Full Paper Transactions, SMiRT 28
Toronto, Canada, August 10-15, 2025

INVESTIGATION OF LEACHING AND THAUMASITE SULFATE ATTACKS IN CEMENTITIOUS MATERIALS FOR LOW AND INTERMEDIATE LEVEL WASTE REPOSITORY STRUCTURES

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INTRODUCTION

In Finnish nuclear waste repositories, the usage of reinforced concrete in the engineered barriers is significant. Reinforced concrete is designed for a long effective life, hundreds of years. The barriers are used for Low and Intermediate Level Waste (LILW) repositories. Throughout this usage period, the concrete structures must withstand a wide range of degradation drivers present in the underground cavern environment, especially regarding the long-term contact with flowing groundwater containing mineral ions. The presence of sulfate ions in the groundwater, as well as the flow of the groundwater and the pH gradient can cause sulfate and thaumasite degradation, as well as leaching of calcium from the cementitious matrix. The objective of this paper is to assess the performance of different binders against sulfate and thaumasite attacks, as well as calcium leaching

LEACHING OF CEMENTITIOUS MATERIALS

Calcium phases can leach out of cementitious materials with long-term contact with groundwater, which can occur in underground nuclear waste repositories (post-closure). The pH level of the cement paste can be reduced by leaching, in which the calcium phases are dissolved in stages (Ekström, 2003). Calcium hydroxide (CH), which is the more soluble calcium form in cement paste is dissolved first, followed by a gradual dissolution of the calcium minerals in the calcium-silicate-hydrate phases (CSH), reducing the total calcium in the CSH gradually (Kärnbränslehantering & Olof Höglund, 2001; Phung, Maes, Jacques, Perko, et al., 2016). Leaching can result in weakening of the material, where the porosity increases, and subsequently, the strength drops (Agostini et al., 2006; Carde & François, 1999; Phung, Maes, Jacques, De Schutter, et al., 2016).

THAUMASITE SULFATE ATTACK

Sulfate attacks are also of concern in the underground waste repositories during the post-closure period. The salinity of the groundwater affects the sulfate attack behaviour, where the risk increases with higher concentrations and more soluble phases (Ikumi & Segura, 2019; Zhang et al., 2024). Sulfates typically attack the CH phases in cement paste, producing aluminate phases such as ettringite and gypsum. The thaumasite form of sulfate attack can also occur under special conditions, resulting in a more thorough damage. Thaumasite form attacks the CSH phases directly instead of the CH phases (Crammond, 2002; Song et al., 2017), where the thaumasite product is mushy and weak.

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EXPERIMENTAL INVESTIGATION

This study investigates the performance of different cementitious mixes against leaching and thaumasite sulfate attack. 5 different mortar mixes were prepared for this study. The mix compositions were chosen based on (Al-Neshawy & Ba Ragaa, 2023). The mixes differ in the used binder and the utilized supplementary cementitious materials (SCMs). The mixes utilize Sulfate Resisting (SR) cement, silica fume, and Ground Granulated Blast Furnace Slag (GGBFS). The mixes used in the study are shown in Table *1*. The specimens were prepared in accordance to EN 196-1.

Table 1: Mix design of the mortar specimens

Mix	Binder		w/b
	Portion [%]	Type	
SR-mix	100	CEM I	0.44
SR-SI-mix	90 10	CEM I Silica fume	0.44
KA-mix	100	CEM III/A	0.44
KB-mix	100	CEM III/B	0.44
KB-SI-mix	90 10	CEM III/B Silica fume	0.44

After preparing and curing the specimens, initial testing is conducted to obtain the compressive strength baseline of the specimens. The fresh properties of the mixes, as well as the initial compressive strength testing results are shown in Table *2*. The chemical composition is also assessed using X-Ray methods.

Table 2: Fresh properties and initial strength of the mortar mixes.

Mix	Temperature (Cº)	Slump (cm)	Density (kg/L)	Air content (%)	Compressive strength (MPa)
SR-mix	26	17.9	2.22	3.6	68.4
SR-SI-mix	26.2	13.4	2.24	3.8	74.2
KA-mix	26.1	18.55	2.2	3.8	72.8
KB-mix	27.2	19.15	2.17	3.4	65.5
KB-SI-mix	25.8	15.25	2.16	3.6	60.1

Table 3: Concentration of the aggressive solutions.

