Characterisation of Taal Volcanic Ash as a Potential Raw Material for the Construction Industry

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Abstract

The phreatomagmatic eruption of Taal Volcano in Batangas, Philippines, in January 2020 resulted in a massive ash plume covering a large portion of nearby provinces, including Metro Manila. This event caused damage and disruptions to various sectors, including agriculture, the environment, health, infrastructure, and aviation. The challenge of managing the vast amount of collected tephra environmental waste prompted the initiative of converting it into a useful material. This study characterizes and evaluates the quality of the collected tephra as a potential raw material for the construction industry, based on the Philippine National Standard (PNS) 07:2018, to ensure structural integrity and public safety.

Four ashfall samples from strategic locations, identified by the Philippine Institute of Volcanology and Seismology (PHIVOLCS), were obtained and analysed for specific chemical parameters using various analytical techniques. The results suggest that tephra has potential as a raw material for ground-level structures. However, further treatment is necessary to reduce the concentration of certain constituents. The material met the standard specifications for SiO₂, MgO, and SO₃. However, the levels of Al_2O_3 , Fe₂O₃, total alkali, loss on ignition, and water-soluble and acid-soluble Cl⁻ exceeded the threshold limits set by PNS 07:2018 and EN 197-1:2000.

Keywords

Volcanic ash, construction materials, chemical analysis, oxides, waste management

1 Introduction

In January 2020, the Taal volcano, located in Batangas, Philippines, exhibited a phreatomagmatic eruption.¹ Since it is situated in the middle of a lake, the interaction of magma with water resulted in the explosive ejection of water, steam, and volcanic fragments.² Ashfall subsequently occurred, and the dispersion of emitted ash reached nearby provinces, such as Laguna, Cavite, Rizal, Bulacan, and Metro Manila. This phenomenon caused disruptions to various sectors, including agriculture, the environment, health, infrastructure, and aviation. The damages incurred in the agricultural sector alone were estimated at 3.150 billion pesos.³ Addressing the problem of the vast amount of tephra waste collected from cleaning establishments, buildings, and houses blanketed by wet ash was a primary concern of the local government units and residents after the disaster. This prompted collaboration with the government agencies responsible. Given that several studies have investigated the suitability of tephra waste as an additive in the manufacture of cement, this study evaluated the volcanic ash for its potential as a raw material in cement production.^{4–7} Cement, along with aggregates and water, is one of the key ingredients in making concrete. It is composed of several chemical compounds, the quantities of which

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Note: The findings of this study were presented at the 1st European GREEN Conference (1st EGC), held on May 23–26, 2023, Vodice, Croatia.

dictate its characteristics. These include silica (SiO₂), lime (CaO), alumina (Al₂O₃), ferric oxide (Fe₂O₃), titania (TiO₂), magnesia (MgO), alkalis (Na₂O and K₂O), water content and carbonates, and sulphate (SO₄²⁻). Each of these components influences the properties of the cement, such as durability, setting time, and colour, among others. Therefore, the right formulation is key to achieving the desired property of the cement.⁸⁻¹⁰ Since the chemical and physical properties of construction materials are crucial to structural integrity, the Bureau of Product Standards Technical Committee on Cement and Lime (BPS/TC 3) has set the technical specifications for Portland cement. The Bureau of Philippine Standards – Department of Trade and Industry (BPS-DTI) approved these specifications for adoption in 2018 as the Philippine National Standard (PNS) 07:2018. In terms of chemical properties, it has specified limits for SiO₂, Al₂O₃, Fe₂O₃, MgO, loss on ignition (LOI), insoluble residue, tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), $C_3S + 4.75C_3A$, tetracalcium aluminoferrite + tricalcium aluminoferrite ($C_4AF + 2C_3A$) or $C_4AF + C_2F$, equivalent alkalis (Na₂O + 0.658 K₂O), and sulphur trioxide (SO₃).¹¹

