of the groundwater influences the degradation of the reinforced concrete. The duration of the post-closure phase can be in the hundreds or even thousands of years. In this study, the concrete properties are assessed by using various exposure solutions that simulate the long-term degradation of concrete in the post-closure phase.

DEGRADATION OF CONCRETE IN LILW REPOSITORIES

Reinforcement corrosion

Reinforcement corrosion in LILW repositories can occur via carbonation and chloride attacks. In carbonation induced corrosion, the alkalinity of the concrete forms a passive layer around the reinforcement, preventing the occurrence of corrosion. When carbonation occurs, the portlandite in the concrete phases is transformed into calcite, and the alkalinity of the concrete is slowly reduced. When carbonation reaches the level of the rebars, the passive layer is destroyed, and reinforcement corrosion induce by carbonation commences. In LILW repositories, this is a concern during the operational phase, which can last for around 100 years (Kari & Puttonen, 2014).

Chloride-induced corrosion in LILW repositories is more of a concern during the post-closure period. In this instance, the corrosion is driven by the ingress of chlorides into the concrete, reaching the level of the rebar, and resulting in the pitting corrosion of reinforcement. The chloride content at the rebar level must be above a certain threshold to initiate this corrosion. Because the environment in LILW repository during the post-closure period is anoxic, this threshold level can be higher than that of traditional values used in conventional structures, with some research projects estimating it to be around 2% per weight of cement (Angst et al., 2022). Chloride ingress into the concrete can be a slow process. The duration of the post-closure period is long, and it can be in the hundreds or thousands of years (Kari & Puttonen, 2014), which could result in favourable conditions for chloride-induced corrosion.

Sulfate attack

Sulfate attack in concrete leads to changes in the cementitious phases of the concrete, leading to the formation of expansive materials that cause cracking and spalling of the concrete. In LILW repositories, the concrete is submerged in groundwater in the post-closure phase, which contains some sulfate and magnesium. The sulfate ingress leads to reactions with portlandite, that lead to the formation of gypsum and ettringite. The reactions can propagate further with the presence of magnesium, which can break down the cement phases further to produce brucite and M-S-H, which can be somewhat incohesive and weaker than the original material (Zhang et al., 2014). In certain conditions (which are present in LILW repositories), thaumasite formation can also form in the concrete, in which the C-S-H phases are transformed into thaumasite, which is a mushy weak material (Rahman & Bassuoni, 2014). In this case, the damage to the concrete is more severe.

Leaching.

When the concrete is in contact with water for a long period of time, leaching of cementitious phases can occur. The leaching of cement paste occurs to achieve equilibrium between the pore solution and the exposure solution. This leads to the dissolution and leaching of cementitious phases, leading to the removal of calcium from the concrete. Leaching is typically classified into two stages: the leaching of portlandite, which is followed by the decalcification of C-S-H (Duchesne & Bertron, 2013). The leached concrete is more porous, as some of the material is leached, which can accelerate the effects of leaching and other degradation mechanisms.

MATERIALS AND EXPERIMENTAL INVESTIGATION

In this study, 9 different concrete mixtures with different proportions were used to evaluate the degradation of concrete under environments that simulate repository conditions. The concrete specimens were cast in 1997-1998 and stored in solutions ever since. The chemical composition of the binder is shown in Table 1.

Table 1: Chemical composition of used binders, in % (Ferreira et al., 2015).

Binder	CaO	SiO_2	Fe_2O_3	Al_2O_3	MgO	K_2O	Na_2O
SR Cement (CEM I 42.5 SR)	65	21	4.3	3.2	2	0.34	0.94
“Yleis” cement (CEM II A 42.5 R)	65	22	2.7	5.4	3.5	0.87	0.89
“Mega” cement (CEM I 42.5 R)	61	19	3.1	5.1	4.2	1.6	0.07
Silica fume		> 85					
Blast furnace slag	40	34	-	9.3	11	0.47	0.47

The used concrete mixtures contain different water/binder, aggregate/binder, and binder portions are shown in Table 2.

