

**Research Article**

Investigation on the corrosion resistances of bronze-waste tire-concrete composites

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ABSTRACT

In this study, finely ground CuAl10Ni bronze sawdust and waste tire additives were incorporated into C30 concrete at different amounts and then their corrosion resistances were investigated. SEM/EDX analyses were performed. It was observed that after acids attacks, as the waiting time in the acid solutions increased, electrical surface resistance values increased due to further corrosion. Also, more losses in the weight were observed in the pure concrete than the concretes including bronze sawdust and waste tire grains, then those refractories showed higher corrosion resistances than that of pure concrete.

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1. Introduction

Corrosion is an important parameter for the service life of reinforced concrete structures limited by corrosion deterioration [1]. There have been many academic researches on concrete corrosion. In the study of Congqi Fang et al., it was observed that flat steel bar reinforced concrete, which was kept in 5% NaCl solution for 3 days after curing, was more corroded than the concrete having deformed steel bar. Corrosion degree increased with increasing corrosion time, and also the concretes coated with polyethylene material were less corroded [2]. Similarly, concretes with coated steel reinforcement were less corroded. In addition, it was stated that the degree of corrosion had a significant effect on the bond that decreased with increasing corrosion degree according to Cabrera's study [3]. Guerrero et al. produced the geopolymeric concrete product coated with metakaolin and fly ash for 3, 7 and 28 days. As a result of this study, metakaolin coated concrete had a higher compressive strength and gel polymeric coating exhibited better adhesion than that of hybrid polymer coating. It was concluded that geopolymer material (as a protective coating) showed a much better chlorine permeability resistance than that of uncoated concrete material [4].

Corrosion of reinforcement is the predominant factor causing deterioration of concrete construction, especially located in the marine environment. Chloride ions and carbon dioxide penetrations are the most important causes of corrosion initiation of reinforcing steel. After initiation of the corrosion process, the corrosion products are usually deposited in the concrete around the steel. Then expansive stresses formation occurs cracking the concrete cover [5, 6].

In the study of Thomas et al., the chloride penetrations of concretes in which crumb rubber was replaced up to 7.5% of fine aggregates were lesser than or equal with the value of their control concrete. Also, more losses in the weight and compressive strength were observed in their control concrete than the rubberized concrete after acid attack [7].

In the present study of Oikonomou et al., physical and mechanical properties of cement mortars modified with worn tires from automobiles have been investigated. The reduction in chloride ion penetration in cement mortars and in concrete reduces the potential for corrosion of embedded reinforcement [8].

The aim of this study is to investigate for the use of bronze sawdust and waste tire additives in order to improve corrosion resistances of C30 concrete materials.

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2. Materials and Methods

New concrete materials with different compositions were produced by using bronze waste and fine rubber waste: i) 2.5 wt.% bronze waste and 2.5 wt.% waste tire (2.5%B+2.5%T); and ii) 5 wt.% bronze and 5 wt.% waste tire were added to C30 concrete (5%B+5%T). Ready-mixed dry mortar of C30 concrete was used. After the produced samples were removed from the mold, were kept in water for 28 days for curing.

Corrosion tests were performed according to ASTM C-1152. Three different acid solutions with pH 1.5-2 were prepared by using HCl, H₂SO₄ and HNO₃ acids. Samples from each composition were stored in three different acid solutions for 7 and 28 days. After 7 days, the samples were removed and their electrical resistances were measured. Then the samples were dried and weighed. Same procedures were applied for the samples which were held for 28 days. After corrosion test had completed, microstructure investigations were performed by scanning electron microscopy (SEM) at 1000x magnification with backscattered electron images.

3. Results and Discussion

3.1 Corrosion Test Results

According to corrosion tests results with 3 different acids, for all concrete samples either with or without additives, it has been found that 3 acid types had approximately the same effect weight loss in concretes.

Dissolution and weight losses occurred in pure concrete samples after corrosion tests. In the concrete samples where bronze and tire were used together, it was found that the weight losses were not significant for the corrosion tests performed within 3 acids, also close to the pre-corrosion values and even increased slightly. It was considered that these concrete materials had higher corrosion resistances compared to pure concrete (Table 1).

Similar results of our study were achieved in the study of Blessen Skariah Thomas et al. After acid attack, more losses in the weight were observed in their control mix concrete than the rubberized concrete [7].

As a result of corrosion tests performed with 3 different acids, it was seen that the electrical surface resistance values of all concrete samples increased (Table 2). Ceramics are non-conductive materials and show electrical surface resistance. Metal reinforcements are materials which are electrically conductive but begin to show resistance after corrosion. Then, structural defects caused by corrosion effect in pure concrete (ceramic matrix) and rusting of metallic reinforcement (bronze) in the doped concrete materials caused the increase of electrical surface resistances. Similar to our results, Yung et al. found that the electrical resistance increased as more waste tire rubber powder was added [9].

