Journal of Radioanalytical and Nuclear Chemistry
https://doi.org/10.1007/s10967-023-09023-y

PGAA measurement of chloride diffusion profiles in concrete cylinders

H. Heather Chen-Mayer[1] · **Neal S. Berke**[2] · **Richard A. Livingston**[3]

Received: 18 March 2023 / Accepted: 22 June 2023

Abstract

Chloride diffusion is a critical precursor to corrosion of steel reinforcement in concrete structures. The current standard method for estimating chloride diffusion coefficients involves destructive chemical analysis. This work investigates the feasibility of Prompt Gamma Activation Analysis (PGAA) for in-situ determination of chloride distribution in an intact concrete cylinder which has a chloride diffusion depth profile. The profile thus obtained is in good agreement with the result of the chemical analysis of the profile in a duplicate cylinder. This is a first such direct comparison to our knowledge. A diffusion coefficient can be extracted from the profiles for further evaluation.

Keywords Prompt gamma activation analysis · Chloride in concrete · Non-destructive analysis of diffusion profile

Introduction

Metal reinforcement in concrete is prone to corrosion over time. “Unlike the Pantheon …, virtually all the concrete structures one sees today will eventually need to be replaced, costing us trillions of dollars in the process.” [1] Chloride ingress is one the main contributing factors to corrosion and degradation of concrete [2]. The threshold of corrosion initiation is about 0.1% chloride by weight of cement, although the corrosion process is complicated by numerous influencing factors, such that the service life prediction based on the threshold value can be unreliable [3]. Consequently, the chloride diffusion behavior continues to be under scrutiny, especially with the current emphasis on climate friendly concrete that has new compositions whose corrosion behavior is being actively studied. The diffusion process can be characterized by the diffusion coefficient, which can be derived from a diffusion profile obtained by measuring the chloride concentration at a given depth and time. Currently, such a profile is determined by the industrial standard method of testing such as the ASTM C1152 “Acid-Soluble Chloride in Mortar and Concrete” [4], which is a destructive chemical analysis involving drilling or milling samples from points along a cylinder followed by chemical processes, including acid-digestion as preparation for the titration process. (The choice of using C1152 does not preclude other ASTM rapid testing methods involving electrical, electrochemical or mechanical processes, and the evaluation of their merits is beyond the scope of this study.) There are many other techniques for measuring the chloride profile in concrete, such as LA-ICP-MS (destructive), uXRF (limited penetration), and Cl-36 radiotracer (requiring injection of tracers and subsequent measurements), each with its limitation for rapid testing. It is desirable to have a nondestructive technique for this task for in-situ measurements by eliminating the need for these destructive processes. Prompt Gamma Activation Analysis (PGAA) [5] has long been recognized as a tool for concrete analysis. Neutrons needed by this technique can be generated from a compact accelerator driven generator [6–8] or a radioactive source [9], both of which are portable for on-site measurements. Radiation transport simulations can be used to optimize these types of systems [10, 11], and particularly to correct the neutron self-shielding and gamma ray self-absorption necessary for bulk samples [12]. A non-portable but much more powerful nuclear reactor offers higher neutron intensity and therefore higher gamma yield and better detection limit, Reactor-based PGAA of concrete is performed usually by taking portions of concrete powder that are irradiated

✉ H. Heather Chen-Mayer
chen-mayer@nist.gov

[1] National Institute of Standards and Technology, 100 Bureau Dr, Gaithersburg, MD 20899, USA

