

Article

Not peer-reviewed version

The Synthesis and Performance of a Novel Lignin Modified Salt Resistance Branched High-Performance Water Reducer

[Haipeng Xin](#)^{*} and [Donggang Guo](#)^{*}

Posted Date: 18 December 2023

doi: 10.20944/preprints202312.1305.v1

Keywords: Water reducer; Salt resistance; Dispersant



Preprints.org is a free multidiscipline platform providing preprint service that is dedicated to making early versions of research outputs permanently available and citable. Preprints posted at Preprints.org appear in Web of Science, Crossref, Google Scholar, Scilit, Europe PMC.

Copyright: This is an open access article distributed under the Creative Commons Attribution License which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Article

The Synthesis and Performance of a Novel Lignin Modified Salt Resistance Branched High-Performance Water Reducer

Haipeng Xin ^{1,*} and Donggang Guo ^{2,3}

¹ Institute of Environmental Science, Shanxi University, Taiyuan, 030006, China

² College of Environment and Resource, Shanxi University, Taiyuan 030006, China; gdghjx@126.com

³ Shanxi Laboratory for Yellow River, Taiyuan 030006, China

* Correspondence: xhp_1986@126.com

Abstract: A lignin modified salt resistance branched high-performance water reducer was prepared via free radical polymerization. The water reducing agent was identified through Fourier transform infrared analysis, thermal gravimetric analysis, and scanning electron microscopy. The experiment conducted on cement paste demonstrates that the water-reducing efficiency can reach a maximum of 44%. Additionally, the significant spatial steric hindrance of the application enhances the dispersal capability of the water-reducing agent, resulting in effective water reduction and reduced viscosity. In addition, its compressive strength is the highest after 3-day curing and 3, 7, 28-day standard curing, and it has the best overall performance both in water and saline water prepared systems. The application in oil cement slurry shows that it exhibits good dispersibility in fresh water, saline water, and substitute ocean water. In the Halfaya and Missan Oilfields of Iraq, BHPWR was used in slurry with a density of 2.28g cm⁻³ for casing the 244.5 mm salt paste layer of five wells. Cementing results exceeded expectations with over 85% excellent and 100% qualified.

Keywords: water reducer; salt resistance; dispersant

1. Introduction

The water reducer is a crucial admixture in the concrete industry, which has witnessed a shift from the conventional polyelectrolyte water reducer to the polycarboxylic acid water reducer [1–6]. The comb type polycarboxylic acid water reducer, characterized by its remarkable adjustability and significant potential for achieving high performance, effectively addresses concerns related to dispersibility and stability, thereby yielding exceptional application outcomes [7–9].

However, it is impossible to directly use seawater, saline water, and alkali water to build coastal wave-resistant dikes and saltwater lake dams due to the decreased flow ability induced by salt resistance, which requires long-distance transportation of fresh water increasing costs and fuel consumption during transportation.

Salt resistant water reducer could effectively increase flow ability of concrete slurry containing salt which could help the direct prepare of slurry by seawater, saline water, and alkali water.

This study is still in its early stages, and there is no relevant research yet. The available salt-resistant water reducer literatures are mostly about resistance of erosion of concrete by sulfate and chloride salts after being added [10–13], rather than to improve its fluidity during construction. Starting from the multi-hydroxyl lignin, a salt resistance branched high-performance water reducer (BHPWR) was prepared by introducing branching structures. The main chain contained carboxyl and sulfonic acid groups as well as long hydrophilic side chains. By utilizing the strong steric hindrance effect, the volume dispersion and electrostatic repulsion lead to Strong dispersing effect which could improve concrete fluidity under saline conditions.

2. Materials and Methods

2.1. Materials

Acrylic acid was obtained from Sinopharm Chemical Reagent Co., Ltd. AMPS was obtained from Nanjing All-Plus chemical Co. Ltd. APEG-2000 was obtained from Haian Petrochemical Plant Co. Ltd. Lignin was obtained from Shandong Gaotang Polymeric Lignin Co., Ltd.

