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Compressive Strength and Electron Paramagnetic Resonance Studies on Waste Glass Admixtured Cement

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ABSTRACT

The present work reports the effect of waste glass (*WG*) *on the properties of Portland cement through Electron Paramagnetic Resonance* (*EPR*) *study. Cement pastes containing* 0, 10, *and* 30% *replacement of waste glass with cement and in a water to cement ratio of* 0.4 *have been prepared. The g factors of Fe*(*III*) *and Mn*(*II*) *impurities at different hydration ages have been calculated. The decreased* g_{Fe} *values and simultaneous increase in* g_{Mn} *values with increase in replacement % of WG are explained due to retardation of cement hydration.*

Keywords**:** *EPR, Cement, Waste Glass, Setting Time, Compressive Strength, G-Factor*

1. Introduction

Cement is an important adhesive used by mankind in all walks of life, right from filling the teeth cavity to the Sky-Scrapers. Clinker, produced by heating a mixture of limestone and clays at 1500°C, is composed of various calcium minerals, e.g. calcium silicates, aluminates and ferrites. The principle minerals are tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) [1]. Hydration products, formed when cement or clinker minerals are mixed with specific amount of water, have chemical and physiccal properties that vary with the conditions of hydration (time, temperatures, pressure etc.,). The hydration products of cement form a colloidal structure (hydrogel), when cement is hydrated with much excess water. There are many methods, which can be used to analyze the succeeding mechanisms in the cement hydration. They are FTIR, XRD, DTA, SEM, Electrical measurement and dielectric methods [2-6].

The utilization of many industrial byproducts in the construction industry is now well developed as it helps in improving the sustainability in two ways. First, reuse of and will be occupying scarce land resource. Second, it minimizes the degradation of land and the environment as a result of comparatively less digging. "Recycling" is an All-Prevailing practice now as it conserves the planet's resources. The construction industry has shown great gains in recycling industrial by products and waste, including waste glass (WG).

Glass is produced in many forms including packaging or container glass (bottles and jars), flat glass (windows and windscreens), bulb glass (TV screens, monitors etc.), all of which have a limited life in the form they are produced and need to be reused/recycled to avoid environmental problems that would be created if they were to be stockpiled or send to landfill. The finely ground waste glass is a mineral additive in cement is another promising direction for waste glass recycling.

The use of recycled waste glass in Portland cement has attracted a lot of interest worldwide due to the increased disposal costs and environmental concerns. Being amorphous and containing relatively large quantities of silicon, aluminium, calcium, glass is, in theory, pozzolanic or even cementitious in nature when it is finely ground. Thus, it can be used as a cement replacement in Portland cement. Recently, many studies have focused on the uses of wastes glasses as aggregates for cement concrete or as cement replacement [7-9]. Recently some attempts have been made to use the waste glasses as raw siliceous materials for the production of Portland cement [10-12]. Studies have been done on the possibility of reusing waste glasses as asphalt additive or rode filler [13].

Electron Paramagnetic Resonance (EPR) is an ideal

complementary technique for other methods in a wide range of studies in the area of chemistry, biology, medicine and physics. EPR spectroscopy offers information on the equilibrium structure as well as the dynamic properties (dynamic or time dependent Hamiltonian) of system containing one or more unpaired electrons. EPR has been successfully applied to hydration of waste glass admixtured cement paste, following the behaviors of iron and manganese ions. According to Bruckner *et al.* [14], EPR and Mossbauer investigations confirm that in addition to oxygen, the internal cement components such as Fe(III) and Mn(III) act as oxidizing agents being reduced to Fe(II) and Mn(II) ions respectively. From X-band EPR spectra of unhydrated cement, Lubomir Lapcik and Zdenek Simek [15] have suggested that iron is mainly Fe(III), which is in a tetragonally distorted octahedral symmetry, due to the surrounding ligands. As far as we are aware, EPR studies on hydration of cement are meager and no EPR studies have been reported so far on hydration of soda-lime waste glass admixtured cement paste. The purpose of this paper is to present a detailed EPR study on soda-lime waste glass admixtured cement paste hydrated for different intervals of time.