[2] Tourney Consulting Group, 3401 Midlink Drive, Kalamazoo, Michigan 49048, USA

[3] University of Maryland, College Park, MD 20742, USA

entirely by the neutron beam for gamma counting [13], yielding a bulk average of the entire sample. In this work, we investigate the feasibility of measuring the spatially varying chloride distribution in an intact concrete cylinder, without cutting up it to sections. This type of measurement requires sample scanning and refined gamma ray collimation to achieve spatial specificity. Spatially resolved PGAA has been practiced at other reactor facilities for objects that must be physically preserved, such as archeological artefacts [14, 15] and specific investigation of the role of chloride in corrosion [16]. The current study is focused on the Cl diffusion profile inside concrete cylinders as a function of depth. The Cl gradients were created using the ASTM C1202 "Rapid Chloride Permeability Test" method [17]. Duplicate sets of cylinders were made for each loading protocol; one set was analyzed by PGAA which measures total Cl, and the other by ASTM C1152 destructive chemical analysis which measures acid soluble Cl. The comparison suggests that with further development and standardization of the measurement and automation, the PGAA can be considered as an alternative to destructive analysis,

Theory

The gamma peak count rate for a given isotope of an element is given by

$$c = n\sigma_{\gamma}\varphi\varepsilon_{\gamma} \tag{1}$$

where n denotes the atom number density for the element of interest. σ_{γ} is the partial gamma cross section which is a combination of the neutron capture cross section, the isotopic abundance, and the gamma yield for the capture product. ε_{γ} is the detector efficiency at the gamma energy [5]. By taking the ratio of the count rates of two elements, the thermal neutron flux φ is considered cancelled. For this work, the ratio between the Cl peak at 6.11 MeV and the Si peak at 4.93 MeV is used to arrive at the atom number ratio, and in turn, the mass ratio, between Cl and Si. With further information on the mass fraction of Si to concrete, the Cl mass fraction in concrete, which is the quantity of interest, can be determined. The chain of conversions is as follows:

$$\begin{aligned} \frac{n_{\mathrm{Cl}}}{n_{\mathrm{Si}}} &= \frac{c_{Cl}\sigma_{Si}^{\gamma 4.93}\varepsilon_{\gamma 4.93}}{c_{\mathrm{Si}}\sigma_{\mathrm{Cl}}^{\gamma 6.11}\varepsilon_{\gamma 6.11}} \\ \frac{m_{\mathrm{Cl}}}{m_{\mathrm{Si}}} &= \frac{n_{\mathrm{Cl}}M_{\mathrm{Cl}}}{n_{\mathrm{Si}}M_{\mathrm{Si}}} \\ \frac{m_{\mathrm{Cl}}}{m_{\mathrm{concrete}}} &= \frac{m_{\mathrm{Cl}}}{m_{\mathrm{Si}}}\frac{m_{\mathrm{Si}}}{m_{\mathrm{concrete}}} \end{aligned} \tag{2}$$

The chloride diffusion gradient follows a solution to Fick's second law [18]:

$$C(z,t) = C_s - \left(C_s - C_i\right)\mathrm{erf}\left(\frac{z}{\sqrt{4D_a t}}\right) \tag{3}$$

where $C(z, t)$ is the Cl concentration at a given time t and location z. Parameters C_s and C_i are the surface and initial Cl concentration, respectively, and D_a denotes the effective diffusion coefficient, in the unit of m^2/s. After a profile $C(z, t)$ is obtained experimentally, it can be fitted to Eq. (3) by varying the three parameters to get an estimate of the diffusion coefficient.

Sample preparation

Concrete cylinders of 10 cm diameter by 5 cm length were cast from a mix of cement, coarse and fine aggregates (limestone or granite) and sand. Two types of concrete mixes were prepared. One with limestone aggregate (labeled L) and the other with granite aggregate (labeled G). The Cl gradients were created using the Rapid Chloride Permeability Test (ASTM C1202). Each cylinder was preconditioned in a vacuum and then was placed in a test cell with one side in contact with a NaCl solution and the other in contact with NaOH solution, with a 60 V electrical voltage applied across the two sides. Cylinders were treated in the test cell at exposure times 0.5, 1, 3 h, respectively. Duplicate sets of cylinders were prepared, one set for PGAA and the other for ASTM C1152 destructive testing. After chloride loading, the center 5 cm diameter was cored out of the original 10 cm cylinders to reduce the gamma ray attenuation thickness relevant to the PGAA measurement.

