

The Resistance to Magnesium sulphate of Mortars Modified with GGBS and Flue Gas Desulphurisation (FGD) Waste

P S Mangat¹, J M Khatib², L Wright³

¹Centre for Infrastructure Management, MERI, Sheffield Hallam University, Howard Street, Sheffield, S1 1WB, UK, <Email: p.s.mangat@shu.ac.uk>

²School of Engineering and the Built Environment, University of Wolverhampton, Wulfruna Street, Wolverhampton, WV1 1SB, <Email: j.m.khatib@wlv.ac.uk>

³Pick Everard, Halford House, Charles Street, Leicester, LE2 7DQ, UK, <Email: LeeWright@Pickeverard.co.uk>

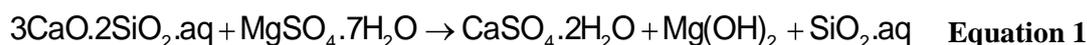
ABSTRACT

This work is part of a wide ranging research project on the optimum use of waste from the dry and semi dry flue gas desulphurisation (FGD) processes in concrete. It reports the resistance of mortars containing ground granulated blastfurnace slag (S) and a typical simulated desulphurised waste (SDW) to a magnesium sulphate solution. The binder consists of cement (C), S and SDW. The cement content was kept constant (10%) and then the slag was replaced with increasing levels of SDW. The mortar consists of 1 part binder to 3 parts sand and the water to binder ratio was 0.55. Samples were exposed to 2.44% magnesium sulphate solution. The samples containing cement-slag-simulated desulphurised waste (C-S-SDW) were compared to a reference sample of 100% cement. All C-S-SDW mortars exhibited superior sulphate resistance compared to reference mortars. This was attributed to reduction in the reactive phases that contribute the sulphate attack. Increasing the SDW content in the C-S-SDW blend also lead to an improvement in sulphate resistance.

Keywords: Desulphurised waste, ground granulated blastfurnace slag, FGD waste, strength, sulphate resistance

INTRODUCTION

The presence of magnesium sulphates in soil and ground water can reduce the service life of concrete structures. In a solid state these sulphates are harmless to concrete, however, once present in solution above a certain threshold they can have serious effects on concrete, causing expansion, cracking, spalling and loss of strength. The attack occurs when the sulphates present in the water react with calcium aluminates (C₃A) present in the cement and phases formed during hydration such as calcium hydroxide (CH). The reactions are somewhat complex and are dependent on many factors, such as the concentration of sulphate ions, temperature, and types and content of cementitious material, water content and curing type and duration. However, the general attack is associated with the formation of gypsum and ettringite, which is reported to result in large expansions [Lea 1998, Neville 1995]. Magnesium sulphate (MgSO₄) reacts with the CH, C-A-H phases and the calcium silicate hydrate (C-S-H) phases, as shown in Equation 1.



Given magnesium sulphate reacts with all phases of cement-based materials, the attack is more severe than other types of sulphate attack. The beneficial use of replacement materials in cement-based materials has been well documented with respect to sulphate resistance [Freeman 1995, Mangat and El Khatib 1992, Rasheedduzzafar et al 1994]. Replacement materials generally dilute the C₃A present in the cement which reduces the amount of CH produced. Materials such as fly ash and GGBS can also improve the transport properties of the hydrated material by reducing permeability, which also increases the sulphate resistance of cement-based materials [Lea 1998]. However, when exposed to magnesium sulphate the use of low C₃A cements may be inadequate because it attacks also the C-S-H formed. This paper is concerned with the sulphate resistance of mortar containing desulphurised waste exposed to magnesium sulphate solution.