Base Cement: Jidong Cement Co. Ltd provided P·O 52.5 Cement. Hebei Huakai Mining Co. Ltd supplied Quartz Sand ranging from 20 to 120 mesh. Gansu Sanyuan Silicon Material Co., Ltd provided Silica fume with a SiO₂ content exceeding 94% and a specific surface area of 20 m²/g. Shandong Shunke Building Materials Technology Co., Ltd supplied Class I fly ash with a density of 2200 kg/m³. Xingtai Guangqing Refractory Material Distribution Co., Ltd provided Glass bead with a density of 412 kg/m³ and a particle size of approximately 0.1 mm. Changzhou Tianyi Engineering Fiber Co., Ltd supplied Steel Fiber with a diameter of 0.22 mm and a length ranging from 13 to 15 mm. Jiangsu Liqi Environmental Technology Co., Ltd provided the defoaming agent.

2.2. Characterization

The Bruker Tensor 27 spectrometer was used to record Fourier transform infrared (FTIR) spectra of the BHPWR in KBr pellets at room temperature. The spectra were recorded in the range of 4000-400 cm⁻¹.

The Scanning Electron Microscope (SEM) measurement was obtained using an JEOL JSM-7600 Thermal Field Emission Scanning Electron Microscope, and the surface of the gel particles was treated with gold spraying previously.

The consistency of cement paste was examined following the guidelines of GB 8077-2012 'Test Method for Consistency of Concrete Admixture' using a water-to-cement ratio of 0.29, and the solid content of the water reducing agent was 0.12%.

The water reduction rate was tested according to GB 8076-2008 "Concrete Admixtures". The concrete mix ratio is: m (Jidong Cement): m (sand): m (stone) = 360: 810: 990.

Concrete viscosity was tested according to T500 in JGJ/T 283-2012 "Technical Specification for Application of Self-Compacting Concrete".

The mechanical properties of concrete are tested in accordance with the GB/T 50081-2019 standard through the process of standard steam curing. The specimens, after being exposed to an experimental setting for 24 hours at a temperature of (20±5)°C and a relative humidity above 50%, are transferred to a curing box. They are then gradually heated, not surpassing a rate of 15°C/h, until reaching a temperature of (90±1) °C. The specimens are maintained at a constant temperature for 48 hours before being cooled down, again not exceeding a rate of 15°C/h, until reaching (20±5) °C.

The process of curing at the typical temperature of a room is conducted in accordance with the guidelines provided by GB/T 50081-2019, which outlines the standard procedures for evaluating the mechanical properties of concrete. Samples are placed in a typical curing chamber at a temperature of (20±2) °C and a relative humidity exceeding 95%.

A ZNN-D6 rotational viscometer was used to conduct the rheological test at 85°C and atmospheric pressure, following the guidelines of SY/T 5504.3-2008 "Evaluation Method for Oil Well Cement Additives Part 3 Friction Reducers".

The thickening test was conducted according to GB/T19139-2012 "Test Methods for Oil Well Cement" using an OWC-9480C pressurized thickening meter.

3. Synthesis and Characterization of BHPWR

3.1. The Synthesis of BHPWR

Five BHPWR samples were produced through the process of free radical polymerization. 2-acrylamide-2-methylpropanesulfonic acid (AMPS) (100g, 0.48mol), acrylic acid (15 g, 0.21mol), allyl polyethylene glycol APEG-2000 (10 g, 0.0050mol), Lignin (0.5 g for BHPWR-1, 0.7 g for BHPWR-1, 0.9 g for BHPWR-1, 1.1 g for BHPWR-1, and 1.3 g for BHPWR-1,) and water (375 g) were added in one

portion and stirred to dissolve at 70 °C, then Initiator was added and the solution was kept warm at 70 °C for 3 h. Resulting pale yellow liquid was filtered while still hot. In this system, the presence of acrylic acid enhances the attachment of dispersant to cement particles, resulting in three-dimensional dispersion effects when combined with APEG-2000 and lignin, while AMPS provides resistance to salt.

3.2. The Characterization of BHPWR

The IR spectrum of the dispersant is presented in Figure 1, with the main absorption bands of the dispersant assigned as follows: a) OH stretching (H₂O, APEG-2000) at 3500 cm⁻¹, b) CH₂ and CH₃ stretching (AMPS, APEG-2000, lignin) at 2880 cm⁻¹, c) C=O symmetric stretching (acrylic acid) at 1720 cm⁻¹, d) Aromatic ring skeleton stretching (lignin) at 1653 cm⁻¹ and 1467 cm⁻¹, e) COO-symmetric stretching (acrylic acid) at 1345 cm⁻¹, f) C-O-C stretching (APEG-2000, lignin) at 1114 cm⁻¹, and g) S-O bending (sulfonic acid group of AMPS) at 626 cm⁻¹.

