

Experimental on effect of steel slag activator on mechanical properties and durability of offshore concrete

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Abstract: To improve the durability of offshore concrete and the incorporation of steel slag powder within the concrete matrix, a series of tests were conducted to evaluate the fluidity, setting time, mechanical properties, carbonation depth, and chloride ion electric flux of steel slag concrete. The study investigated the influence of three different activators—sodium sulfate, desulfurization gypsum, and desulfurization ash—on the activity of steel slag, as well as the concrete's resistance to chloride ions and carbonation. The findings indicate that the inclusion of steel slag reduces the fluidity of cement paste and extends the setting time. Notably, sodium sulfate (Na_2SO_4) as an activator has the potential to marginally decrease the setting time. Both mineral powder and steel slag powder can mitigate the loss of concrete slump over time to a certain degree; however, the presence of a specific quantity of activator may diminish this effect. The use of desulfurization ash (at a concentration of 2%), sodium sulfate (at 3%), and desulfurization gypsum (at 4%) significantly enhanced the flexural strength of the concrete, with the 3% Na_2SO_4 (designated as SS-N) demonstrating the most substantial contribution to flexural strength. The combination of sodium sulfate and desulfurization gypsum (referred to as SS-NG) exhibited a greater impact on the flexural strength of the concrete compared to the combination of sodium sulfate and desulfurization ash (SS-ND) or the use of individual activators. When the three activators were applied independently, a slight improvement in the 7-day compressive strength of concrete containing steel slag-slag powder was observed, although the enhancement in later compressive strength was not pronounced. Conversely, the composite activator demonstrated a significant influence on the compressive strength of the concrete, particularly the combination of 3% sodium sulfate and 4% desulfurization gypsum, which markedly affected the mechanical properties. Furthermore, sodium sulfate improved the carbonation resistance and chloride ion penetration resistance of the concrete by 23.9% and 43.7%, respectively. The durability benefits of the composite activator comprising sodium sulfate and desulfurization gypsum surpassed those of any single activator. Overall, the three activators—desulfurization ash, desulfurization gypsum, and sodium sulfate—enhanced the activity of steel slag, thereby improving the microstructure, mechanical properties, and durability of offshore concrete.

Keywords: road engineering; the improvement of activity of steel slag; composite activator; mechanical properties; durability

1 Introduction

In recent years, new construction projects such as cross-sea bridges and coastal highways have been increasing. Offshore and marine concrete are facing serious chloride ion erosion problems due to coastal atmospheric environment or seawater immersion, and steel corrosion caused by chloride ion erosion is one of the main reasons for the premature failure of reinforced con-

crete members in coastal areas^[1-2]. In the coastal environment with high chlorine and high humidity, concrete structures are inevitably affected by carbonization while suffering from chloride ion erosion^[3]. Carbonation will reduce the alkalinity of concrete and may also lead to the re-release of bound chloride ions^[4], which makes the steel bars face more serious chloride ion erosion. Therefore, it is necessary to study the durability of offshore concrete projects subjected to chloride ion erosion and

Received: 7 January 2024; Revised: 25 April 2024; Accepted: 31 July 2024

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Translated from *Journal of Highway and Transportation Research and Development* (Chinese, ISSN1002-0268), 2024, 41(9): 106–112.

carbonization.

Offshore concrete is in great demand due to the development of the marine economy, and important admixtures such as slag powder and fly ash that can improve the durability of concrete will be difficult to fully supply the market demand^[5]. From the perspective of feasibility, the large-scale promotion of high-activity steel slag as a concrete admixture not only meets the needs of engineering construction and development but also realizes the high value-added utilization of metallurgical waste, which is in line with Chinese strategic policy of vigorously developing circular economy, increasing environmental protection and promoting marine economic development. Steel slag powder is a solid waste produced in large quantities by using lime to extract impurities in steelmaking. It has micropores and is grayish brown^[6]. The emission of steel slag accounts for about 10%–15% of steel production. The total output of steel slag in China is more than 160 million tons in 2020, and the amount of steel slag is up to 1.468 million tons. The comprehensive utilization rate is only 10%–30%, but most of them are low value-added utilization^[7]. Therefore, studying the characteristics of steel slag and preparing building materials that can be used on a large scale is an important direction to improve its resource utilization rate.