EXPERIMENTAL

Mortar mixes consists of 42.5N Portland cement (C), ground granulated blastfurnace slag (S), fly ash (FA), gypsum (G), fine aggregate complied with class M sand (BS 882:1983), and water. Further information regarding composition is given elsewhere [Khatib et al 2008]. The mixes (M1-M7) used in this study are presented in Table 1. The mortar proportions were 1:3 of binder to sand respectively. The water/binder was kept constant at 0.55. Mix 1 represents a reference mix containing 100% C. Mixes 2 to 7 contain different blends of C, S and SDW. In these mixes the cement content was kept constant at 10%. The remaining 90% was a blend of slag and SDW. The level of SDW was increased from 0 to 70%. The SDW contained 85% fly ash and 15% gypsum. The basis for the proportion of the SDW can be found elsewhere [Khatib et al 2008].

Table 1. Binder constituents

Mix No	Mix ID	Proportions (% weight of binder)		
		Cement (C)	Slag (S)	SDW
1	REF (100 _C)	100	0	0
2	10 _C 90 _S 0 _{SDW}	10	90	0
3	10 _C 80 _S 10 _{SDW}	10	80	10
4	10 _C 70 _S 20 _{SDW}	10	70	20
5	10 _C 60 _S 30 _{SDW}	10	60	30
6	10 _C 50 _S 40 _{SDW}	10	50	40
7	10 _C 20 _S 70 _{SDW}	10	20	70

The mortar samples consisted of 40mm x 40mm x 160mm prisms. After casting, all samples were placed in a mist curing room at 20°C±1°C and 95%±5% relative humidity until demoulding. For most samples this initial mist curing was for 24 hours, however, several samples required a longer initial period (48 hours) due to an increase in setting times. After demoulding, all cubes were cured in water at 20°C for a total of 28 days (from casting). After 28 days of water curing, three samples were left immersed in water at 20°C (reference) and three samples were immersed in a 5% magnesium sulphate solution (MgSO₄·10H₂O or 2.44% MgSO₄). The sulphate solution was replaced monthly to replenish the sulphate concentration in the solution. Weight change, length change and visual observations were then recorded at regular intervals up to 450 days.

RESULTS AND DISCUSSION

Figures 1 and 2 show the change in length with time for samples submerged in water and magnesium sulphate respectively, and Figure 3 show the net change in length with time. Over the 450 day monitoring period only the reference mix showed any significant expansions when immersed in magnesium sulphate. This indicates that replacing cement with the S-SDW blends improves sulphate resistance. Previous researchers have reported that failure occurs once expansions exceed 0.5% [Mangat and El-Khatib 1992, Brown 1981]. Based on this limit the reference samples fail between 330 and 365 days.