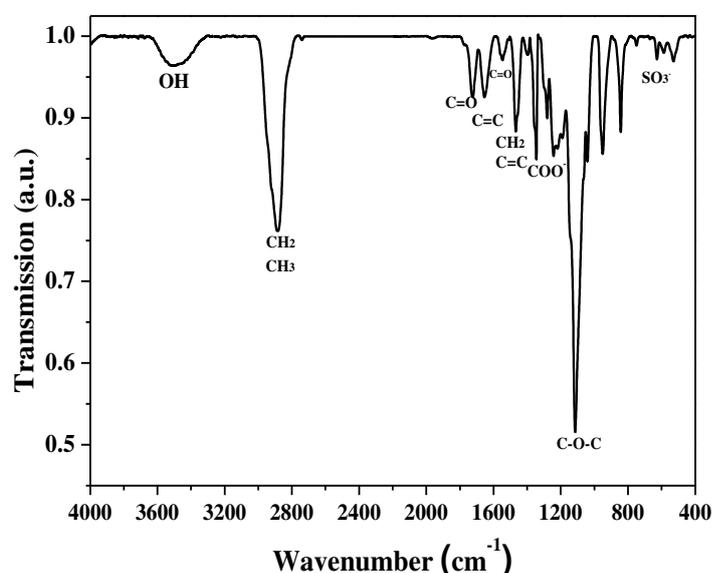


Figure 1. Infrared spectra of the BHPWR.

Electron microscopy tests were conducted to further study the stereostructure of water reducer in solution, using scanning electron microscopy (SEM). BHPWR does not exhibit a single regular shape due to the free rotation of its main chain and side chains. In addition, due to the thermal motion of molecules, the shape of water reducer is constantly changing. Despite the adsorption of the primary chain onto the cement particle surface in cement slurry, the secondary chain exhibits erratic movement as well. Figure 2 shows the aggregate state of water reducer at the micrometer scale, which is a dendritic shape. The primary chain of the polymer attaches to the cement particles in the cement slurry through carboxyl and sulfonic acid groups, while the polymer's secondary chains are long side chains that can extend without restriction when the primary chain is attached to the cement slurry. The response of water and mechanical radius increases due to the significant molecular weight of the side chains, resulting in a substantial spatial steric hindrance. Due to this large spatial steric hindrance effect, the side chains have strong three-dimensional dispersing ability on cement particles, which leads to good dispersion of cement slurry and further increases its rheology.

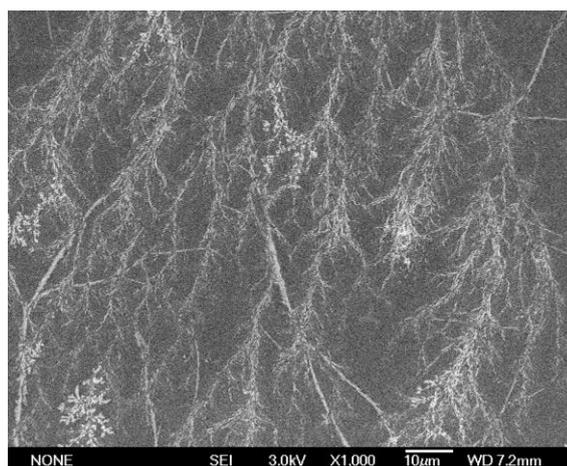


Figure 2. The SEM of BHPWR.

4. Concrete and Cement Slurry Performance

4.1. Concrete Performance

Tables 1 and 2 displayed the performance of concrete made with freshwater and saltwater, correspondingly. The water-reducing rate of BHPWR-3 can reach up to 45% in fresh water and 44% in saline water, and its large spatial steric hindrance improves the dispersibility of the water reducer, achieving high water reduction and low viscosity. In addition, its compressive strength is the highest after 3-day curing and 3, 7, 28-day standard curing, and it has the best overall performance both in fresh water and saline water prepared systems.

Table 1. Performance of concrete prepared by fresh water.