Table 2: The used concrete mixtures in the program.

Concrete code	Cement type	Cement portion	Silica fume portion	Slag portion	Aggregate /binder ratio	Water / binder ratio
B1	CEM I 42.5 SR	100%	0	0	4	0,35
B2	CEM I 42.5 SR	100%	0	0	5	0,425
B3	CEM I 42.5 SR	100%	0	0	6	0,5
B4	CEM II A 42.5 R	90%	10%	0	4	0,35
B5	CEM II A 42.5 R	90%	10%	0	5	0,425
B6	CEM II A 42.5 R	90%	10%	0	6	0,5
B7	CEM I 42.5 R	20%	5%	75%	4	0,35
B8	CEM I 42.5 R	20%	5%	75%	5	0,425
B9	CEM I 42.5 R	20%	5%	75%	6	0,5

In this study, the concrete specimens were stored in various solutions that simulate repository groundwater conditions. Those solutions contain differing amounts of chloride, magnesium, and sulfate. The chemicals are used to simulate the ingress of the aggressive ions, and if the concrete’s microstructural properties were affected due to the exposure to the ions. The concrete’s performance is also evaluated based on the obtained results. In general, 3 main solutions are used in this report, to study the effect of chloride ingress, sulfate attack, and combined chloride/sulfate/magnesium attack in concrete. An authentic groundwater solution is also used in the study (labelled GW), which contains a small proportion of aggressive ions. This groundwater solution is taken from the cavern repositories in Olkiluoto, Finland. The chemical composition is, of course, fluctuating in the caver, and can be much more severe in different locations. The chemical composition of the used solutions is shown in Table 3.

Table 3: Solutions and aggressive ions

Code	SO_4 content (mg/L)	Cl content (mg/L)	Mg content (mg/L)
GW	45	17	0.16
L1	1000	0	0
L2	0	10000	0
L3	1000	10000	300

The testing program of the study consists of testing the compressive strength of the concrete specimens (150mm cubes), as well as the chloride ingress (potentiometric titration), sulfur and magnesium content (micro-X-Ray Fluorescence) and a petrographic thin section analysis of the concrete's microstructure. The sulfur magnesium, chloride, and petrographic analysis is done on concrete prisms that have been sealed off with epoxy, to facilitate 1 dimensional ingress of ionic species into the concrete, which resembles the conditions in the LILW repositories. The obtained results are compared to the previous iterations of the project, to investigate the changes of the concrete properties with time. Table 4 summarizes the experimental program in this study.

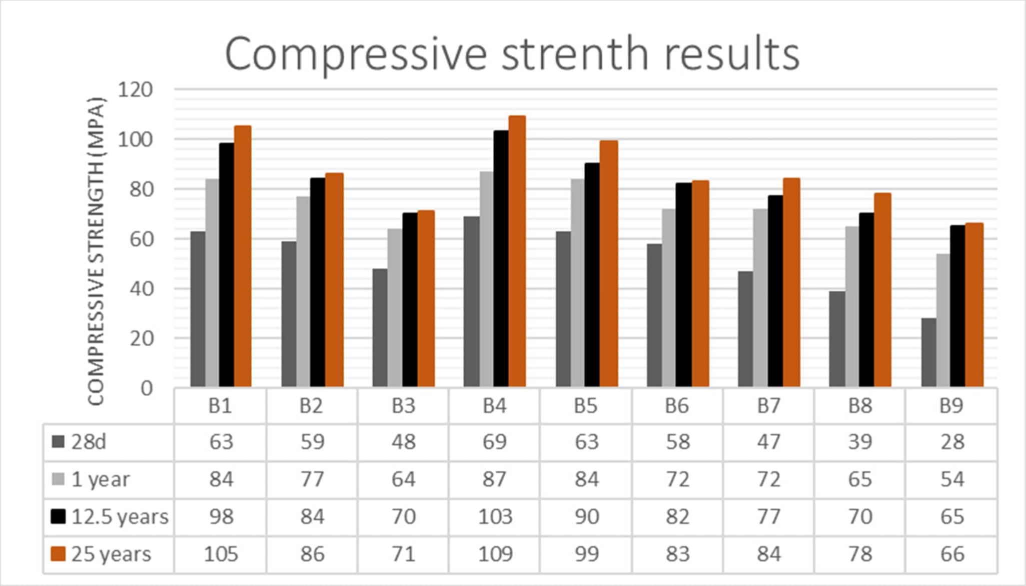
Table 4: The experimental program of the research