Solution	Information	
Leaching	Chemical	NH_4NO_3
	Concentration	6 mol
Thaumasite Sulfate	Chemical	$MgSO_4 . 7 H_2o$
	Concentration	Mg: 20 mg/L SO4: 80 mg/L

The remaining specimens are stored separately into two solutions, which simulate the behaviour of leaching or sulfate attack. The leaching solution contains ammonium nitrate (NH_4NO_3), and the sulfate solution has Epsom salt. The concentration of the aggressive ions is detailed in Table *3*. The storage containers are placed in the research tunnel in Aalto University, which has an ambient temperature around 15ºC, which is suitable for thaumasite formation (Ashraf et al., 2014). The specimens in their storage containers are shown in Figure 1. The testing program includes periodic monitoring of the specimens' mass change. The compressive strength of the specimens is also determined before and after storage.

Figure 1. Storage containers for the sulfate specimens (left) and leaching specimens (right).

RESULTS

Compressive strength, leaching

In this section, we display some of the obtained results. The compressive strength results showcase the current drops in strength of the stored specimens. The results vary by mix, with higher strength losses associated with mixes that contain more cement. The KB and KB-SI mix, which have more slag had much lower strength drops of 8.7% and 7.7%, respectively, while the KA mix, which has less slag in comparison had a compressive strength reduction of 17.8%. The SR mix had the biggest drop, with 32.6% strength drop. The presence of added silica fume decreased this fall in compressive strength slightly, where the SR-SI mix had a strength reduction of 23.1%.

Table 4: Compressive strength of the mortar specimens, before and after storage in the leaching solution.

Mix	Compressive strength (MPa)	
	Initial	4-month storage
SR-mix	68.4	46.12
SR-SI-mix	74.22	57.09
KA-mix	72.79	59.82
KB-mix	65.45	59.78
KB-SI-mix	60.08	55.46

Testing of pH, leaching

Using the phenolphthalein method, the drops in pH of the specimens under the leaching solution was also measured. The pH reduction means that the colour of the degraded part of the tested specimen will not change to pink (Huang & Qian, 2011; Larrard et al., 2010). The testing is conducted monthly to assess the degree of leaching throughout the storage period. Figure *2* shows one instance of testing the colour changes of the different mixes.

Figure 2. Phenolphthalein test in the mortar mixes.

The progression of the leached front is highlighted in Table *5*. The results showcase the progression of the leached front, where the specimens in the SR mix (no SCMs) started with a lower relative pH reduction, which progressed deeper into the specimen faster than some of the other mixes. The slower start can be attributed to the high alkalinity in cement, whilst the faster progression can be due to the higher CH content in mixes without SCMs, leading to more losses in alkalinity and subsequent pH reductions. The SR-SI and KA mixes generally had good performance in relation to the progression of the leached front with time.

Table 5: Progression of the reduced pH front.

Mix	Depth (mm)		
	1st month	2nd month	3rd month
SR	1.37	3.2	4.89
SR-SI	1.64	3.26	4.74
KA	1.92	3.22	4.35
KB	2.18	3.72	5.34
KB-SI	3.17	4.52	4.79

Mass changes, leaching

The mass changes of the specimens stored in the ammonium nitrate solution were tracked monthly. Table *6* shows the mass variations in the first four months of the investigation. Based on the results, it can be seen that the SR mix has the most gradual decrease in mass, which follows the results obtained in the phenolphthalein assessment. SR-SI has a relatively higher mass decrease as well compared to the remaining mixes (containing slag) which had much lower drops.

Table 6: Mass change in the specimens under the leaching solution

Mix	Mass changes within months, %		
	2nd	3rd	4th
SR	-1.23	-0.51	-0.27
SR-SI	-0.63	-0.32	-0.05
KA	-0.28	-0.18	0.02
KB	0.16	-0.13	-0.01
KB-SI	0.18	-0.14	0.07

Mass changes, thaumasite

The changes to the mass in the specimens stored in the Epsom salt solution are shown in Table *7*. Based on the results, the mixes have had varying degrees of mass gain in the first month, with higher magnitudes in the KB and KB-SI mortars. These two mixes have also showcased the biggest mass drops in the following month, with higher signs of degradation in these mixes, especially KB-SI. The remaining mixes show more moderate mass losses, and less visible degradation. Figure *3* shows the degradation of the KB and KB-SI mixes.

Table 7: Mass change in the specimens under the Epsom salt solution.

Mix	Mass changes within months, %		
	2nd	3rd	4th
SR	0.73	-0.12	-0.04
SR-SI	0.74	-0.17	-0.16
KA	0.60	-0.16	-0.04
KB	1.31	-0.67	0.03
KB-SI	2.08	-1.13	0.01

Figure 3. The visual degradation after 2 months.