This study aimed to conduct a preliminary characterisation of the Taal Volcano ashfall from strategic locations impacted by the plume caused by the January 2020 Taal Volcano eruption. Specifically, the study: (1) characterised the Taal Volcano ashfall for complete chemical analysis (SiO₂, Al₂O₃, TiO₂, Fe₂O₃, CaO, MgO, Na₂O, K₂O, loss on ignition), acid-soluble and water-soluble sulphate, and ac-

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id-soluble and water-soluble chloride; and (2) evaluated the quality of the ashfall as a potential construction material against the criteria set by PNS 07:2018 and European Standard EN 197-1:2000.²⁹

2 Experimental

2.1 Sampling

Tephra samples were collected from the four strategic locations identified by PHIVOLCS. Fig. 1 shows the geographical locations (latitude and longitude) where the samples, coded as B13, B48, B73, and B78, were obtained. One location (B73) was near the centre of the volcano, while the other three locations (B13, B48, and B78) were near the periphery of the volcano.

2.2 Characterisation

Various analytical techniques were used to determine the metal oxides, and water-soluble and acid-soluble Cl⁻ and $SO_4^{2^-}$ in the volcanic ash samples. Gravimetric techniques were employed to analyse LOI and SiO₂. Titrimety was utilized for Al₂O₃ and acid-soluble Cl⁻. Flame atomic absorption spectrophotometry was used for Na₂O, K₂O, CaO, MgO, and Fe₂O₃. Ion chromatography was applied to measure water-soluble Cl⁻ and water-soluble $SO_4^{2^-}$. UV-visible spectrophotometry was used for the analysis of TiO₂ and acid-soluble $SO_4^{2^-}$. Table 1 shows the specific methods used in the determination.



Fig. 1 – Tephra sampling sites

Test parameter	Test method	Remarks (comparison against BS EN 196-2:1995 ²⁷ and 196-21:1992 ²⁸)
Silica (SiO ₂)	JIS M 8853:1998 ²⁰	Similar except that the cement is fused with Na_2CO_3 first before addition of HCl, and no NH_4Cl is used
Alumina (Al ₂ O ₃)	ASTM C 25 – 93a ²¹ (modified)	Both use EDTA as titrant, but work at different pH ranges
Ferric oxide (Fe ₂ O ₃)	JIS M 8853:1998 ²⁰	Both use EDTA as titrant, but work at different pH ranges
Loss on ignition (LOI)	JIS M 8853:1998 ²⁰	Similar
Titania (TiO ₂)	JIS M 8853:1998 ²⁰	
Calcium oxide (CaO)	JIS M 8853:1998 ²⁰	Both use EDTA as titrant, but work at different pH range and use different indicators
Magnesium oxide (MgO)	JIS M 8853:1998 ²⁰	Both use EDTA as titrant, but work at different pH range and use different indicators
Sodium oxide (Na ₂ O)	JIS M 8853:1998 ²⁰	Flame atomic absorption spectrophotometer was used instead of flame photometer
Potassium oxide (K_2O)	JIS M 8853:1998 ²⁰	Flame atomic absorption spectrophotometer was used instead of flame photometer
Acid-soluble chloride (Cl-)	ASTM C1152/C1152M – 04 ²² (modified, titrimetry)	Both use Volhard method
Water-soluble chloride (Cl ⁻)	ASTM C 1218/ C1218M – 99 ²³ (modified, ion chromatography)	
Acid-soluble sulphate (as SO ₃)	CS3:2013 ²⁴ /US EPA 9038 ²⁵ (modified)	Sample preparation part is the same, but the gravimetric technique is replaced by UV-visible spectrophotometry
Water-soluble sulphate (as SO_3)	ASTM C 1580 – 15 ²⁶ (modified, ion chromatography)	