The increase in resistance means that the metal reinforcement is corroded. According to the resistance results, similar to the weight losses, 3 strong acids have approximately the same corrosion effect. As the waiting time in the acid solutions increased, electrical surface resistance values increased due to further corrosion.

which contained porosity, microcracks and also deep cracks.

According to the elemental analysis, the distributions of Cu, Al, Ni elements were in the same regions and it was seen that the grains were bronze.

According to the microstructure and elemental analysis of the concrete sample containing 2.5% bronze and 2.5% waste tire, which were tested for corrosion in HCl solution for 28 days (Figure 2), the oxygen distribution was in the region where the bronze grains were found. Then, it was thought that bronze grains were oxidized, new phase formation occurred. Waste tire grains could also absorb some acid solutions. These situations were thought to be effective in weight gain (Table 1).

Table 1. Dry weights of samples that were stored in acid solutions with pH 2 for 7 and 28 days

Acid Solution Type	Material	Dry weights before corrosion test (g)	Dry weights after corrosion test for 7 days (g)	Weight change after corrosion test for 7 days (%)	Dry weights after corrosion test for 28 days (g)	Weight change after corrosion test for 28 days (%)
HCl solution	Pure	302.63	291.56	-3.65793	291.83	-3.56871
	2.5%B+2.5%T	298.42	299.64	0.509349	299.97	0.284833
	5%B+5%T	287.97	288.73	0.263916	289.16	0.239608
H ₂ SO ₄ solution	Pure	304.01	292.95	-3.63804	293.75	-3.37489
	2.5%B+2.5%T	292.32	293.65	0.454981	293.98	0.465244
	5%B+5%T	283.20	283.65	0.158898	283.99	0.173023
HNO ₃ solution	Pure	301.24	291.06	-3.37937	292.82	-2.79511
	2.5%B+2.5%T	293.17	294.81	0.24218	294.86	0.235358
	5%B+5%T	277.80	278.70	-0.036	278.87	0.025198

Table 2. Electrical surface resistances of samples kept in pure water and acid solutions

Sample	After soaking in pure water (kΩcm)	After corrosion test for 7 days (kΩcm)			After corrosion test for 28 days (kΩcm)		
		HCl	H ₂ SO ₄	HNO ₃	HCl	H ₂ SO ₄	HNO ₃
Pure	51.5	140	135.5	126	346	265	160
2.5%B+2.5%T	128	160	174	183	172	196	190
5%B+5%T	175	214	212	201	230	228	215

Similarly, since the Cl ions were in the regions where both the concrete matrix and the Cu element were present, it was thought that the concrete matrix and the bronze reinforcement were affected by the HCl acid solution and that the corrosion type known as bronze cancer occurred (Figure 3).

3.2 SEM Analysis of Concretes Before and After Corrosion Tests

Before corrosion test, according to SEM images of 2.5%B+2.5%T concrete (Figure 1), it was observed that there was no strong bonding between the concrete matrix, bronze and waste tire interfaces in the concrete structure

According to study of Dermaj et al., similar to our results given as above, bronzes are subjected to corrosion, which results in the formation of an oxide or salt layer (Cl in our study) on its surface. The corrosion products formed on bronze surface acquire the barrier property preventing a complete destruction of the object [10].

When EDX analysis (Table 3) were examined, it was

seen that before corrosion test, besides the Ca, Si, Al elements, which are mainly in the cement phase, Cu, Al, Ni elements forming the bronze material increased and the percentage of C increased with increasing the amount of waste tire.

After corrosion tests, the decrease in Ca and Si amounts indicated the dissolution of the concrete matrix. According to results of corrosion test in HCl solution, the amount of Cu decreased slightly from the pre-corrosion value suggested that the oxidation could be passive oxidation (protective oxide layer on the surface). The fact that the resistance values did not increase too much confirmed this situation.

According to the EDX analysis of corrosion test, where H₂SO₄ solution was used, as the amount of Cu did not decrease, passive oxidation could be the same as in HCl solution.

Also, it was seen that the amount of C and O increased. It was thought that tire reinforcements were not affected by acid unlike the concrete matrix.

