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Research Article

Long Term Corrosion Experiment of Steel Rebar in Fly Ash-Based Geopolymer Concrete in NaCl Solution

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This research focuses on an experimental investigation to identify the effects of fly ash on the electrochemical process of concrete during the curing time. A rebar was analysed using potentiostat to measure the rest potential, polarization diagram, and corrosion rate. Water-to-cement ratio and amount of fly ash were varied. After being cured for 24 hours at a temperature of 65°C, the samples were immersed in 3.5% of NaCl solution for 365 days for electrochemical measurement. Measurements of the half-cell potential and corrosion current density indicated that the fly ash has significant effects on corrosion behaviour of concrete. Although fly ash tends to create passivity on anodic current, it increases corrosion rate. The corrosion potential of this concrete mixture decreases compared to concrete without fly ash. From the result, it can be summarized that concrete mixture with 70% of OPC (Ordinary Portland Cement) and 30% fly ash has shown the best corrosion resistance.

1. Introduction

In aggressive environments, early degradation of reinforced concrete structures is caused by steel corrosion. In concrete, steel is passive due to alkalinity of concrete which is protective of steel surface. However, effects of carbon, chlorine, and acid conditions can damage the passive film which makes reinforcing steel exposed to the active environments to corrode. Some efforts have been conducted to prevent the corrosion of reinforcing steel by improving the quality of the concrete. Recently, the uses of polymer to improve quality of concrete have attracted and obtained great attention. Combination of concrete with polymer, so-called geopolymer, has advantages such as good tensile strength, light weight, high corrosion resistance, and durability.

Therefore, in recent years, geopolymer concrete has become a potential alternative to replace the conventional Portland cement concrete (OPC) used in the infrastructure construction. In contrast, with OPC, most geopolymer systems rely on the minimally processed natural materials to provide the binding agents. Geopolymer is based on the chemistry of alkali activated inorganic binders. This chemistry is involved in antique binders [1] and has been accidentally rediscovered by Purdon during the contemporary era [2]. In the 1950s, geopolymer was already used as a cement replacement binder [3]. These binders were made with alkali and slag called geopolymer. A binder had been developed which resulted from the hydroxylation and polycondensation reaction of thermally activated kaolin (metakaolin) in an alkaline solution in the 1950s [4]. The strength of geopolymer concrete can be modified to obtain the best properties. However, the researchers are still in the progress of finding the best composition of geopolymer to provide the best protection of the rebar and reduce the corrosion rate which can increase the time for the initial deterioration of concrete.

Some researchers such as Perná and Hanzlíček [5], in 2014, have studied solid product which can be used as building material that has a good thermal insulation material. Rashad [6] (2015) and McLellan et al. (2011) [7, 8] used combination of fly ash and cement to improve mechanical of geopolymer concrete. They concluded that geopolymer concrete has a prospective material which can be used as

Table 1: Mixture proportion of geopolymer concrete.

		Water	Cement	Fly ash	Fine aggregate	Coarse aggregate	
OPC	A	1.09	1.84	0	3.88	5.62	
OPC + 10% FA	B	1.09	1.65	0.19	3.88	5.62	
OPC + 30% FA	C	1.09	1.29	0.55	3.88	5.62	
OPC + 50% FA	D	1.09	0.92	0.92	3.88	5.62	
		NaOH solution	Na_2SiO_3 solution	Fly ash	Fine aggregate	Coarse aggregate	Extra water
Geopolymer concrete	E	0.25	0.54	2.15	3.34	6.22	0.16

an alternative structural material to replace the role of OPC. Upon further investigation, they found that the main chemicals in fly ash contributing improving compressive stress are calcium compounds (CaO and $Ca(OH)_2$). The compressive stress of geopolymer concrete, in their experiments, reached up to 29.2 MPa for 3% CaO and 3% $Ca(OH)_2$ additions.

Most of the studies on geopolymer have shown relationship of fundamental aspects of chemical and binder system on concrete strength, yet the role of concrete in preventing reinforcing steel corrosion has not yet been fully understood. Hence, to improve the corrosion resistance of concrete, environment-friendly concrete which is geopolymer will be introduced. In this study, the corrosion rate tests and corrosion polarization tests of reinforcing steel concrete were tested in 3.5% NaCl concentrations and were investigated. This study was also conducted to describe ability of geopolymer concrete combined with fly ash to protect reinforcing steel bar on corrosion.

