Coventry University and
The University of Wisconsin Milwaukee Centre for By-products Utilization,
Second International Conference on Sustainable Construction Materials and Technologies
June 28 - June 30, 2010, Università Politecnica delle Marche, Ancona, Italy.
Special Technical Proceedings ed. P Claisse, E Ganjian, F Canpolat and T Naik
ISBN 978-1-4507-1488-4 http://www.claisse.info/Proceedings.htm

Effect of Simulated Desulphurised Waste Content on Resistance to Sodium Sulphate

J M Khatib[1], L Wright[2], and P S Mangat[3]

[1]*School of Engineering and the Built Environment, University of Wolverhampton, Wulfruna Street, Wolverhampton, WV1 1SB, UK, E-mail: <j.m.khatib@wlv.ac.uk>.*

[2]*Pick Everard, Halford House, Charles Street, Leicester, LE2 7DQ, UK. E-mail: <LeeWright@PickEeverad.co.uk>.*

[3]*Centre for Infrastructure Management, MERI, Sheffield Hallam University, Sheffield, S1 1WB, UK. E-mail: < p.s.mangat@shu.ac.uk>.*

ABSTRACT

Desulphurised wastes are solids residues produced as a result of the desulphurisation process in coal power generation plants. If the waste is to be used in construction application such as concrete pavement, its performance under different environments needs to be investigated. Concrete pavement may be subjected to sulphate bearing environment. This paper investigates the performance of mortar containing different amounts of desulphurised waste as partial substitution of cement. Cement was replaced with 0-70% simulated desulphurised waste (SDW). SDW was a combination of fly ash (85%) and gypsum (15%). Mortar consists of 1 part binder (cement + SDW) and 3 parts sand. Mortar specimens were subjected to sodium sulphate solution for 450 days. The results suggest that the sulphate resistance of mortar is enhanced in the presence of SDW.

INTRODUCTION

If concrete is to be used in practice such as pavement applications, it is necessary that its performance (e.g. strength and durability) is satisfactory. However, during the service life of concrete structures it is common that elements are subjected to external factors that cause deterioration and wear which may lead to an unserviceable structure if left untreated. Hence, the durability of concrete determines the concretes ability to resist such attacks and subsequent deterioration. One of the most common forms of concrete deterioration is from sulphate attack, which occurs due to the presence of sulphates in surrounding ground water. Sulphate attack occurs through the reaction of aggressive sulphate ions with constituents of the hydrated material such as tricalcium aluminate (C_3A) and calcium hydroxide (CH). These reactions generally result in the formation of gypsum ($CaSO_4.H_2O$) and ettringite ($C_3AS_3H_{32}$). This can cause excessive expansion, which can lead to cracking and strength loss [Lee 1998, Collepardi 2001].

The sulphate resistance of concrete depends mainly on the amount of minerals present within the concrete that contribute to the attack. It also relies on its ability to resist the transport of sulphate ions throughout the body of the material that initiates the chemical attack process. In normal concretes, the C_3A in cement is an important factor in the sulphate resistance of cement. Generally, the sulphate resistance is improved by reducing the amount of C_3A present. One other way of reducing the amount of C_3A in the system is to replace the cement with pozzolanic materials such as fly ash [Dunstan 1980, Tikalsky and Carrasquillo 1993, Poon el al 2000]. The pozzolanic reactions occurring from the inclusion of fly ash consumes CH, which also increases sulphate resistance [Mehta 1986]. Reducing porosity and permeability of the concrete matrix improves the resistance to sulphate by reducing the flow of water through the concrete. In concrete, permeability can be improved by reducing the water to cement ratio and by providing adequate curing, which produces a much denser structure by reducing voids and pores present in the concrete. Materials such as fly ash also improve durability by increasing pore refinement and reducing permeability. This paper investigates the resistance to sodium sulphate of mortar containing varying amounts of desulphurised waste.

EXPERIMENTAL

Sulphate resistance tests were carried out on mortars. The proportions of binder to sand were 1:3 respectively. The water/binder was kept constant at 0.55. The binder consists of cement and a typical simulated desulphurised waste. Mix 1 represents a reference mix of 100% cement. Mixes 2 to 6 contain different blends of cement (C) and a typical simulated desulphurised waste (SDW). The cement was replaced with increasing levels of SDW from 0 to 90%. The proportion of the SDW was 85% fly ash and 15% gypsum. Table 1 shows the proportion of mixes evaluated. The mix ID (column 2) in mixes 2 to 6 represents the constituent of the binder. For example, mix 70_C30_{SDW} represents a binder containing 70% cement and 30% of SDW by weight of binder. Columns 3 and 4 show the cement (C) and typical simulated desulphurised waste (SDW) content respectively.