Test	Specifications	Storage solution
Strength	150mm cubes B1 – B9	GW
Chloride ingress	Grinded powder (concrete prism) B2, B5, B8 Potentiometric titration	GW, L2, L3
Sulfur and magnesium content	Concrete prism B2, B5, B8 µXRF	GW, L1, L3
Petrographic analysis	Concrete prism B2, B5, B8 Thin section slices	GW, L1, L2, L3

RESULTS AND DISCUSSION

Compressive strength

The compressive strength results of the concrete cube samples in this study are shown in Figure 1. The strength development of the concrete throughout the 25-year project duration is shown in Figure 2. Based on the results, the constant (but slow) development of the concrete's strength properties can be seen. The results have slightly increased in the 25-year investigation compared to the previous results. This is in accordance with the relevant literature, which suggest that the concrete's strength keeps developing slowly with time.



	B1	B2	B3	B4	B5	B6	B7	B8	B9
■ 28d	63	59	48	69	63	58	47	39	28
■ 1 year	84	77	64	87	84	72	72	65	54
■ 12.5 years	98	84	70	103	90	82	77	70	65
■ 25 years	105	86	71	109	99	83	84	78	66

Figure 1: Compressive strength test results.

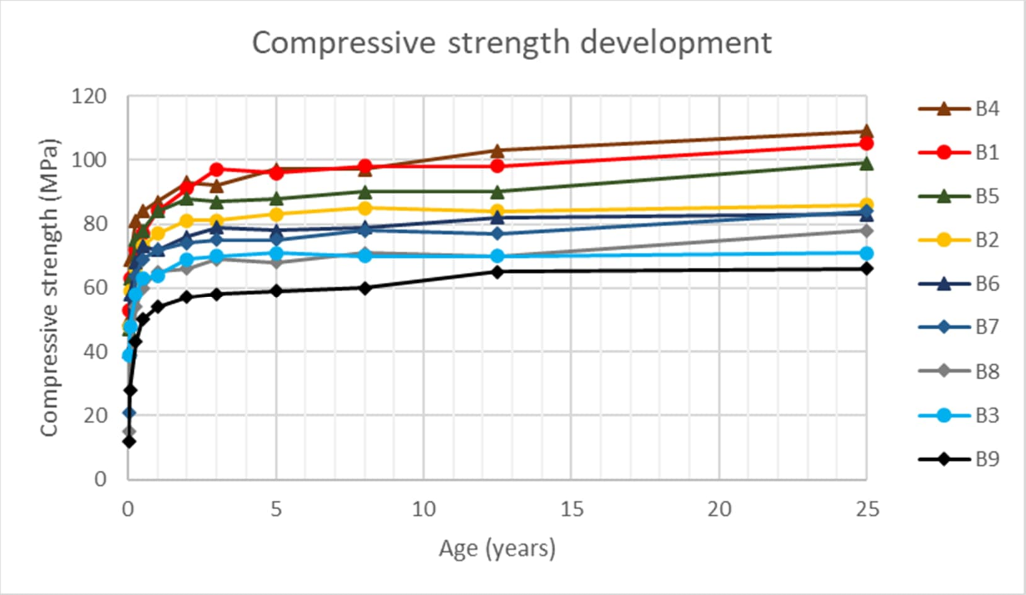


Figure 2: Compressive strength development throughout the 25-year program period (Ferreira et al., 2015)

Chloride ingress

The chloride ingress results into the concrete are shown in Figure 3. The graph shows the ingress in the current study (25-year storage period) compared to the previous investigation at around 15-years of storage (Ferreira et al., 2015; Vesikari & Koskinen, 2012). Based on the obtained results, the effects of both the storage period and the binder type are noticeable. The chloride ingress into the specimens has generally increased over time. The 25-year tests mostly showcase higher chloride content at a deeper depth compared to the previous results. The results also show that the concrete mixtures with cement replacement (both B2 with silica fume, and B8 with silica fume + slag) contribute to better properties against chloride attack.