2. Methodology

2.1. Concrete Mix Design. The ratios of fly ash to the cement used in the mix design were 0%, 10%, 30%, and 50% noted as A, B, C, and D in Table 1, the same as in [9]. The specimens were air-cured for seven days before removing from the mould. The standard minimum compressive strength of concrete was set to 25 MPa. One kg of 8 M sodium hydroxide (NaOH) solution was prepared by diluting 297 grams of NaOH pellets with 703 grams of water. NaOH solid used was in 99% purity and sodium silicate solutions (Na_2SiO_3, Na_2O = 14.7%, SiO_2 = 29.4%, and water = 55.9% by mass) were used as the alkaline activators [10]. More detail of the concrete mix design was presented in Tables 1 and 2.

The concrete specimens were placed in a shaded area in room temperature. These specimens were protected from the exposure to sunlight and rainfall. The specimens were subjected to immersion in the artificial seawater that contains sodium chloride (NaCl) with 3.5% concentration. The specimens were immersed in the solution for 365 days.

2.2. Corrosion Rate Test. The corrosion rate of the reinforcement steel bar was determined by the linear polarization resistance (LPR). The electrochemical tests were performed on the Ordinary Portland Cement concrete, pozzolan concrete, and fly ash-based geopolymer concrete specimens using potentiostat. LPR measurements are generally used to determine the instantaneous corrosion rate of an electrode.

Table 2: Concrete properties and mix design.

Strength	25 N/mm^2
Aggregate type: coarse	Crashed
Aggregate type: fine	Crashed
Free water-cement ratio	0.59
Slump: 30–60 mm, VB (time)	3–6 second
Max aggregate size	20 mm
Free water content	210 kg/m^3
Cement content (C1)	355 kg/m^3
Concrete density	2400 kg/m^3
Total aggregate content	1834.09 kg/m^3
Fine aggregate content	3514.7 kg/m^3
Coarse aggregate content	1052.10 kg/m^3
Curing time	28 days

The IR drop value in the cover concrete is significant and may vary among the specimens as concrete is a high resistive medium. The IR drop values of the concrete have to be determined and compensated for determining the corrosion current density in mAm^{-2} relative to steel area. The linear polarization resistance is defined as the slope of this curve ($R_p = dE/dI$) at E_{corr}. It can experimentally be obtained in a few millivolts (normally 10 mV) into anodic and cathodic direction and the required current was recorded. The reinforcement bar in the specimens as the working electrode (WE) was polarized to ±20 mV from the equilibrium potential at a scan rate of 0.1 mV per second based on ASTM G-59-97 standard for electro-polarization test.

2.3. Experimental Setup. Three electrodes connected with the potentiostat were working electrode, reference electrode, and counter electrode. The rebar was embedded in the concrete as the working electrode. The saturated calomel electrode used was an electrode made of silver immersed in saturated potassium chloride (KCl) solution. A carbon rod was the counter electrode. Figure 1 shows the rebar for corrosion test. Figure 2 shows the experimental test.

3. Results and Discussion

3.1. Effects of the Curing Time on Corrosion Potential. The results of the calculation are tabulated in Table 1. As shown in this table, corrosion rates are ranged from 0.01 to 0.03 μm/yr.

Table 3: Effects of types of concrete on corrosion rate and corrosion potential.

Types of concrete	Corrosion potential (E_{corr}), V	Corrosion current (I_{corr}), μA/cm^2	Corrosion rate (C_R), μm/yr
A	−0.539	1.2512	0.0154
B	−0.549	1.1258	0.0131
C	−0.574	1.2208	0.0142
D	−0.585	1.0908	0.0126
E	−0.670	1.0728	0.0264

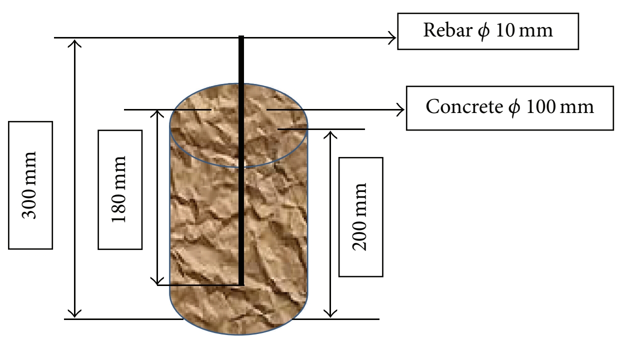

Figure 1: Experiment setup of the corrosion test.

