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Recycling waste Nix particles for ultra-high-performance concrete: A practical way towards the sustainability

Nguyen Cong Thang[1,2*], Tran Duc Binh[2,3], Phung Quoc Tri[2,4], Nguyen Van Tuan[1,2]

[1] Faculty of Building Materials, Hanoi University of Civil Engineering, 55 Giai Phong road, Hai Ba Trung district, Hanoi, Vietnam

[2] Key research group of Advanced Building Materials (HUCEMAT), Hanoi University of Civil Engineering, 55 Giai Phong road, Hai Ba Trung district, Hanoi, Vietnam

[3] Faculty of Construction Economics and Management, 55 Giai Phong road, Hai Ba Trung district, Hanoi, Vietnam

[4] Expert Group Waste and Disposal, Belgian Nuclear Research Centre (SCK CEN), Boeretang 200, 2400, Mol, Belgium

KEYWORDS

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Mechanical properties
Chloride ion penetration resistance

ABSTRACT

Research on Ultra-High-Performance Concrete (UHPC) has demonstrated the feasibility of utilizing various types of industrial and agricultural waste as partial substitutes for cement or aggregates. Previous studies have mainly focused on using waste materials as mineral admixtures to replace cement in UHPC. However, it is worth noting that sand, a key ingredient in UHPC, constitutes a significant proportion of the concrete's mass, accounting for approximately 50%. Therefore the use of sand in large volumes can adversely affect natural resources and lead to increased costs. This study investigates the possibility of using Nix particle waste from ship cleaning as partial or complete substitute for quartz sand in UHPC. Experimental results show that Nix particle waste, which has been cleaned with an average particle size of about 300 µm, can be used to produce UHPC with high flowability, compressive strength exceeding 120 MPa, and high chloride ion penetration resistance. Furthermore, a life cycle assessment of concrete mixes reveals that incorporating Nix particles as a sand substitute enhances the environmental performance of the concrete. This is evident in the reduction of all six environmental impact assessment indicators. It is important to note that although the reduction levels are not substantial, ranging from 0.95 % to 6.44 % depending on the specific indicator, the utilization of waste materials presents socio-economic benefits by reducing the need for waste treatment activities and promoting resource efficiency, as natural sand is used in large quantities.

1. Introduction

The global construction industry is making major changes in minimizing its impact on the environment and protecting natural resources. The focus of this revolution is research, the application of new or advanced materials and processes, and the reuse or recycling of waste materials to reduce manufacturing energy and environmental impacts. In the development of advanced concrete systems, ultra-high performance concrete (UHPC) has become a potential construction material, characterized by excellent mechanical properties and durability such as compressive strength greater than 120 MPa, flexural strength up to 15 MPa, elastic modulus up to 45 GPa and excellent durability when working in aggressive environments [1-3]. With these great characteristics, UHPC can address the economic problem by reducing the cross-sectional area of the structure, increasing maintenance time as well as extending the life of the project.

In terms of materials used to make concrete, UHPC constitutes about 40-50 % binder (CKD), 50 % sand by weight of concrete (800-1200 kg/1 m^3 of concrete), about 10-20 % mineral admixtures (by weight of binder), dispersed steel fiber (about 2 % by volume of concrete), water and chemical admixtures [4-6]. Thus, it can be seen that the use of both cement and aggregates (usually quartz sand) in very large quantities will pose environmental challenges and scarcity of natural resources. Overexploitation of natural materials not only causes habitat destruction but also affects the ecosystem, consumes significant energy, and has adverse impacts on the environment. Currently, researchers are actively looking for alternative material sources, especially the use of industrial and agricultural waste and construction demolition waste. By recycling waste, it is possible to reduce dependence on resources, minimize the amount of solid waste and reduce environmental pollution. Furthermore, the use of waste in concrete production can improve technical properties while bringing economic and environmental benefits.

One of the waste materials used in this study is waste Nix particles, which is a type of granular material formed from iron, limestone, and silica during the copper smelting process. During this refining process, due to sudden solidification from the molten state by

*Corresponding author: thangnc@huce.edu.vn

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the blowing of cold air and washing with high pressure steam, the finished product is copper slag. [7]. Copper slag (Nix particles) is a by-product of copper extraction by smelting, which is then collected, classified and refined into hard, black particles.