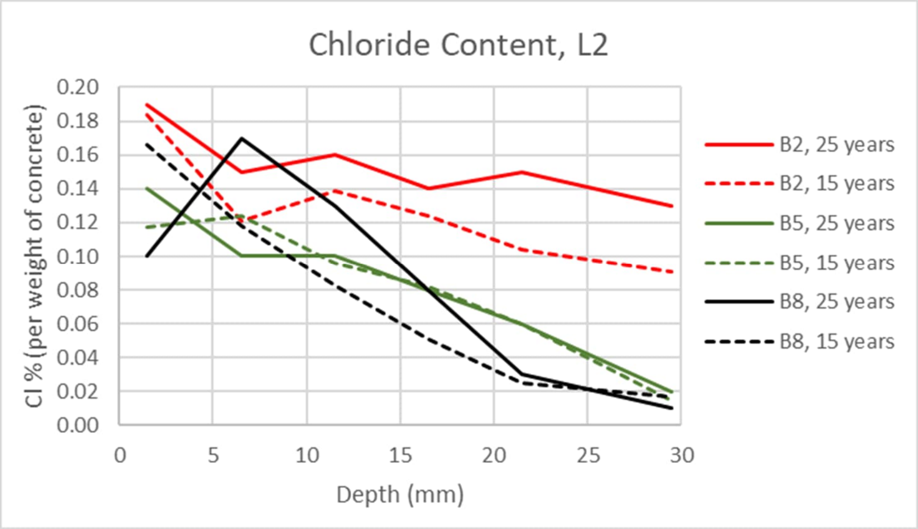


Figure 3: Chloride ingress into the concrete (25-year and 15-year storage period in NaCl solution, L2)

Sulfur and magnesium attack

The sulfur content in the concrete is shown in Figure 4 (in mixed solution, L3). The results show relatively low values in the concrete. The storage period and the depth of measurement did not show any significant impact that suggests the diffusion of ionic species into the concrete. The values have remained relatively low. This is also reinforced by the petrographic test results that are discussed in the following section. This pattern of "low" concentration of ionic species is also seen in the other storage solutions, where the distribution pattern remained relatively 'flat' with values that are close to the sulfur levels that were originally observed in the concrete which were between 0.15 – 0.3 % per weight of concrete (Ferreira et al., 2015). In the outer edges of some of the specimens (B8 mainly), slightly higher sulfur levels were observed, suggesting that very minimal ingress might have occurred.

Some of the magnesium profiles are shown in Figure 5. The results, which mostly follow the sulfur trend, do not show any significant sign of magnesium ingress into the concrete. The magnesium levels are relatively low and flat for the most part, with slightly higher levels in slag concrete (due to the chemical composition of slag). Only one sample (B8, tested at 15 years) showed some signs of ingress on the edge of the specimen, suggesting very minimal ingress of magnesium as well. The original magnesium content of the tested concrete ranged between 0.3 to 1.4 % per weight of concrete, with slag concrete, B8 being on the upper end of this range (Ferreira et al., 2015).

