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INTERNAL SULFATE ATTACK CAUSED BY GYPSUM CONTAMINATION OF RECYCLED AGGREGATES: DEVELOPMENT OF A SWELLING TEST PROTOCOL

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RÉSUMÉ: L'attaque du béton par les sulfates est un processus qui engendre une détérioration du béton au travers de la formation de minéraux expansifs tels que l'ettringite. Les sulfates nécessaires à cette réaction peuvent provenir d'une source externe (telle que l'eau de mer ou l'eau souterraine) ou interne (comme le ciment ou les granulats). La situation spécifique décrite ici est la contamination des granulats recyclés avec du gypse provenant du site de démolition. Pour évaluer l'étendue des dommages que cette contamination peut causer, la variation de dimensions des mélanges cimentaires qui incorporent des granulats recyclés doit être surveillée. Le défi posé dans cette recherche concerne le choix d’un protocole de test pour suivre le développement de l'attaque par les sulfates. Étant une réaction lente qui peut prendre plusieurs mois, des procédures accélérées peuvent être nécessaires. Différentes méthodes sont décrites et discutées, mais ne semblent pas directement applicables dans ce contexte spécifique de contamination par le gypse. Dans cet article, des granulats recyclés finement contaminés avec différents niveaux de gypse sont soumis à diverses conditions de stockage et / ou cycles de vieillissement. Les résultats montrent que les protocoles existants, mis en place spécifiquement pour l'attaque de sulfate interne, ne fournissent pas l'accélération ou l'aggravation de la réaction comme cela a déjà été observé auparavant. Un protocole de test définitif, à utiliser dans cette situation spécifique, est finalement proposé.

ABSTRACT: Sulfate attack is a deteriorating process for concrete, where the formation of expansive minerals such as ettringite causes the swelling of a material. The sulfates necessary for this reaction can come from an external (such as sea- or groundwater) or an internal (such as cement or aggregates) source. A specific situation within this problematic is the contamination of recycled aggregates with gypsum from the demolition site. To assess the extent of the damage that this gypsum contamination can cause, the length of cementitious mixes that incorporated recycled aggregates needs to be monitored. The challenge in this research exists in finding the right testing protocol to follow the development of sulfate attack. Being a slow reaction which can take several months, accelerating procedures could be necessary. Different methods are described, but do not seem to be applicable in this specific context of gypsum contamination. In this paper, fine recycled aggregates contaminated with different levels of gypsum are subjected to a set of various storage conditions and/or aging cycles. The results show that existing protocols, set up specifically for internal sulfate attack, do not provide the acceleration or aggravation of the reaction as might have been shown before. A definitive testing protocol, to be used in this specific situation, is eventually proposed.

1. INTRODUCTION

Construction and Demolition Waste (C&DW) represents a considerable part of the total amount of generated waste (1.5 tonnes per year and per person in Europe in 2014 [1]), and consists mostly of crushed concrete or other construction materials such as bricks, masonry, etc [2]. An important fraction of this C&DW is not yet valorized. The objective of the interreg VALDEM '*Solutions intégrées de valorisation des flux Matériaux issus de la démolition*' project (http://www.valdem-interreg.eu) is the development of a mobile waste treatment tool, capable of separating different useful waste fractions on the demolition site. In the scope of this VALDEM project, research units are focused on the identification of different problematic waste fluxes, and the study of their properties.

1.1 Fine recycled aggregates

C&DW can be valorized by using the demolished concrete inside a new structure as a replacement for natural aggregates, and the use of coarse recycled aggregates has been shown to produce concrete with acceptable properties [3].

Fine recycled aggregates (FRA) however, have more nefarious characteristics and their incorporation into a new concrete is up to now generally avoided [4]. These properties include - amongst others - a higher water absorption [5], a lower density, and the presence of contaminations from the construction or demolition site such as glass, plastic, wood, etc [6]. Existing studies often focus on mechanical properties, and research is needed on the durability aspects of concrete with an incorporation of FRA [4].

