REDUCTION OF DISSOLVED OXYGEN IN MINIMIZING CORROSION

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Abstract.

Concrete structures are susceptible to corrosion especially when exposed to marine environment. In order to minimize the corrosion in reinforced concrete, reduction of dissolved Oxygen (DO) in mixing water is recommended. The DO is the measurement of the amount of free Oxygen that is dissolved in water which is proportional to the corrosion rate of steel bars inside concrete. In this paper, the use of industrial waste/by-products, agricultural waste, natural minerals, and green inhibitors as additive for cement in reducing the DO level of the mixing water was explored. Candidate materials from different types of agricultural waste, industrial waste, natural minerals, and green inhibitors. The percentage difference of DO were computed for all types of materials as ash or powder or extract in room temperature. This is the percentage difference of DO level in distilled water and the solution mixed with the candidate material having a mass ratio of 3: 2 and/or 3: 1. Results showed that more than 90% reduction of DO level were achieved when mixed with ginger extract, ginger powder, aloe vera extract, ginger pulp, and rice hull ash. Future experimental studies using the candidate materials producing reinforced concrete specimens with high reduction of DO level in mixing water is recommended.

KEYWORDS: Corrosion, dissolved oxygen, waste.

1. INTRODUCTION

Concrete is considered as most extensively used construction material globally and each component has contributed to an environmental impact [1]. It is made up of aggregates (coarse and fine) and paste (cement and water). Concrete industry is one of the largest consumers of natural resources, therefore attaining reliable, vigorous, sustainable and economical concrete products has been proposed. Cost of concrete products has increased over the years resulting to increase in the shortage of aggregates and worsens situation. Use of industrial and agricultural byproducts have gained interests as a potential replacement to concrete manufacturing process [2] since they are rich in silica as well as alumina which are suited as supplementary cementitious material and superior reactivity [3]. Through the years, there is scarcity of natural resources. To address such issues, substitution to concretes components could be an answer to environmental impacts, however, substitute materials should impart comparable or enhanced attributes compared to the natural concrete [2].

Several factors affect the durability of reinforced concrete structures such as change in temperature that could lead to cracks due to shrinkage, amount of moisture that could permeate concrete, physical factors (strength, resistance to wear and tear, and

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abrasion), chemical factors like aggressive agents that could interfere with the cement paste and biological factors (organisms) that could damage concrete. One way of achieving durable concrete is to study corrosion which can be defined as "destruction of metal by either chemical, electrochemical or electrolytic reaction within its environment" according to American Concrete Institute. It is a global problem that deteriorates the durability of concrete structures [5]. Also, corrosion of steel in concrete is one of the main reasons for premature failure where in marine environment, chloride ingress is the probable cause for breaking the passivating layer and the onset of extreme corrosion [6]. Most marine structures are susceptible to corrosion as it is located near marine environment and may trigger chloride intrusion [7]. Nowadays, it is necessary to inspect and alleviate corrosion to extend serviceability of RC structures and is accepted worldwide [4]. Three parameters that greatly affect corrosion of reinforcing bars in concrete are shown in Figure 1. These are Oxygen, pH level, and the permeability of concrete. In this research, reduction of Oxygen through dissolved Oxygen (DO) level in mixing water is the main focus to prevent corrosion inside concrete.

Additives such as industrial waste/by-products, agricultural waste, natural minerals, and green in-



FIGURE 1. Graph showing relationship of Embodied Carbon for cements by clinker content, source [4]

hibitors are considered as candidate materials in reducing the DO level of mixing water that could affect concretes resistivity to corrosion. The selection of these materials is based on the result of related studies utilizing them as replacement to cement or aggregate that enhances concrete's durability. Industrial wastes are known to have high pH level which is being measured under varying temperatures to enhance its reactivity [8]. Since these wastes no longer have industrial application, converting them to construction materials could improve its properties. In addition, agricultural waste is also found to contain minerals that could improve various properties of concrete. Natural minerals as admixture could enhance resistance of concrete to chloride penetration [9]. Plant extracts are also considered as these were proven to be good corrosion inhibitors [10]. Shown in Table 1 is the process of accumulation of the candidate materials from previous researchers.

Numerous literatures are available considering corrosion in reinforced concrete structures. However, researches associated with Oxygen - reducing materials haven't been thoroughly studied. Using keyword searches "Oxygen", "permeability", "concrete" and "corrosion" resulted to 34 published journals. It is evident that researches concerning on the effects of DO in concrete corrosion has an average of only two publications per year and in which approximately one publication per year under Cement and Concrete Research. This study introduces the use of waste materials, plants and natural minerals to contribute significantly in the performance of reinforced concrete, particularly, in the reduction of Oxygen that can inhibit corrosion on the steel bars.

