Technical Report

XYPEX AUSTRALIA

Resistance Of Concrete To Harsh Environments

Ammonium Sulphate

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Abstract

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RESISTANCE OF CONCRETE TO HARSH ENVIRONMENTS AMMONIUM SULPHATE

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1.0 INTRODUCTION

Concrete technologists are often required to recommend concrete mixes for use in aggressive environments where the achievement of desired service life rather than design strength is the controlling criteria for concrete design. In such instances, the concrete technologists must consider both the concretes capacity to prevent reinforcement corrosion and the cement matrixes resistance to chemical attack. Commonly reinforcement corrosion is initiated in environments that contain high chloride levels where as environments with low pH or high sulphate concentrations are the most likely to lead to a breakdown of the cement matrix.

Typical examples of environments where sulphate attack is the dominant deterioration mechanism include the Goldfields region of Western Australia where extremely high sulphate contaminated groundwaters are experienced and the fertiliser industry where ammonium sulphate exposure may lead to rapid deterioration of reinforced concrete.

A number of approaches can be taken to improve the performance of concrete in these environments. Some of the alternative procedures being:

- Use of sulphate resistant cements
- Use of conventional mixes with w/c ratio of approximately 0.32
- Use of blast furnace slag and or fly ash

- Use of silica fume
- Use of water proofing or other performance enhancing admixtures.

Although it is recognised that all the above enhancement methods will lead to improved performance of concrete in the extreme environments there is little information upon which the relative performance of these various enhancement methods can be determined. Furthermore there is a lack of technical information on the performance of concrete (rather than mortars) under real life operating environments.

To fill this lack of information on relative performance an internally funded programme of testing has been commenced. The objective being to develop an accelerated fitness for purpose test which can be used to determine the relative performance of various durability enhancing mechanisms. In the process of developing the test method the relative performance of a selection of commonly available durability enhancing mechanisms will be measured.

In developing the fitness for purpose test it is intended that the performance of 10 or more commonly recommended durability enhancing mechanisms will be assessed under four harsh environments including:

- exposure to ammonium sulphate (fertiliser industry)
- exposure to sodium sulphate (sulphate ground water)
- exposure to high alkalinities (Aluminum refining)
- exposure to low pH (chemical processing)

The findings of Laboratory Testing will be compared to insitu testing to ensure that the relative performance of accelerated testing replicates that observed in real life situations.

This paper presents results for exposure of 6 concrete types in the first of the environments listed above.

2.0 BACKGROUND

Sulphate environments are found in numerous situations from ground water to sewer systems to industry. It is the considerable damage that is caused to concrete structures built in these conditions which led to extensive research in this area. Industries that have high concentrations of ammonium sulphate are fertiliser, steel making, and mineral processing industries. These industries can have concentrations of up to 760 g/L at 25^{o}C.

The chemical reactions that can occur when a cementitious material is in contact with sulphate solution are wide ranged. They can include processes such as alkali-aggregate reactions, stress corrosion, decomposition and dissolution of hydrates. The chemistry of the sulphate solution, particularly the types and concentrations of cations, are the triggers of these reactions which can be very serious in the particular environment. (Cao 1997) Sulphates react with C_3A in hydrating Portland cement, this reaction is expansive, and the resulting compounds are about double the size of the original compounds. (Perkins 1997)

In general there are two main mechanisms of attack on concrete that result due to the presence of sulphate ions. The first of these reactions is the production of gypsum and the second is ettringite formation, as shown in the equations below. In most cases, the formation of gypsum is associated with loss of mass and strength rather than expansion. The reactions that are involved with ammonium sulphate are: -

$$Ca(OH)_2 + (NH_4)_2SO_4 \rightarrow \underset{\text{Gypsum}}{CaSO_4.2H_2O} + \underset{\text{gas}}{NH_3}$$

$$3CaO.Al_2O_3.6H_2O + 3CaSO_4.2H_2O + 24H_2O \rightarrow \underset{\text{Ettringite}}{3CaO.Al_2O_3.3CaSO_4.32H_2O}$$