Sample added	Water reduction rate %	concrete slump mm	T500 s	3-day compressive strength under steam curing MPa	Compressive strength, MPa		
					3d	7d	28d
BHPWR-1	36	766	6.62	120.1	83.1	115.4	118.6
BHPWR-2	41	799	6.13	135.2	85.7	120.3	135.7
BHPWR-3	45	832	4.85	147.6	94.3	129.9	144.6
BHPWR-4	32	763	5.27	127.1	79.8	110.2	129.3
BHPWR-5	35	771	5.96	119.3	81.2	112.7	130.4

Concrete batching: Cement 700 g + Fly ash 105 g + Silica fume 150 g + Foaming agent 50 g + Quartz sand 1200 g + Water 170 g + Steel fiber 150 g + Water reducing agent 21.4 g.

Table 2. Performance of concrete prepared by saline water.

Sample added	Water reduction rate %	concrete slump mm	T500 s	3-day compressive strength under steam curing MPa	Compressive strength, MPa		
					3d	7d	28d
BHPWR-1	30	650	6.97	81.3	44.6	62.1	84.2
BHPWR-2	39	710	6.44	97.5	48.9	69.7	93.1
BHPWR-3	44	812	4.91	123.6	70.2	100.2	125.7
BHPWR-4	29	702	5.83	100.4	50.3	71.3	99.8
BHPWR-5	28	680	6.22	90.2	52.7	73.2	98.9

Concrete batching: Cement 700 g + Fly ash 105 g + Silica fume 150 g + Foaming agent 50 g + Quartz sand 1200 g + Water 170 g + NaCl 61.2 g + Steel fiber 150 g + Water reducing agent 21.4 g.

4.2. Cement Slurry Performance

BHPWR could also be used as oil cement dispersant. BHPWR-3 was added to the slurry prepared with fresh water, saline water with 36 % NaCl by weight of water, and substitute ocean water which is prepared according to Designation D1141-98 (D1141-98). The dispersant underwent evaluation in accordance with SY/T 5504.3-2008 and the important indicators are flow behavior index n and consistency index K calculated from θ_{300} and θ_{100} , the reading of viscometer at the shearing rate of 100 r/min and 300 r/min. Good dispersant should result to bigger n and lower k .

$$n = 2.096 \times \lg \frac{\theta_{300}}{\theta_{100}} \quad (1)$$

$$K = \frac{0.511 \times \theta_{300}}{511^n} \quad (2)$$

Rheology of slurries prepared with fresh water, saline water, and substitute ocean water is listed in Table 3. With the addition of 1.5 %BWOC, $n = 0.78-0.93$ and $K = 0.04-0.16 \text{ Pa.s}^n$ at 52 °C and atmospheric pressure while $n = 0.73-0.92$ and $K = 0.16-0.19 \text{ Pa.s}^n$ at 85 °C and atmospheric pressure, which indicates that BHPWR-3 exhibits good dispersibility in fresh water, saline water, and substitute ocean water.

Table 3. Rheology of slurries prepared with different kind of water.

Water type	Addition of BHPWR-3 %BWOC	Temperature °C	Shear rate					n	$K \text{ Pa.s}^n$
			θ_3	θ_6	θ_{100}	θ_{200}	θ_{300}		
Fresh water	0	52	14	20	68	81	92	0.28	8.45
Fresh water	1.5	52	--	--	6	10	15	0.83	0.04
Saline water	0	52	14	19	36	47	60	0.46	1.68
Saline water	1.5	52	3	4	9	16	25	0.93	0.04
Substitute ocean water	0	52	20	29	90	95	105	0.14	22.4
Substitute ocean water	1.5	52	6	9	17	26	40	0.78	0.16
Fresh water	0	85	12	17	111	133	143	0.23	17.3
Fresh water	1.5	85	--	--	4	7	11	0.92	0.18
Saline water	0	85	16	21	49	59	65	0.26	6.67
Saline water	1.5	85	5	6	13	22	29	0.73	0.16
Substitute ocean water	0	85	20	26	145	153	162	0.10	44.2
Substitute ocean water	1.5	85	8	13	16	25	36	0.74	0.19

* Slurry formulation: G class cement + water + BHPWER with water-solid ratio of 0.44.

5. The Application of BHPWR

The cement slurries used in Iraq's Halfaya and Missan Oilfield are prepared by saline water with low fluidity, significant thixotropy, and high initial consistency due to its high solid and salt content.