Nix particles are used to clean ship hulls, then emitted during this process will include dust, grease, paints, etc. Although Nix particles are highly effective and economical, many countries do not encourage their use because after cleaning the ship's hull and being released into the environment, they cause very serious dust and noise pollution. In the dust composition, there is dust from paint peeling off from the ship's hull, dust from metal rust, grease but the main component is dust from Nix particles after spraying. In the mixture, there contains many impurities and many toxic heavy metals that negatively affect the soil, water and air environment due to exceeding allowable standards and endangering public health, it can cause death if using groundwater highly contaminated with Nix. In addition, Nix particles that are washed after use are completely inert materials and do not react with water, and have no negative impact on the environment. With a fineness modulus of about 2.0 and a mean particle size of about 300 μm, Nix particles are considered suitable to substitute sand in producing concrete [8-10].

This paper presents research findings on the impact of incorporating Nix particles as a substitute for sand in Ultra-High Performance Concrete on various mechanical properties and resistance against chloride ion penetration. Moreover, this study employs the life cycle assessment method to effectively evaluate the environmental implications associated with employing waste Nix particles as a replacement for sand in order to promote sustainable development of UHPC concrete in Vietnam.

2. Materials and methods

2.1. Materials

In this study, Portland cement PC40 Nghi Son (C), Condensed silica fume (SF) from Elkem were used to produce UHPC. The physical and mechanical properties of the cement comply with Vietnamese standard TCVN 2682:2009. The physical and mechanical properties of cement and silica fume are shown in **Error! Reference source not found.**. Polycarboxylate-based superplasticizer (SP) with powder form was used for controlling the workability of UHPC mixtures. Straight steel fiber was a commercial product of Dramix with 13 mm in length, 0.2 mm in diameter (l/d=65) and tensile strength of 2750 MPa. The chemical properties of cement and SF were shown in Table 2.

Quartz sand (S) and Nix particles (N) were used as aggregate. Quartz sand with a mean particle size of 300 μm, with density of 2.64 g/cm^3. Waste Nix particles were washed and sieved using the 0.14 mm sieve in order to remove clay and organic impurities. The physical and mechanical properties of Nix particles are shown in Table 3. Some photos of Nix particles on the site and after being washed are shown in Figure 1.

Table 1. Physical properties of cementitious materials.

Properties		Units	Cement	SF
Retained percentage on 0.09 mm sieve		%	0.58	-
Specific gravity			3.15	2.20
Standard consistency		%	29.5	
Setting time	Initial	Min.	115	
	Final	Min.	225	
Strength activity index		%		113.5
Mean particle size		μm	11.4	0.15
Compressive strength	3 days	MPa	29.8	-
	28 days	MPa	52.2	-

Table 2. Chemical composition of cementitious materials.

Materials	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	L.O.I
Cement, wt.%	20.60	5.13	3.56	63.26	3.07	0.24	0.25	-	1.86
Silica fume, wt.%	92.30	1.91	0.86	0.32	0.85	0.38	1.22	0.30	1.68

Note: L.O.I: Loss on Ignition

Table 3. Mechanical properties of Nix particles.

No	Properties	Units	Value	Note			
1	Specific gravity		3.48				
2	Water absorption	%	0.16				
3	Fineness modulus	-	2.236				
4	Particle size distribution						
	Sieve, mm	2.5	1.25	0.63	0.315	0.14	<0.14
	Mass, g	2.6	50.2	407.5	305.9	187.8	42.5
	Fraction content, % retained	0.26	5.02	40.75	30.59	18.78	
	Cumulative distribution, %	0.26	5.28	46.03	76.62	95.4	

(a) Nix particles on the site (b) Nix particles after washing

Figure 1. Nix particles used in the study.