Ammonium compounds (sulphate, nitrate, super-phosphate) cause serious deterioration of concrete in a relatively short time. (Perkins 1997) Actual time depends on concentration, period of contact, abrasion of concrete, and concrete quality in terms of porosity, penetrability, cement content and cement type. (Perkins 1997) The aggressive action of ammonium sulphate is thought to be connected with the increased solubility of gypsum in ammonium sulphate solutions. (Lea 1970) Another contributory mechanism is likely to be the formation of ammonia gas. (Collins and Green 1990) Upon formation, ammonia gas will readily diffuse from the concrete enabling the gypsum formation reaction to eventually proceed to completion rather than to establish equilibrium. (Collins and Green 1990) Diffusion of ammonia gas from the concrete will also render the concrete more porous and permeable and thus more susceptible to further attack from ammonium sulphate solution. (Collins and Green 1990)

There are three main ways to increase the sulphate resistance of concrete, these are;

- Prevent the contact of concrete and the sulphate environment.
- Change the chemical composition of the cementitious binder.
- Decrease the penetrability of the concrete.

Of the above it is only the last two means which offer possible solutions to increasing the durability of concretes in a sulphate environment. Changing the cementitious binder to a more sulphate resisting binder will slow the rate of chemical attack, and decreasing the penetrability will prolong the time it takes for the sulphate ions to migrate into the concrete to react with the cementitious binder.

3.0 LABORATORY TESTING

3.1 Testing Regime

At present there is no Australian Standard method for the performance assessment of concrete in aggressive environments. Therefore it has been necessary to develop a fitness for purpose test that is relevant to "real world" conditions.

Exposure trials were conducted on a nominal N50 grade mix to simulate typical construction grade concrete (using a W/C ratio of 0.43). The samples being cast in accordance with AS1012.2. To replicate real life conditions only commercially available aggregates, sand, cements and admixtures were used and all trials were conducted on concrete (20 mm aggregates) rather than mortars or cement pastes. The aggregate consisted of Darling Range granite and the sand was quartz sand from Jandakot.

To simulate typical construction practice the curing of the concrete was restricted to 7 days in limewater. After curing the samples were placed in the accelerated exposure environment for a period of 180 days. The rate of attack experienced by the samples was determined by measurement of the weight loss and length change of the samples.

3.2 Mix Designs

A total of six mixes were included in the trials (Table 1). All mixes had the same combined aggregate but differed in the composition of their cementitious binder. Four commercially available cement blends (GP, GP80, LH, SR), a GP/Silica fume blend and a GP with waterproof admixture were used.

All materials were obtained from the local Perth market. It should be noted that the sulphate resistant cement supplied to the local Western Australian market is a blend of Portland cement and silica fume, which complies with AS 3972-1997.

	Mix Designation					
Component	GB80	GP	LH	SR	SF	Admix
20mm Aggregate	635	625	625	625	655	630
14/10mm Aggregate	420	415	415	410	430	415
7mm Aggregate	210	205	205	205	215	210
Jandakot Sand	680	675	675	670	705	675
Type GP80 Cement	420					
Type GP Cement		415			315	415
Type LH Cement			415			
Type MGP Cement				415		
Silica Fume					30	
Catalytic crystalline waterproofing admixture						3.3
Water reducer (mls/m^3)	1675	1655	1655	1650	1650	1655
Water added	180	180	180	180	150	180
Slump prior to SP addition (mm)	57	55	30	0	0	57
Superplasticiser (mls/m^3)	600	590	295	1325	4265	595
Post Superplasticiser Slump	100	90	108	110	102	97

Note 1: Jandakot sand was sourced from CSR quarry in Jandakot, WA.
Note 2: All coarse aggregate was sourced from the CSR quarry in Gosnells, WA.
Note 3: All cement is from the Cockburn Cement plant in Munster, WA.
Note 4: All water reducing admixtures are supplied by W.R. Grace
Note 5: Catalytic crystalline waterproofing admixture from XYPEX Australia
Note 6: All values given as kg/m^3, except where stated otherwise.

Cement Compositions

Type GB80 - 20% Ground Granulated Blast Furnace Slag
80% General Purpose Cement

Type GP - General Purpose Cement

Type LH - 70% Ground Granulated Blast Furnace Slag
30% General Purpose Cement

Type SR - 8% Silica Fume
(Type MGP) 92% General Purpose Cement

Table 1. Mix Designs

3.3 Sample Preparation

All mixes were batched in accordance with the requirements of AS 1012.2-1994. Mixes were batched with the same water cement ratio of 0.43 and dosage of water reducing admixture. The slump of each mix was then measured (AS 1012.3) prior to the addition of sufficient superplasticiser to achieve a workable slump of approximately 100mm.