The sample results for all the types of concrete are summarized in Table 3. The table shows the corrosion potential, corrosion current, and lastly corrosion rate. For the corrosion potential (E_{corr}), sample E showed the highest positive value which is 0.670 V and sample A showed more negative value which is 0.539 V. For the corrosion current result, concrete A is the highest with the value 1.2512 μA/cm^2 and concrete E shows the lowest value. The lowest corrosion rate is from concrete D which is 0.0126 μm/yr.

The pozzolan concrete (samples B, C, and D) contains a different percentage of cement and fly ash that has low corrosion rate compared with the Ordinary Portland Cement concrete and geopolymer concrete. With the presence of fly ash, it helps to control the alkali-silica reaction by reducing the permeability to water and the diffusivity to alkali supplied by external sources from the seawater or sodium chloride solution. The pozzolanic reaction, in which calcium hydroxide formed on the hydration of the cement reacts with silica in the supplementary cementing material to form calcium silicate hydrate, fills in the pores and reduces their connectivity.

From Figure 3, the corrosion potential (E_{corr}) for concrete E showed the highest value which is 0.670 V followed by concrete D which is 0.545 V and concrete C which is 0.574. The second lowest value is concrete B which is 0.549 and the lowest E_{corr} is concrete A, 0.539 V. Corrosion potential is defined as the only point in the system where the total rate of oxidation is equal to that of reduction at the intersection. Reference [11] has already mentioned that E_{corr} happened when the rate of hydrogen reduction is equal to the rate of metal dissolution. Due to this reason, the highest value of corrosion potential obtained leads to the result getting better. Corrosion potential and a decrease in the corrosion rate with time are consistent with this time dependence of the anodic reaction.

3.2. Effect of Rebar on Scan Polarization. Figure 4 shows the polarization graph of the different mixtures of concrete after 10 weeks. Based on the figure, the corrosion potential of the decrease is from concrete samples E, D, C, B, and A. Concrete A was fully OPC concrete. Concrete samples B, C, and D were mixed with OPC cement and fly ash. Concrete E was a geopolymer in which the fly ash was mixed with the alkaline solution, NaOH. Concrete B shows the smallest value of absolute current and concrete E is the highest.

All of the concrete samples A, B, C, D, and E showed the presence of the stable passive film formed in the circle. The formation of a passivating oxide film on metal surfaces is an important aspect of corrosion protection [12]. The passage of metal ions through an oxide film takes place very slowly so the current due to metal ions leaving the metal becomes very small when the surface is completely covered with an oxide film. The metal is, thus, protected against corrosion by passivation. Passive layer is able to prevent further dissolution of the underlying metal and, thus, reduces the corrosion rate to insignificantly low levels [13]. This passive film does not actually stop corrosion but reduces the corrosion rate to an insignificant level [14].

3.3. Effects of Concrete on Corrosion Rate. Based on Figure 5, it is shown that an increase in the percentage of fly ash substitute in the concrete to a certain amount will only reduce the corrosion potential of the concrete. From the experiment, concrete C (70% OPC and 30% fly ash) had the lowest corrosion potential. For concrete D (50% OPC and 50% fly ash), the corrosion potential was lower than concrete C. Concrete E (geopolymer concrete) had the highest negativity of corrosion potential although it contained a high amount of fly ash. The reason for this could be that the fly ash contained a high amount of metal oxide. If there is too much metal oxide contamination, the electric conductivity would be high. High conductivity will allow the transfer of metal ions of rebar to the concrete since there was a potential difference. The substitution of fly ash improved the corrosion resistance of concrete. The increase of substitution percentage of fly ash decreases the corrosion potential of the rebar. As fly ash has smaller particle size compared to cement particles, the fly ash particles fill more the pores structure of the concrete than cement particles [14]. Consequently, the porosity of the concrete will be reduced and the chloride ions cannot penetrate the concrete easily.

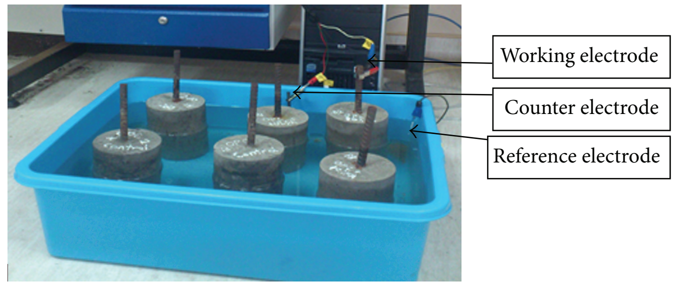

FIGURE 2: Setup of corrosion test.