Table 1: Details of binder

		Proportions (% weight of binder)	
Mix No	**Mix ID**	Cement (C)	SDW
1	REF (100_C)	100	0
2	90_C10_{SDW}	90	10
3	80_C20_{SDW}	80	20
4	70_C30_{SDW}	70	30
5	60_C40_{SDW}	60	40
6	30_C70_{SDW}	30	70

After 28 days of water curing, specimens (40mmx40mmx160mm) were either immersed in water at 20ºC or 5% sodium sulphate solution ($Na_2SO_4.10H_2O$ or 2.2% Na_2SO_4). The length and weight change in sodium sulphate solution and water was monitored at different intervals. The net length and weight change was calculated by subtracting those immersed in water from those immersed in sodium sulphate solution. The sulphate solution was replaced every month to replenish the sulphate concentration in the solution.

RESULTS AND DISCUSSION

The effect of incorporating simulated desulphurised waste (SDW) on length and weight change of mortar subjected to water and sulphate solution and also the net length and weight change is presented in Figures 1 to 6. Figures 1-3 show the length change while Figures 4-6 show the weight change. The net length and weight change are presented in Figures 3 and 6 respectively. The results suggest that the incorporation of SDW improves the sulphate resistance of mortar at all replacement levels. The sulphate resistance is drastically improved when cement is partially replaced with SDW beyond 10%. The sulphate resistance of C-SDW mortars increased as the SDW content in the mix increases. Below is possible explanation on the reasons for this enhanced performance.

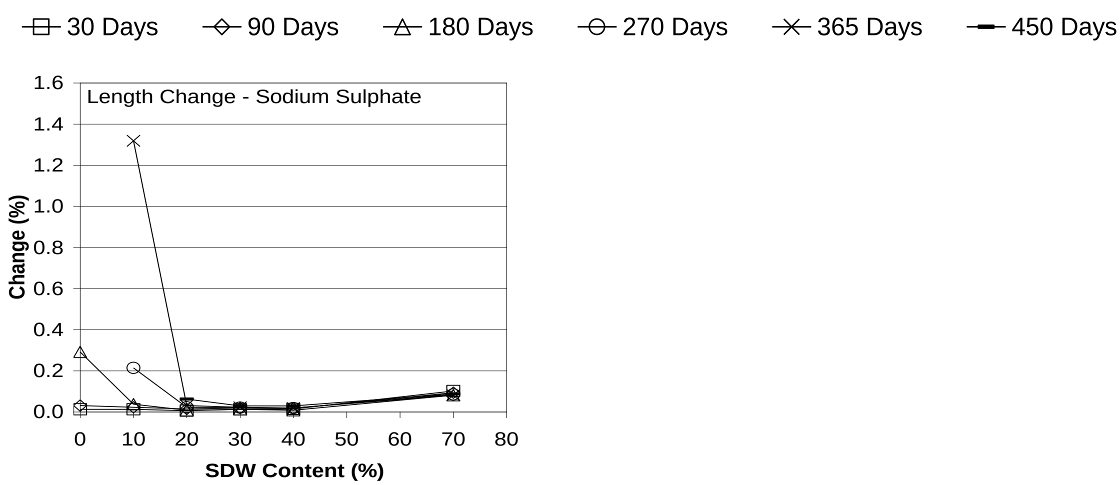

Fig. 1. Effect of SDW content on length change of mortar specimens immersed in sodium sulphate solution