Samples as listed in Table 2 were cast from each batch and cured in accordance with AS 1012.8.

Purpose	**Dimension**	**Number**	**Curing**
Compressive Strength	200 x 100	3	28 days water cured
Volume Water Permeable Voids	200 x 100	3	28 days water cured
Exposure Trials	280 x 75 x 75	3	7 days water cured

Table 2 Sample Preparation

3.4 Exposure Conditions

The accelerated exposure environment to which the samples were subjected to is an in-house method. The method is based on the Australian Standard for Soundness (by use of Sodium Sulphate Solution), AS 1141.24-1974 and a similar method developed by the US Bureau of Reclamation the "Procedure for Length Change of Hardened Concrete Exposed to Alkali Sulphates".

The exposure environment consists of alternate wetting and drying cycles, where the samples are immersed in 1M (132g/L) ammonium sulphate for 18 hours and dried at 50^{o}C for 6 hours.

3.5 Performance Assessment

A number of methods of measuring the relative performance of samples were considered and trialed. It was however found that the most representative and reproducible methods are the measurement of weight loss/gain and length loss/gain. These both have been measured over weekly intervals over the exposure period.

4.0 RESULTS AND DISCUSSION

4.1 Relationship between Cementitious Binder and Water Demand

Mixes containing silica fume (SR & SF) required significantly greater quantities of superplasticiser to achieve the desired slump. This being attributable to the high water demand of the silica fume associated with its high surface area to weight ratio.

Furthermore, as the SF mix had a lower cementitious content than all other mixes its total water was reduced from 180 to 150 kg/m^3 to maintain the same w/c ratio. As a consequence the amount of free water is also reduced. Therefore there is a greater requirement for superplasticiser than other mixes to achieve the same level of workability.

4.2 Measurement of Volume Water Permeable Voids and Compressive Strength

The volume of water permeable voids (to ASTM C 642-90) and compressive strength (AS 1012.9) were determined on samples cured in limewater for 28 days. The results of testing being presented in Table 3.

	Mix Designation					
	GB80	GP	LH	SR	SF	Admix
Compressive Strength (MPa)	66	64	58	79	69	62
Volume Water Permeable Voids (%)	11.8	11.4	12.8	10.9	9.5	11.4

Note 1: Compressive Strength test was performed in accordance with AS 1012.9.
Note 2: Volume Water Permeable Voids test was performed in accordance with ASTM C 642-90.

Table 3

Volume Permeable Voids and Compressive Strength (Average of 3 samples)

4.3 Measurement of Weight Loss During Ammonium Sulphate Exposure

The level of attack of the concrete by the sulphate solution was determined by measuring the weight loss of samples with time. Total weight loss over the 25 week exposure period for each mix type is presented in Table 4. Figure 1, shows a graph of the average weight change with time (of 3 samples) for each of the trial mixes.

The SR mix experienced the lowest level of weight loss for all samples tested. This is not surprising as the mix had a strength 15MPa higher than the average of all other mixes. It is considered likely that SR mixes with strengths equivalent to other mixes would have exhibited similar weight loss to that experienced by the SF and Admix mixes.

The performance of the SF and Admix mixes were similar and only marginally worse than the SR mix. These three mixes exhibited significantly less weight loss than the GP mix, which in turn performed better than the GB80 mix. The low heat mix (LH) was by far the worst performing of all mixes.