At present, steel slag has been widely used in the field of building materials, mainly used as cement admixture and concrete mineral admixture, aggregate, etc.^[8–10]. As a concrete admixture, steel slag powder can replace cement, which not only realizes the utilization of solid waste but also helps to reduce the amount of cement, the costs, energy consumption and carbon emissions in cement production. Steel slag contains a certain amount of C_2S , C_3S and other minerals similar to cement clinker, but the crystal is large and the hydration rate is slow^[11–12]. Previous studies have shown that steel slag can effectively improve its activity and utilization efficiency through mechanical excitation, chemical excitation and thermodynamic excitation^[13]. Studies have shown that the incorporation of 10% steel slag is beneficial to improve the compressive strength of concrete, but when the content is 20%, the compressive strength of concrete decreases^[14]. Due to the low activity of steel slag, increasing the amount of steel slag is equivalent to increasing

the water-binder ratio. The filling effect of steel slag particles cannot fully compensate for the problems of coarse pores and poor compactness caused by the increase in water-binder ratio^[13,15–16], which ultimately reduces the strength and durability of concrete. Therefore, the use of steel slag as a mineral admixture alone may have limited or even decreased the performance of concrete. On the other hand, the incorporation of mineral powder will reduce the alkalinity of concrete and cause corrosion of steel bars. However, the preparation of high-performance admixtures with steel slag and mineral powder can improve the alkalinity of the system and effectively enhance the stability of concrete^[17]. In addition, the combination of slag powder and steel slag can improve the bulk density of the cementitious system and make the concrete system more compact. However, the research on the influence of various activators on the durability of steel slag-slag powder composite admixtures is very limited^[18]. Therefore, it is necessary to study high-performance activators to improve the activity of steel slag and slag powder, the utilization rate of steel slag and the durability of offshore concrete.

In this paper, the effects of different activators on the mechanical and durability of steel slag concrete are studied using single and compound activators. The effect of the activator on steel slag activity and durability of concrete was studied by testing the working performance of the slurry, the mechanical properties of concrete, carbonization resistance and chloride ion penetration resistance. The mechanism of action was analyzed by combining the characteristics of the activator, which provided a theoretical reference for the use of high performance activator in marine concrete to improve the utilization and durability of steel slag.

2 Experiment

2.1 Material

Cement: The cement used in the test is ordinary Portland cement (PO 42.5) produced by Shanghai Haibao Cement Plant, and its chemical composition is shown in Table 1.

Steel slag powder: The steel slag powder is from Baogang. The specific surface area was $450 \text{ m}^2/\text{kg}$, and the chemical composition is shown in Table 1. The main mineral composition of steel slag powder is C_2S and sol-

Table 1 Chemical composition of raw materials (%)

Composition	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	SO ₃	Loss	f-CaO
Cement	21.08	62.68	4.55	2.7	—	2.05	2.9	2.94	0.77
Steel slag	15.77	39.44	5.21	7.41	8.87	10.03	—	—	10
Slag	33.26	40.35	14.95	1.07	—	8.58	0.05	—	—

id solution RO phase formed by FeO and MgO, with the content of 40% and 21.6% respectively. The steel slag powder used in this experiment meets the standard GB/T 20491—2017.

Slag powder: produced by Shanghai Baotian Company, the chemical composition is shown in Table 1.

Water reducer: Shandong Wanshan FDN naphthalene superplasticizer, solid content of 30%.

2.2 Mix proportion

The mix ratio of concrete is shown in Table 2. The steel slag powder is used to replace the slag powder (S) in equal amounts to configure the steel slag-slag powder composite mineral admixture, and then the composite admixture is used to replace 1/3 cement, and the water-cement ratio is fixed at 0.5. The type and content of the activator (the percentage of steel slag powder mass) are shown in Table 2.

2.3 Test method

(1) Workability

According to the industry standard JC/T 1083—2008, the compatibility of steel slag-slag powder composite admixture and water reducer was studied by slurry fluidity. The cement paste ratio is steel slag powder: slag powder: cement = 16.67 : 16.67 : 66.66, water-binder ratio is 0.29.

According to GB/T 50080—2002, the slump reten-

tion value and setting time of concrete mixture samples were measured.

