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Utilization of Electrolytic Manganese Dioxide (E.M.D.) waste in concrete exposed to salt crystallization

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HIGHLIGHTS

- Durable composite concretes with EMDW addition may be produced.
- EMDW induces a positive effect on the pitting corrosion of reinforcement steel.
- 5% w/w EMDW addition slightly improves the elastic modulus of concrete in NaCl.
- Composite EMDW concretes exhibit lower porosity values than OPC concrete.
- The sorptivity of EMDW concrete is lower than that of OPC concrete at late ages.

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ABSTRACT

In the present study, the physico-mechanical properties and corrosion resistance of reinforced concrete containing Electrolytic Manganese Dioxide (E.M.D.) waste were investigated. Concrete samples prepared in the lab with and without the use of EMD waste were exposed to sulfate and chloride salt solutions. In particular, the test samples were placed in 5% w/w Na_2SO_4 solution, while chloride penetration resistance was studied in 3.5% w/w NaCl solution. The concrete mixtures were prepared with 0%, 5% and 10% w/w replacement of Ordinary Portland Cement (OPC) with the aforementioned waste additive. For testing, specimens of varying shapes and dimensions were cast; cylindrical reinforced cement mortar specimens were also prepared. Tests for estimating the physico-mechanical properties (compressive strength, modulus of elasticity, porosity and sorptivity), mass loss of steel and thermal response of concrete (DTA/TG) were performed; the carbonation depth of mortars exposed to atmospheric conditions was also estimated. The experimental results generally suggest that the EMD waste additive does not affect negatively the properties of concrete partially immersed in chloride salt solution; in addition, the anticorrosive effect of EMD waste on steel rebars embedded in cement mortars was also observed. On the other hand, the composite concretes immersed in sulfate salt solution exhibited inferior values for all measured properties.

1. Introduction

The chemical reaction between Portland cement and water, which is widely known as cement hydration, plays a decisive role in the performance and durability of hardened concrete [1,2]. The use of additives as cement replacement, which is currently gaining popularity in an effort to reduce the carbon footprint of concrete production, affects the aforementioned chemical reaction. At the same time, the chemical composition of concrete constituents and the presence of heavy, toxic or trace chemical elements within the waste additives may cause deterioration to the end-product and contamination of the immediate surroundings [3].

Traditional additives used in cement manufacturing, such as fly ash, natural pozzolans, slags, silica fume etc., generally improve the physico-mechanical performance of concrete, but may consist of heavy metals or harmful elements [4–6]. The leaching of these metals from concrete elements [7] contaminates the underground water and soil.

Besides the traditional concrete additives, other industrial hazardous materials are also utilized in concrete design. A generally unknown material used in concrete production is the gamma Electrolytic Manganese Dioxide (γ-MnO_2). The aforementioned

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material, known commercially as EMD, is a black/dark brown fine powder used in the manufacturing of batteries. The raw material used for EMD production is the mineral pyrolusite (MnO_2). The latter is initially washed with sulfuric acid (H_2SO_4) to form manganese sulfate ($MnSO_4$); Electrolytic Manganese Dioxide is produced from the electrolysis of the bath of manganese sulfate and sulfuric acid. During this electrolysis, the Electrolytic Manganese Dioxide deposits on a titanium or carbon anode [8,9]; the γ-MnO_2 polymorphic type is removed from the anode, crushed, washed and rotary dried. Its outstanding electrochemical properties, low impurities and high specific surface contribute to the design of high performance alkaline batteries and dry cells [10].

EMD manufacturing produces significant amounts of environmentally unfriendly solid waste, the burning or disposal of which in landfills is complicated and costly. The aforementioned waste contains considerable amounts of raw jarosite, small amounts of gypsum and a variety of heavy metals (Table 1). Jarosite is a hydrous sulfate of potassium and iron and its formula is $KFe_3^{3+}[OH]_6[SO_4]_2$; it has a triangular crystal structure, it is classified in the alunite ($KAl_3[SO_4]_2[OH]_6$) group and it commonly occurs with limonite ($FeO[OH]{\cdot}nH_2O$) or goethite ($FeO[OH]$), known in mineralogy as mineral paragenesis. Jarosite is a secondary mineral, forming under weathering conditions; it is considered a hazardous waste and its toxicity is attributed to the presence of heavy metals, such as Co, Cu, Ni, Zn and As. Raw jarosite also contains approximately 50% iron and its utilization for producing construction materials has been patented by Mymrin and Vazquez Vaamonde [11]. In Europe the amount of Mn – Fe solid wastes is estimated to be around 55,000 tons per annum. Greece (TOSOH HELLAS A.I.C.) is the main producer of Electrolytic Manganese Dioxide, with more than 25,000 tons produced per year. Other European electrolytic MnO_2 producers are Spain, with 6,000 tons produced per year, and Ireland with 15,000 tons per year [12].