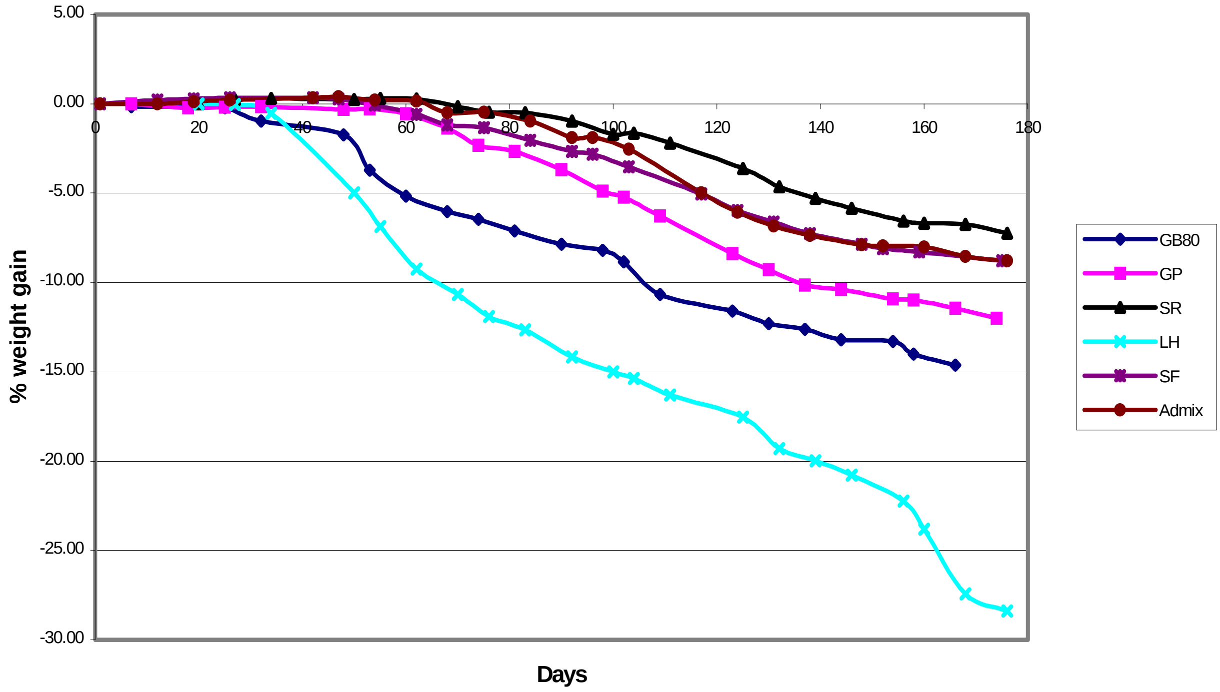

Figure 1

Change in weight with time for samples exposed to cycling Ammonium Sulphate exposure

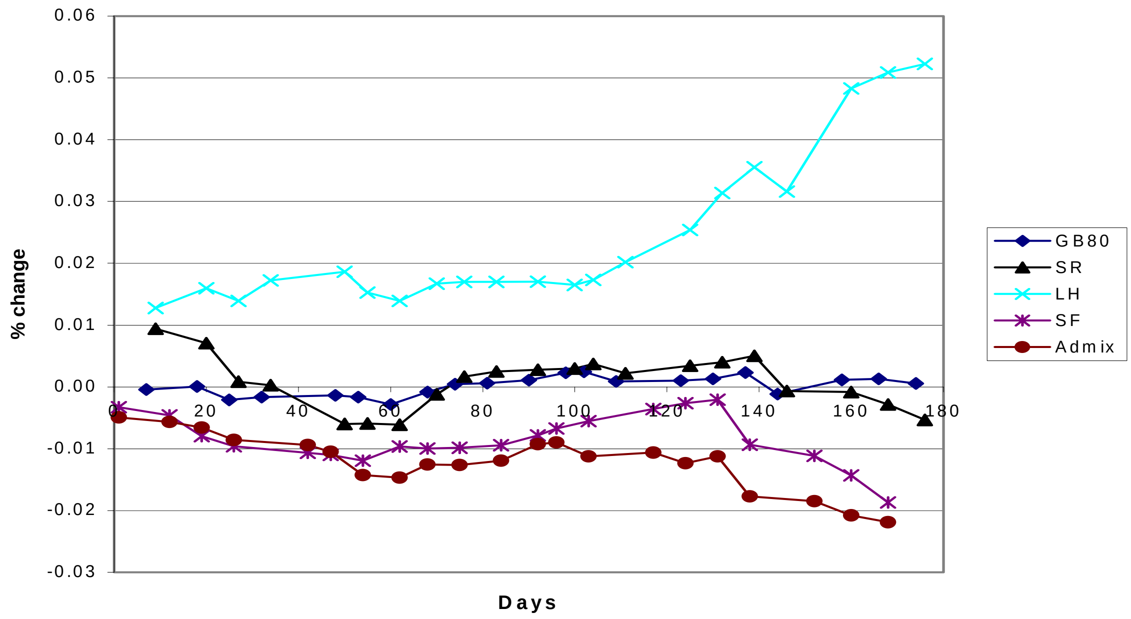

Figure 2

Change in Sample Length compared to that of GP mix during exposure to Ammonium Sulphate