2. Materials and Methods

2.1. Experimental Methods

Initial setting time and final setting time has been measured on OPC and WG admixtured cement paste in a water to cement ratio of 0.4 [17] and reported in **Table 2.**

Compressive strength has been measured on OPC and WG admixtured cement in a water to cement ratio of 0.4 and sand: cement ratio of 1:3 [17]. The proportions of the cement, sand and water were calculated according to Indian standard (IS No. 650 - 1960). The standard size building sand was used. The mixtures were filled into 7 × 7 × 7 cm cubes tightly and were allowed to dry and then cured. After 1 day, 1 week and 4 weeks, the cubes were split open and subjected to compression testing, which the average of three cubes and the results are shown in **Table 3**.

EPR spectra are recorded using JEOL JES-TE100 ESR Spectrometer operating at X-band frequencies, having a 100 KHz field modulation. DPPH is used as the standard reference for magnetic field correction. For all samples the experimental parameters are the same and g-values are obtained from the equation $g = h\nu/\beta B$, where β is the Bohr magneton, h is the Planck's constant, ν is the frequency and B is the center field at which the resonance occurred [18]. The g-value is the key parameter in identifying paramagnetic results in a particular symmetry.

2.2. Materials

In the present study, the commercial available Ordinary Portland Cement (OPC) and soda lime Waste glass were used. Waste glasses are grinded in laboratory for 5 h. Before grinding, bottles were crushed by a hammer to granulate it. The chemical properties of cement and Waste glass are given in **Table 1**. From the chemical analysis, the OPC and WG contain small amounts of iron and manganese and are in the oxidation state of + 3.

2.3. Sample Preparation

Present investigation, Ordinary Portland cement and Waste glass admixtured cement paste was prepared by mixing double distilled water in water to cement ratio (W/C) of

Table 1. Oxide Composition (%) of Ordinary Portland cement and Waste Glass.

Constituents	Oxide Composition (%) Cement	Oxide Composition (%) Waste glass
CaO	63.32	12.89
SiO2	21.70	70.40
Al2O3	5.40	1.98
Fe2O3	3.40	1.41
MgO	2.09	0.87
SO3	2.10	-
MnO	0.12	0.97
Na2O	nil	12.90
K2O	nil	0.85
Loss on ignition	0.79	0.54
Insoluble residue	1.08	0.19

Table 2. Setting time of Waste glass admixtured cement paste.

Sample	Initial setting time hr.min	Final setting time hr.min
OPC + 0% WG	5.05	6.50
OPC + 10% WG	5.20	7.15
OPC + 30% WG	5.55	8.05

Table 3. Compressive strength (MPa) of Waste glass admixtured cement.

Sample	1 day	1 week	4 weeks
OPC + 0% WG	10.4	32.6	47.7
OPC + 10% WG	8.7	31.2	45.4
OPC + 30% WG	7.1	28.3	46.7

0.4. OPC is partially replaced with 0%, 10% and 30% of WG by weight. The samples were thoroughly mixed with water using a glass rod for two minutes and then allowed to hydrate in Air-Tight plastic containers. Samples hydrated for periods 1 hour, 1 day, 1 week and 4 weeks were subjected to acetone. To remove water content the hydrated samples were Oven-Dried at $105^{\circ}C$ for 1 hour [16]. The samples hydrated more than 1 day were cured. The dried samples were powdered using agate mortar and used EPR methods.

3. Results and Discussion

The Electron Paramagnetic Resonance spectrum of anhydrous cement and powdered waste glass are shown in **Figure 1**.

From the **Figure 1(a)**, the broad and strong EPR signal at g = 4.13 pertains to the Fe(III) ion, which is in a tetragonally distorted octahedral environment, surrounded by six ligands [15]. The spectrum consists of a sextet having a g-value of 2.14 and a hyperfine coupling constant of 9.1 mT is also present. This is owing to Mn(II), replacing Ca(II) ions in the lattice positions of calcium hydroxide. The observed values in the present work also agree with those reported by Bruckner *et al*., [14].

The EPR spectrum of anhydrous WG powder [**Figure 1(b)**], the broad and strong EPR signal at g = 4.21 pertains to the Fe(III) ion which is generally present in glasses. In addition, a six peak spectrum observed and having a g-value of 2.16 indicates the characteristics of to Mn(II) impurity. In both these spectra, the Fe(III) signal at g ≈ 2 is superimposed by a hyperfine spiliting sextet arising from manganese ions, which is due to the population of another Kramer's doublet [19].