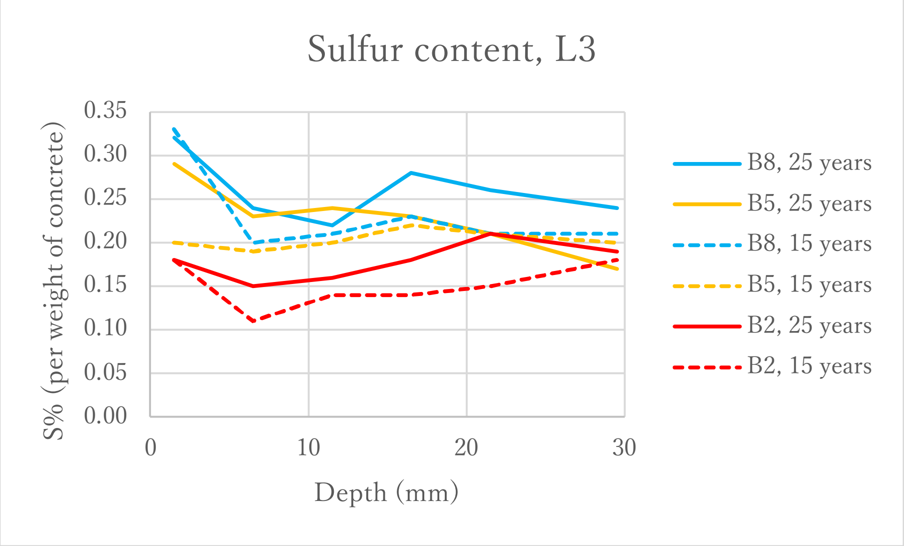


Figure 4: Sulfur content in the concrete, 25-year and 15-year storage period in mixed solution L3 *(Vesikari & Koskinen, 2012)*

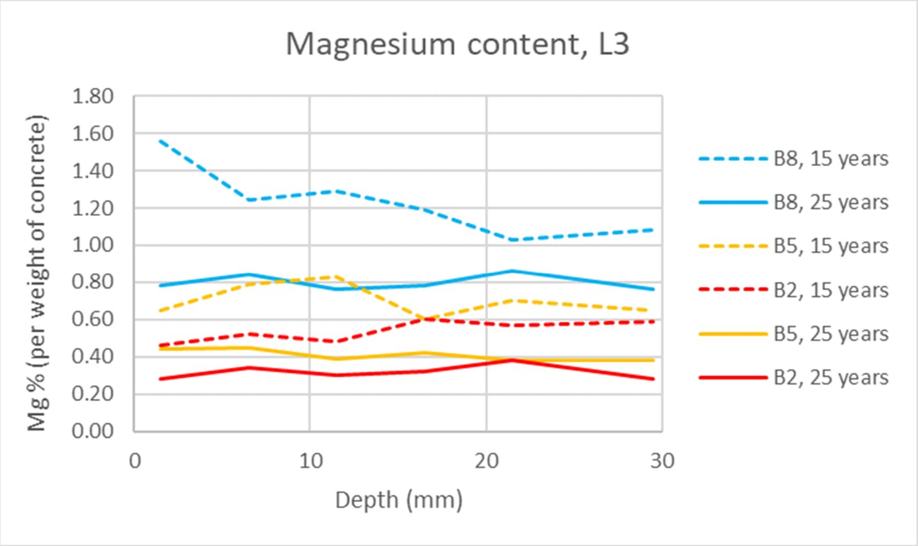


Figure 5: Magnesium content in the concrete, 25-year and 15-year storage period in mixed solution L3 *(Vesikari & Koskinen, 2012)*.

Petrographic analysis

The results of the thin section petrographic analysis have shown some of the physical properties of concrete. In general, the tested concrete specimens appear to be of good quality, with minimal and local defects. The concrete specimens (which had a w/c ratio of 0.425) have shown a relatively low degree of hydration, which is typically the case in concrete mixed with low w/c ratios. The portlandite in the concrete did not show signs of leaching, and it is evenly distributed. The aggregates were mostly evenly distributed, and the interfaces appear to be good. Depth of carbonation was very low (which is expected, due to the specimens being stored in anoxic environments).