1.2 Gypsum contamination

Gypsum drywall is by far the most important contaminant that can be present in FRA [7]. Gypsum – or $CaSO_4.2H_2O$ – is a source of sulfates who will dissolute to leach into the environment [8], causing ecotoxicological problems [9]. When these contaminated aggregates are used inside cementitious materials, the sulfates will give rise to an internal form of the sulfate attack reaction and cause dimensional instabilities, which is detrimental to the durability of a structure [10]. A sulfate limit of 0.2% was established in NF EN 206/CN:2014 and NBN B15-001:2012, to restrict the risk of sulfate attack to a level considered as acceptable [11][12].

Gypsum itself, despite being the most important one, is however not the only possible source of harmful sulfates that can be present in FRA. Depending on the FRA source, treatment, and storage, soil particles or groundwater could also contain sulfates.

A number of methods have been developed to remove gypsum contaminations from coarse recycled aggregates, based on differences in density [13], color [14], solubility [15] or infrared absorptivity [16] between gypsum particles and the other components of C&DW. Those methods are however not applicable on the finer fraction of C&DW. This confirms the need of research to determine the consequences of gypsum contaminations in FRA.

1.3 Sulfate attack

Sulfate attack is a deteriorating process where sulfates react with water and aluminate hydrates (AFm) in a hardened cement paste to form the mineral ettringite (AFt). The high volume of this product exerts an internal pressure on its surrounding cement paste and causes a volumetric deformation [17]. Macroscopically, the concrete structure will show swelling behavior and the formation of cracks [18]. Ettringite is a normal hydration product in the cement paste: its formation only becomes dangerous when it occurs after setting, in a rigid cement matrix.

Depending on the source of the sulfates responsible for the reaction, a distinction can be made between an external and an internal form. To experience external sulfate attack, the structure is submerged in a sulfate rich environment such as soil or seawater, where the sulfates enter via capillary pores or microcracks. Internal sulfate attack happens when there is a delayed release of sulfates from the hardened cement matrix, which is possible when high curing temperatures have destroyed the sulfate hydrates that were initially formed [19]. This reaction is also known as Delayed Ettringite Formation (DEF).

While external sulfate attack and DEF are well researched and understood concepts, the reaction caused by the presence of gypsum is not. The gypsum residues contaminating FRA are another internal source of sulfates who can complicate, accelerate or enhance the effects of sulfate attack, and the extent to which the swelling reaction can manifest itself in this situation is not yet known.

1.4 Swelling protocols

The effect of this internal sulfate attack reaction will be seen macroscopically as a swelling of the material. Up to now, no standards exist describing the procedure of following this swelling reaction in this specific context. More specifically, the ideal storage conditions and treatments of the samples remain a question.

Most of the authors prefer to submerge their samples into water at room temperature for the duration of the swelling monitoring [20] [21] [22] [23]. However, in this specific situation where the culprit of the swelling reaction is a water soluble source of sulfates, it is clear that leaching needs to be considered. Significant leaching will lead to an underestimation of the level of sulfates in the sample that is able to contribute to internal sulfate attack.

Seeing as it can take months to evaluate the full swelling potential of the sulfate attack reaction, some treatments are described that aim to ameliorate the visible effects. Specifically for internal sulfate attack, a protocol has been developed that consists of drying and wetting cycles [23]. Here, it is theorized that drying has an influence on the porosity, letting the ettringite crystallize in a confined space. While wetting, new water is provided to take part in the reaction and to transport sulfate ions.

1.5 Objective

The goal of this research was to find a testing protocol that allows to accurately determine the swelling potential of a given cementitious mix contaminated with gypsum. Because sulfate attack is a slow reaction, a testing protocol where the response would be exaggerated and/or accelerated could be interesting.

The different testing procedures described by other authors [20] [21] [22] [23] at first do not seem to not be applicable in the situation of an internal gypsum contamination: a submersion in water could pose risks in terms of leaching. Furthermore, the added value of the proposed treatments – the mechanics as to how they influence the swelling process - are not clear. In these experiments, it was tested whether the described procedures do indeed have a non-negligible effect on the swelling kinetics, and whether or not there is a significant leaching of sulfates in the treatment solutions.

2. MATERIALS AND METHODS

2.1 Fine recycled aggregates

A laboratory-made concrete was crushed after 90 days of aging in the humid chamber, to obtain model recycled aggregates from which the resulting 0/4 mm fraction was chosen to incorporate into mortars. A normalized sand was used as a non-porous reference. The relevant physical properties of these materials are presented in Table 1 and Figure 1.