4.4 Length Change of Samples Exposed to Ammonium Sulphate Environment

The length of each sample was measured weekly using a vertical comparator. To compensate for changes in length resulting from shrinkage and thermal effects of the experimental procedure variations in length have been expressed as the difference in the percentage change in length and the percentage change for the GP control mix. To distinguish the underlying trends this is displayed as a five point moving average, as seen in Figure 2 above.

Over the period of exposure to the experimental environment the GB and LH mixes, both of which contained ground granulated blast furnace slag, experienced expansions in excess of that of the GP mix indicating that a greater level of sulphate attack was being experienced. The Admix, SR and SF samples experienced significantly less expansion than the GP mix indicating that substantially less sulphate attack had occurred during the period of exposure.

The measurement of length gain can be related to bulk expansion of the samples as distinct from weight loss, which is more, associated with surface effects. These results clearly show that the Admix mix containing catalytic crystalline waterproofing admixture achieved the highest level of protection. This presumably is a result of the inability of water, containing dissolved ammonium sulphate, to penetrate to the centre of the samples under test. It is therefore a reflection of the waterproofing abilities of the catalytic crystalline waterproofing admixture.

	Mix Designation					
	GB80	GP	LH	SR	SF	Admix
Total Percentage Weight Loss	14.6	12.0	28.4	7.2	8.8	8.8
Percentage Length Change	0.01	-	0.12	0.00	-0.01	-0.02

Note 1: Total Percentage Weight Loss is given for 25 weeks exposure.
Note 2: Percentage Length Change is given as the change compared to the GP mix, at 25 weeks.

Table 4 Results of Exposure Trials

4.5 Relationship Between Water Permeable Void Volume and Sulphate Resistance

The measure of water permeable void volume of a concrete mix is commonly used as an indication of potential concrete durability. As shown in Table 3, the overall variation in permeable voids was small but as expected mixes containing silica fume achieved the lowest values. This result was expected as the addition of silica fume is known to result in a finer pore structure.

The relatively high level of water permeable voids for the Admix mixes was not representative of its performance in exposure trials as they experienced the lowest level of sulphate attack (based on relative length change). As a consequence water permeable void volume testing is considered an inappropriate method for measuring resistance to sulphate attack most particularly when admixtures have been used to improve the performance of the mix.

4.6 Relationship Between Concrete Strength and Sulphate Resistance

By maintaining a standard water cement ratio with all mixes the variability in strength was minimised. The SR mix (8% silica fume addition) did have a significantly higher strength than all other mixes. This mix also experienced the lowest level of weight loss (marginally less than SF and Admix). Its length variation during exposure trials however was not significantly different to that experienced by the GP mix. Similarly, with the exception of the Admix mix, the mixes with the highest strengths tended to have the lowest weight loss. The Admix mix performed better than mixes with significantly higher strengths.

4.7 Performance of mixes Containing Ground Granulated Blast Furnace Slag

The addition of Ground Granulated Blast Furnace Slag (20% in GB80 and 70% in LH) had a detrimental effect on performance during exposure trials as measured by both weight loss and length change. This result was unexpected as the pozzolanic effect of the slag was expected to make the concrete more resistant to sulphate attack by reducing the amount of free calcium hydroxide available for reaction with the sulphate ions. Figure 3, shows the level of surface attack experienced by the GB80 mix after 25 weeks.

Figure 3

The visual appearance of GB80 concrete after 25 weeks of testing in ammonium sulphate

The poor performance of the GGBFS blends could be attributed to the longer curing time required to achieve full hydration or to the chemical composition of the slag itself. Slag with high aluminate contents reduces resistance to sulphate attack.