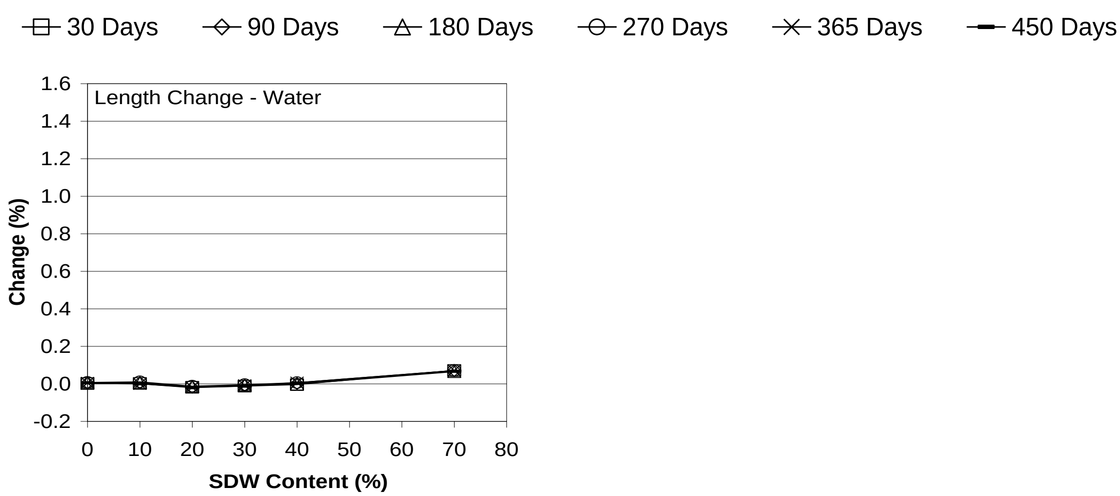

Fig. 2. Effect of SDW content on length change of mortar immersed in water

The improvement in sulphate resistance manifests itself in the form of reduced expansions and weight gain, in addition to reduced cracking and deterioration. The samples also retain strength compared to samples cured in water, and in some cases, a strength increase was observed. The composition of the SDW is predominantly fly ash. The sulphate resisting properties of fly ash in cement is well documented, and generally leads to improved resistance to sulphate when exposed to sulphate environments [Mehta 1986].

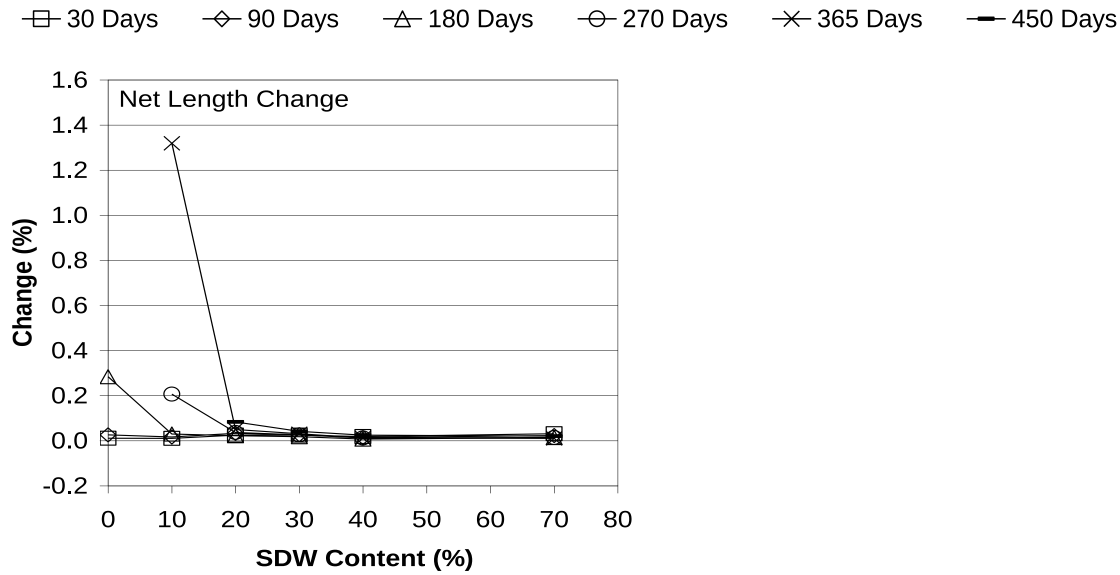

Fig. 3. Effect of SDW content on net length change of mortar

Sulphate attack occurs when alumina (C_3A) in the cement and calcium hydroxide (CH), formed during cement hydration, react with sulphates in the solution (e.g. Na_2SO_4). This results in the formation of gypsum and/or ettringite that leads to the deterioration and destruction of the samples. The improved sulphate resistance due to the replacement of cement with SDW can be attributed to its chemical and mineralogical composition. Unfortunately, no attempts were made to determine the mineralogical composition of the SDW. The replacement of cement with SDW firstly reduced the C_3A and CH content of the mix available for reaction. Secondly, the fly ash in the SDW undergoes long-term pozzolanic reactions, which consumes CH, one of the main reaction products in sulphate attack, to form additional cementing C-S-H and low calcium C-A-H phases [Poon et al 2000].