Table 1: relevant physical characteristics of the used 0/4 mm aggregates

	Recycled sand	Normalized sand
Water absorption	9.78 %	0 %
Particle density	$1.95 \cdot 10^3$ kg/m³	$2.60 \cdot 10^3$ kg/m³

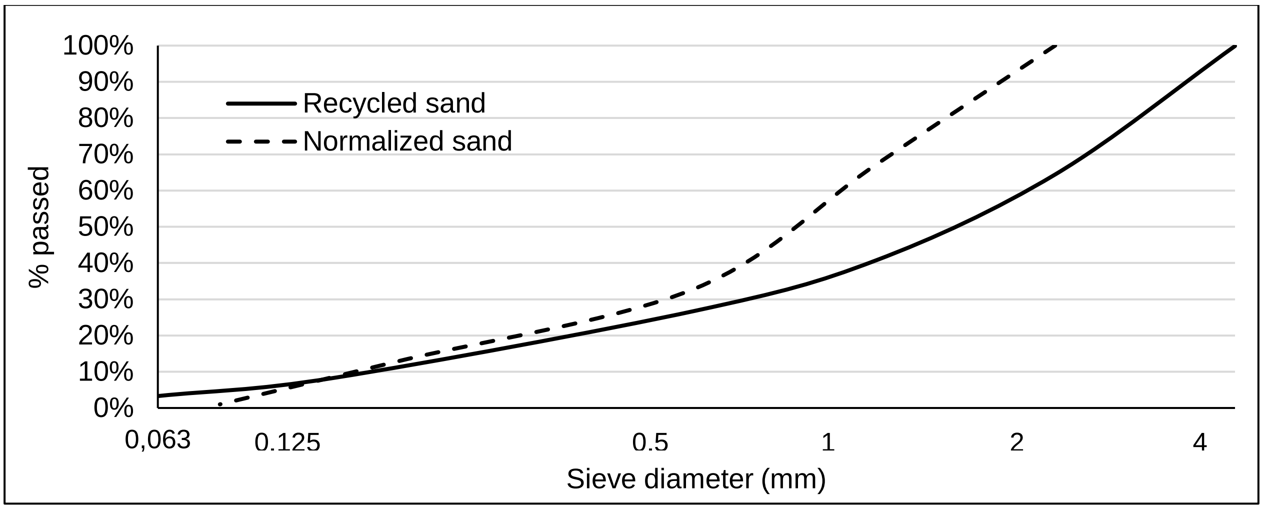

Figure 1: particle size distribution of the model recycled aggregates

The mortars used in this research were fabricated according to standard EN 196-1 [24]. Using the data from Table 1, normalized sand was replaced by an equivalent volume of recycled sand, and the absorbed water was added to the recycled sand one week before the mixing took place in order to saturate it. These compositions can be found in Table 2.

The gypsum used to contaminate the mortar mixes is a $CaSO_4.2H_2O$ powder (D50: 13µm) obtained from VWR Chemicals. It was found that, due to their similar particle sizes, mixing the gypsum powder with cement shortly before mixing, yields the most homogeneous results.

Table 2: compositions (g) of the mortar mixes

Gypsum content	0%		0.5%		1%		5%	
Demineralized water	324.0	225.0	323.5	225.0	323.0	225.0	319.1	225.0
CEM I 52.5 N	450.0	450.0	450.0	450.0	450.0	450.0	450.0	450.0
Recycled sand	1012.5	0	1007.4	0	1002.4	0	961.9	0
Normalized sand	0	1350.0	0	1343.3	0	1336.5	0	1282.5
Gypsum	0	0	5.1	6.7	10.1	13.5	50.6	67.5

2.2 Tested swelling protocols

A first procedure existed in testing the ideal storage conditions that prevent leaching, without trying to accelerate the swelling process. The mortar bars are placed in the humid chamber, where they have access to the humidity needed for the sulfate attack reaction, but are not in direct contact with water so the sulfates cannot leach.

The second treatment plan consisted of the drying/wetting cycles proposed by Pavoine et al. in their 'Méthode d'essai des lpc n°66' [23]. After demolding, the mortar bars were placed at 38°C for 7 days to dry, and afterwards submerged in water at 21°C for 7 days. This cycle is repeated once more. After these 28 days of drying/wetting cycles, the mortars are placed into the humid chamber in the same way as the first procedure, where their length is monitored for the remainder of the test.