Furthermore, the elevated temperature during the summer in Iraq speeds up the process of cement hydration, ultimately causing a decrease in the rheology of the cement slurry. Due to the persistent high ground temperature, which can reach up to 60°C during the summer in Iraq, the cement slurry experienced significant hydration while being mixed, leading to a decrease in its fluidity as shown in Table 4 which shows θ_{300} unreadable at 60 °C, strong thixotropy and high initial consistency leading to difficulty in pumping and unstable density which seriously impacts on on-site construction safety and cementing quality.

Table 4. Rheology of 2.28 g cm⁻³ slurry at different ambient temperature.

Ambient temperature °C	θ_3	θ_6	θ_{100}	θ_{200}	θ_{300}	n	K Pa.s ⁿ
27	3	10	79	138	195	0.82	0.59
40	16	20	88	158	212	0.8	0.74
50	17	28	108	162	235	0.71	1.45
60	19	25	138	200	--	--	--

Slurry formulation: Oman G class cement 450 g+ hematite 300 g + manganese ore fines BH-WS 22.5 g + fluid loss additive BH-F101L 18 g + dispersant BH-D301L 15.7 g + retarder BZR101 0.1 g + defoamer XP-1 0.9 g + salt NaCl 40.5 g+ water 214.7 g.

BHPWR could enhance the flow characteristics of slurry, making it easier to mix and place. Rheology is a metric that gauges the ability to resist fluid motion and the decrease in such resistance when subjected to pressure. Upon substitution of the dispersant in Table 5 with BHPWR-3, the slurry displayed favorable rheological characteristics, with a flow behavior index of $n=0.74$ and a consistency factor of $K=1.08$ Pa.sⁿ at 60 °C from which we can learn that the BHPWR-3 is a kind of good performance dispersant.

Table 5. Rheology of 2.28 g cm⁻³ slurry using BHPWR-3 at different ambient temperature.

Ambient temperature °C	θ_3	θ_6	θ_{100}	θ_{200}	θ_{300}	n	K Pa.s ⁿ
27	2	8	59	102	150	0.85	0.38
40	6	14	73	125	173	0.79	0.66
50	8	19	86	146	195	0.75	0.95
60	9	23	96	158	217	0.74	1.08

Slurry formulation: Oman G class cement 450 g+ hematite 300 g + manganese ore fines BH-WS 22.5 g + fluid loss additive BH-F101L 18 g + dispersant BHPWR-3 15.7 g + retarder BZR101 0.1 g + defoamer XP-1 0.9 g + salt NaCl 40.5 g+ water 214.7 g.

To cement the 244.5 mm salt paste layer casing for five wells in Halfaya and Missan Oilfield in Iraq, the BHPWR-3 was utilized with high-density (2.28 g cm⁻³) saline cement slurry under the ambient temperature of 55-58 °C. It is worth noting that over 85% of each cementing job executed was deemed outstanding. One of the wells, namely FQCS-44H, serves as a prime example, involving the sealing of the Lower Fars formation containing high-pressure saltwater zones via casing measuring 244.5 mm in diameter placed in 311.1 mm open holes, with the shoe being at 2957.7 m as opposed to the previous 339.7 mm casing at 2081.5 m. However, it is challenging to conduct cementing under these circumstances given that higher mud weight (2.23 g cm⁻³) requires denser slurry, potentially narrowing the cementing window. Despite these complications, the Segment Bond Tool evaluation indicates that the cementing job was qualified at 100%, with 85% of the job regarded as excellent.

6. Conclusions

BHPWR prepared via free radical polymerization demonstrates excellent performance as a water reducer, with reduction rates of up to 45% in fresh water and 44% in saline water. After 3-day curing and standard curing for 3, 7, and 28 days, it shows the highest compressive strength and overall best performance in both water and saline water systems. Furthermore, it has been found to exhibit good dispersibility in fresh water, saline water, and substitute ocean water, making it a suitable dispersant for oil cement slurries. Rheological testing of slurries prepared with BHPWR-3 showed $n=0.78-0.93$ and $K=0.04-0.16 \text{ Pa}\cdot\text{s}^n$ at 52°C and atmospheric pressure, and $n=0.73-0.92$ and $K=0.16-0.19 \text{ Pa}\cdot\text{s}^n$ at 85°C and atmospheric pressure. This indicates that BHPWR-3 is effective in fresh water, saline water, and substitute ocean water. In the Halfaya and Missan Oilfields of Iraq, BHPWR was used in slurry with a density of 2.28g cm^{-3} for casing the 244.5 mm salt paste layer of five wells. Cementing results exceeded expectations with over 85% excellent and 100% qualified.