(2) Mechanical properties of concrete

Referring to GB/T 50081—2002, the compressive strength and flexural strength of concrete blocks at different ages were measured.

(3) Concrete carbonation test

According to GB/T 50082—2009, carbonation test method, the carbonation depth (mm) of each group of specimens at different ages was tested.

(4) Chloride ion penetration test of concrete

According to GB/T 50082—2009, the direct current flux of the specimens after 18 h vacuum saturation and 6 h electrification was measured by the CABR-RCP9 concrete chloride ion flux tester.

3 Test results and analysis

3.1 The workability of concrete

3.1.1 Adaptability analysis of steel slag powder to water reducing agent of cementitious materials

Figure 1 shows the effect of different amounts of FDN series superplasticizer on the fluidity of cement paste. As shown in Figure 1, the fluidity increased rapidly and then maintained a slow growth during the increase of FDN superplasticizer dosage. When the content of water reducer is about 0.6%, the fluidity is close to the maximum

Table 2 Steel slag-slag concrete mix ratio (unit: kg/m³)

	Cement	Water	Steel slag	Slag	Activator	Medium sand	Gravel	Superplasticizer
R	378	189	—	—	—	788	1 004	5.67
S	252	189	—	126	—	788	1 004	5.67
SS	252	189	63	63	—	788	1 004	5.67
SS-D	252	189	63	63	Desulfurization ash (2%, wt.)	788	1 004	5.67
SS-N	252	189	63	63	Sodium Sulfate (3%, wt.)	788	1 004	5.67
SS-G	252	189	63	63	Desulfurization Gypsum (4%, wt.)	788	1 004	5.67
SS-ND	252	189	63	63	Sodium Sulfate (3%, wt.)+ Desulfurization ash (2%, wt.)	788	1 004	5.67
SS-NG	252	189	63	63	Sodium Sulfate (3%, wt.)+ Desulfurization Gypsum (4%, wt.)	788	1 004	5.67

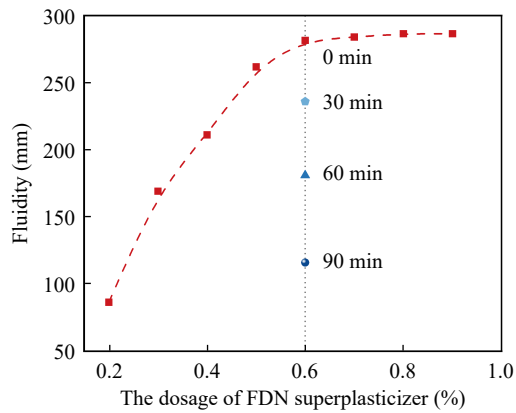


Fig. 1 The fluidity of paste with different dosage of FDN water reducer

value of 281 mm. When the dosage of water reducer was 0.6%, the fluidity decreased in turn at 30 mm, 60 mm and 90 min. The loss was 100 mm at 60 min, and 165 mm at 90 min, and the loss rate was 59%. It can be seen that under the action of water reducing agent, the fluidity of the composite cementitious material paste is good, and the water retention is good, indicating that the adaptability of steel slag powder and FDN series superplasticizer is good. When the amount of water-reducing agent is 0.6%, it has good fluidity and can meet the construction requirements of concrete.

3.1.2 Concrete slump

It can be seen from Figure 2 that the concrete with an initial slump greater than 180 mm can be prepared by adding steel slag-slag composite admixture. When the water-binder ratio and the amount of water reducer are kept unchanged, the initial slump of steel slag-slag concrete is about 5–10 mm higher than that of the control group. Slag powder and steel slag powder can reduce the time loss of slump to a certain extent, but a certain amount of activator will weaken this effect, which may

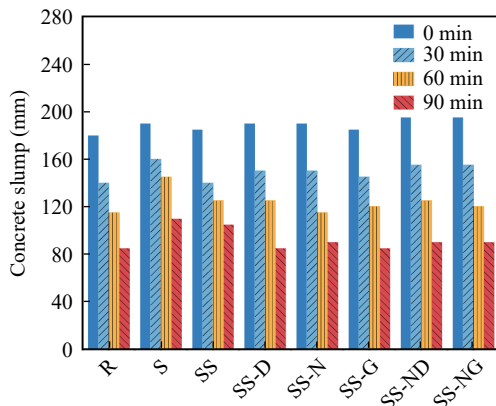


Fig. 2 The concrete slump and slump retention value

be related to the activator improving the activity of steel slag and promoting cement hydration^[15].