Wild el al [1997], Mangat and El Khatib [1992] and Brown [1981] have tried to quantify the failure due to sulphate attack by monitoring expansion and proposing limits for failure, for example, once the expansion had exceeded 0.5% the samples were assumed to have failed. However, the actual failure mechanism due to exposure to sulphate is subject to great debate.

The mechanism of attack is dependent on factors such as concentrations of sulphate ions, type of sulphate, temperature, and type and content of cementitious material, water content and curing type and duration. The formation of ettringite during sulphate attack was generally associated with expansive failure, whereas, gypsum formation tends to lead to a decalcification of the C-S-H resulting in a loss of strength. Therefore, the evaluation of expansion alone may be insufficient in determining sulphate attack [Collepardi 2001, Santhanan et al 2001].

30 Days 90 Days 180 Days 270 Days 365 Days 450 Days

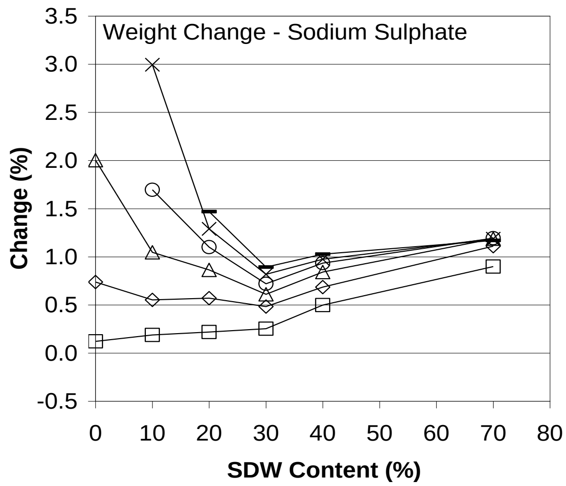

Fig. 4. Effect of SDW content on weight change of mortar specimens immersed in sodium sulphate solution