Author Contributions: Conceptualization, H.X.; methodology, D.G.; software, H.X.; validation, D.G.; formal analysis, H.X.; investigation, H.X.; resources, D.G.; data curation, H.X.; writing—original draft preparation, H.X.; writing—review and editing, D.G.; visualization, H.X.; supervision, D.G.; project administration, H.X.; funding acquisition, H.X. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Shanxi Province Postdoctoral Special Subsidy, grant number 205521029.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Flávio, A.; Rodrigues, I.J. Water reducing agents of low molecular weight: Suppression of air entrapment and slump loss by addition of an organic solvent. *Cem. Concr. Res.* **1994**, *24*, 987–992.
2. Chen, J.; Li, L.; Wu, G.; Zhou, M.; Jiang, T.; Pu, Q.; Wei, M. Study on the effect of fly ash and polycarboxylic acid water reducer on the properties of recycled concrete. *IOP Conf. Ser. Earth Environ. Sci.* **2019**. <https://doi.org/10.1088/1755-1315/218/1/012068>.
3. Chen, Y. Research and application of polycarboxylate water reducer for precast components. *IOP Conf. Ser. Earth Environ. Sci.* **2021**. <https://doi.org/10.1088/1755-1315/621/1/012112>.
4. Pang, L.; Zhou, X. Research of polycarboxy acid water-reducer with modified ployether and its effect on concrete's workability. *Adv. Mater. Res.* **2011**, *250–253*, 2032–2035.
5. Liu, B.; Yu, K.; Yang, Y.; Miao, D.; He, C. Research and application of polycarboxylic acid water reducer with different molecular weight. *E3S Web Conf.* **2020**. <https://doi.org/10.1051/e3sconf/202017901021>.
6. Yan, Q.; Yao, L.; Xia, Y.; Liu, S.; Chen, L. Synthesis and characterization of a high performance polycarboxylic acid water reducing agent. *E3S Web Conf.* **2020**. <https://doi.org/10.1051/e3sconf/202019801018>.
7. Süleyman, Ö.; Muhammet, G.; Ali, M.; Kambiz, R. Effect of main and side chain length change of polycarboxylate-ether-based water-reducing admixtures on the fresh state and mechanical properties of cementitious systems. *Struct. Concr.* **2021**, *22*, E607–E618.
8. Li, C.; Feng, N.; Li, Y.; Chen, R. Effects of polyethylene oxide chains on the performance of polycarboxylate-type water-reducers. *Cem. Concr. Res.* **2005**, *35*, 867–873.
9. Liu, Y.; Li, H.; Wang, K.; Wu, H.; Cui, B. Effects of accelerator–water reducer admixture on performance of cemented paste backfill. *Constr. Build. Mater.* **2020**, *242*, 118187.
10. Wang, J.; Shen, L.; Niu, K. Study on the salt scaling resistance of pavement cement concrete. *J. Highw. Transp. Res. Dev.* **2014**, *8*, 7–10.
11. Konzilia, J.; Matthias, E.; Jürgen, F. Experimental investigation on salt frost scaling of textile-reinforced concrete. *Struct. Concr.* **2022**, *23*, 954–969.

12. Brun, M.; Shpak, A.; Jacobsen, S. Shape and size of particles scaled from concrete surfaces during salt frost testing and rapid freeze/thaw in water. *Nord. Concr. Res.* **2021**, *64*, 53–68.
13. Kryvenko, P.; Rudenko, I.; Konstantynovskyi, O.; Boiko, O. Restriction of Cl⁻ and SO₄²⁻ ions transport in alkali activated slag cement concrete in seawater. *IOP Conf. Ser. Mater. Sci. Eng.* **2021**, *1164*. [https://doi.org/10.37538/2224-9494-2022-2\(33\)-183-193](https://doi.org/10.37538/2224-9494-2022-2(33)-183-193).

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.