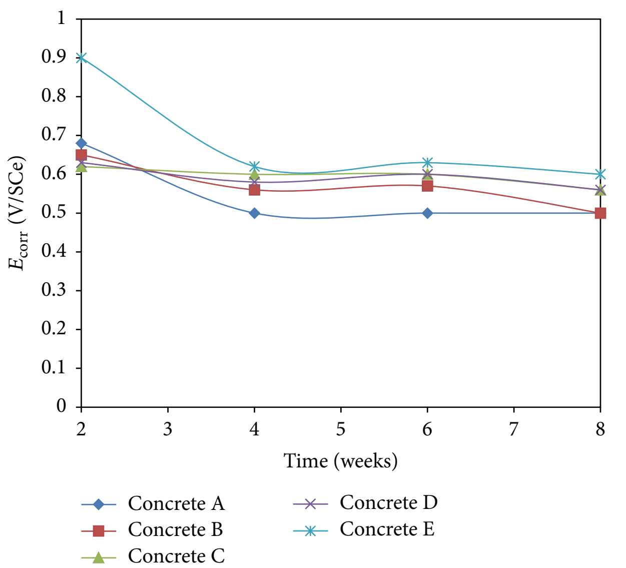

FIGURE 3: Effects of rebar on corrosion potential in 3.5% NaCl solution after immersion for 365 days.

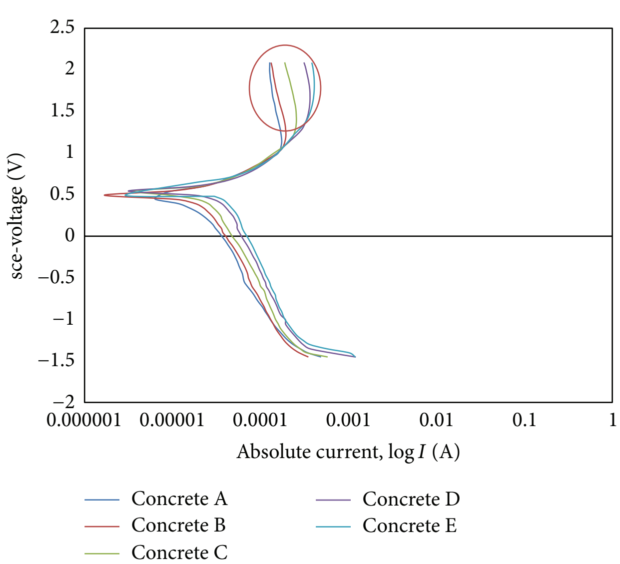

FIGURE 4: Polarization scan of rebar in 3.5% NaCl solution after immersion for 365 days.

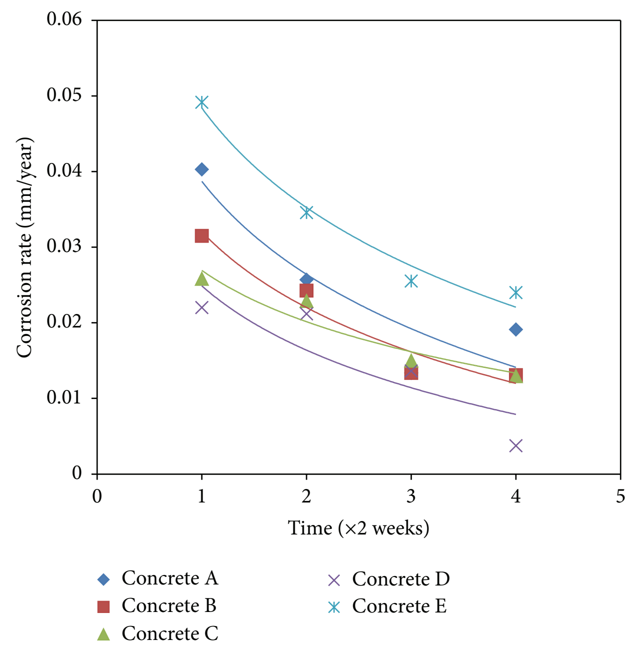

FIGURE 5: Corrosion rate of several types of concrete in 3.5% NaCl solution after immersion for 365 days.