A third protocol involved an immediate submersion in water after demolding. This procedure is the one most often found in literature and seems to give elevated swelling results, the risk here being once again the leaching of the added sulfates into the solution. To limit leaching when submerged, mortar bars are placed in very limited amounts of water, which are not changed.

For the first protocol, the mortars are fabricated with a recycled sand as well as a normalized sand. This allows the comparison between aggregates with respectively a high and a low porosity, and makes it possible to correctly interpret the results obtained with FRA. For all subsequent protocols, only FRA is used, and the results between the different protocols can be compared.

3. RESULTS AND DISCUSSION

3.1 Protocol 1

In a first series of tests, the mortars bars were placed in the humid chamber without undergoing additional treatment. This testing protocol was used for a series of mortars made with normalized sand, as well as a series with recycled sand, to allow the comparison between materials with a different porosity.

Figure 2 shows a clear swelling for highly contaminated samples. However, the swelling reaction has still not attained its maximum potential after almost a year of monitoring. This confirms the need of a testing protocol designated to accelerating the reaction.

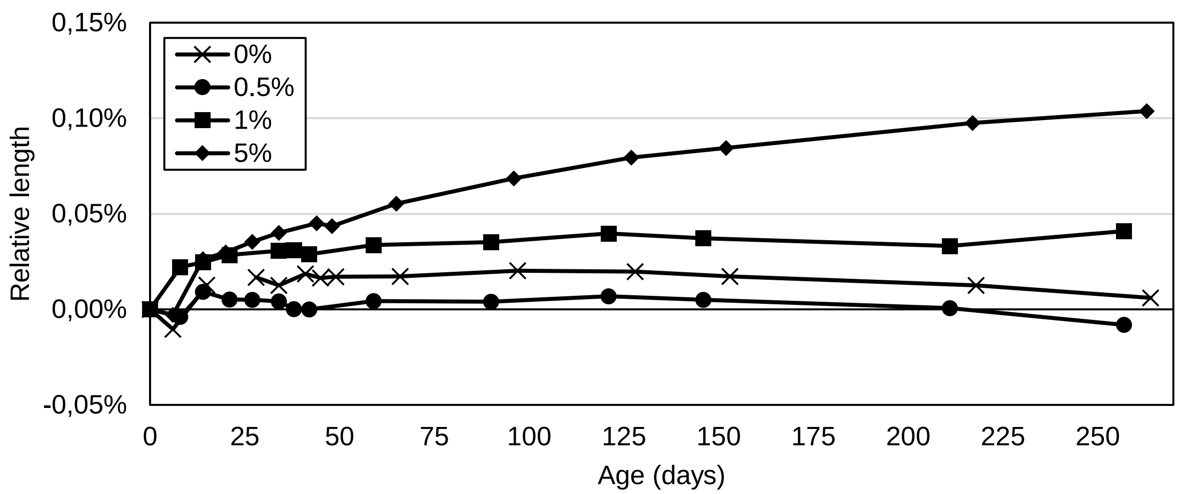

Figure 2: length change of samples with normalized sand during protocol 1: immediate storage in the humid chamber

In Figure 3, the results of this same storage method can be seen for the samples containing recycled sand. Initial hesitations about the kinetics of the reaction seem to be unfounded, seeing as the sample with 5% gypsum attains its maximum length change of 0.04% already after several weeks. This ultimate swelling level is however much lower than that observed for the normalized sand samples. This can be explained by the nature of the recycled aggregates: FRA are much more porous than natural sand, giving more space and less confinement for ettringite crystals to grow.