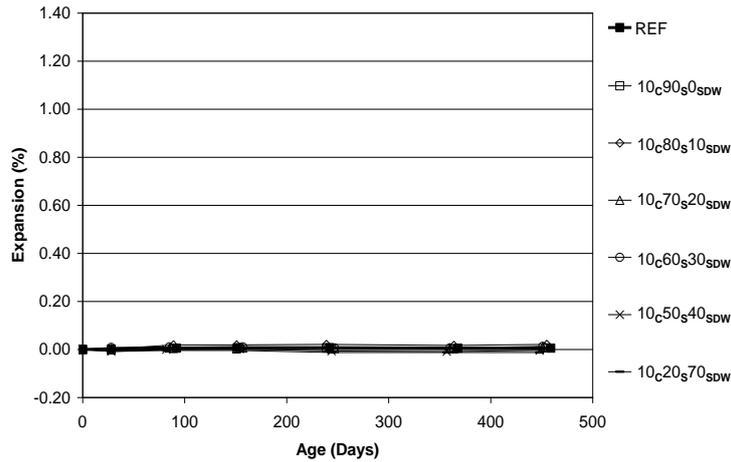


Fig. 1. Change in length of samples immersed in water

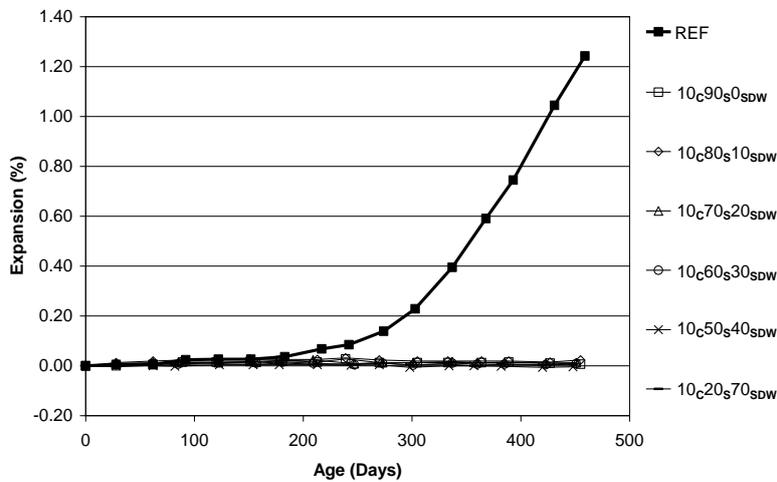


Fig. 2. Change in length of samples immersed in magnesium sulphate

Figure 4 and Figure 5 show the change in weight with time for samples submerged in water and magnesium sulphate respectively, and Figure 6 shows the net change in weight with time. During the first 200 days of exposure to magnesium sulphate, the change in weight for all C-S-SDW mortars was similar to the reference mix. Beyond 200 days, replacing cement with the S-SDW blends reduced the weight change of the samples. Increasing the SDW content in the S-SDW blends resulted in a reduced increase in weight. At 450 days the reference mix continued to show an increase in weight, whereas, the increase in weight change of C-S-SDW blends had slowed significantly, and in a couple of cases a weight loss was observed, i.e. mixes 10_C90_S0_{SDW}, 10_C80_S10_{SDW} and 10_C70_S20_{SDW}.

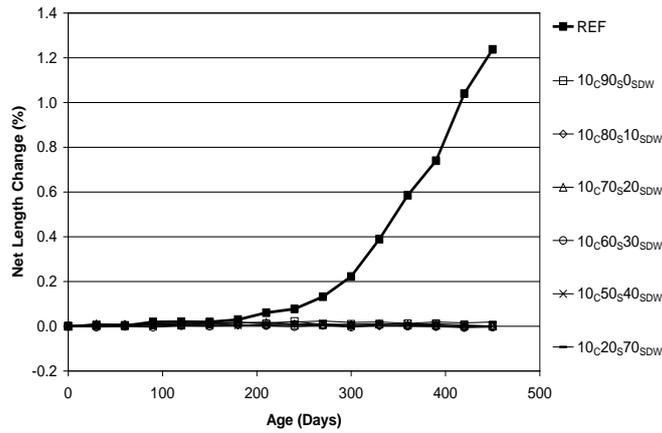


Fig. 3. Net change in length of samples [Khatib et al 2008]