2.2. Testing methods

Determine the flow of freshly mixed UHPC was measured using a flow table test in accordance with Test Method ASTM C1437 [11]. The mold and flow table met the requirements of ASTM C230/C230M. Testing apparatus and flow testing of UHPC mixtures are shown in Figure 2 and Figure 3.

Figure 2. Mini-cone test.

Figure 3. Flow testing of UHPC mixtures.

The density of UHPC was measured according to TCVN 3115:2022, with the exceptions described in this section. UHPC sample size of 50 × 50 × 50 mm was used in this measurement.

Compressive strength of UHPC was determined on a sample with dimensions of 50 × 50 × 50 mm (Figure 4). After casting, the samples were cured under standard conditions, with temperature at 27 ± 2ºC, relative humidity exceed of 95 % until the testing. The load was applied at a stress rate on the sample of 1.0 ± 0.05 MPa/s.

Figure 4. Casting and UHPC samples.

The chloride ion penetration resistance of UHPC samples was performed according to ASTM C1202 [12]. The experimental method is based on the principle of measuring the charge transmitted through a cylindrical concrete sample with a diameter of 100 mm and a thickness of 50 mm over a period of 6 hours. One DC potential of 60 V was applied to both sides of the cylindrical sample where one side was contacted with the NaOH solution, the other side was contacted with the NaCl solution. UHPC samples were tested at the age of 28 days. Under the effect of an electric field, chloride ions will diffuse through the capillary pores, forming an electric current. The total current transmitted, in measured coulombs, is related to the chloride ion resistance of the concrete. The test samples and chloride ion permeability test procedure are shown in Figure 5 and Figure 6.

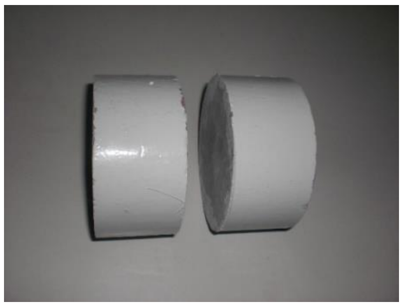

Figure 5. UHPC samples for test.

Figure 6. Applied voltage cell.

2.3. UHPC mix compositions

Based on the research that has been done on optimizing granular composition and selecting material composition for UHPC [13, 14], the sand-to-binder (s/b) ratio was fixed to 1.0. The binder (b) herein is the total of the cement and silica fume, in which SF revealed a value of 20 % by mass of binder; six UHPC mixtures were proposed which had the same water to binder ratio of 0.16 (w/b = 0.16); The superplasticizer (SP) was used to control the workability of the mixtures, with dosages of 1.0 % by mass of binder. The weight of steel fiber was calculated with 1 % by vol. of the UHPC mixture. Quartz sand was substituted by Nix particles ranging from 0 % to 100 % by vol. Details of the mixture composition are summarized in Table 4. It should be noted in Table 4 that the concrete mixtures for N0–N20–N40–N60–N80–N100 corresponds to replacing sand by 0–20–40–60–80–100 % Nix particles, respectively.

Table 4. Mix proportion of UHPC mixtures

Mix	Concrete constituents, kg/m^3						
	Cement	Sand	Nix particles	Silica fume	SP	Water	Steel fiber
N0	880	1100	0	220	11	176	78.5
N20	880	883	290	220	11	176	78.5
N40	880	663	580	220	11	176	78.5
N60	880	442	870	220	11	176	78.5
N80	880	221	1160	220	11	176	78.5
N100	880	0	1450	220	11	176	78.5

3. Results and discussions

3.1. Flowability of UHPC mixtures

Experimental results of the effect of the Nix particle content on the workability of UHPC mixtures are shown in Figure 7. It can be seen that the flowability of UHPC mixtures tends to slightly increase with the increase in Nix particle content of up to 40 %. However, the flowability significantly increases with the Nix particle content of 80 % and 100 %, about 9 % higher compared to that of the control sample (0 % of Nix particles). The improvement of flowability of UHPC mixtures can be explained by the fact that the Nix particles have a spherical shape, smooth surface after spraying to clean the steel surface of the ship, and especially do not absorb water. This can help improve the flowability of the concrete mixture.