Figures 2 - 4 shows the EPR spectra of hydrated cement paste and WG admixtured cement paste (10% & 30%) at various time intervals viz., 1 hour, 1 day, 1 week, 4 weeks. In order to have a better view in the changes of g-values, the g-values have been plotted as a function of WG admixtured cement for Fe(III) and Mn(II) and shown in **Figures 5** and **6** respectively.

For hydrated cement paste (**Figure 2**), both g_{Fe} and g_{Mn} values are found to higher at 1 hour when compared to anhydrous. When cement mixed with water, immediately due to dissolution of the hydroxyl (OH^-) and Calcium (Ca^{2+}) ions concentration increases. C_3A and C_4AF are responsible for the setting of cement and its containing aluminate and ferrite phases having high amount of iron and also some miner elements soluted in the structure. Ettringite (AF_t) is the first hydration products in cement,

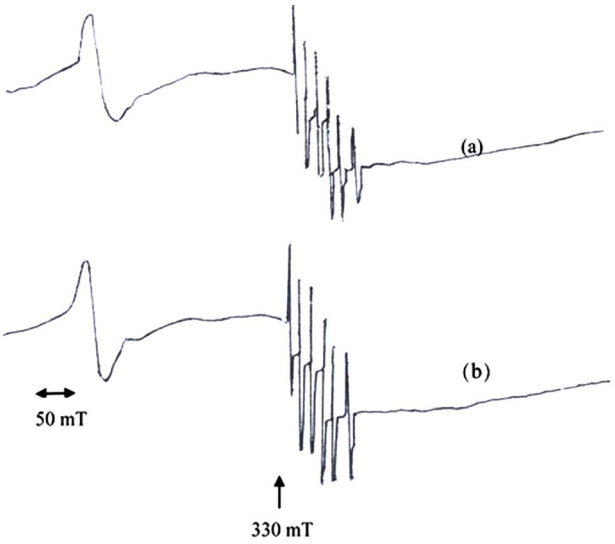

Figure 1. EPR spectra of anhydrous a) Cement (Frequency = 9.39624 GHz) and b) Waste glass powder (Frequency = 9.39729 GHz).

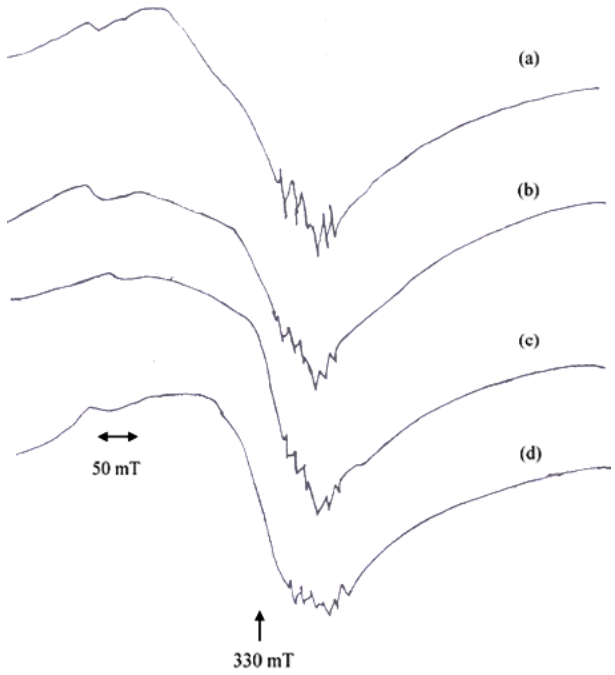

Figure 2. EPR spectra of OPC paste hydrated with (a) 1 hour (Frequency = 9.39723 GHz) (b) 1 day (Frequency = 9.37654 GHz) (c) 1 week (Frequency = 9.39465 GHz) (d) 4 weeks (Frequency = 9.39873 GHz).

rich in iron content, produced through the consumption of gypsum by C_3A. The reaction of C_3A be represented by the following equation [20].

$$3CaO.Al_2O_3 + 3CaSO_4 + 32H_2O \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12}.26\,H_2O$$

Tricalcium Aluminate — gypsum — water — ettringite

(1)