3.1.3 Setting Time

The setting time of steel slag-slag concrete is shown in Figure 3. It can be seen from Figure 3 that the initial setting time and final setting time of the test group are longer than those of the control group (R) to varying degrees. The initial setting time of the steel slag-slag composite admixture group is extended by nearly 35 min, and the final setting time is extended by 65 min. The initial setting time and final setting time are longer than those of the concrete with the same amount of slag powder. This is due to the substitution of steel slag and slag powder, and the amount of cement clinker is reduced. The early reaction of composite admixture is slow, and the activity of steel slag is lower than that of slag powder, so the setting time is prolonged^[15]. In addition, the effect of a single activator on the initial setting time is not significant, but the final setting time of cement-steel slag slurry is shortened. The composite activator of Na_2SO_4 and desulfurized gypsum shortens the final setting time by 60 min, and the initial-final setting time difference is shortened.

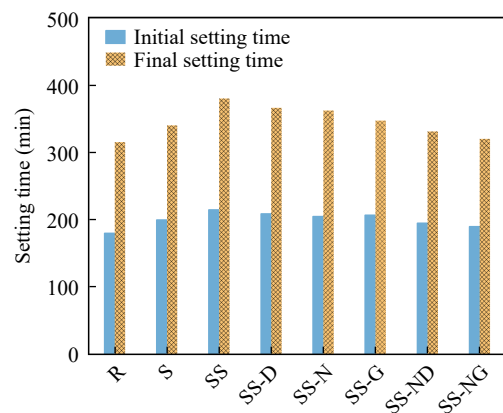


Fig. 3 The effect of activator on setting time

3.2 The effect of steel slag powder and activator on mechanical properties and durability of concrete

3.2.1 Mechanical property

Figure 4 shows the flexural strength of concrete at 7 d, 28 d, 60 d and 90 d. From Figure 4, it can be seen that the flexural strength of the group containing steel slag and slag powder is significantly lower than that of the control group at 7 d. The flexural strength of 28 d concrete mixed with steel slag and slag powder is close to

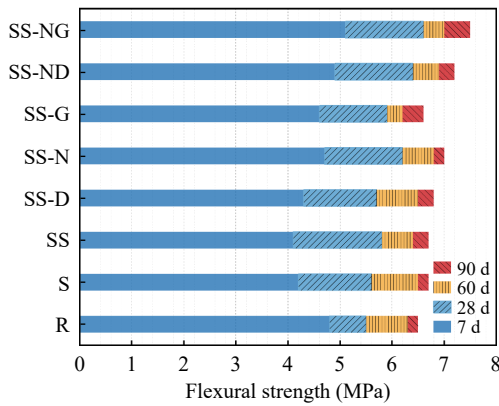


Fig. 4 The flexural strength of concrete

that of the reference concrete, and the flexural strength of 60 d and 90 d is slightly higher than that of the reference concrete. The flexural strength of concrete is significantly improved by three activators of desulfurization ash (2%, wt.), Na_2SO_4 (3%, wt.) and desulfurization gypsum (4%, wt.), especially Na_2SO_4 (SS-N). The contribution of flexural strength is larger, and the effect of Na_2SO_4 and desulfurization gypsum composite activator (SS-NG) on the flexural strength of concrete is greater than that of Na_2SO_4 and desulfurization ash composite activator (SS-ND) and single activator.