This paper mainly concerns the PGAA work, and therefore the destructive testing procedures are described here briefly rather than in the experimental section. The cylinders were sampled at 1–3 mm intervals by milling or sawing slices. The slices were pulverized into a fine powder which was then digested in nitric acid. The filtered solution was analyzed by titration with a silver nitrate solution to determine the Cl mass. This was converted to Cl/concrete mass fraction by dividing by the sample mass. The results were compiled to obtain a Cl mass fraction as a function of depth from the surface of the cylinder.

Experimental

The PGAA measurements were conducted at the NIST Center for Neutron Research (NCNR) 20 MW reactor at Neutron guide D (NGD) cold neutron PGAA station [19]. The Cold neutron beam flux is 5×10^9 n/cm^2-s (thermal

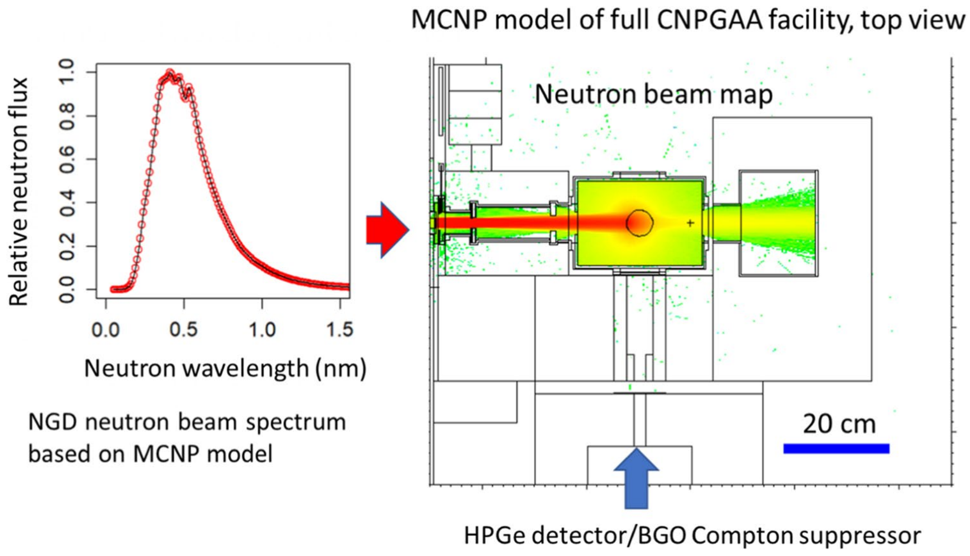

Fig. 1 Neutron beam spectrum and map (MCNP simulation) of the PGAA instrument

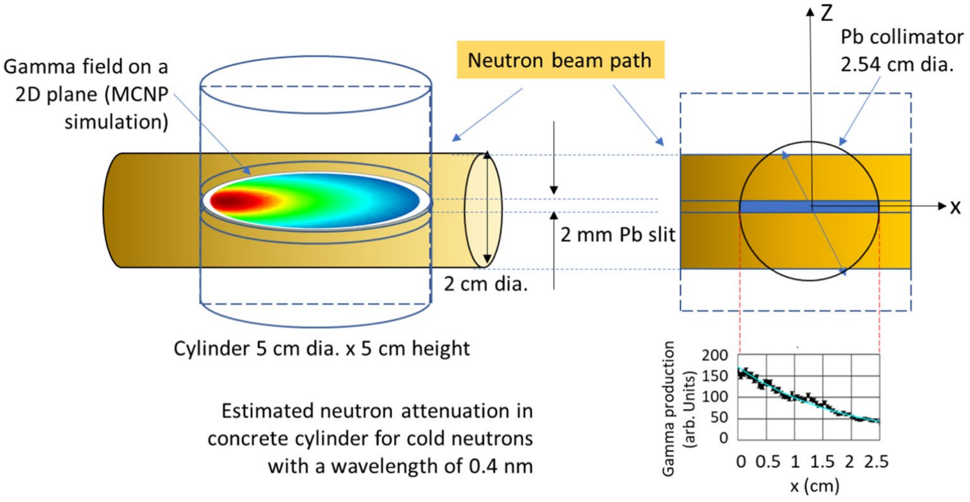

Fig. 2 Schematic illustration of the PGAA of a cylinder. The neutron beam is about 2 cm diameter entering the side wall of the cylinder. As the cylinder is scanned in the vertical direction, gamma emission from a slice of the cylinder is collected at 2 mm resolution. A 2D slice of the gamma response from MCNP simulation based on the cold neutron beam spectrum is shown as false color image, and the integrated intensity within the 2 mm field of view is plotted as a function of the location relative to the leading edge of the slit. The decrease in the signal across the slice reflects the attenuation of the neutron beam inside the cylinder

equivalent) at the sample position. The neutron wavelength spectrum is shown in Fig. 1, along with the instrument model developed [20] for the radiation transport simulation program MCNP [21]. The gamma ray spectrum is obtained by a high purity germanium detector (HPGe) with a relative efficiency of 41% and an energy resolution of 1.75 keV at 1 MeV, which is surrounded by a bismuth germanium oxide gamma ray detector which operates in an anti-Compton coincidence mode. The electronics are provided by a Lynx multichannel analyzer (Mirion Technologies[1]).

The concrete cylinder measurement setup is schematically shown in Fig. 2. The standard Pb collimator for the detector is further restricted by a slit formed by two Pb bricks with a 2 mm gap, defining the field of view of the detector to a slice of the cylinder. The gamma response map and integrated intensity obtained from MCNP simulation based on the