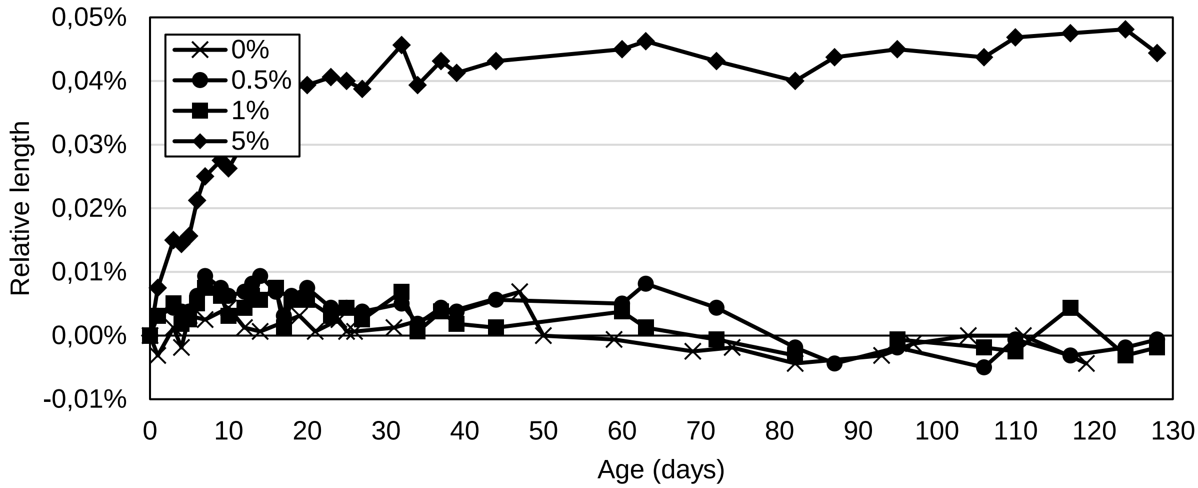

Figure 3: length change of samples with recycled sand during protocol 1: immediate storage in the humid chamber

3.2 Protocol 2

Protocol 2 consisted of 1 week of drying, 1 week of wetting, and again 1 week of drying and 1 week of wetting. During those wetting periods, the sulfate concentration in the solution was monitored. Figure 4 shows that there is indeed a flow of sulfates from the mortar bars into the solution, but it stays relatively limited. Taking the 5% sample as an example, 80 mg/L of sulfate ions corresponds in this case to 2.2% of the added gypsum that leached into the solution. This means that this mortar bar contained 4.89% of gypsum instead of 5%, which is an acceptable deviation.

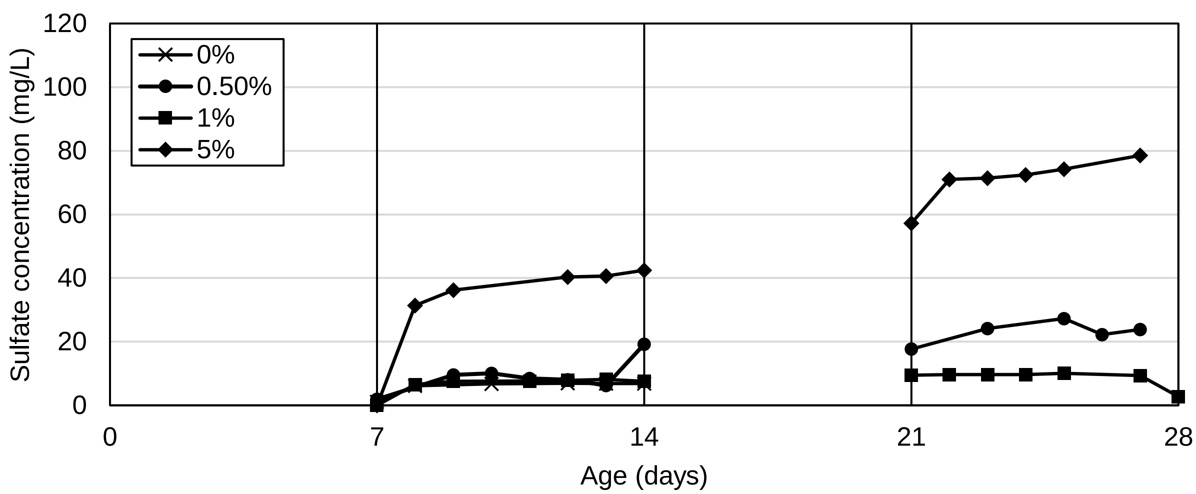

Figure 4: sulfate leaching during the wetting periods of protocol 2

During the cycles, normal shrinkage during drying and swelling during wetting is observed, as shown in Figure 5.