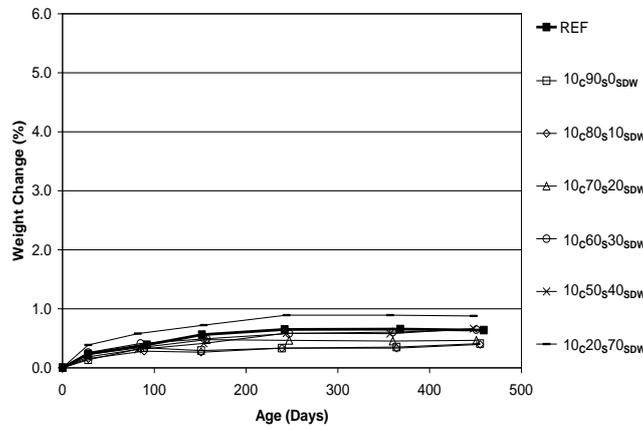


Fig. 4. Change in weight of samples immersed in water

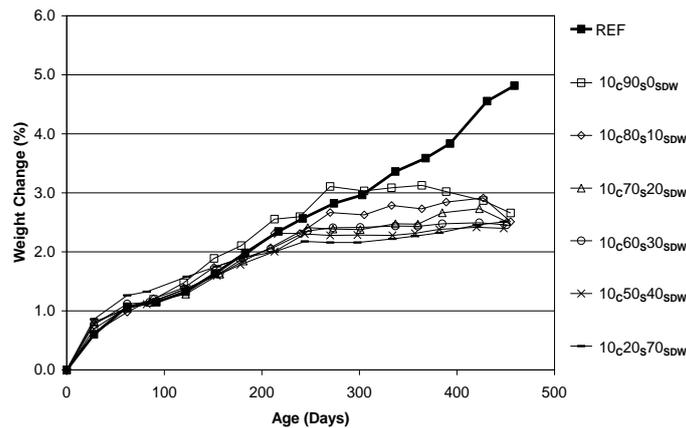


Fig. 5. Change in weight of samples immersed in magnesium Sulphate

During the first 60 days of immersion, a white layer forms on the surface of the reference sample. The formation of the white layer became thicker with time. No cracking was observed with the reference mix after 150 days, however, the presence of the white layer may have masked the start of cracking. After 180 days, the edges and corners of the

reference mix had started to soften, which resulted in loss of material on handling. Slight cracking was observed, and was more prominent around the edges and corners.

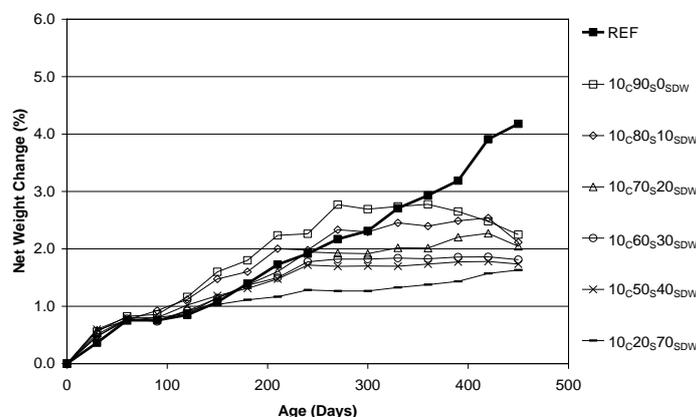


Fig. 6. Net change in weight of samples [Khatib et al 2008]

The formation of the white layer on the reference samples after 60 days of exposure was not observed for the C-S-SDW mortars. During the first 90 days of exposure, the C-S-SDW mortars containing 0% and 10% SDW (10_C90_S0_{SDW}, 10_C80_S10_{SDW}) start to exhibit advanced deterioration in the form of friable surfaces and cracking around the edges and corners. This resulted in flaking of material on handling. As the SDW content increased beyond 10%, the amount of cracking observed decreased until almost no signs of deterioration were observed in the mix containing 70% SDW (10_C20_S70_{SDW}). Exposure to magnesium sulphate beyond 365 days lead to a continual deterioration of the samples, where the edges and corners of reference samples continued to soften, which resulted in a loss of material on handling. The deterioration of the C-S-SDW mortars was more defined by widening of cracks around the edges and corners. This led to a loss of material, which was accompanied by a decrease in weight once the cracks formed. However, the loss of material from the reference samples was accompanied by a continual weight and length increase. This indicated that the failure mechanism for the C-S-SDW mortars was different to the reference mix, or that the reference mix was more susceptible to attack from magnesium sulphate.