2. Apparatus and materials

2.1. DISSOLVED OXYGEN METER

Sufficient amount of free Oxygen at the initial curing stage is critical in the formation of the passive layer protecting the reinforcing steel bars [26]. There is a relevant connection when aggregates in concrete have open porosity as it could increase the permeability of Oxygen [27]. Corrosion rate of steel is higher on areas with high Oxygen contents. Measuring the Oxygen level of water at a certain location can be used to foresee the performance of different alloys in the same environment [28]. Oxygen permeability in reinforced concrete is high using deformed bars which makes it more susceptible to corrosion than plain bars since cracks begin at the ribs of the rebars and eventually becomes surface cracks [29]. DO is the measure of the amount of free Oxygen that is dissolved in water. Factors such as atmospheric pressure, temperature and salinity determine the amount of Oxygen that can be dissolved physically in water. Rate of corrosion process on the reinforcing steel bars in concrete can be controlled by DO on pore solution, thus, reduced DO could enhance corrosion resistance [30].

2.2. CANDIDATE MATERIALS

Materials were chosen based on its effect on the performance of concrete. Related studies as presented in Table 1, utilized the use of these candidate materials as an additive or replacement to either cement and aggregates. Table 2 to 4 summarize the candidate

Corrosion inhibitors				
	Candidate materials		Process of Accumulation	Source
		Blast Furnace Slag	Acquired from industry as it is a by-product of steel manufacturing	[11]
Wastes	Industrial waste	Bottom Ash	Acquired from industry as it is a by-product of coal power plants	[12]
		Fly Ash	Acquired from industry as it is a by-product of coal power plants	[13]
		Granite / Marble Dust Waste Glass Powder Wood Waste Ash	Acquired from industry producing marble / granite as tiles	[14]
			Crushing, Sieving using Ball Mill	[15]
			Incineration, Combustion	[16, 17]
		Coconut Husk Ash	Burning under controlled temperature or incineration, pyrolysis	[18]
	Agri- cultural	Rice Husk Ash	Burning under controlled temperature or incineration, through annealing furnace	[19]
	waste	Corn Cob Ash	Burning under controlled temperature	[20]
		Sugarcane Bagasse Ash	Burning under controlled temperature or incineration, combustion, acquired from sugar mill	[13, 17]
		Seashell	Cleaning, Drying, Crushing / Pulverizing, Furnace	[21]
Nε	atural	Volcanic Ash	Readily available on areas near volcanoes	[22]
minerals		Natural Zeolite	Mining Fotos stiene Dravin a Cain dia a	[23]
Р	Plant	Mater Hyacinth	Extraction, Drying, Grinding	[24] [10]
ex	tracts	Ginger	Extraction, Drying	[25]

TABLE 1. Process of accumulation adapted from previous researches.

Agricultural wastes					
Craciman	Ash		Powder		
Specimen	3:2	3:1	3:2	3:1	
Bagasse ash					
Bagasse ash	AW-BA-2	AW-BA-1			
	C	oconut husk ash			
Coconut husk ash	AW-CHA-2	AW-CHA-1			
Corn cob ash					
Corn cob ash	AW-CCA-2	AW-CCA-1			
		Rice hull ash			
Rice hull ash	AW-RHA-2	AW-RHA-1			
		C1 11-			
Oyster snen	AW-55-A-U5-2	AW-55-A-05-1	AW-55-P-05-2	AW - 55 - P - 05 - 1	
Yellow cockles	AW-55-A-YC-2	AW-SS-A-YC-1	AW-55-P-YC-2	AW-55-P-YC-1	
Strombus sicad	AW-SS-A-SC-2	AW-SS-A-SC-1	AW-SS-P-SC-2	AW-SS-P-SC-1	
Brown scallop	AW-SS-A-BS-2	AW-SS-A-BS-1	AW-SS-P-BS-2	AW-SS-P-BS-1	
Clamrose big	AW-SS-A-CB-2	AW-SS-A-CB-1	AW-SS-P-CB-2	AW-SS-P-CB-1	
Granular ark	AW-SS-A-GA-2	AW-SS-A-GA-1	AW-SS-P-GA-2	AW-SS-P-GA-1	
Distant scallop	AW-SS-A-DS-2	AW-SS-A-DS-1	AW-SS-P-DS-2	AW-SS-P-DS-1	
Green mussel	AW-SS-A-GM-2	AW-SS-A-GM-1	AW-SS-P-GM-2	AW-SS-P-GM-1	

TABLE 2. Agricultural wastes as candidate materials in reducing DO level.