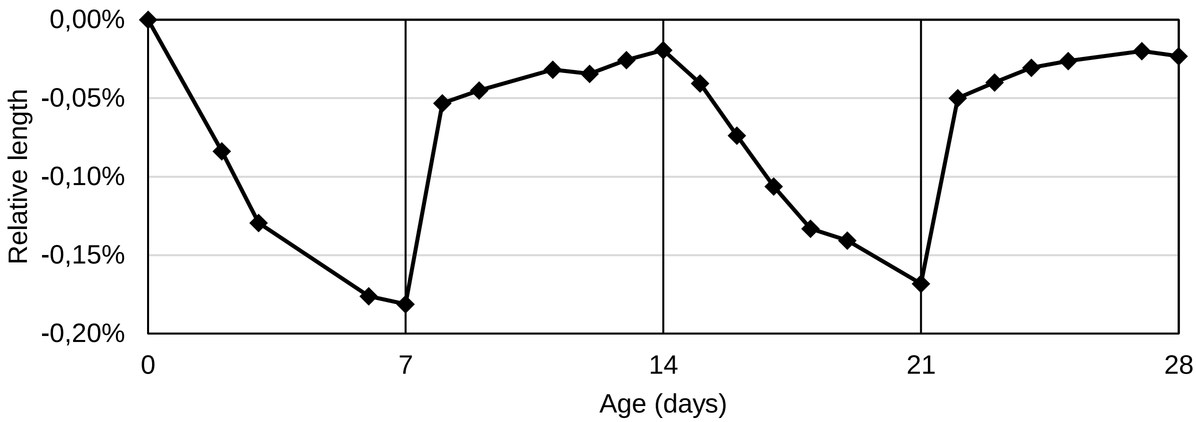

Figure 5: length change of the 5% samples with recycled sand during the drying/wetting cycles of protocol 2

The question posed by the application of these cycles was whether they could magnify the swelling potential that can be measured afterwards. With the length of the sample at the end of the cycles (day 28) taken as a zero value, the subsequent swelling is shown in Figure 6.

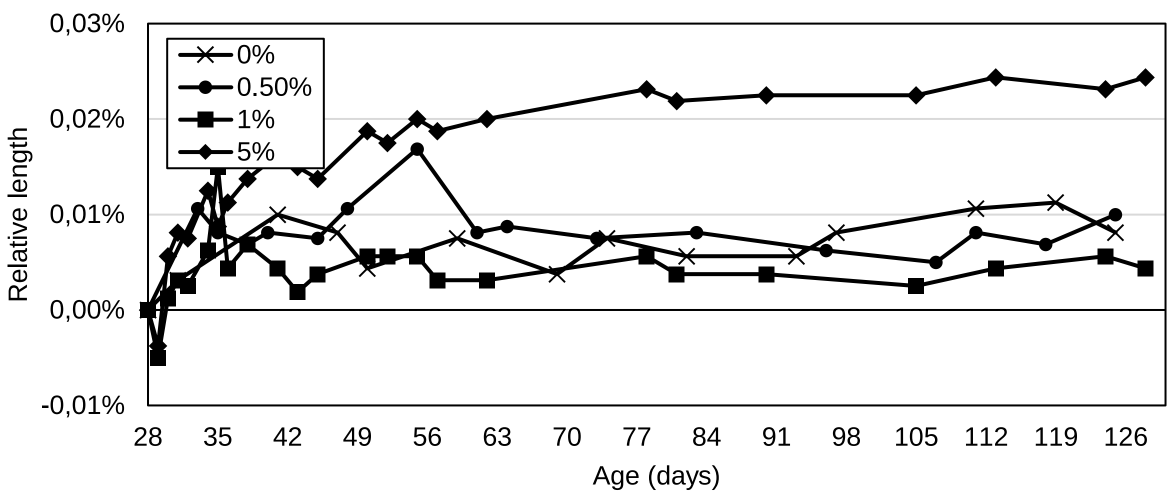

Figure 6: length change of samples with recycled sand after the drying/wetting cycles of protocol 2

The same trend as in Figure 3 can be seen: the samples 0%, 0.5% and 1% do not surpass a 0.01% length change and 5% of gypsum contamination shows a significant swelling compared to the other samples.

On the other hand, the samples from protocol 1 attained their maximum swelling potential much earlier. The results also show that the application of wetting/drying cycles does not boost the amplitude of the reaction – on the contrary.