Table 1 – Test method for each parameter

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Test parameter		Result (DNIC 07,2010 (trues II)		
lest parameter	B13	B48	B78	B73	PINS 07:2018 (type II)
SiO ₂ , % w/w	51.9	50.8	50.6	50.6	20.0 min.
Al ₂ O ₃ , % w/w	13.2	17.0	15.1	15.1	6.0 max.
Fe ₂ O ₃ , %w/w	10.8	11.5	10.8	11.0	6.0 max.
LOI, %w/w	7.15	5.47	6.11	7.47	3.0 max.
TiO ₂ , %w/w	0.942	0.964	0.927	0.890	_
CaO, %w/w	7.91	7.99	6.79	7.79	-
MgO, %w/w	3.09	2.93	2.74	2.85	6.0 max.
Na ₂ O, %w/w	3.66	3.46	3.23	3.40	
K ₂ O, %w/w	1.73	1.76	1.71	1.65	0.60 max.
Total alkali (Na ₂ O + 0.658 K ₂ O), % w/w	4.80	4.62	4.36	4.49	

Table 2 – Measurement results for oxide analyses of tephra samples

2.3 Evaluation

For most of the parameters, the quality of the ashfall as a raw material for the production of cement was evaluated using PNS 07:2018. This included SiO₂, Al₂O₃, Fe₂O₃, MgO, loss on ignition (LOI), equivalent alkalis (Na₂O + 0.658 K₂O), and acid-soluble and water-soluble SO₄^{2–} (as SO₃). Meanwhile, the acid-soluble and water-soluble Cl⁻ concentrations were evaluated against the requirements of EN 197-1:2000.

3 Results and discussion

3.1 Oxide analyses of tephra samples

Table 2 depicts the measurement results of the oxide analyses conducted for the tephra samples collected from the four sampling sites. SiO_2 , Al_2O_3 , Fe_2O_3 , and CaO are the primary components of cement, as they are involved in forming the four major compounds that mainly contribute to the properties of cement, such as strength, setting time, and colour. These compounds are alite or tricalcium silicate (C₃S or 3CaO \cdot SiO₂), belite or dicalcium silicate $(C_2A \text{ or } 2CaO \cdot SiO_2)$, celite or tricalcium aluminate $(C_3A$ or $3CaO \cdot Al_2O_3$) and felite or tetracalcium aluminoferrite $(C_4AF \text{ or } 4CaO \cdot Al_2O_3 \cdot Fe_2O_3)$. Alite and belite are the constituents mainly responsible for concrete strength, as their hydration results in the production of calcium silicate hydrate or C–S–H gel (3CaO \cdot 2SiO₂ \cdot 3H₂O). Celite does not significantly contribute to the strength and is responsible for the undesirable flash setting of cement during hydration. Felite does not contribute to the strength but helps prevent unwanted sulphate attack. All the tephra samples met the 20.0 %w/w minimum requirement for SiO₂ of PNS 07:2018. However, they exceeded the 6.0 %w/w limit for both Al_2O_3 and Fe_2O_3 . This could affect the hydration of the cement, potentially impacting its strength and workability.8-10,19

LOI refers to the mass loss of a sample upon heating at very high temperatures (e.g., 1000 °C). The mass loss accounts for the water content and/or carbonation, which reduce the quality of the cement. A high loss on ignition can indicate pre-hydration and/or carbonation.^{12–13} All the tephra samples indicated LOI values greater than the regulation limit of 3.0 %w/w. This was somewhat expected as the volcano is within a lake, and carbon dioxide emissions from the volcano may have oxidised to carbonates. High MgO may be detrimental to the firmness of the cement, contributing to strength reduction by altering the heat of hydration.^{8,14–15} All the tephra samples were below the 6 % w/w regulation limit.

The presence of alkalis increases the pH up to 13.5, which is beneficial for protecting reinforcement steel from corrosion. However, excessive alkalis are undesirable as they react with aggregates in concrete, causing efflorescence. Efflorescence is a white or greyish crystalline deposit of salts formed on surfaces after water evaporates.^{8–10,16} The tephra samples exceeded the 0.60 %w/w total alkali threshold limit.