Industrial wastes					
Specimen	Ash		Powder		
specimen	3:2	3:1	3:2	3:1	
Blast furnace slag					
Blast furnace slag	IW-BFS-2	IW-BFAS-1			
	Bottom ash				
Bottom ash	IW-BA-2	IW-BA-1			
Fly ash					
Fly ash	IW-FA-2	IW-FA-1			
Marble / Granite waste dust					
Marble / Granite waste dust			IW-WWA-2	IW-WWA-1	

	Natural mineral		Dowdon		
Specimen	ASH		Powder		
opeemien	3:2	3:1	3:2	3:1	
Volcanic pumice					
Volcanic pumice		-	NM-VP-2	NM-VP-1	
	Natura	l zeolite			
NATURAL ZEOLITE			NM-NZ-2	NM-NZ-1	
Natural mineral					
Plants					
a :	Extract		Powder		
Specimen	3:2	3:1	3:2	3:1	
	Aloe	vera			
Aloe vera	P-AV-2	P-AV-1			
Ginger					
Ginger extract 1	P-GE1-2	P-GE1-1			
Ginger extract 2	P-GE2-2	P-GE2-1			
Ginger pulp			P-GP-2	P-GP-1	
Ginger powder			P-GPW-2	P- GPW -1	
Water hyacinth					
Water hyacinth			P-WH-2	P-WH-1	

TABLE 3. Industrial waste as candidate materials in reducing DO level.

TABLE 4. Natural and plants as candidate materials in reducing DO level.

materials based on their ratio with water and type whether powder, ash or extract. A reducibility effect in the DO was found using 3 : 1 and 3 : 2 mass ratio (Water : Specimen Ratio), therefore, it was adapted and was considered that it may have a possibility in obtaining the same effect when combined with concrete [31].

Candidate materials that were burned, powdered and extracted have composition similar to cement and aggregates that may replace them or be added to enhance concrete properties. Usually, those materials that were burned and became ash are associated with cement properties, powdered materials are associated with aggregates while extracted materials may serve as coating to metals to reduce corrosion. In this study, candidate materials are used as an additive to mixing water in reducing DO level. Figure 2 shows the DO meter used and the sample candidate materials.

3. Methodology

Candidate materials were gathered from different sources such as industrial plants, farms, quarries and plantation. Industrial wastes were readily available since these are by-products being disposed, whereas, agricultural wastes were burned to form ash which can produce properties similar to cement. Moreover, minerals are also readily available as they are part of natural resources while plants, on the other side, were gathered from plantation and were extracted.

3.1. MIXING PROCEDURE

300ml of distilled water was used to determine the baseline value of DO to identify the percentage dif-



FIGURE 2. DO meter and sample candidate materials.



FIGURE 3. Candidate materials for DO testing.

ference of DO when mixed with the candidate materials. DO of water was found out to be 5.08ppm. DO of the mixture were measured by placing 100grams and 200grams of materials into a bottle with 300ml of distilled water (3:1 and 3:2 ratio), stirred until thoroughly mixed to form a solution. At room temperature (average 26 degrees Celsius), DO level was measured using DO meter. Except for the case of garlic powder and RHA, the ratio used was 10:1 since these materials were observed to be low density, thus, bagasse ash and wood waste ash were tested only in 3:1 ratio. Figure 3 shows how the specimens were prepared prior to DO testing.

3.2. Percentage difference of DO

The equation used to determine the DO is shown below.

$$\% DO_{diff} = \frac{DO_{water} - DO_{solution}}{DO_{water}} \cdot 100 \quad (1)$$

where:

• DO_{water} = DO level of distilled water at room temperature

• DO_{solution} = DO level of mixed solution at room temperature

3.3. Results and Discussion

Shown in Table 5 are the materials with highest DO level reduction represented by the percentage difference resulted to a reduction of more than 90% which include ginger extract, ginger powder, aloe vera, ginger pulp, and rice hull ash.

Materials	DO diff. (ppm or mg/L)	% DO diff
P-GE-1	4.99	98.23
P-GE-2	4.98	98.03
P-GPW	4.97	97.83
P-AV-1	4.96	97.64
P-AV-2	4.91	96.65
P-GP-1	4.81	94.69
AW-RHA	4.77	93.90

TABLE 5. Top percentage DO difference of the candidate materials.