Generally cement replacement materials are used to dilute the chemical components in the cementitious material that contribute to the reaction processes, such as C₃A, and CH, as well as decrease permeability through improvement in the pore structure. When immersed in magnesium sulphate the reference mix went through an attack process, which resulted in the formation of a white layer on the surface of the samples during the first 90 days of hydration. The white layer was not observed in water cured samples. This was followed by a rapid increase in weight and expansion, during which time the samples underwent softening of the edges and corners resulting in spalling of material. The C-S-SDW mortars performed very differently to the reference in that no white layer formed during the early stages of attack. In addition, the increase in weight of the C-S-SDW mortars was not accompanied by expansion. Instead, the surfaces of the samples were friable at an early age, which lead to cracking around the edges and sides leading to a loss of material. The severity of the attack decreased in the C-S-SDW mortars as the SDW content in the mixes increased. At 450 days, the appearance of the C-S-SDW mortars was better than the reference mix, and the improvement in sulphate resistance increased with increasing SDW contents. However, large cracking was observed in almost all samples.

Rasheeduzzafar et al [1986] reported the sulphate resistance of normal and blended cements in more aggressive solutions such as sodium-magnesium sulphate solutions ($\text{N}\bar{\text{S}}\text{-M}\bar{\text{S}}$ - 2.1% SO_4^{2-}). Compared to the samples cured in sodium sulphate, the $\text{N}\bar{\text{S}}\text{-M}\bar{\text{S}}$ environment was much more aggressive. The deterioration of samples immersed in $\text{N}\bar{\text{S}}\text{-M}\bar{\text{S}}$ was characterised by scaling, spalling and softening associated gypsum-magnesium type of attack. The failure of the plain cements was attributed to the attack of CH, however, in the slag cement, pozzolanic type reactions occur which consume the CH to form additional C-S-H. In addition, because magnesium sulphate also reacts with the C-S-H phases formed, the absence of CH meant that that magnesium sulphate directly reacted with the C-S-H to form large deposits of gypsum. This could explain the inferior performance of the cement containing slag compared to the reference cement. Hime and Mather [1999] reported that if concrete was exposed to magnesium sulphate (MgSO_4), brucite (MH) was formed as shown below in Equation 2.



The formation of brucite was said to occur at the sample surface, which may enhance sulphate resistance. Bonen and Sarker [1993] reported the formation of a brucite layer on cement pastes cured in magnesium sulphate. The retardation of the sulphate attack was attributed to the low solubility of the brucite, which restricted the penetration of the Mg^{2+} into the interior of the sample. During this investigation, C-SDW mortars cured in magnesium sulphate solution did form a white layer on the surface of the samples at an early age. Unfortunately, no tests were carried out to identify the composition of the white formation. The C-S-SDW cements evaluated in the current investigation show no formation of a white layer on the surface of the samples like that observed with the reference mixes. This may explain why the C-S-SDW cements start to deteriorate sooner in the presence of magnesium sulphate. However, increasing the SDW content decreased the rate at which deterioration occurred in the C-S-SDW mortars. The softening and spalling of material associated with the C-S-SDW mortars indicated decalcification of the C-S-H gel due to excessive gypsum formation, however, with the reference mix large expansions were observed indicating possible ettringite formation. Several researchers have reported that expansion may be present during gypsum formation when exposed to sulphate environments [Tian Bing and Cohen 2000, Bonen and Sarker 1993].

Gollop and Taylor [1996] reported that by increasing the slag content in cement mortars from 69% to 92%, sulphate resistance could be significantly improved when exposed to magnesium sulphate. It was reported that the Al_2O_3 available for reaction was an important factor in the sulphate resistance of slag cements. For mixes containing the same amount of slag, if the Al_2O_3 content of the slag increased the sulphate resistance worsened. However, if the same slag type was used, increasing the slag content (increasing the Al_2O_3) improved the sulphate resistance. It was suggested that the improvement in sulphate resistance by increasing the slag content resulted from the reduction in the available Al_2O_3 for reaction, which was taken up in the formation of additional C-S-H. The reduction in the available Al_2O_3 , which would reduce the amount of expansive products formed, such as ettringite, may explain why cements containing slag may be more susceptible to destruction of the C-S-H phase and subsequent loss of adhesion and strength rather than expansion and cracking. This would also explain why the C-S-SDW blends evaluated in the current investigation showed no signs of expansion when exposed to sodium and magnesium sulphate solutions. Gollop and Taylor [1996] reported that by adding 5% gypsum to a cement containing 65% slag, an improvement in the sulphate resistance could be achieved. The addition of gypsum was