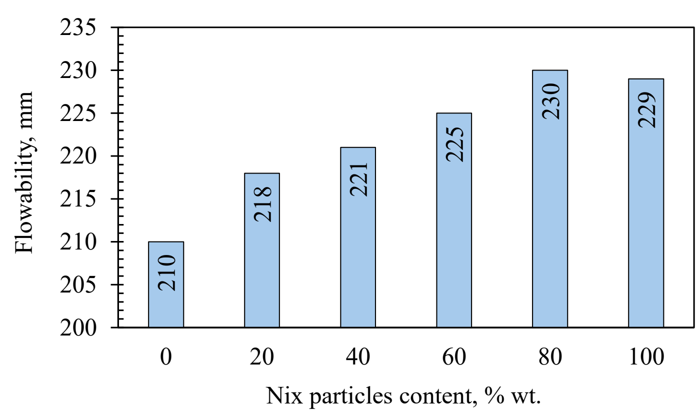

Figure 7. Flowability of UHPC mixtures.

3.2. Unit weight of UHPC

Figure 8 shows the effect of Nix particle content to the unit weight of UHPC mixtures. Experimental results show that the unit weight of concrete mixtures increases with increasing the Nix particle content. This can be explained because the density of Nix is 3.48 g/cm^3, larger than that of sand (2.64 g/cm^3) and the volume of aggregate is kept constant. It should be noted that the substitution of 20 % Nix particles increases the unit weight of concrete but not significantly, about 4 % compared to the control sample. When substituting Nix particles up to 60 %, 80 % and 100 %, the unit weight of concrete increases gradually by 11 %, 15.5 % and 18 %, respectively, compared to the control sample. The highest unit weight is attained 2820 kg/m^3 with the substitution of 100 % Nix particles. The results reveal that a very heavy weight concrete for nuclear power plants or other structures can be made by this substitution.

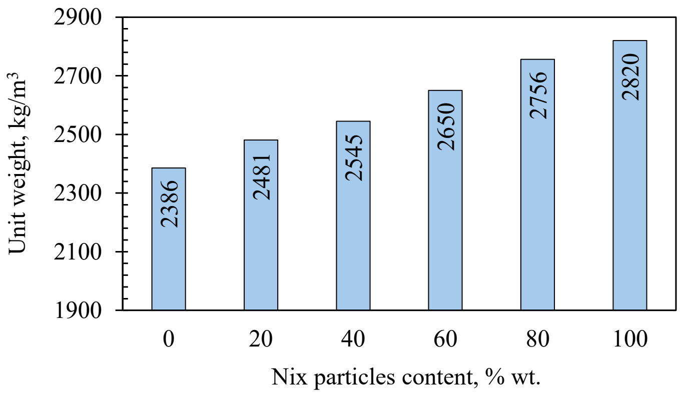

Figure 8. Effect of the Nix particle content on the unit weight of UHPC mixtures.

3.3. Compressive strength of UHPC

Figure 9 shows the effect of Nix particle content on the compressive strength of UHPC samples at different ages. Experimental results show that the 28-day compressive strength of the control sample (using 0 % Nix) achieved over 161 MPa. When increasing the Nix particle content to 40 %, the 28 day-compressive strength of UHPC is not changed significantly, i.e. 6 % lower compared to that of the control sample. However, this reduction is very small, within the deviation range. Whereas, for the sample with a higher Nix particle content of 80 and 100 %, the strength developments were a bit lower, i.e., 16.5 % and 20.3 %, respectively. With substituting 100 % Nix particles, the 28 day-compressive strength of concrete can reach the maximum value of 128.5 MPa. Although the strength is reduced when substituting 100 % Nix particles, the strength of UHPC still attained over 120 MPa. The reduction in strength of concrete when using Nix particles can be explained by the presence of flat particles in the composition, the surface of the particles being very inert and smooth, and especially on the surface of the particles there is still grease, not too cleaned, which will affect the bond between the surface of Nix particles and the matrix.