4. CONCLUSION

Corrosion inside concrete is very complex with a lot of factors contributing to it. In this study, the objective is to reduce the DO level of mixing water that can reduce the corrosion of steel rebars inside concrete. Identification of candidate materials from agricultural waste, industrial waste, minerals, and plants were made in the region. Among the candidate materials, it can be observed that plants such as ginger and aloe extracts have the highest capacity to reduce Oxygen in a solution due to its inherent properties and constituents that may inhibit corrosion followed by agricultural and industrial wastes. Future studies are recommended to test the candidate materials as an additive to mixing water in concrete by conducting permeability test and evaluating through Scanning Electron Microscope SEM, to identify its efficiency as part of the binding material in the reduction of corrosion.

References

- B. Bhardwaj, P. Kumar. Waste foundry sand in concrete: A review. Construction and Building Materials 156:661-74, 2017. https: //doi.org/10.1016/j.conbuildmat.2017.09.010.
- [2] A. Tiwari, S. Singh, R. Nagar. Feasibility assessment for partial replacement of fine aggregate to attain cleaner production perspective in concrete: A review. *Journal of Cleaner Production* 135:490-507, 2016. https://doi.org/10.1016/j.jclepro.2016.06.130.
- [3] S. Deepika, G. Anand, A. Bahurudeen, et al. Construction Products with Sugarcane Bagasse Ash Binder. Journal of Materials in Civil Engineering 29(10), 2017. https: //doi.org/10.1061/(asce)mt.1943-5533.0001999.
- [4] Y. Zhou, B. Gencturk, K. Willam, et al. Carbonation-Induced and Chloride-Induced Corrosion in Reinforced Concrete Structures. *Journal of Materials in Civil Engineering* 27(9), 2015. https: //doi.org/10.1061/(asce)mt.1943-5533.0001209.
- [5] M. W. T. Mak, P. Desnerck, J. M. Lees. Corrosion-induced cracking and bond strength in reinforced concrete. *Construction and Building Materials* 208:228-41, 2019. https: //doi.org/10.1016/j.conbuildmat.2019.02.151.
- [6] N. S. Berke, M. C. Hicks. Predicting Times to Corrosion from Field and Laboratory Chloride Data. Techniques to Assess the Corrosion Activity of Steel Reinforced Concrete Structures. p. 41-17, 1996. https://doi.org/10.1520/stp16966s.
- [7] N. C. Concha. Bond Strength Prediction Model of Corroded Reinforcement in Concrete Using Neural Network. *International Journal of GEOMATE* 16(54), 2019. https://doi.org/10.21660/2019.54.4785.
- [8] M. Ramesh, K. Karthic, T. Karthikeyan, et al. Construction materials from industrial wastes - a review of current practices. Intl. j. of environmental research and development. 2014(4):317-24. https://www.ripu blication.com/ijerd_spl/ijerdv4n4spl_08.pdf.

 Y. T. Tran, J. Lee, P. Kumar, et al. Natural zeolite and its application in concrete composite production. *Composites Part B: Engineering* 165:354-64, 2019. https:

//doi.org/10.1016/j.compositesb.2018.12.084.