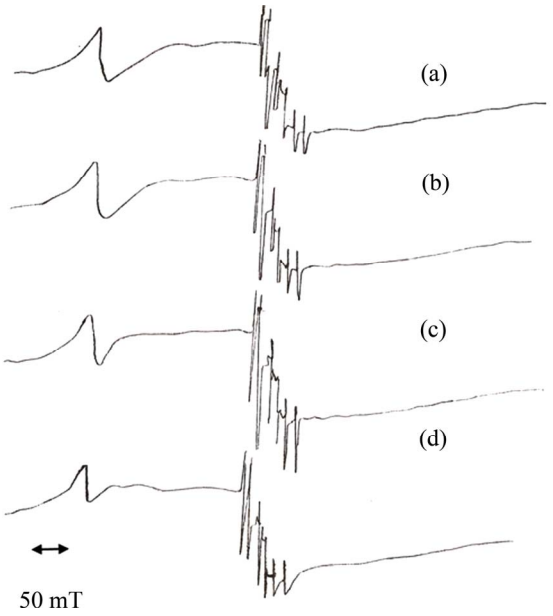

Figure 3. EPR spectra of OPC + 10% WG admixtured paste hydrated with (a) 1 hour (Frequency = 9.39428 GHz) (b) 1 day (Frequency = 9.39566 GHz) (c) 1 week (Frequency = 9.39728 GHz) (d) 4 weeks (Frequency = 9.39874 GHz).

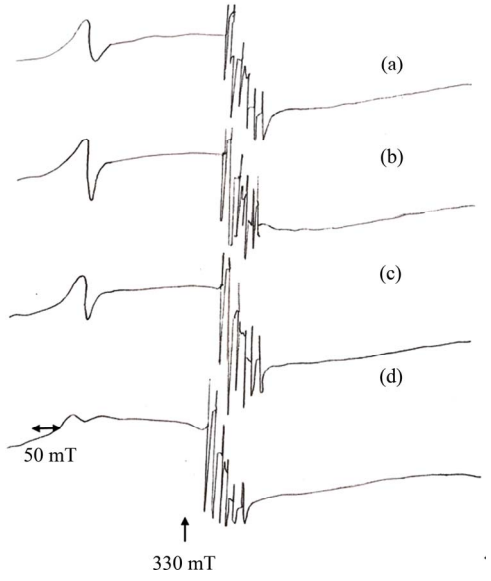

Figure 4. EPR spectra of OPC + 30% WG admixtured paste hydrated with (a) 1 hour (Frequency = 9.39537 GHz) (b) 1 day (Frequency = 9.39584 GHz) (c) 1week (Frequency = 9.39734 GHz) (d) 4 weeks (Frequency = 9.39790 GHz).

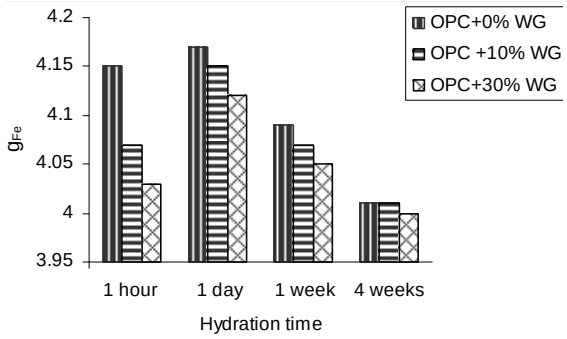

Figure 5. g_{Fe} values *Vs* hydration of waste glass admixture cement paste.

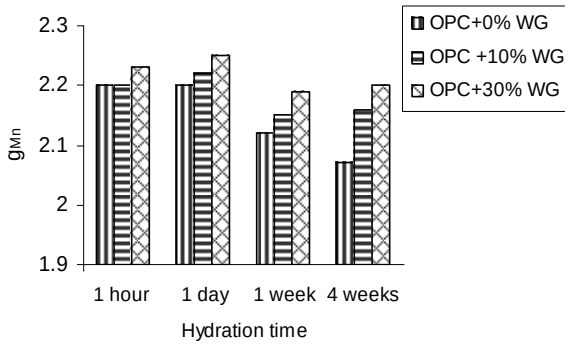

Figure 6. g_{Mn} values *Vs* hydration of waste glass admixtured cement paste.

Due to increase in iron content (AF_t), the resonance line due to Fe(III) species becomes broader and distributed over the whole range of spectrum. The broad signal is attributed to magnetically ordered Fe-O-Fe species with Ferri/Ferro or antiferro magnetic behaviour. The high g_{Fe} value (4.17) of the OPC paste is caused by Fe(III) ions in sites of strong rhombic distortion [21].