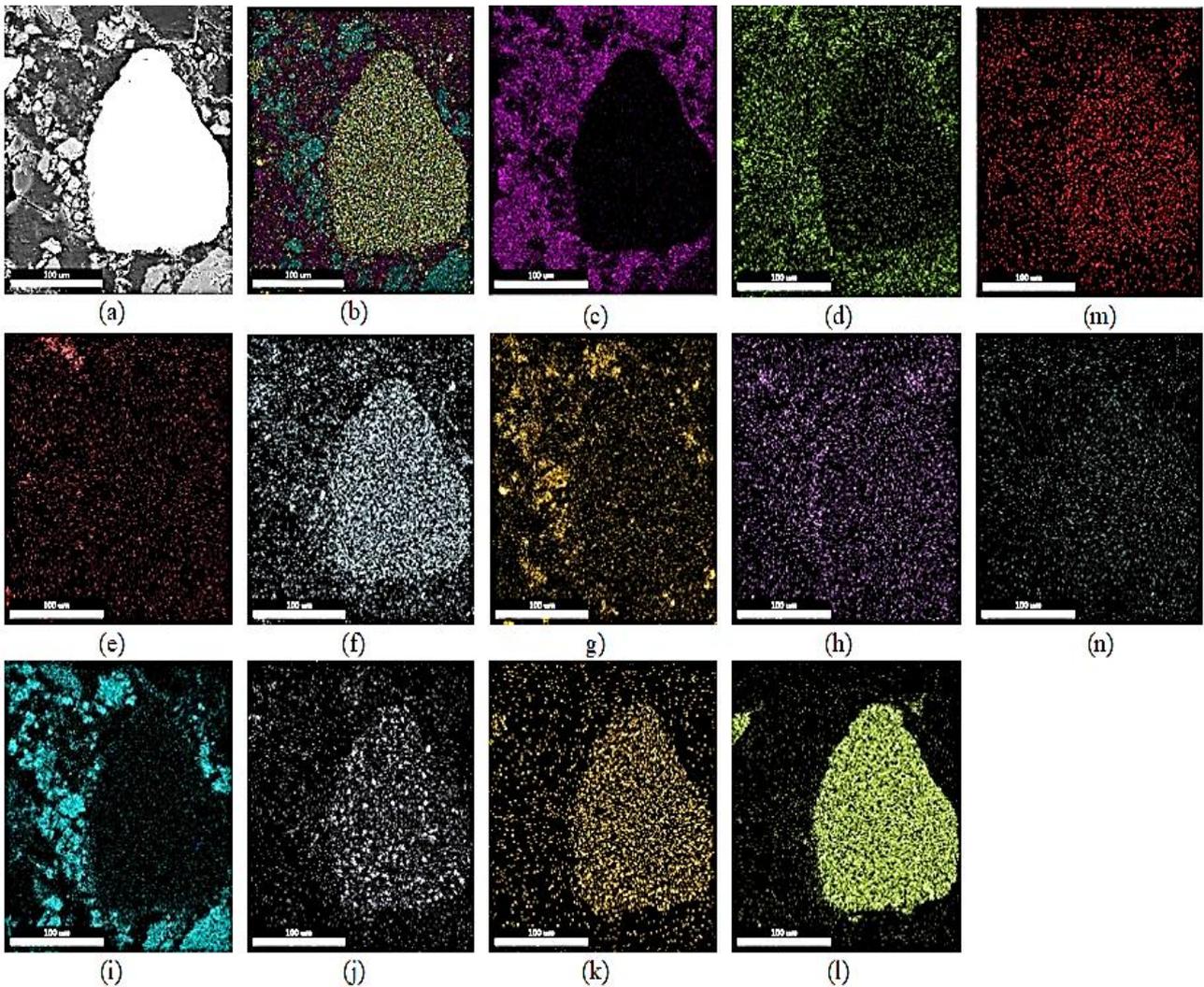


Figure 1. Before corrosion test in HCl solution, a) Microstructure, b) Colored microstructure of 2.5%B+2.5%T concrete and distribution of elements: c) C, d) O, e) Na, f) Mg, g) Al, h) Si, i) S, j) K, k) Ca, l) Fe, m) Ni, n) Cu (1000X-SEM backscattered electron image).