4.8 Performance of mixes Containing Silica Fume

The addition of silica fume (SR and SF mixes) lead to increased performance when compared to the GP mix. This result can be attributed to the silicon dioxide component (86 to 98%) of the silica fume, which reacts with the calcium hydroxide. This being the component of the concrete that the sulphate reacts with to produce gypsum. The reduction in calcium hydroxide along with the reduced penetrability caused from the refinement in the pore structure is what gives silica fume concrete its sulphate resistant qualities. Figure 4, shows the level of surface attack experienced by the SF mix after 25 weeks.

Figure 4

The visual appearance of SF concrete after 25 weeks of testing in ammonium sulphate

4.9 Performance of the Admix Mix

As noted previously there is a general relationship between increasing strength and reduced weight loss and between reduced permeable voids and reduced expansion (as measured by relative length gain). The exception to this general trend being the Admix mixes which achieved one of the lowest (with the exception of the LH mix) compressive strengths but achieved the second lowest weight loss and the lowest relative length gain of all samples tested.

The improved performance may be attributable to the waterproofing properties of the admixture. This restricts access of the sulphate ions to the bulk of the concrete limiting the area of attack to the very surface of the concrete. Figure 5, shows the level of surface attack experienced by the Admix mix after 25 weeks. Figure 6, shows the level of surface attack experienced by the GP mix after 25 weeks.

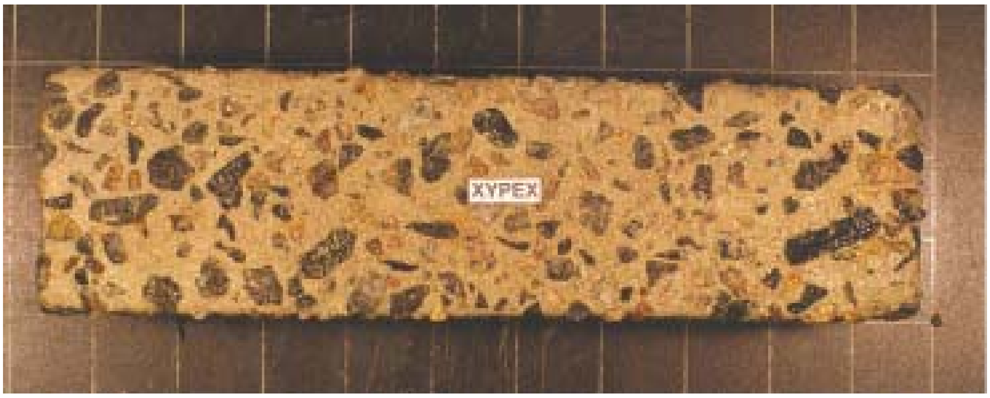

Figure 5

The visual appearance of Admix concrete after 25 weeks of testing in ammonium sulphate

Figure 6

The visual appearance of GP concrete after 25 weeks of testing in ammonium sulphate

5.0 SUMMARY

Concrete technologists are often required to recommend concrete mixes for use in aggressive environments where the achievement of desired service life rather than design strength is the controlling criteria for concrete design. Technical papers on the development of high durability concretes and performance enhancing admixtures describe a number of approaches, which can be taken to improve the performance of concrete in these environments. Some of the alternative procedures being use of sulphate resistant cements, use of conventional mixes with w/c ratio of approximately 0.32, use of a pozzolan, and use of water proofing or other performance enhancing admixtures.

There is, however, little information upon which the relative performance of these various enhancement methods can be determined. Furthermore, there is a lack of technical information on the performance of concrete (rather than mortars) under real life operating environments. To fill this lack of information on relative performance an internally funded research program to develop an accelerated fitness for purpose test has been undertaken, which can be used to determine the relative performance of commonly available durability enhancing mechanisms.

The performance of various concrete blends exposed to ammonium sulphate environments has been assessed by measure of weight loss and relative change in length of samples placed in a wetting and drying cycle. It has been found that the addition of catalytic crystalline waterproofing admixture substantially improves the performance of the concrete compared to GP mixes with the same cement content and approximate compressive strength. The level of performance being greater than which would be predicted from consideration of either concrete strength or water permeable void volume.

The addition of silica fume in combination with a reduction in GP content sufficient to achieve equivalent strengths resulted in a smaller increase in performance to the addition of catalytic crystalline waterproofing admixture. Finally, the replacement of GP with blast furnace slag resulted in a significant reduction in performance.

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