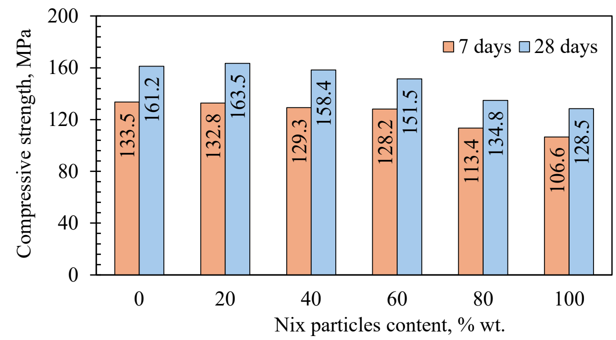

Figure 9. Effect of the Nix particle content on the compressive strength of UHPC.

3.4. Chloride ion penetration resistance of UHPC

Penetration of chlorides through concrete is one of the factors which aimed at the depassivation of reinforcing bars and thus, may shorten the service life of the structure. The ions pass through the sample by the pore solution of concrete, which acts as an electrolyte. As the amount and continuity of pores existing in concrete samples affect the passage of ions and thus affect the current rate, it is expected that porous samples with continuous pores have high passing ions, and samples with low porosity have low passing ions. The time needed by these ions to reach the rebar depends first, on the mechanism of intrusion and secondly, on the external concentration of the chlorides and the microstructure of the concrete. In UHPC, the low water-to-binder (W/B) ratio and the use of silica fume will lead to the formation of a very dense microstructure in the hardened paste [15], which greatly reduces the permeability. UHPC differs from conventional concrete not only in terms of strength, but also in terms of durability. Therefore, chloride ion penetration is one of the important criteria of UHPC to increase the durability of UHPC structures.

In this study, three UHPC samples were selected to evaluate the effect of Nix particle content on the chloride ion penetration of UHPC samples containing different Nix particle contents of 0 % (a control sample-N0), 60 % (N60) and 100 % (N100). The chloride ion penetration test was performed according to ASTM C1202. The test results in Table show that the substitution of Nix particles seems to have no effect on the resistance to chloride penetration. According to ASTM C1202 and the chloride penetration results shown in Table , three UHPC samples in this study can be considered as having “negligible” effect on chloride penetration.

Table 5. Chloride ion penetration test results.

Sample	Chloride ion penetration, Coulombs
N0	36
N60	38
N100	56

3.5. Environmental impact assessment of UHPC using waste Nix particles

The environmental impacts of UHPC using waste Nix particles to substitute sand are measured by six indicators as recommended by the Green Building Rating System LEED (Leadership in Energy and Environmental Design) [16] as shown in Table 6. These indicators will then be calculated based on the Ecoinvent 3.10 database (Table 7) [17], using Life Cycle Impact Assessment method (LCIA) CML v4.8 2016 [18].

Table 6. Environmental impact indicators of UHPC using waste Nix particles [16].

No	Indicators	Unit	Symbol
1	Global Warming Potential	kg CO_2-Eq	GWP
2	Ozone Depletion Potential	kg CFC 11-Eq	ODP
3	Acidification Potential	kg SO_2-Eq	AP
4	Photochemical Ozone Creation Potential	kg ethylene-Eq	POCP
5	Eutrophication Potential	kg PO_4-Eq	EP
6	Abiotic Depletion Potential	MJ	ADP

Six UHPC samples were made from different mix compositions as shown in Table 4. As presented above, Nix particles are a waste product from ship hull cleaning activities. Nix released during this process is washed and transported to the UHPC production site. Therefore, the environmental impacts of the production process (smelting copper and cleaning ship hulls) of Nix particles will not be taken into account. Only one activity of washing Nix particles was taken into account in which 1 m^3 of water was consumed to clean 3.48 tons of Nix particles. The environmental impact of Nix particles is shown in Table 8.

Table 7. Use of data sets.