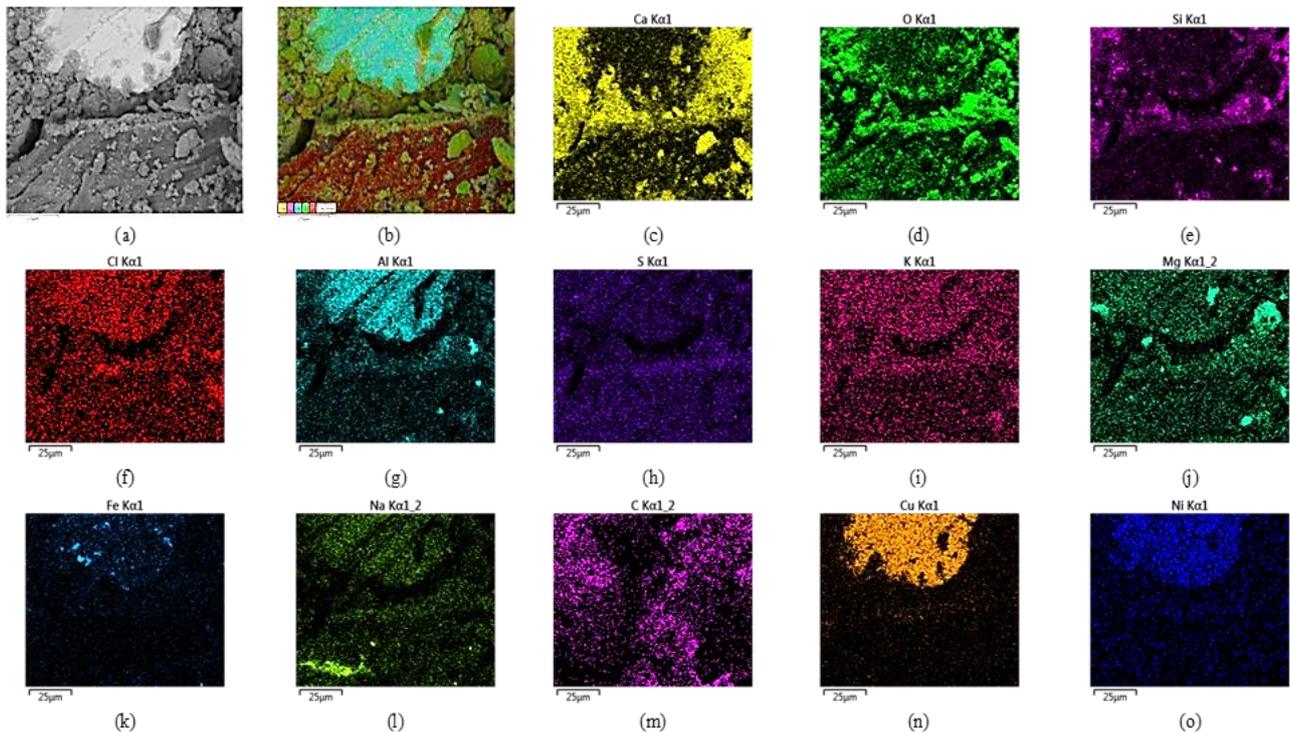


Figure 2. After corrosion test in HCl solution, a) Microstructure, b) Colored microstructure of 2.5%B+2.5%T concrete and distribution of elements: c) Ca, d) O, e) Si, f) Cl, g) Al, h) S, i) K, j) Mg, k) Fe, l) Na, m) C, n) Cu, o) Ni (1000X-SEM back scattered electron image).

Table 3. EDX analysis after corrosion tests of bronze and tire doped concrete samples

Elements (%)	2.5%B+2.5%T		
	Before corrosion test	After corrosion test in HCl solution	After corrosion test in H ₂ SO ₄ solution
C	7	54.32	33.75
O	8	27.51	28.18
Na	1	0.42	0.18
Mg	2	0.58	0.60
Al	6	1.34	1.80
Si	12	1.12	3.55
S	4	0.00	0.00
K	2	0.18	0.30
Ca	46	6.64	17.00
Fe	3	0.59	2.18
Ni	1	0.45	1.11
Cu	8	6.78	11.34
Cl	0	0.07	0

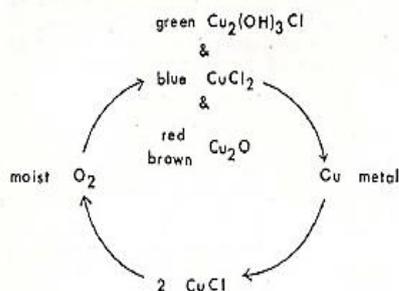
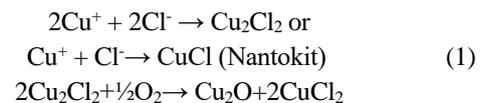
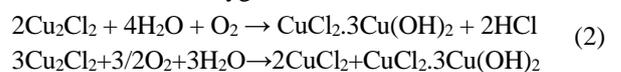


Figure 3. Schematic depiction of the cyclic nature of bronze cancer.