3.2 Extractable anions analyses of tephra samples

Excessive chloride may cause corrosion of reinforcement steel bars embedded in the concrete, whereas excessive sulphate may cause expansion and subsequent cracking of the concrete. Extractable anions are categorised into water-soluble and acid-soluble. Water-soluble anions refer to the free or available anions that can be extracted by using only water. Acid-soluble anions pertain to the total extractable anions that can be extracted under extreme conditions such as an acidic medium. In normal settings, only the water-soluble anions are available for reaction with the components of the concrete and cause detrimental effects. However, under extreme conditions, other more tightly held anions may be extracted, thus acid-soluble

Test never stor	Result			Standard an acification		
lest parameter	B13	B48	B78	B73	standard specification	
Acid-soluble Cl ⁻ , % w/w	0.586	0.156	0.243	0.325	< 0.10.0// (EN 107.1.2000)	
Water-soluble Cl ⁻ , % w/w	0.549	0.161	0.217	0.320	$\leq 0.10 \%$ W/W (EIN 197-1:2000)	
Acid-soluble SO4 ²⁻ , % w/w	1.15	1.11	1.32	1.40	2.0.9// (DNC 07-2019 - trac II)	
Water-soluble SO ₄ ²⁻ , % w/w	2.89	1.86	2.36	2.88	5.0 % w/w (FINS 07:2018 – type II)	

Table 3 – Measurement results for extractable chloride and sulphate in tephra samples

anions must also be determined.^{17–18} Table 3 shows the measurement results for the extractable anions (chloride and sulphate) in the tephra samples. All the tephra samples exceeded the 0.1 % w/w chloride maximum requirement set by the European Standard (Cement – Part 1: Composition, specifications, and conformity criteria for common cements (EN 197-1:2000)). Meanwhile, all the tephra samples met the 3.0 % w/w sulphate (as SO₃) limit set by the PNS 07:2018.

In summary, it was found that the Taal volcanic ash contained most of the vital components of cement. Moreover, there were selected chemical parameters that conformed to the specifications set by relevant standards. However, as some parameters exceeded the threshold limits, careful considerations must be given to these constituents when formulating cement using the volcanic ash as a raw material.

4 Conclusion

The results suggested that Taal volcanic ash has the potential to be a raw material for the production of cement, as it contains the essential components. However, the cement to be produced is recommended for use in ground-level structures only. For other applications, further treatment is necessary to reduce the concentration of certain constituents. Based on the PNS 07:2018, the material met the standard specifications for SiO₂, MgO, and water-soluble and acid-soluble SO_4^{2-} (as SO_3). In contrast, the results for Al₂O₃, Fe₂O₃, total alkali, loss on ignition, and water-soluble and acid-soluble Cl- exceeded the threshold limits set by the standards. These preliminary data will help the construction industry and local government units plan for the utilisation of volcanic ashfall in the event of a volcanic eruption. Furthermore, this study promotes a circular economy, wherein waste generated from natural disasters such as volcanic eruptions is converted into useful material. As a way forward, it is recommended to conduct studies on optimising cement formulation using the volcanic ash, incorporating it into actual construction, and testing the physical properties of the resulting concrete.

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List of abbreviations and symbols Popis kratica i simbola

PNS	 Philippine National Standards
PHIVOLCS	 Philippine Institute of Volcanology and Seismology
BPS/TC	 Bureau of Product Standards Technical Committee
BPS-DTI	 Bureau of Philippine Standards – Department of Trade and Industry
JIS	– Japan Industrial Standards
ASTM	– American Society for Testing and Materials
CS	- Construction Standard
US EPA	- United States Environmental Protection Agency
EN	– European Standards
BS	– British Standards
LOI	– loss on ignition
C ₃ S	– tricalcium silicate
C_2S	– dicalcium silicate
C ₃ A	- tricalcium aluminate
C_4AF	- tetracalcium aluminoferrite
C ₃ A	- tricalcium aluminoferrite
C_2F	– dicalcium ferrite
% w/w	– percent weight <i>per</i> weight