---

[1] Trade names and commercial products are identified in this paper to specify the experimental procedures in adequate detail. This identification does not imply recommendation or endorsement by the authors or by the National Institute of Standards and Technology,

Footnote 1 (continued)

nor does it imply that the products identified are necessarily the best available for the purpose.

actual neutron spectrum and an assumed concrete composition and density are also shown, with the intensity showing a diminishing response along the direction of the beam path, as expected from neutron attenuation due to absorption and scattering. The gamma intensity map and curve serve as an assessment of the experimental conditions for a bulk sample which exacerbates the spatial non-uniformity compared to the standard sample size of 1 cm diameter and a few mm thickness. It is noted that although the spectrum acquired is considered the total emission from the slice accepted into the detector, additional gamma ray attenuation from within the slice before reaching the detector can also have an effect. It is assumed that the ratio method can eliminate these effects even for the bulky sample, and no special correction is made for these analyses.

Results and discussion

PGAA

A total of 5 cylinders were measured: Type L with 0.5, 1, and 2 h chloride exposure times, and type G with 1 and 3 h exposure times. For each cylinder, seven to nine heights were measured, extending to a depth of about 20–25 mm. A spectrum from each slice is collected for about 1000 s live counting time, yielding a relative uncertainty of about 1% based on counting statistics.

The spectrum from each height of the cylinder was analyzed using an open-source software OpenAGS [22]. It performs both the peak fitting and the counts to mass conversion steps. The gamma peak for Cl at 6.11 MeV and for Si at 4.93 MeV was fitted to a Gaussian model with baseline to obtain a net peak count rate, which were then converted to mass ratio between Cl and Si by Eq. (2). To make a direct comparison with the C1152 analysis, the Cl/Si mass ratio was further converted to Cl/concrete mass ratio, by using a previously determined Si/concrete mass ratio obtained from a small quantity of powder sample taken from the same batch as the cylinder. This ratio was 0.123 ± 0.0020 for the L type, and 0.379 ± 0.0022 for the G type. The mass ratio along with the propagated uncertainty are plotted in Fig. 3, overlayed with the C1152 results. The data are also listed in Supplemental Tables S1-S3.