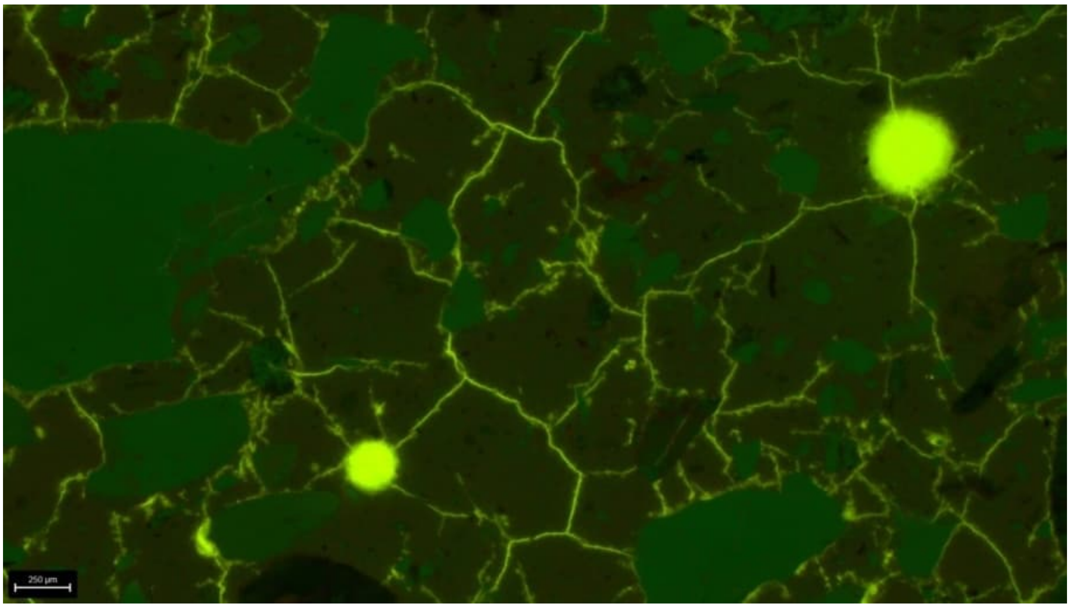


Figure 6: Very fine mesh micro-cracks (< 0.01mm) were present in all tested samples.

All the specimens had very fine mesh microcracking (thickness < 0.01mm), which is also typical in concretes with low w/c ratios, shown in Figure 6. Some of the tested specimens have shown some minor signs of degradation, such as the presence of cracks on the margins of aggregates in Figure 7, and the formation of small amounts of secondary ettringite shown in Figure 8.

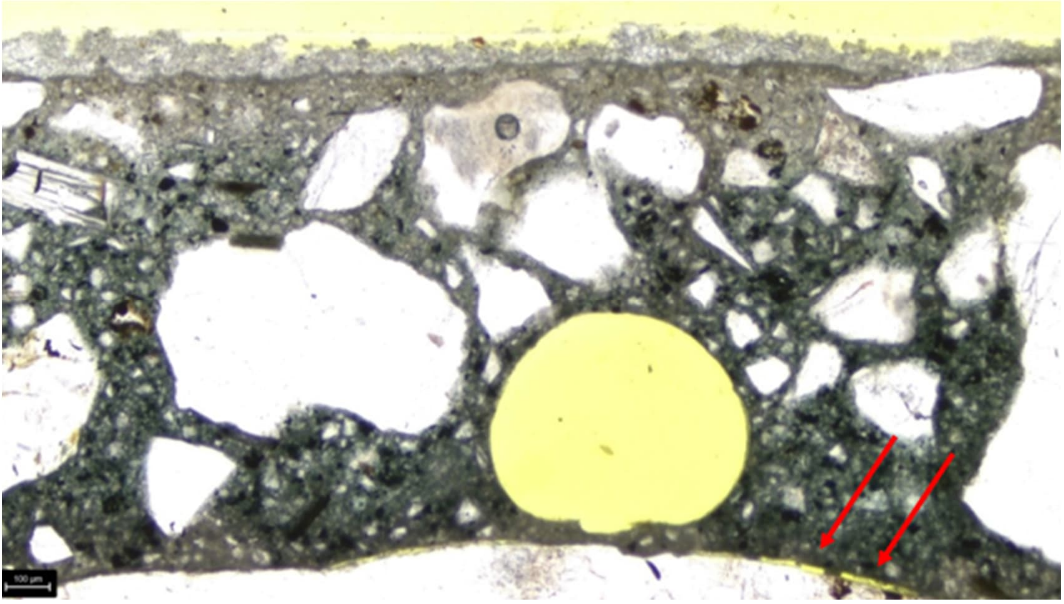


Figure 7: Some minor local imperfections were observed, such as the highlighted crack in the margin of aggregates in a B8 slag concrete sample.