3.3 Protocol 3

After demolding, the samples are immediately placed in water. The sulfate leaching data is shown in Figure 7. Less sulfates have leached than in protocol 2: even at the highest measured sulfate concentration of 60 mg/L, the 5% samples have only lost 1.6% of its sulfates, rendering its actual gypsum content to 4.9%. Moreover, the leaching behavior for the less contaminated sulfates is indistinguishable from the 0% sample.

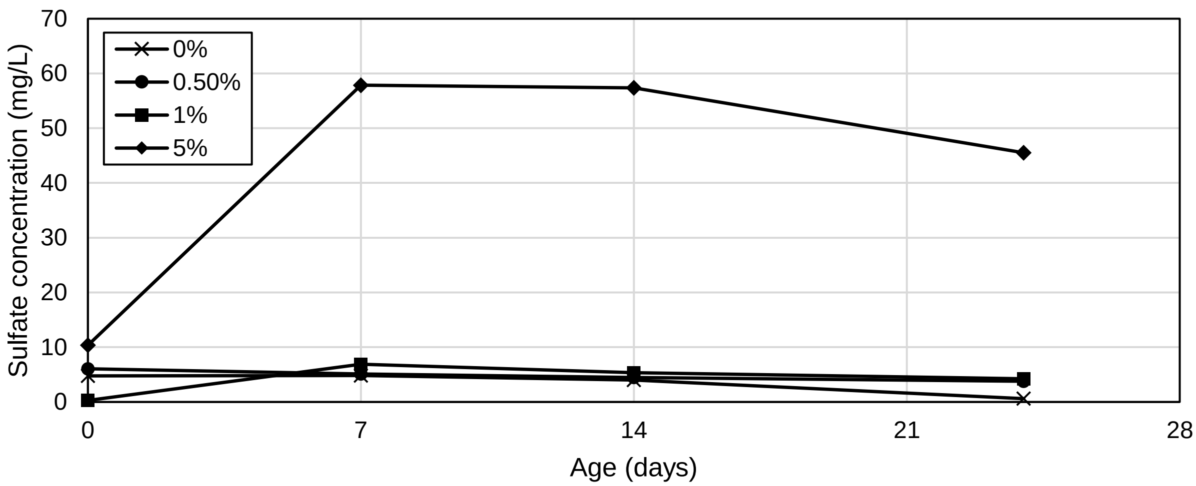

Figure 7: sulfate leaching during protocol 3

Figure 8 shows that immediate submersion after demolding indeed augments the swelling amplitude: a higher swelling potential than in protocol 1 or 2 is seen. The maximum value is attained already after approximately 2 weeks, which is somewhat faster than in protocol 1.

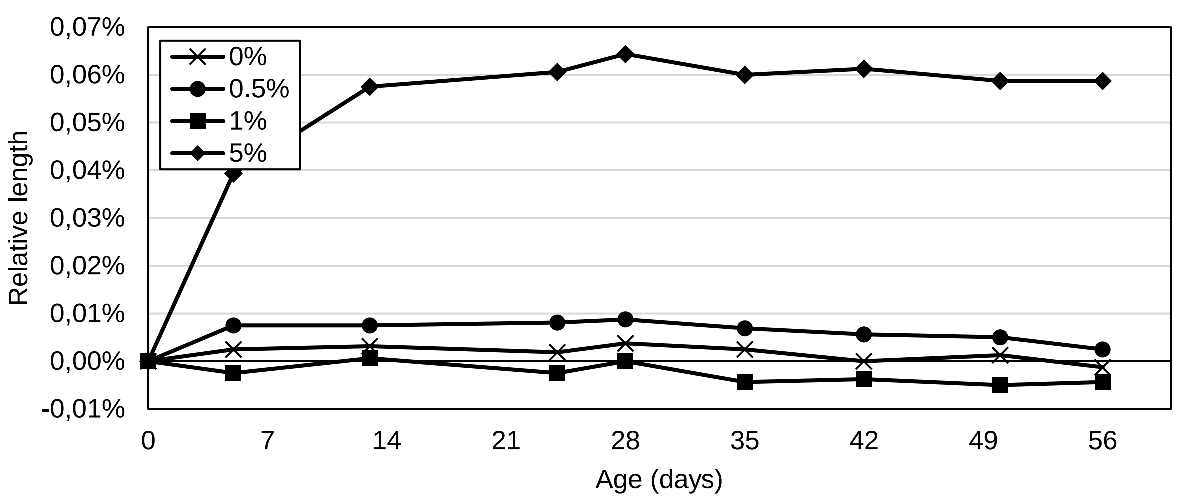

Figure 8: length change of samples with recycled sand during protocol 3: immediate submersion in water

4. CONCLUSION

The question posed at the beginning of this article was twofold: are existing treatment protocols applicable in the case of a contamination with water soluble sulfates, and what is the added benefit of these procedures?