The diffusion curves were then fitted to Eq. (3) using Python Scipy curve fitting library [23]. The entire set of parameters for the fit is tabulated in Supplemental Tables S4 and S5. The diffusion coefficients, D_a, are depicted in the box plot in Fig. 4, showing the range of distribution by both PGAA and C1152. The two methods are in closer agreement for the L type cylinders than for the G type, perhaps due to greater sample to sample variations in the Si/concrete mass ratio in the G series associated with local variations in the granite mineralogy. The measured diffusion depth profiles show that the Cl diffusion occurred to a greater extent for the L type than for the G type for the same exposure time. The higher values for the G type at depth zero to about 10 mm appear to be a surface build-up, in conjunction with the slower inward diffusion. The more rapid diffusion observed in the L type could be attributed to the fact that limestone tends to have more porous morphology than igneous rocks such as granite, giving rise to the greater likelihood of Cl diffusion.

A main source of systematic error in the PGAA determination of Cl in concrete is in the conversion of mass ratio from Cl/Si to Cl/concrete. This conversion depends on the mass ratio of Si/concrete, which in turn depends on sample uniformity. This can be alleviated by taking multiple samples for averaging.

Finally, the value of D_a, of the order of 10^{-9} m^2/s, can be put into context with the example for a concrete exposed to marine conditions in Ref. [18], where the time dependent D_a, normally measured in years,[2] could be extrapolated down to hours, which yielded a D_a of about 10^{-8} m^2/s. The Cl diffusion coefficients obtained from these samples were higher than the marine condition, which is not entirely surprising given the accelerated loading times under an applied electrical voltage for the cylinders used in this work.

Limit of detection

Assume the gamma counts follows the Poisson statistics, i. e. for N net peak counts, $N = N_T – N_B$ (total count minus background), the standard deviation is $\sigma_N = \sqrt{2}\ \sigma_B = \sqrt{(2N_B)}$, then a random event can be considered above background if it is above N_B by z σ_N, referred to as the critical level $L_C = z\ \sqrt{(2N_B)}$, and the limit of detection (LOD) is defined as $L_D = 2\ L_C + z^2$, where $z = 1.645$ for 95% probability [24]. The LOD thus estimated for this measurement setup is shown in Table 1. For comparison, the LOD is also shown for the small sample in the form of a 1.3 cm diameter pellet, which better conforms with the standard PGAA practice. As expected, the LOD for the cylinder is worse than for the pellet due to the higher amount of mass in the measured region of the slice of about 2 g which contributes to the higher gamma background rate. These estimate shows that the PGAA can detector levels of Cl in concrete below the threshold level–at 0.06% Cl by weight of cement, or about

---

[2] In the classic Fick's theory the diffusion coefficient is a constant. However, over long D_a versus loading time decreases approximately with the square root of time. This phenomenon of exposure dependent diffusion has been observed in samples taken from actual concrete structures. This indicates that other factors affect the transport of Cl in concrete including reaction with aluminum to form Friedel's salt.