No	Material	Data set	Unit	Geography
1	Cement	Cement OPC, EPD, INSEE	kg	Vietnam
2	Silica fume	Market for silica fume, densified	kg	GLO
3	Quartz sand	Silica sand production	kg	RoW
4	Water	Tap water production, conventional treatment	kg	RoW
5	Superplasticizer	Polycarboxylates production, 40 % condensed	kg	RoW
6	Steel fiber	Dramix® steel fibers, EPD 215/2021	kg	EU
7	Nix particles (copper slag)	Calculation	kg	Vietnam

Table 8. Environmental impacts of 1 kg of Nix particles (copper slag) used in producing UHPC.

Process	Data set	Geography	GWP	ODP	AP	POCP	EP	ADP
Water	Tap water production, conventional treatment	RoW	1.26×10^{-4}	8.07×10^{-13}	5.78×10^{-7}	3.22×10^{-8}	2.44×10^{-7}	1.33×10^{-3}

Other raw materials are imported and used locally, so environmental impacts during the exploitation and production process, except transportation, are taken into account. The results of calculating the environmental impact of 6 UHPC samples are shown in Figure 10.

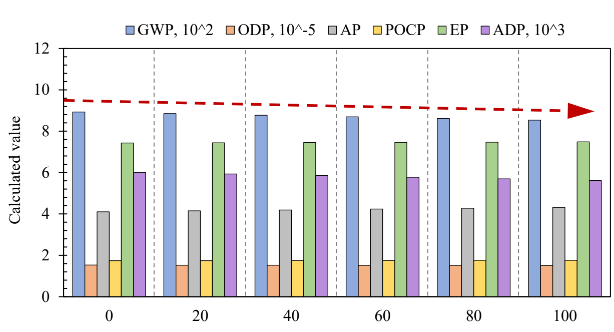

Figure 10. Environmental impacts of six UHPC samples.

The results in Figure 10 show that when increasing the Nix particle content to gradually substitute quartz sand, all environmental impact indicators are improved. Regarding the GWP indicator, the control UHPC sample without Nix particles emits greenhouse gas emissions equivalent to 892.7 kg CO_2, but this emission was reduced to 885.1 kg CO_2 when increasing Nix particle content up to 20 %. This demonstrates that using Nix to substitute sand is effective in reducing the environmental impact of UHPC production. When increasing the Nix particle content to 40, 60, and 80 %, the GWP indicator of UHPC decreases by 1.72, 2.59, and 3.46 % respectively, compared to the control sample. Especially, the substitution of 100 % Nix particles achieves the best GWP indicator of 854.1 kg CO_2, meaning that 4.32 % of greenhouse gas emissions are reduced.

The analysis also shows similar results for the remaining five environmental indicators, namely ODP, AP, POCP, EP and ADP. UHPC samples with higher Nix particle content have a lower environmental impact. Among these six indicators, the one with the greatest improvement is ADP, a decrease of 6.44 %, followed by AP with a decrease of 6.4%. The ODP, POCP and AP indicators have the lowest decrease, 1.29; 0.95 and 0.95 % respectively. It is clear that using Nix particles to substitute sand in producing UHPC brings better environmental performance, expressed by the impact reduction in all six assessment indicators, however, the reduction is not significant.

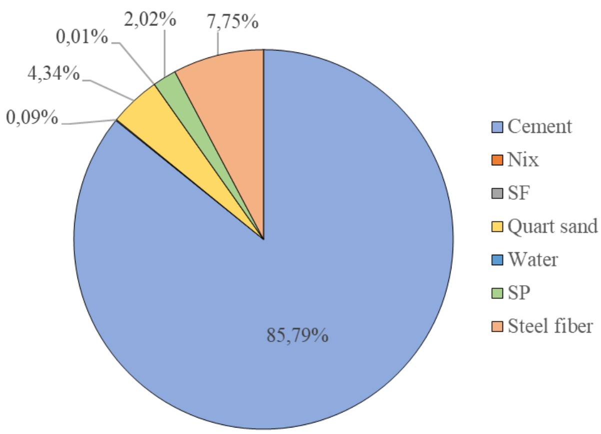

Figure 11. GWP contribution of UHPC sample's components (60 % Nix)

The better environmental impacts can be explained because the contribution of quartz sand to the environmental impact of UHPC is insignificant. Although quartz sand accounts for 44.6 % by wt. of the UHPC, it only contributes 4.34 % to the GWP indicator (Figure 11). Therefore, more sand is substituted by Nix particles, more the environmental impact of UHPC can be reduced. The waste Nix particles are a by-product discharged after two operations (copper smelting and ship hull washing), it is no longer of use value and is usually disposed of by landfilling. However, when substituting sand to produce UHPC, this will help significantly reduce copper slag waste, and also help save copper slag waste treatment activities. From there, it brings invisible effects to the environment, economy and society.