The influence of Electrolytic Manganese Dioxide waste (EMDW) addition in the performance of reinforced concrete exposed to sulfate ions has not been studied extensively to-date; previous experimental research [13] has proved the increased mechanical strength of EMDW concrete under water-cured conditions, and the reduction of its porosity in sodium chloride (NaCl) solution. Mehra et al. [14] indicated that, using jarosite as partial replacement of sand in concrete production improves the strength of the composite material; in addition, the same researchers observed a reduction in the amount of heavy metals in the jarosite concrete compared to raw jarosite. The findings of Mymrin et al. [15] and Mehra et al. [16] also confirm the high compressive strength and water resistance of jarosite concrete and its potential use as an engineering material. The aforementioned researchers proved that jarosite concrete strength increases during the hydration process. The solid particles of jarosite are initially dissolved, following the growth of amorphous gel compounds, before being transformed to a stone-like condition; thus, a reduction in concrete porosity results in the increase of its compressive strength. In previous research [17], it has also been mentioned that, if the additive consists of high amounts of iron, chloride ingress is reduced, whilst the strength of concrete is improved; this may be attributed to the filling of pores with iron carbonates (siderite, ankerite). Katsioti et el. [18] and Tsakiridis et al. [19] also showed that the jarosite-alunite residue can be utilized as a raw material in concrete production, improving the strength of the hardened composite, without affecting its setting time and expansion.

The present research investigates the physical and mechanical properties of concrete containing Electrochemical Manganese Dioxide waste (EMDW) as partial replacement to cement, and looks into the possibility of using the end-product as a construction material. The anticorrosive effect of EMDW on reinforcing steel is also studied in this paper. Prior to testing, all the specimens were partially immersed in sodium chloride (NaCl) and sodium sulfate (Na_2SO_4) solutions, while the carbonation depth of cement mortars produced with EMDW was also estimated following their exposure to the atmosphere.

2. Experimental program

2.1. Raw materials

Cement I 42.5 N, water from the Nicosia supply network and crushed coarse/fine limestone aggregates were used for the preparation of the test specimens. Table 2 presents the physico-mechanical properties, chemical composition and mineralogy of cement; the chemical compounds of cement were calculated using Bogue's equations [20]. The Electrolytic Manganese Dioxide waste (EMDW) replaced the cement by 5% w/w and 10% w/w during the production of the test specimens. The aforementioned additive consists of large amounts of calcium, iron and sodium, while according to the XRD analysis (Fig. 1), it contains jarosite, gypsum and small amounts of alunite. Aluminum (ca. 5%), silicon oxide (ca. 5%) and manganese (ca. 13%) are also present in EMDW [12]. The chemical composition of EMDW also includes significant amounts of heavy metals (Table 1), the values of which generally exceed the permissible limits set by the United States Environmental Protection Agency (US EPA), the European Union (EU) and the World Health Organization (WHO) for drinking water. Nevertheless, a number of studies (e.g. [21]) confirm the insignificant leaching of heavy metals from cement-based composites containing waste materials, due to the high alkalinity of the composites. In particular, the high *pH* values of the pore solution within concrete is responsible for the stabilization of hazardous metals; as a result, the latter are not released to the environment [22–24]. Shirazi and Marandi [25] evaluated the concentrations of leached metals for concrete containing municipal wastewater sludge in different proportions (0, 25, 50, 75 and 100 w/w replacing of sludge with water). The authors reported that water leaching out of the aforementioned concrete contained only small amounts of hazardous metals (lower than the limits determined in EPA standards). They commented that the main reasons for that might had been the gradual and slow diluting process of the heavy metals and the immobilization effect of cement on the latter. This provides strong evidence that the use of EMDW in concrete may not be harmful to the environment in the long term, despite the presence of significant amounts of heavy metals in its chemical composition.

The addition of EMDW in concrete possibly induces a latent pozollanic effect to cement hydration products, while its high fineness (430 m^2/kg) compared to that of cement (400 m^2/kg) leads to decreased permeability [26]. In general, ultrafine

Table 1
Concentrations of heavy metals/trace elements in EMD/EMDW and permissible limits in drinking water set by various international organizations. All values are given in ppm. (1:1.000.000) except for the sulfate SO_4^{2-} ions (%).

Electrolytic Manganese Dioxide waste (EMDW)							
Cobalt	Nikelium	Zinc	Copper	Lead	Chromium	Arsenic	Cadmium
2200	1200	1200	820	70	52	41	14
Electrolytic Manganese Dioxide (E.M.D.) raw material							
Iron	Calcium	Copper	Lead	Potassium	Sodium	Magnesium	SO_4^{2-} [%]
40	300	5	5	50	2500	50	1.66

Permissible limits of heavy metals in drinking water set by different international organizations							
	Nikelium	Zinc	Copper	Lead	Chromium	Arsenic	Cadmium
US EPA, 2008	<100	<5000	<1300	<15	<100	<10	<5
EU, 1998	<20	–	<2000	<10	<50	<10	<5
WHO, 2008	<70	–	<2000	<10	<50	<10	<3