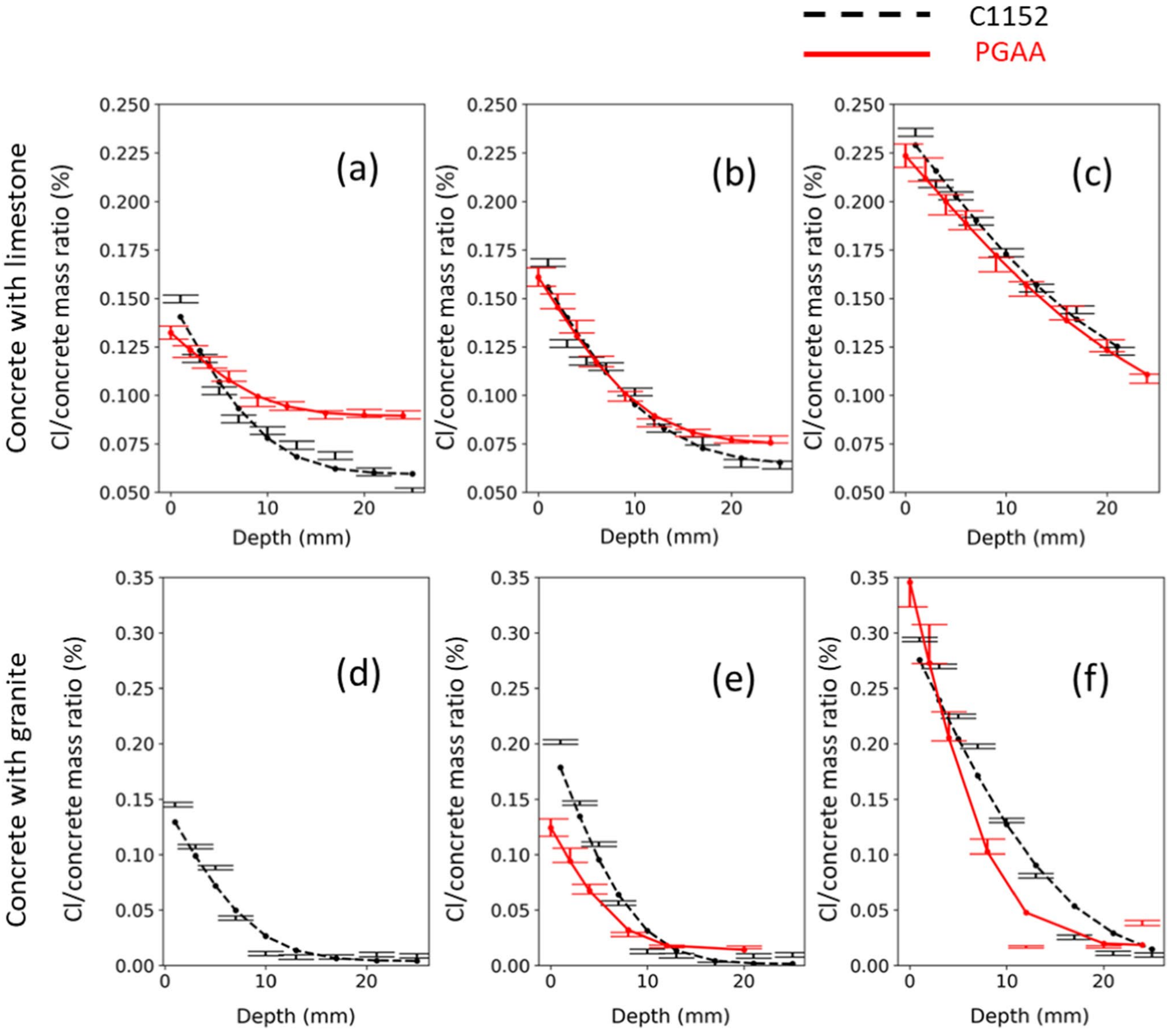

Fig. 3 Mass ratio of Cl to concrete as a function of distance from the top surface of the cylinder. Graphs **a**–**c** are the L-type cylinders at loading times of 0.5 h, 1 h, and 3 h, respectively. Graphs **d**–**f** are the G-type cylinders at the same 3 loading times. PGAA measurement was not performed for (d). The uncertainties for the PGAA data are propagated from the 1 s counting statistics for the gamma peaks used in obtaining the ratio. The uncertainties for the C1152 data are uniformly assigned to be 0.002% (note –this is an absolute uncertainty – the ratio data carries a % sign) based on the ASTMC1152 multilibrary standard

0.015% Cl by weight of concrete, as specified by the American Concrete Institute for pre-stressed concrete [25].

Conclusions

This study investigated the feasibility of using PGAA to determine the Cl diffusion profile in intact concrete cylinders non-destructively. The Cl depth profiles were measured successfully with a 2 mm resolution. The profiles were fitted to Fick's 2nd law model to determine the diffusion coefficients. These results were compared to the standard destructive testing method. The agreement was good for two of the more highly concentrated Cl profiles in concrete cylinders with limestone aggregate, but poor in other cases, which could be due to sample non-uniformity and the difficulty of creating the same Cl depth profile in duplicate cylinders. The estimated limit of detection using the experimental setup can detect Cl mass fraction at levels relevant to the initiation of the corrosion of metal reinforcement. Further development of the PGAA by automating the measurement process will enable more efficient implementation, paving the way for a non-destructive testing method for Cl diffusion in concrete.