4. Conclusion

From the results, it can be summarized that concrete mixture with 70% of OPC (Ordinary Portland Cement) and 30% fly ash had the best corrosion resistance reinforcing steel bar. It gave the lowest corrosion rate. Scanning polarization showed that geopolymer increased corrosion potential to the magnitude of 50 mV. When fly ash was combined with geopolymer, the concrete indicated decrease of corrosion potential. The formations of passive films on steel surfaces were also found in geopolymer concrete. When the more fly ash concentration is contained in the geopolymer concrete, the tendency for formation of passive films on the rebar is higher. Geopolymers concrete has given positive impacts on anodic polarization on the steel. However, due to low resistivity of fly ash, it caused increase of corrosion rate on the steel. The lowest corrosion rate achieved by this mixture was 6.248×10^{-3} mm/year on the 60th day of immersion test. Meanwhile, the geopolymer concrete had a corrosion rate of 71.312 × 10^{-3} mm/year. The corrosion potential that was shown by geopolymer concrete was −0.905 mV.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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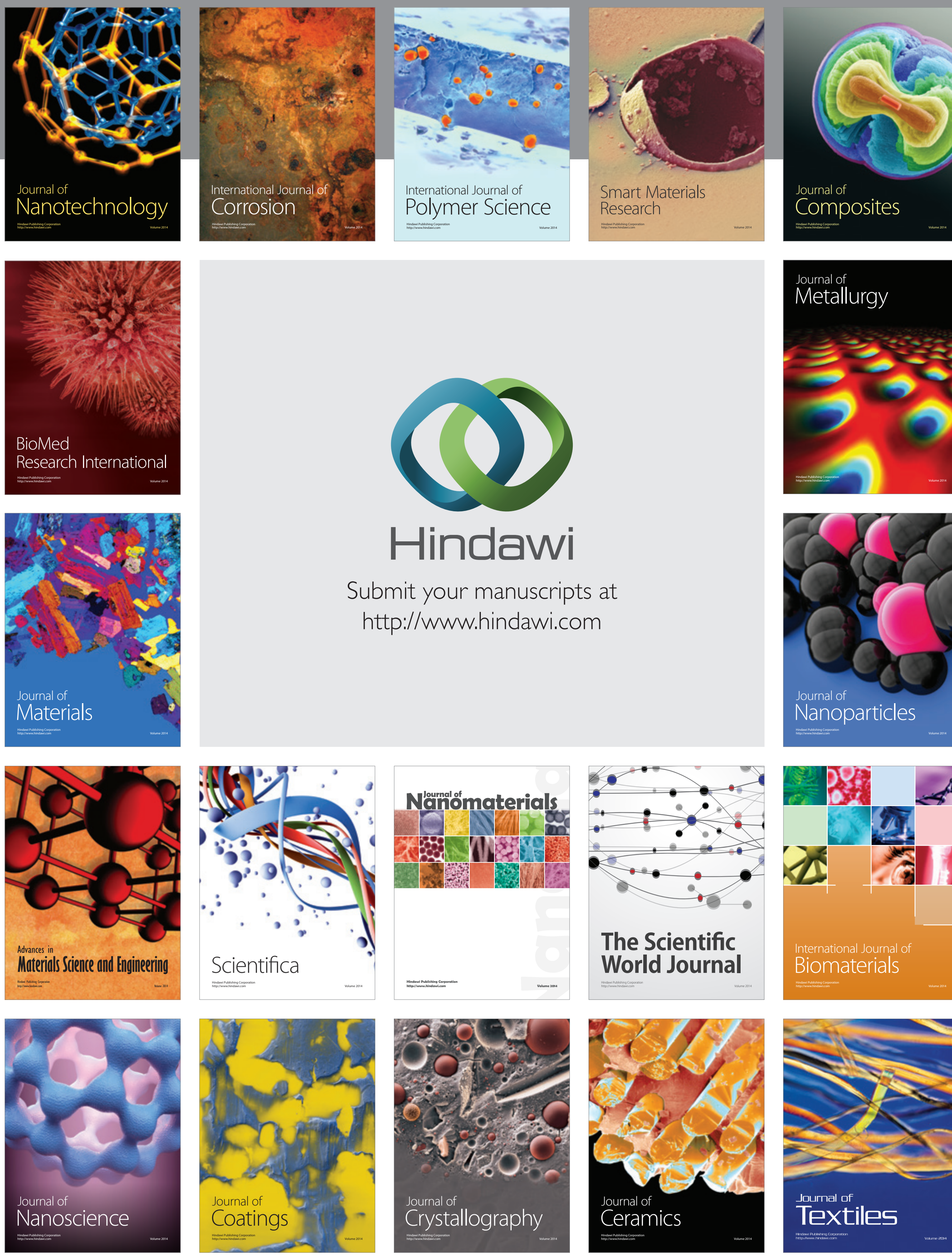
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