In the process of bronze cancer (Figure 3), free chlorine ions in the environment reacts with ionizing copper ions such as below:



Under humid and oxygenated environment:



A portion of the copper chloride reacts with the additional copper in the alloy to form more copper chloride:

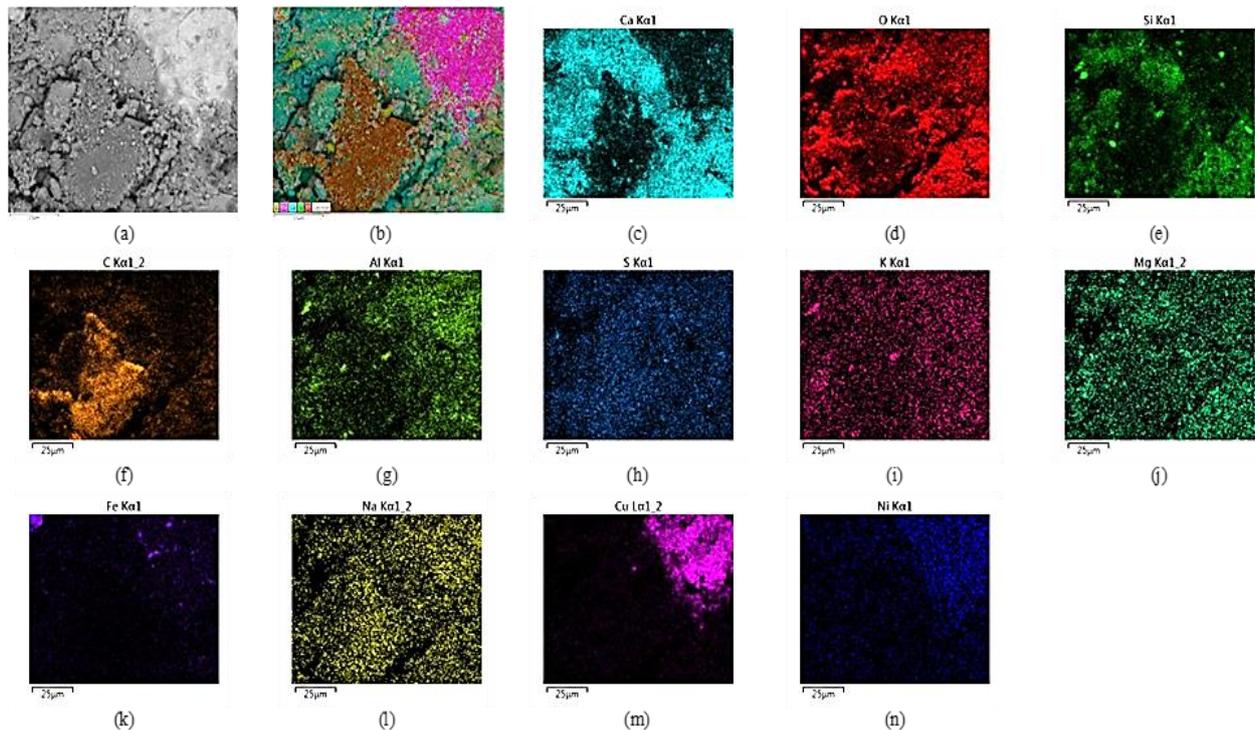


Figure 4. After corrosion test in H_2SO_4 solution, a) Microstructure, b) Colored microstructure of 2.5%B+2.5%T concrete and distribution of elements: c) Ca, d) O, e) Si, f) C, g) Al, h) S, i) K, j) Mg, k) Fe, l) Na, m) Cu, n) Ni (1000X-SEM back scattered electron image).



The reaction sequence of the bronze disease process occurs repeatedly until all the copper and copper compounds in the alloy turn into waste [11].

When the SEM results of the concrete containing 2.5% bronze and 2.5% waste tire were tested for corrosion in H_2SO_4 solution (Figure 4), it was thought that bronze was oxidized due to the coincidence of the distribution regions of oxygen and Cu. However, the amount of Cu did not decrease, then passive oxidation could be on the surface of bronze grains.

4. Conclusions

After the corrosion tests carried out in different acid solutions of the concrete sample containing 2.5% bronze and 2.5% waste tire, it was seen that the amount of Ca and Si decreased considerably, and the amount of O increased. Also, Cu did not decrease much more than the pre-corrosion value. Electrical surface resistance values did not increase too much. Then it was thought that while the concrete matrix was affected by acid solutions, the rubber components were not affected. The corrosion called bronze cancer occurred on bronze grain surfaces at low levels. Those results showed that there was a lower level of corrosion in the concrete sample containing 2.5% bronze and 2.5% waste tire compared to pure concrete.

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Nomenclature

B : Bronze
 T : Waste tire

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