From Figure 4 and Figure 7, it can be concluded that even though sulfates do leach from the highly contaminated 5% sample, the leaching stays within acceptable limits. This makes it possible to choose a test protocol based only on the observed speed and amplitude of the swelling reaction.

A comparison between the swelling results of protocol 1 (Figure 3), protocol 2 (Figure 6), and protocol 3 (Figure 8) is visualized in Figure 9 and demonstrates two points. Firstly, the drying/wetting cycles do not influence the swelling reaction in the desired way. On the contrary, the swelling process is slower than for the other tested storage methods. Secondly, a submersion in water gives rise to significantly faster and higher swelling results.

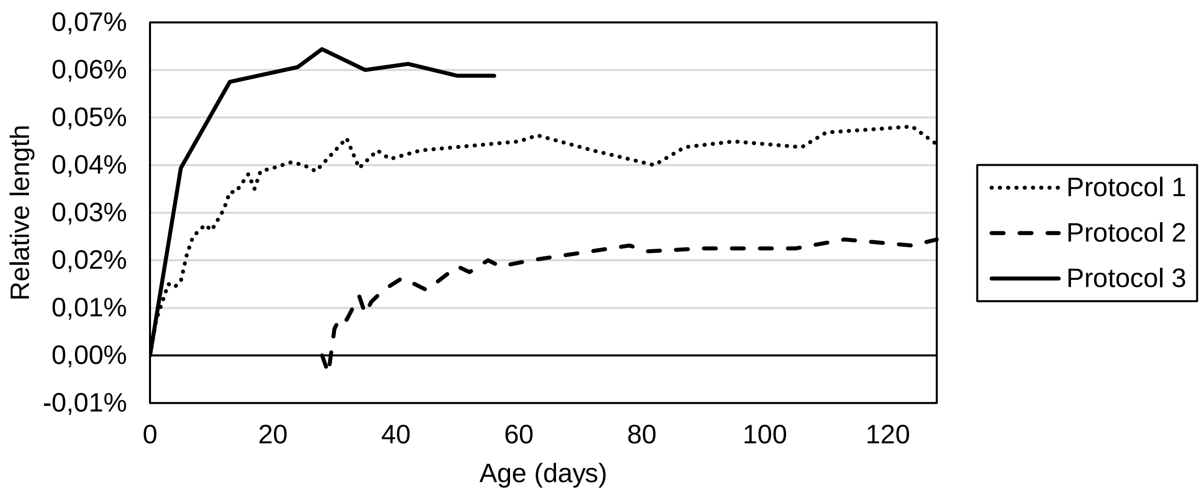

Figure 9: comparison between the swelling results of the 5% samples with recycled sand for the three tested protocols

Ultimately, protocol 3, which entails an immediate placement in water, seems the best choice. It shows a higher swelling potential much quicker than the other treatments tested, while sulfate leaching stays within acceptable limits.

Comparing swelling results of a recycled sand with a normalized sand (Figure 2 and Figure 3) shows a larger deformation for the non-porous material. The higher porosity of recycled sand, which is often seen as a negative characteristic, actually seems to improve the material's behavior in terms of swelling. The extra space inside the material counteracts the sulfate contamination in a way.

This article tried to answer how the swelling caused by a gypsum contamination could be assessed, since ready-to-use testing protocols are not available for this specific context. While storing samples submerged could pose leaching risks, results now show this is not excessive, effectively validating this method in the situation of a gypsum contamination. Results also show the significant influence of the storage method on the swelling reaction. When comparing swelling levels from different experiments and authors, the storage conditions should always be accounted for: similar contamination levels could give rise to vastly different swelling results.

Acknowledgements

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