From the **Figure 2(a)**, the observed sextet at g_{Mn} = 2.20 is due to Mn(II) impurity ions and incorporated into Ca lattice positions of $Ca(OH)_2$. The g_{Mn} values gradually increases up to 1 day due to less incorporation of formed Mn(II) in $Ca(OH)_2$.[14]. Since before 1 day the formation of $Ca(OH)_2$ is very less.

At 1 day, the Ca(II) concentration reaches the saturation level and the crystallization of calcium hydroxide occurs and C-S-H gel is formed moreover the availability of ions and water is also reduced. The formation of C-S-H and $Ca(OH)_2$ is represented by the following equations

$$2\left(3CaO.SiO_2\right) + 6H_2O \rightarrow 3CaO.2SiO_2.3H_2O + 3Ca\left(OH\right)_2$$

Tricalcium Silicate — water — C-S-H — Calcium hydroxide (2)

$$2\left(2CaO.SiO_2\right) + 4H_2O \rightarrow 3CaO.2SiO_2.3H_2O + Ca\left(OH\right)_2$$

Dicalcium Silicate — water — C-S-H — Calcium hydroxide (3)

The C-S-H gel is one of the major strength rendering components of the hydrated cement and it possesses sparse dispersibility, numerous interior structural effects and coarse particle surfaces. After 1 day, the availability of Fe(III) and Mn(II) ions are reduced and hence the g-values have gradually decreased. This is because these two ions in cements are responsible for the kinetics of solidification and hardening of the main silicate component. This may be that the mobility of this particular silicate aggregate is reflected in the vigorous changes in polycrystalline quasi-isotropic character of electron paramagnetic spectra of Fe(III), Fe(II) ions to the anisotropic [15]. Also the decreased g-factor values reflect the structural changes of Fe(III) ions to Fe(II) ions. These characteristics generally decrease the g-values of Fe and Mn but increase the strength of cement up to 4 weeks.

From the **Figures 3** and **4**, it is observed that WG admixtured cement also follows the same fashion as that of OPC. In WG admixtured cement paste exhibit a lower g_{Fe} then that of the plain cement paste, the lowest being observed for the mixture with the highest amount of WG (30%). This is due to well known retarding effect of WG. The WG admixtured cement showed longer setting times than the pure cement. Since, as the increase of WG content reduces the cement in the mix (cement dilution). As a result, hydration process slows down and hence the volume of hydration products is less causing setting time to increase.

At all hydration periods, the WG admixtured cement paste shows higher g_{Mn} values than the plain cement paste. This is attributed to the reduction in the amount of $Ca(OH)_2$ retarded by the clinker phases because of the reduced cement content, leading to less incorporation of formed Mn(II) in $Ca(OH)_2$. This effect is reflected in EPR spectrum (**Figure 3** and **4**) that as replacement % of WG increase in cement, the intensity of the Mn(II) signal is also increases.

Table 3 depicts the compressive strength of waste glass powder modified cement pastes at different hydrated period. The compressive strength decrease with increase in WG powder contents, the reason being the reduction in cement content and increase porosity. At early age no secondary growth of C-S-H gel, because of the poor pozzolanic reaction between $Ca(OH)_2$ and WG.

4. Conclusions

The effect of Waste glass powder on the properties of Portland cement is studied through Electron Paramagnetic Resonance with different hydrated periods. The following conclusions emerge:

1) The results indicate that EPR studies can be effectively used as a powerful tool in delineating the complexities of chemical reactions in cement hydration and to detect very small concentrations of Fe(III) and Mn(II) ions present in cement.

2) Setting time and compressive strength results is a confirmation of the retarding effect of WG in the hydration of the Portland cement.

3) The use WG for cement makes it possible to solve some environmental problems well but it may be considered after studying about its long term reactions, shrinkage properties, Alkali-Silica reaction, Porosity and adhesive capacity.

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Cement nomenclature: C = CaO; S = SiO_2; H = H_2O; C_3S = $3CaO.SiO_2$; C_2S = $2CaO.SiO_2$; C_3A = $3CaO.Al_2O_3$; C_4AF = $4CaO.Al_2O_3.Fe_2O_3$; CH = $Ca(OH)_2$