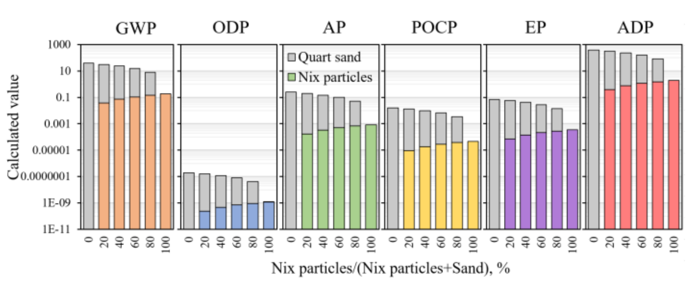

Figure 12. The environmental impact assessment indicators of UHPC using waste Nix particles to substitute quartz sand.

Figure 12 represents the reduction level of six environmental impact assessment indicators calculated for six UHPC samples with Nix particle content ranging from 0 to 100 %. The composition of the six UHPC samples only differs in the content of quartz sand and Nix, the remaining components are the same. Therefore, the emission reduction effect only comes from these two materials. The GWP indicator shows that using Nix to substitute quartz sand in this study helps reduce greenhouse gas emissions by an amount equivalent to 38.60 kg CO_2, similarly reduced 1.97×10^{-7} kg CFC 11-Eq (ODP), 0.25 kg SO_2-Eq (AP), 0.02 kg ethylene-Eq (POCP), 0.07 kg PO_4-Eq (EP), and 386.59 MJ (ADP).

4. Conclusions

Based on research findings regarding the properties and environmental impacts of Ultra-High Performance Concrete using waste Nix particles as a substitute for sand, several conclusions can be drawn:

- It is feasible to utilize waste Nix particles in the production of UHPC while still ensuring adequate compressive strength and durability. The incorporation of Nix particles enhances the flowability of the concrete mixture. Specifically, substituting 80 % of the sand with Nix particles increases the workability of the concrete mixture by 9 % compared to the control sample. Furthermore, when 100 % of the sand is replaced by Nix particles, the unit weight of the concrete reaches 2820 kg/m^3.

- The substitution of Nix particles up to 40 % does not have an impact on the compressive strength of UHPC. However, as the content of Nix particles increases, the compressive strength decreases. For instance, when substituting 80 % and 100 % of the sand with Nix particles, the compressive strength of the concrete is reduced by 16.5 % and 20.3 % respectively, in comparison to the control sample. On the other hand, the substitution of Nix particles does not affect the chloride ion resistance of UHPC. When substituting sand up to 60 % and 100 % with Nix particles, the level of chloride ion penetration remains impermeable.

- The use of Nix particles as a substitute for quartz sand in UHPC production contributes to an improvement in the environmental performance of the concrete. This is evidenced by a decrease in six environmental impact assessment indicators. The environmental impact reduction percentages are as follows: 6.44 % for abiotic depletion potential (ADP), 6.4 % for acidification potential (AP), 4.32 % for global warming potential (GWP), 1.29 % for ozone depletion potential (ODP), 0.95 % for photochemical ozone creation potential (POCP), and 0.95% for eutrophication potential (EP). Notably, the maximum reduction in global warming potential amounts to 38.6 kg CO2-Eq in the UHPC sample containing 100 % Nix particle content.

Although there is an improvement in environmental performance, its significance remains limited. This is due to the fact that emissions from quartz sand only represent a small portion of the total emissions associated with UHPC. However, the substitution of Nix particles also brings about socio-economic benefits by reducing waste and waste treatment activities.

Acknowledgements

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