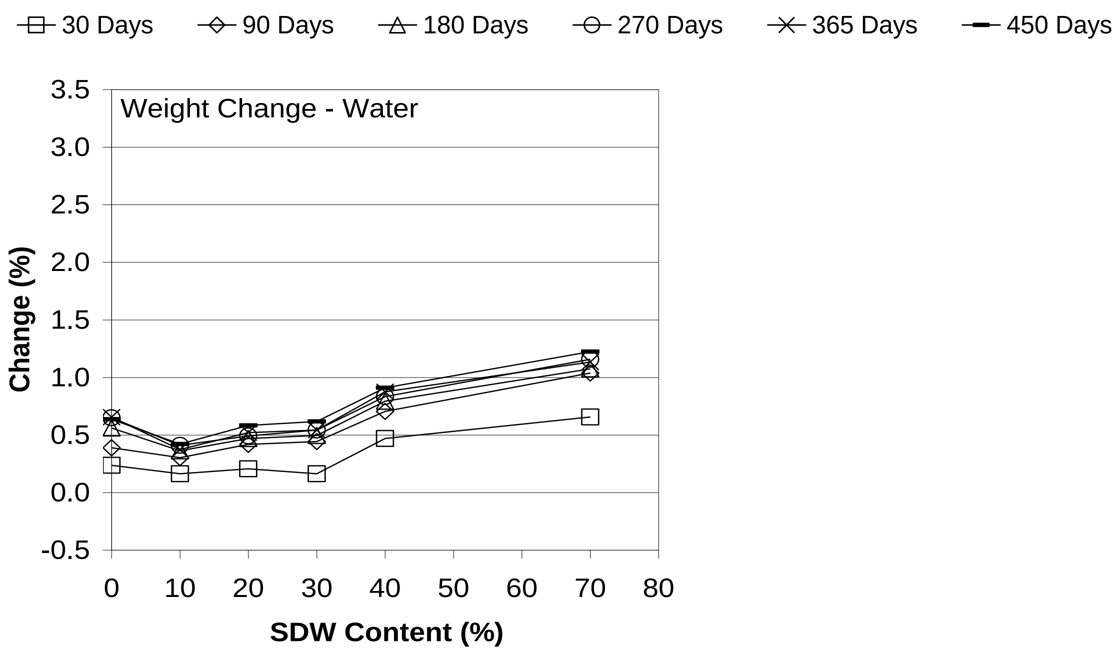

Fig. 5. Effect of SDW content on weight change of mortar immersed in water

Dunstan [1980] tried to predict the sulphate resistance of fly ash in concrete by using a simple resistance factor 'R' based on the calcium and iron oxide content of the fly ash. It was suggested that increasing the CaO content in the fly ash above 5% would decrease sulphate resistance and increasing the Fe_2O_3 content would improve sulphate resistance by reducing the expansive nature of the alumina-sulphate reactions. Values of 'R' less than 1.5 (for 25% replacement) were shown to increase sulphate resistance, whereas 'R' values greater than 3, decreased the sulphate resistance when exposed to sodium sulphate. The 'R' factor for the SDW used in the current investigation was 1.54, which according to Dunstan would have no significant effect on the sulphate resistance at 25% cement replacement. However, the investigation clearly shows that when cement was replaced with SDW the sulphate resistance was significantly improved, especially when the SDW content was increased above 10%. The

SDW is predominantly fly ash, which has an 'R' value of 0.38 in the current investigation. This complements the improvement in sulphate resistance associated with the C-SDW mortars investigated. However, other investigators showed that the measure of chemical composition and the 'R' factor was insufficient in determining the sulphate resistance of the fly ash cements [Mehta 1986, Rasheeduzzafar et al 1986, Hartmann and Mangotich 1987]. The performance of fly ash cements is also dependent on the actual fly ash content, and generally, the optimum fly ash content lies between 20% and 30%.

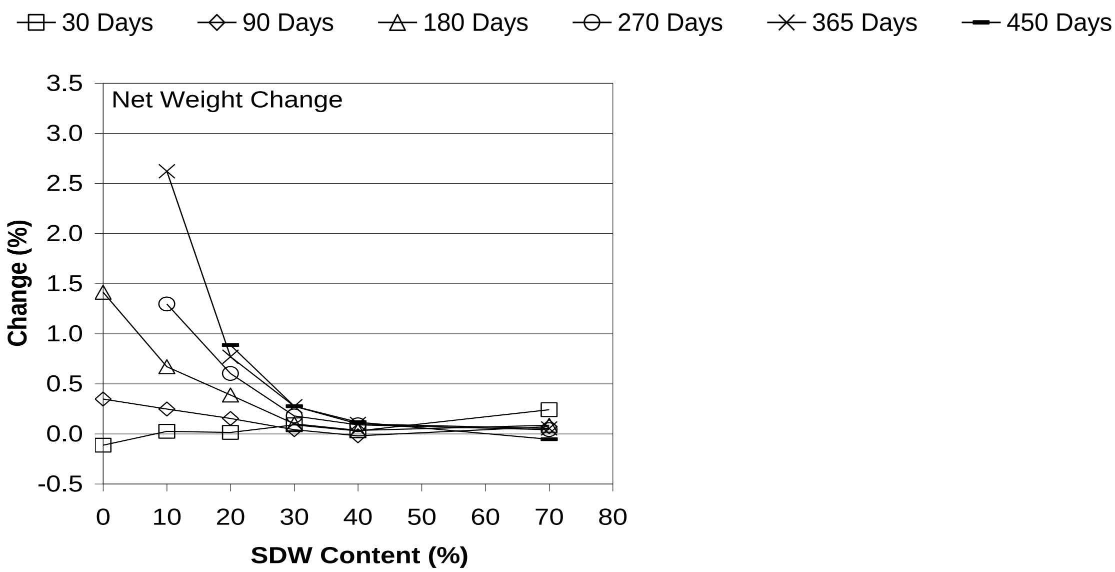

Fig. 6. Effect of SDW content on net weight change of mortar

Mangat and El Khatib (1992) reported that when cement was replaced with 10% fly ash the sulphate resistance was reduced compared to normal cements. This could be attributed to the curing regime adopted. Hartman and Mangotich [1987] proposed an alternative method to determine the sulphate resistance of concretes based on the oxide contents of all the cementitious parts, which was referred to as the oxide durability factor (ODF). It was suggested that sulphate resistance was improved if the ODF was lower than that of the reference cement. Unfortunately, no tests were carried out to determine the free lime content of constituent materials during this investigation, therefore no comparison were made.