Figure 5 shows the compressive strength of concrete at 7 d, 28 d, 60 d and 90 d. It can be seen from Figure 5 that the 7 d compressive strength of concrete mixed with steel slag-slag powder is significantly lower than that of reference concrete, and also lower than that of concrete mixed with slag powder alone. The compressive strength of 28 d and later is slightly higher than that of the control group. The influence of the activator on the compressive strength of concrete is similar to that of flexural strength, that is, the three activators have a slight improvement effect on the 7 d compressive strength of con-

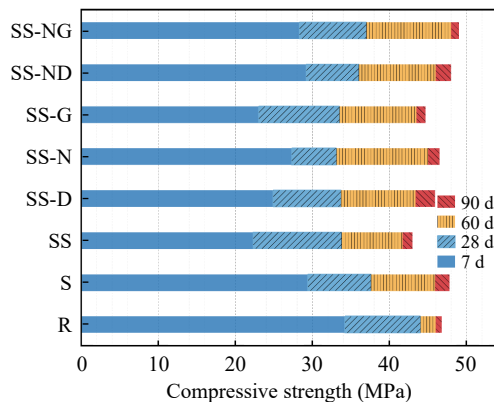


Fig. 5 The compression strength of concrete

crete mixed with steel slag-slag powder, and the improvement effect on the later compressive strength is not obvious, but the two composite activators have a significant improvement on the compressive strength of concrete, which shows that the excitation effect of single activator on steel slag is not as good as that of composite activator.

The key to the chemical excitation of steel slag is to create an alkaline environment in which the vitreous body in steel slag can be fully depolymerized and hydrated^[19]. Since the solubility of CaSO_4 is less than that of Ca(OH)_2 , the addition of Na_2SO_4 can increase the pH value of the liquid phase^[20]. Promoting the formation of ettringite is conducive to the development of early strength^[21]. At the same time, compared with gypsum as an activator, Na_2SO_4 has higher solubility and can provide SO_4^{2-} faster. The direct formation of AFt in the reaction^[15] avoids the process of mutual transformation between substances, and the structure can be stabilized earlier. This explains that the SS-N group can shorten the setting time of the system (Figure 3) and improve the early mechanical properties of concrete (Figures 4 and 5). Sodium sulfate and desulfurization gypsum can provide a large amount of sulfate and calcium ions for the formation of ettringite, while desulfurization ash can only provide calcium ions. Therefore, the composite activator of sodium sulfate and desulfurization gypsum has the most significant effect on the mechanical properties of steel slag-slag powder concrete.

3.2.2 Carbonation Resistance

The carbonation test was carried out on the specimens with standard curing for 28 d, and the results are shown in Figure 6. Compared with the reference concrete, the carbonation depth of concrete can be reduced to varying degrees by adding steel slag-slag powder, and this decreasing trend becomes more obvious with the prolongation of carbonation time. It shows that the incorporation of steel slag-slag powder composite admixture can improve the carbonation resistance of concrete to a certain extent. This is due to the incorporation of steel slag and mineral powder, which optimizes the particle gradation and improves the packing density of the system. At the same time, the carbonation depth of the steel slag-slag powder group (SS) is slightly higher than that of the single mineral powder group (S). After adding three ac-

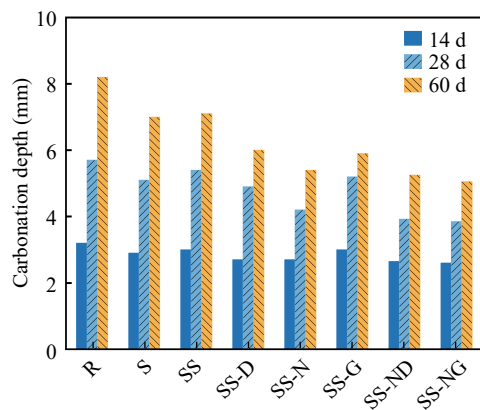


Fig. 6 The test results of concrete carbonation resistance

tivators, especially 3% Na_2SO_4 (SS-N), the carbonation depth of steel slag-slag powder concrete is significantly reduced, which is 23.9% lower than that of the SS group and 34.1% lower than that of the R group. At the same time, the two composite activators further reduce the carbonation depth of concrete. On the one hand, under the action of the activator, the pH of the concrete system increases, so that the activity of steel slag and slag powder is stimulated, and the generated reaction products fill the pores. On the other hand, both steel slag powder and slag powder contain about 40% CaO . After the activity of steel slag and slag powder is activated, the calcium ions in the system increase and CO_2 combines with calcium ions to form CaCO_3 , which is filled in the pores to improve the compactness of the matrix, so that the carbonization depth of the test group at 60 d is significantly lower than that of the control group.