reported to reduce the available Al_2O_3 or more correctly, the amount of aluminate ions for reaction by binding some of the aluminate formed in ettringite during the early stages of hydration. The paste can accommodate the formation of ettringite during the early stages of hydration without causing any significant volume change.

CONCLUSIONS

All cement, slag and typical simulated desulphurised waste mortars (C-S-SDW) exhibited sulphate attack when immersed in magnesium sulphate. The reason being that the magnesium sulphate reacts with the C-S-H phases as well as aluminate and CH phases. Increasing the SDW content in the C-S-SDW from 0 to 70% improved sulphate resistance. An increase in SDW reduced expansion, weight gain, softening and deterioration of the edges and corners commonly associated with exposure to magnesium sulphate.

REFERENCES

- Bonen D, Sarker SL, Replacement of portlandite by gypsum in the interfacial zone and cracking related to crystallization pressure, *Ceramics Transactions*, Vol.37, Cement Based Materials: Present, Future, and Environmental Aspect, American Ceramic Society, Westerville, OH, pp.49-59, 1993
- Bonen D, Cohen MD, Magnesium sulphate attack on Portland cement paste: II. Chemical and mineralogical analysis, *Cement and Concrete Research*, Vol.22, pp.707-718, 1992
- Brown PW, An evaluation of the sulphate resistance of cements in a controlled environment, *Cement and Concrete Research*, Vol.11, pp.719-727, 1981
- Freeman RB, Carrasquillo RL, Adjustments in gypsum content for production of sulphate-resistant blended cements containing high-calcium fly ash, *ACI materials Journal*, pp.411-418, Jul-Aug 1995
- Gollop RS, Taylor HFW, Microstructural and microanalytical studies of sulphate attack: V. Comparison of different slag blends, *Cement and Concrete Research*, Vo.26, No.7, pp.1029-1044, 1996
- Hime WG, Mather B, "Sulphate attack" or is it? *Cement and Concrete Research*, 29, pp.789-791, 1999
- Khatib JM, Mangat PS, Wright L (2008), Sulphate resistance of simulated desulphurised waste, *Proceedings of the ICE- Construction Materials Journal*, CM3, 20-27
- Lea FM, LEA'S Chemistry of Cement and Concrete, Forth Edition, Arnold, ISBN 0 340 56589 6, Chapter 1 - Pozzolana and Pozzolanic Cements, pp.471-633, 1998
- Mangat PS, EL-Khatib JM, Influence of initial curing on sulphate resistance of blended cement concrete, *Cement and Concrete Research*, Vol.22, pp.1089-1100, 1992
- Neville AM, Properties of Concrete, Fourth edition, Longman Group Ltd, ISBN 0-582-23070-5, Chapter 10-Durability of Concrete, pp.482-537, 1995
- Tian Bing, Cohen MD, Does gypsum formation during sulphate attack on concrete lead to expansion? *Cement and Concrete Research*, Vol.30, pp.117-123, 2000
- Rasheeduzzafar, Al-Amoudi OSB, Abduljauwad SN, Maslehuddin M, Magnesium-sodium sulphate attack in plain and blended cements, *Journal of Materials in Civil Engineering*, Vol.6, No.2, pp.201-222, May 1994
- Rasheeduzzafar, Al-Mana A, Haneef M, Maslehuddin M, Effect of cement replacement, content, and type on the durability performance of fly ash concrete in the middle east, *Cement, Concrete and aggregate* 3, Vol.8, pp. 86-96, Winter 1986