Tikalsky and Carrasquillo [1993] reported that fly ash with high amounts of calcium oxide and amorphous calcium aluminate were more susceptible to sulphate attack than concretes containing low lime fly ash (ASTM class F). Samples were considered failed once the expansion of samples exposed to a 10% sodium sulphate solution exceeded 10%. Mixes containing low lime fly ash exhibit less than 0.1% expansion after 540 days. Although the correlation between sulphate resistance and chemical and/or mineralogical composition were not conclusive, the major factors behind improving sulphate resistance lie in reducing the CaO content, and increasing the presence of crystalline phases, such as mullite, quartz, ferrite spinal and hematite. Further it was reported that fly ash containing calcium aluminate-rich glasses were more susceptible to sulphate attack compared to fly ash containing silica or silica-aluminate rich glasses. It was reported that as the CaO content of the glassy phase increased the resistance to sulphate was decreased through increased expansions. This phenomenon does not appear to be restricted to fly ash alone.
O'Farrell et al [1999] reported that the resistance of mortars containing cement and ground brick exposed to sodium sulphate was significantly increased as the CaO:glass ratio

(excluding the CaO combined with sulphate) decreased. The CaO introduced into the C-SDW blends was minimal and was generally supplied by the gypsum component.

CONCLUSIONS

Partial replacement of cement with simulated desulphurised waste improves the sulphate resistance of mortar beyond a replacement level of 20%. The resistance is drastically enhanced when the replacement level is beyond 20% and up to at least 70%. The enhanced resistance may be due to the early formation of ettringite where expansion can be accommodated during the early stages of hydration. Further analysis is required to assess the formation of various phases.

REFERENCES

Brown PW (1981), An evaluation of the sulphate resistance of cements in a controlled environment, Cement and Concrete Research, Vol.11, pp.719-727

Collepardi M (2001), Ettringite formation and sulphate attack on concrete, Fifth CANMET/ACI International Conference, Recent Advances in Concrete Technology, Ed. Malhotra VM, SP 200-2, pp.21-37

Dunstan ER (1980), A possible method for identifying fly ashes that will improve the sulphate resistance of concrete, Cement, Concrete, and Aggregates, Vo.2, No.1, pp.20-30, Summer

Hartmann C, Mangotich E (1987), A method for predicting sulphate durability of concrete, Bryant and Katherine Mather Symposium on concrete durability, American Concrete Institute, SP 100, pp.2135-2151

Lea FM (1998), LEA'S Chemistry of Cement and Concrete, Forth Edition, Arnold, ISBN 0 340 56589 6, Chapter 10 - Pozzolana and Pozzolanic Cements, pp.471-633

Mangat PS, EL-Khatib JM (1992), Influence of initial curing on sulphate resistance of blended cement concrete, Cement and Concrete Research, Vol.22, pp.1089-1100

Mehta PK (1986), Effect of fly ash composition on sulphate resistance of cement, ACI Journal, pp.994-1000, Nov-Dec

O'Farrell M, Wild S, Sabir BB (1999), Resistance to chemical attack of ground brick-PC mortar Part 1. Sodium sulphate solution, Cement and Concrete Research, No.29, pp.1781-1790

Poon CS, lam L, Wong YL (2000), A study on high strength concrete prepared with large volumes of low calcium fly ash, Cement and Concrete Research, Vol. 30, pp.447-455

Rasheeduzzafar, Al-Mana A, Haneef M, Maslehuddin M (1986), 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

Santhanam M, Cohen MD, Olek J (2001), Sulphate attack research - whither now? Cement and Concrete Research, 31, pp.845-851

Tikalsky PJ, Carrasquillo RL (1993), Fly ash evaluation and selection for use in sulphate resistant concrete, ACI Materials Journal, Vol.90, No.6, pp.545-551

Wild S, Khatib JM, O'Farrell M (1997), Sulphate resistance of mortar, containing ground brick clay calcined at different temperatures, Cement and Concrete Research, Vol.27, No.5, pp.697-709