- [10] A. J. Wei, B. Feng, X. Zhang, et al. Inhibition of Aloe in Corrosion Experimental Research. Advanced Materials Research 233-235:648-51, 2011. https://doi.org/10.4028/www.scientific.net/AMR .233-235.648.
- [11] Pal S, Mukherjee A and Pathak S. Corrosion behavior of reinforcement in slag concrete. *Materials Journal* 99(6):521-7, 2002.
- [12] A. Abdulmatin, W. Tangchirapat, C. Jaturapitakkul. An investigation of bottom ash as a pozzolanic material. *Construction and Building Materials* 186:155-62, 2018. https://doi.org/10.1016/j.conbuildmat.2018.07.101.
- [13] A. K. Anupam, P. Kumar, G. D. Ransinchung, et al. Study on Performance and Efficacy of Industrial Waste Materials in Road Construction: Fly Ash and Bagasse Ash. Airfield and Highway Pavements, p. 45-56, 2017. https://doi.org/10.1061/9780784480946.005.
- [14] S. Ghorbani, I. Taji, M. Tavakkolizadeh, et al. Improving corrosion resistance of steel rebars in concrete with marble and granite waste dust as partial cement replacement. *Construction and Building Materials* 185:110-9, 2018. https: //doi.org/10.1016/j.conbuildmat.2018.07.066.
- [15] S. Kumar, B. Nagar. Effects of Waste Glass Powder on Compressive Strength of Concrete. International Journal of Trend in Scientific Research and Development 1:289-98, 2017.
- [16] Udoeyo FF, Inyang H, Young DT and Oparadu EE. Potential of wood waste ash as an additive in concrete. J. of matls. in civil engineering. 2006;18(4):605-11.
- [17] F. Grau, H. Choo, J. Hu, et al. Engineering Behavior and Characteristics of Wood Ash and Sugarcane Bagasse Ash. *Materials* 8(10):6962-77, 2015. https://doi.org/10.3390/ma8105353.
- [18] V. K. Nagarajan, S. A. Devi, S. Manohari, et al. Experimental study on partial replacement of cement with coconut shell ash in concrete. *International Journal of Science and Research* 3:651-61, 2014. https: //www.ijsr.net/archive/v3i3/MDIwMTMxMjYw.pdf.
- [19] J. Safari, M. Mirzaei, H. Rooholamini, et al. Effect of rice husk ash and macro-synthetic fibre on the properties of self-compacting concrete. *Construction* and Building Materials 175:371-80, 2018. https: //doi.org/10.1016/j.conbuildmat.2018.04.207.
- [20] H. Binici, O. Aksogan. The use of ground blast furnace slag, chrome slag and corn stem ash mixture as a coating against corrosion. *Construction and Building Materials* 25(11):4197-201, 2011. https: //doi.org/10.1016/j.conbuildmat.2011.04.057.
- [21] N. H. D. Binag. Utilization of Shell Wastes for Locally Based Cement Mortar and Bricks Production: Its Impact to the Community. *KnE Social Sciences* 3(6), 2018. https://doi.org/10.18502/kss.v3i6.2435.

[22] K. M. Hossain, M. Lachemi. Development of volcanic ash concrete: strength, durability, and microstructural investigations. ACI Materials Journal 103(1):11-17, 2006.

[23] F. A. Sabet, N. A. Libre, M. Shekarchi. Mechanical and durability properties of self consolidating high performance concrete incorporating natural zeolite, silica fume and fly ash. *Construction and Building Materials* 44:175-84, 2013. https: //doi.org/10.1016/j.conbuildmat.2013.02.069.

[24] G. D. O. Okwadha, D. M. Makomele. Evaluation of water hyacinth extract as an admixture in concrete production. *Journal of Building Engineering* 16:129-33, 2018.
https://doi.org/10.1016/j.jobe.2018.01.002.

[25] Y. Liu, Z. Song, W. Wang, et al. Effect of ginger extract as green inhibitor on chloride-induced corrosion of carbon steel in simulated concrete pore solutions. *Journal of Cleaner Production* 214:298-307, 2019. https://doi.org/10.1016/j.jclepro.2018.12.299.

[26] A. Alhozaimy, R. R. Hussain, A. Al-Negheimish. Significance of oxygen concentration on the quality of passive film formation for steel reinforced concrete structures during the initial curing of concrete. *Cement* and Concrete Composites 65:171-6, 2016. https: //doi.org/10.1016/j.cemconcomp.2015.10.022. [27] S. Real, J. A. Bogas. Oxygen permeability of structural lightweight aggregate concrete. *Construction* and Building Materials 137:21-34, 2017. https: //doi.org/10.1016/j.conbuildmat.2017.01.075.

[28] J. F. Jenkins. Metallic Materials for Marine Structures. Treatise on Materials Science & Technology, Elsevier, p. 277-350, 1998.

[29] T. U. Mohammed, N. Otsuki, H. Hamada. Oxygen permeability in cracked concrete reinforced with plain and deformed bars. *Cement and Concrete Research* 31(5):829-34, 2001.

https://doi.org/10.1016/s0008-8846(01)00482-3.

- [30] K. Kawaai, T. Nishida, A. Saito, et al. Corrosion resistance of steel bars in mortar mixtures mixed with organic matter, microbial or other. *Cement and Concrete Research* 124, 2019. https: //doi.org/10.1016/j.cemconres.2019.105822.
- [31] T. Nishida, N. Otsuki, A. Saito, et al., editors. Influence of Reducibility Environment around Steel Bars on Steel Corrosion in Concrete. Proceedings of the Seminar Workshop on the Utilization of Waste Materials E, 2017.