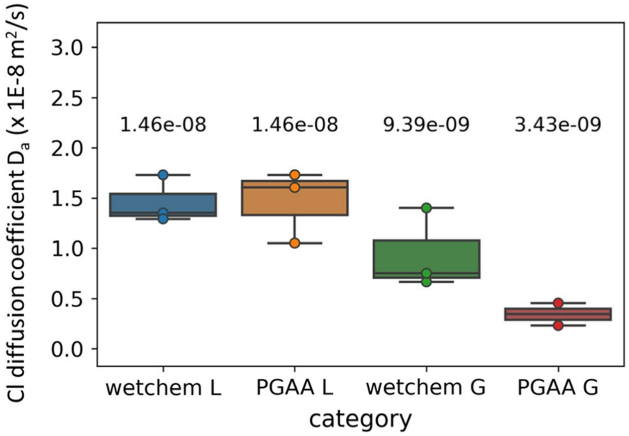

Fig. 4 Box plot of the fitted diffusion coefficient of the L and G cylinders form C1152 and PGAA. The mean values for each category are shown on top of each box. The lower and upper bounds of the box represent the expected boundaries from first to the third quartiles. The horizontal line in the box is the median value

Table 1 The limit of detection for Cl estimated based on measurement data for the concrete cylinder, and for the standard small sample pellet of about 600 mg mass

Sample	Count time (s)	L_D (cps)	L_D Cl mass (mg)	L_D mass fraction Cl/concrete (%)
Cylinder	1000	0.64	0.15	0.0075
Pellet	4000	0.16	0.022	0.0037

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10967-023-09023-y.

Acknowledgements NB and RL acknowledge the grant support from the 2018 National Institute of Standards and Technology Small Business Innovation Research Phase I (70NANB19H049). This paper was presented at the International Conference on Nuclear Analytical Techniques in 2022 (NAT2022).

Data availability All processed data have been presented in the Supplemental Information section. Raw prompt gamma ray spectra are available upon request.

Declarations

Conflict of Interest The authors have no known conflict of interest.