3.2.3 The Resistance to Chloride Ion Permeability

Figure 7 is the result of 28 d chloride ion penetration resistance test of concrete. According to the classification of chloride ion penetration resistance of concrete in

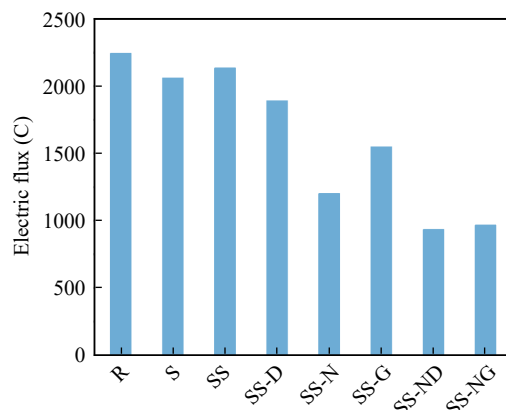


Fig. 7 The electric flux of concrete specimen

JGJ/T 193—2009, the chloride ion flux of R and S (slag group) and SS (steel-slag group) belongs to Qs- II grade, the three groups of single-doped activators belong to Qs- III grade, and the composite activator group belongs to Qs- IV grade. The results of chloride ion flux test show that the incorporation of steel slag and slag powder can reduce the chloride ion flux, and the addition of activator can further reduce the electric flux. In particular, 3% Na_2SO_4 (SS-N) significantly improves the chloride ion penetration resistance of steel slag-slag powder concrete, which is 43.7% lower than SS and 46.5% lower than R. The effect of composite activator is better than that of single activator.

Slag powder and steel slag powder have an active effect and filling effect. After the activity of slag powder and steel slag powder is activated, it can react with $\text{Ca}(\text{OH})_2$, and the reaction product fills the pores and blocks the capillary pores^[22], so that the pore size of the slurry is refined, the pore tortuosity is increased and the connected pores are reduced, the concrete compactness is improved, and the chloride ion transport coefficient is reduced. Studies have shown that due to the Na^+ provided by Na_2SO_4 , the glass in steel slag can be destroyed more thoroughly and decomposed more completely. The active $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ from steel slag dissociation react with Ca^{2+} to form hydrated calcium silicate, hydrated calcium aluminate and other products, and hydrated calcium aluminate reacts with SO_4^{2-} to form hydrated calcium sulphoaluminate^[23-24]. This reaction continuously promotes the decomposition and depolymerization of ionic groups, thus accelerating the hydration of steel slag minerals. On the other hand, at the same time, these hydration products are intertwined with each other to form a network structure, which quickly fills and plugs capillary pores, accelerates the condensation of composite cementitious materials and reduces porosity. And steel slag has a certain degree of improvement on the interface area^[25]. The activity of steel slag under three activators of desulfurization ash, desulfurization gypsum and Na_2SO_4 is improved, which further improves the microstructure of offshore concrete, the mechanical properties and the durability of concrete.

4 Conclusions

(1) The concrete with the initial slump greater than

180 mm can be prepared by adding steel slag-slag composite admixture and FDN series superplasticizer. Slag powder and steel slag powder can reduce the time loss of slump to a certain extent, and the effect of activator on fluidity is not obvious. Steel slag will significantly prolong the setting time of the system, and the single activator shortens the final setting time of the cement-steel slag slurry. The composite activator of Na_2SO_4 and desulfurization gypsum shortens the final setting time by 60 min.

(2) The three single-doped activators can improve the mechanical properties of steel slag-slag concrete, and the effect of 3% Na_2SO_4 and 4% desulfurized gypsum composite activator on the mechanical properties is more significant.

(3) The steel slag-slag powder composite admixture can improve the carbonation resistance of concrete. Three activators can further improve the carbonation resistance of steel slag concrete, and the composite activator of sodium sulfate and desulfurization gypsum has the best effect.

(4) The addition of steel slag and slag powder reduces the chloride ion electric flux, and the addition of activator can further reduce the electric flux. Especially when desulfurization gypsum and sodium sulfate are used as activators at the same time, the chloride ion penetration resistance of steel slag-slag powder concrete is significantly improved. By adding activator, the chloride resistance and carbonation resistance of concrete such as offshore highways and bridges can be improved.

Declaration of competing interest

The author has no competing interests to declare that are relevant to the content of this article.

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