References Literatura

- A. M. Lagmay, Taal Volcano Eruption: The Importance of Science and Science Communication, National Academy of Science and Technology Philippines, 2020, pp. 1–6.
- B. Houghton, J. D. L. White, A. R. V. Eaton, Chapter 30 Phreatomagmatic and Related Eruption Styles, in: The Encyclopedia of Volcanoes, H. Sigurdsson (ed.), Vol. 2, 2015, Elsevier Inc., USA, pp. 537–552, doi: https://doi.org/10.1016/ B978-0-12-385938-9.00030-4.
- M. F. P. Del Castillo, P. M. J. Paraiso, M. C. T. M. Vicente, M. L. P. Jamero, G. T. Narisma, Impacts of Taal Volcano Phreatic Eruption (12 January 2020) on the Environment and Population: Satellite-Based Observations Compared with Historical Records, Manila Observatory (2020), URL: https:// www.observatory.ph/2020/04/20/impacts-of-taal-volcano-phreatic-eruption-12-january-2020-on-the-environment-and-population-satellite-based-observations-compared-with-historical-records (10. 5. 2023).
- D. Susanti, R. Tambunan, A. Waruwu, A. M. Syamsuddin, Studies on concrete by partial replacement of cement with volcanic ash, J. Appl. Eng. Sci. 16 (2) (2018) 161–165, doi: https://doi.org/10.5937/jaes16-16494.
- 5. *R. Siddique*, Properties of concrete made with volcanic ash, Resour. Conserv. Recycl. **66** (2012) 40–44, doi: https://doi. org/10.1016/j.resconrec.2012.06.010.
- Paint Square: Cement with Volcanic Ash Stronger, Greener 2018. URL: https://www.paintsquare.com/news/view/?18263#:~:text=The%20production%20of%20concrete%20contributes%20to%20percent%20of,goes%20into%20producing%20concrete%2C%20thus%20lessening%20overall%20pollution (10. 5. 2023).
- J. Rosales, M. Rosales, J. L. Diaz-Lopez, F. Agrela, F. M. Cabrera, Effect of Processed Volcanic Ash as Active Mineral Addition for Cement Manufacture, Materials 15 (18) (2022) 6305, doi: https://doi.org/10.3390/ma15186305.
- 8. The Constructor, "Concrete Technology", URL: https://theconstructor.org/concrete/ (10. 5. 2023).
- University of Illinois, "Concrete: Scientific Principles", URL: http://matse1.matse.illinois.edu/concrete/prin.html (10. 5. 2023).
- Penn State College of Engineering, "Composition of Cement", URL: https://www.engr.psu.edu/ce/courses/ce584/ concrete/library/construction/curing/Composition%20 of%20cement.htm (10. 5. 2023).
- 11. Bureau of Philippine Standards Philippine National Standard, PNS 07:2018 Portland Cement Specification, 2018.
- LECO Determination of Split Loss on Ignition in Cement, Application Note, 2019, URL: https://eu.leco.com/images/ Analytical-Application Library/TGA801_SPLIT_LOI_CE-MENT_203-821-595.pdf (10. 5. 2023).