CONCLUSION

This paper focuses on the degradation of cementitious materials under sulfate attacks and leaching. The goal of the study is to investigate the accelerated degradation of mortar specimens under simulating solutions. In this study, different mixes were used for the assessment, where the binder type changes per mixture. The performance is assessed by the reduction of the mortar's compressive strength. The depth of leaching is also monitored periodically for the specimens under the leaching solutions. The results show the weaker performance of specimens without SCMs when exposed to leaching. The sulfate attack results also demonstrate the weaker performance of the KB and KB-SI specimens, which had more visible degradation.

REFERENCES

Agostini, F., Lafhaj, Z., Skoczylas, F., & Loodsveldt, H. (2006). *Experimental study of accelerated leaching on hollow cylinders of mortar*. https://doi.org/10.1016/j.cemconres.2006.09.018

Al-Neshawy, F., & Ba Ragaa, A. (2023). *Concrete mixtures, specimen preparations, storage solutions and testing plan WP2-Design new durable concretes for the LILW repositories*. http://civileng.aalto.fi

Ashraf, :, Abdalkader, H. M., Lynsdale, C., & Cripps, J. (2014). *Thaumasite Sulfate Attack in Cement Mortars Exposed to Sulfate and Chloride and Implications to Rebar Corrosion*.

Carde, C., & François, R. (1999). Modelling the loss of strength and porosity increase due to the leaching of cement pastes. *Cement and Concrete Composites*, *21*(3), 181–188. https://doi.org/10.1016/S0958-9465(98)00046-8

Carde', C., & Franqois, R. (1997). EFFECT OF THE LEACHING OF CALCIUM HYDROXIDE FROM CEMENT PASTE ON MECHANICAL AND PHYSICAL PROPERTIES. *Cement and Concrete Research*, *27*(4), 539–550.

Crammond, N. (2002). The occurrence of thaumasite in modern construction – a review. *Cement and Concrete Composites*, *24*(3–4), 393–402. https://doi.org/10.1016/S0958-9465(01)00092-0

Ekström, T. (2003). *Leaching of concrete : the leaching process and its effects*. https://portal.research.lu.se/en/publications/leaching-of-concrete-the-leaching-process-and-its-effects

Huang, B., & Qian, C. (2011). Experiment study of chemo-mechanical coupling behavior of leached concrete. *Construction and Building Materials*, *25*(5), 2649–2654. https://doi.org/10.1016/J.CONBUILDMAT.2010.12.014

Ikumi, T., & Segura, I. (2019). Numerical assessment of external sulfate attack in concrete structures. A review. *Cement and Concrete Research*, *121*, 91–105. https://doi.org/10.1016/J.CEMCONRES.2019.04.010

Kärnbränslehantering, S. A., & Olof Höglund, L. (2001). *R-01-08 Project SAFE Modelling of long-term concrete degradation processes in the Swedish SFR repository*.

Larrard, T., Benboudjema, F., Colliat, J.-B., Torrenti, J.-M., Deleruyelle, F., de Larrard, T., Benboudjema, F., Colliat, J., Torrenti, J., & Deleruyelle, F. (2010). Concrete calcium leaching at variable temperature: Experimental data and numerical model inverse identification. *Computational Materials Science*, 35–45. https://doi.org/10.1016/j.commatsci.2010.04.017i

Phung, Q. T., Maes, N., Jacques, D., De Schutter, G., & Ye, G. (2016). Investigation of the changes in microstructure and transport properties of leached cement pastes accounting for mix composition. *Cement and Concrete Research*, *79*, 217–234. https://doi.org/10.1016/J.CEMCONRES.2015.09.017

Phung, Q. T., Maes, N., Jacques, D., Perko, J., De Schutter, G., & Ye, G. (2016). Modelling the evolution of microstructure and transport properties of cement pastes under conditions of accelerated leaching. *Construction and Building Materials*, *115*, 179–192. https://doi.org/10.1016/J.CONBUILDMAT.2016.04.049

Song, Y., Zhou, S., Wang, Z., Wang, B., & Qian, J. (2017). Mechanism of thaumasite formation in concrete. *Journal Wuhan University of Technology, Materials Science Edition*, *32*(4), 893–897. https://doi.org/10.1007/S11595-017-1686-7/METRICS

Zhang, C., Li, J., Yu, M., Lu, Y., & Liu, S. (2024). Mechanism and Performance Control Methods of Sulfate Attack on Concrete: A Review. *Materials 2024, Vol. 17, Page 4836*, *17*(19), 4836. https://doi.org/10.3390/MA17194836