References

1. Courtland R (2011) Concrete planet: the strange and fascinating story of the world's most common man-made materia. Prometheus Books, New York
2. Frohnsdorff G (1998) Modelling Service Life and Life-Cycle Cost of Steel-Reinforced Concrete Report from the NIST/ACIIASTM Workshop held in Gaithersburg, MD. https://nvlpubs.nist.gov/nistpubs/Legacy/IR/nistir6327.pdf
3. Angst U, Isgor O, Hansson C, Sagüés A, Geiker M (2022) Beyond the chloride threshold concept for predicting corrosion of steel in concrete. Applied Physics Reviews 9:011321. https://doi.org/10.1063/5.0076320
4. ASTM C1152/C1152M – 04 Standard Test Method for Acid-Soluble Chloride in Mortar and Concrete, ASTM International, West Conshohocken, PA, 2012
5. Molnar G (ed) (2004) Handbook of Prompt Gamma Activation Analysis with Neutron Beams. Kluwer Academic Publishers, Dordrecht
6. Saleh H, Livingston R (2000) Experimental evaluation of a portable neutron-based gamma spectroscopy system for chloride measurements in reinforced concrete. J Radioanal Nucl Chem 244:367–371
7. Naqvi A, Maslehuddin M, Kalakada Z, Al-Amoudi O (2014) Prompt gamma ray evaluation for chlorine analysis in blended cement concrete. Appl Radiat Isot 94:8–13. https://doi.org/10.1016/j.apradiso.2014.06.011
8. Wakabayashi Y, Yoshimura Y, Mizuta M, Otake Y, Ikeda Y (2019) Feasibility study of nondestructive diagnostic method for chlorine in concrete by compact neutron source and PGA. J Adv Concr Technol 17:571–578
9. Wakabayashi Y, Yan M, Takamura M, Ooishi R, Watase H, Ikeda Y, Otake Y (2022) Development of the Neutron Salt-meter RANS- μ for Non-destructive Inspection of concrete structure at on-site use. J Neutron Res 24:411–419. https://doi.org/10.3233/JNR-220031
10. Yan M, Wakabayashi Y, Takamura M, Ikeda Y, Otake Y (2022) Optimization study of chlorine detection sensitivity in concrete based on prompt gamma analysis using 252Cf neutron source. Appl Radiat Isot. https://doi.org/10.1016/j.apradiso.2022.110393
11. Hei D, Jia W, Cheng C, Yao Z, Shan Q, Ling Y, Gao Y (2021) Feasibility study of fast neutron-induced gamma ray imaging of large sample based on D-T neutron generator. nuclear Instruments and Methods in Phys. Res B 492:7–14. https://doi.org/10.1016/j.nimb.2021.01.014
12. Szentmiklósi L, Kis Z, Maróti B, Horvátha L (2021) Correction for neutron self-shielding and gamma-ray self-absorption in prompt-gamma activation analysis for large and irregularly shaped samples. J Anal At Spectrom. https://doi.org/10.1039/D0JA00364F
13. Livingston R, Sridhar P, Berke N, Amde A, Chen-Mayer H (2023) Measurement of Chloride in Concrete by Prompt Gamma Neutron Activation, American Concrete Institute, submitted
14. Szentmiklósi L, Maróti B, Csákvári S, Calligaro T (2022) Position-sensitive bulk and surface element analysis of decorated porcelain artifacts. Materials 15(15):5106. https://doi.org/10.3390/ma15155106
15. Belgya T, Kis Z, Szentmiklósi L, Zs K, Kudejova P, Schulze R, Materna T, Festa G, Caroppi P, The Ancient Charm Collaboration (2008) First elemental imaging experiments on a combined PGAI and NT setup at the Budapest Research Reactor. J Radioanal Nucl Chem 278:751–754. https://doi.org/10.1007/s10967-008-1605-7
16. Watkinson D, Rimmer M, Kasztovszky Z, Kis Z, Maróti B, Szentmiklósi L (2013) The use of neutron analysis techniques for detecting the concentration and distribution of chloride ions in archaeological iron. Archaeometry 56(5):841–859. https://doi.org/10.1111/arcm.12058
17. ASTM C1202, Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration. ASTM International, West Conshohocken, PA, 2012
18. Poulsen E, Mejlbro L (2006) Diffusion of Chloride in Concrete: Theory and Application. Taylor & Francis, Newyork
19. Paul R, Sahin D, Cook J, Brocker C, Lindstrom R, O'Kelly D (2015) NGD cold-neutron prompt gamma-ray activation analysis spectrometer at NIST. J Radioanal Nucl Chem 304(1):189–193

20. Turkoglu D, Downing R, Chen W, Sahin D, Cook J (2017) A 3He beam stop for minimizing gamma-ray and fast-neutron background. J Radioanal Nucl Chem 311:1243–1249
21. Monte Carlo N–Particle® Transport Code System Version 6.2. Los Alamos National Security, LLC
22. Stallar C https://github.com/chris-stallard1/OpenAGS
23. Virtanen P et al (2020) SciPy 1.0: fundamental algorithms for scientific computing in python. Nature Methods 17(3):261–272
24. Currie L (1968) Limits for qualitative detection and quantitative determination. application to radiochemistry. Anal Chem 40:586–593. https://doi.org/10.1021/ac60259a007
25. Obla K, Colin Lobo C, Hong R, and Berke N (2017) Evaluation of Chloride Limits for Reinforced Concrete Phase A, Final report to the RMC Research & Education Foundation (Project 14–01); and Concrete Research Council, ACI Concrete Foundation. https://www.acifoundation.org/Portals/12/Files/PDFs/CRC-94_Evaluation-of-Chloride-Limits.pdf