- S.-H. Ngo, T.-P. Huynh, T.-T. Thi Le, N.-H. Thi Mai, Effect of High Loss on Ignition-Fly Ash on Properties of Concrete Fully Immersed in Sulfate Solution, IOP Conf. Ser.: Mater. Sci. Eng. 371 (2018) 012007, doi: https://doi.org/10.1088/1757-899X/371/1/012007.
- A. A. El-gray, F. B. M. Ahmed, Determination of Major Oxides Percentages in Portland Cement of Some Sudanese Cement Manufactories, Am. J. Appl. Chem. 4 (1) (2016) 14–17, doi: https://doi.org/10.11648/j.ajac.20160401.13.
- Q. Song, J. Su, J. Nie, H. Li, Y. Hu, Y. Chen, R. Li, Y. Deng, The occurrence of MgO and its influence on properties of clinker and cement: A review, Constr. Build. Mater. 293 (2021) 123494, doi: https://doi.org/10.1016/j.conbuildmat.2021.123494.
- J. Bai, 10 Durability of sustainable concrete materials, in: Sustainability of Construction Materials, J. M. Khatib (ed.), Woodhead Publishing, 2009, pp. 239–253, doi: https://doi. org/10.1533/9781845695842.239.
- N. Klein, E. D. Gómez, G. S. Duffó, S. B. Farina, Effect of sulphate on the corrosion of reinforcing steel in concrete, Constr. Build. Mater. 354 (2002) 129214, doi: https://doi. org/10.1016/j.conbuildmat.2022.129214.
- U. A. Birnin-Yauri, S. Garba, The effect and mechanism of chloride ion attack on Portland cement concrete and the structural steel reinforcement, IFE J. Sci. 8 (2) (2006) 131– 134, doi: https://doi.org/10.4314/ijs.v8i2.32211.
- H. M. Nadir, A. Ahmed, The Mechanisms of Sulphate Attack in Concrete – A Review, Mod. App. Matrl. Sci. 5 (2) (2022) 658–670, doi: https://doi.org/10.32474/ MAMS.2022.05.000206.
- 20. JIS M 8853:1998, Methods for chemical analysis of aluminosilicate raw materials for ceramics.
- 21. ASTM C 25 93a, Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime.
- 22. ASTM C1152/C1152M 04, Standard Test Method for Acid-Soluble Chloride in Mortar and Concrete.
- 23. ASTM C 1218/ C1218M 99, Standard Test Method for Water-Soluble Chloride in Mortar and Concrete.
- 24. CS3:2013.
- 25. US EPA 9038, SW-846 Test Method 9038: Sulfate (Turbidimetric).
- 26. ASTM C 1580 1, Standard Test Method for Water-Soluble Sulfate in Soil.
- 27. BS EN 196-2:1995, Methods of testing cement Part 2: Chemical analysis of cement.
- BS EN 196-21:1992, Methods of testing cement Part 21: Determination of chloride, carbon dioxide and alkali content of cement.
- 29. EN 197-1:2000, Cement Part 1: Composition, specifications and conformity criteria for common cements.

SAŽETAK

Karakterizacija pepela vulkana Taal kao potencijalne sirovine u građevinskoj industriji

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Freatska erupcija vulkana Taal u Batangasu na Filipinima u siječnju 2020. izazvala je formiranje masivnog oblaka pepela koji je prekrio veliki dio obližnjih provincija i područje grada Manile. Ovaj događaj prouzročio je štetu i poremećaje u različitim sektorima, uključujući poljoprivredu, okoliš, zdravstvo, infrastrukturu i zrakoplovstvo. Izazov upravljanja ogromnom količinom vulkanskog pepela prikupljenom u okolišu potaknuo je inicijativu da ga se pepeo pokuša pretvoriti u korisnu sirovinu. U ovoj studiji provedena je karakterizaciju prikupljenog pepela i ocijenjena njegova kvaliteta kao potencijalne sirovine u građevinskoj industriji prema Filipinskom nacionalnom standardu PNS 07:2018, ne bi li se osigurao integritet struktura i sigurnost.

Analizirana su četiri uzorka pepela uzorkovana na lokacijama koje je strateškima ocijenio Filipinski institut za vulkanologiju i seizmologiju. Rezultati su pokazali da vulkanski pepeo ima potencijal da se primijeni kao sirovina za prizemne građevinske strukture. Međutim, potrebna je daljnja obrada kako bi se smanjila koncentracija određenih komponenata. Materijal je udovoljio standardnim specifikacijama za SiO₂, MgO i SO₃, dok su razine Al₂O₃ i Fe₂O₃, ukupni alkalitet, gubitak žarenjem, te sadržaj klorida topljivih u vodi odnosno kiselinama premašili granice postavljene standardima PNS 07:2018 i EN 197-1:2000.

Ključne riječi

Vulkanski pepeo, građevinski materijali, kemijska analiza, oksidi, upravljanje otpadom

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