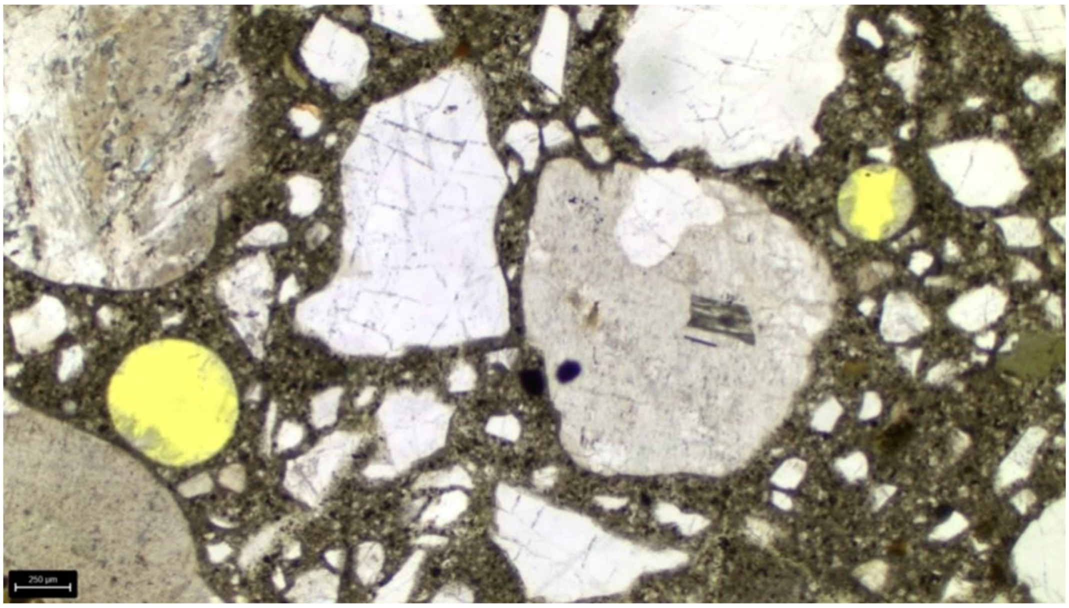


Figure 8: Some secondary ettringite can be seen in the voids in this specimen.

CONCLUSION

In this research, 25 years old concrete specimens stored in different salt solutions, were examined. The testing program included testing the compressive strength, chloride ingress, sulfur and magnesium content, as well as the analysis of the microstructure of the specimens using the petrographic thin section analysis. The concrete mixtures have shown high strength properties, as well as a slight strength development compared to the previous test iterations. The chloride concentrations of the specimens were determined, and it was seen that the specimens with secondary cementitious materials generally had lower chloride content in deeper parts of the concrete (beyond 15mm) compared to the mixes with only Portland cement. The µXRF results did not show any significant ingress of sulfate and magnesium into the concrete, as the values remained similar to the initial results, and the result charts were mostly flat apart from some results being slightly higher at the fat edges of some of the tested specimens. This is also reinforced by the thin section images, which did not show any noticeable sign of sulfate attack. The defects that were seen in the petrographic analysis were mostly local, and no signs of damage as a result of those defects were observed. Investigating the long-term behavior of concrete is significant for waste repositories, due to the long lifespan of those structures. This research was aimed at expanding the knowledge of concrete durability in repository conditions, by testing and assessing the performance of concrete in simulating environments to provide more insight into concrete behavior.

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