Geopolymer-based moisture sensors for reinforced concrete health monitoring

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Abstract

Moisture plays a critical role in reinforced concrete corrosion, underpinning structural degradation which costs the global economy a staggering \$350 bn per year (0.5% GDP). Both moisture sensors and repair materials that limit water ingress are required, but monitoring and maintenance are often viewed as separate challenges. This paper outlines a first-time demonstration of moisture sensors based on low calcium fly ash geopolymers — a class of cementitious, electrolytically conductive repair materials. Electrochemical impedance spectroscopy and equivalent circuit models are used to understand and optimize the electrical response of geopolymer sensors to water content and temperature. Moisture and temperature precisions of 0.1 wt% and 0.1 °C are demonstrated respectively, and sensor drifts over 20 minute periods were found to be within 1–3%. Sensor responses were also shown to be repeatable to within 3% between wetting and thermal cycles. Results from spectrometry and chromatography analyses link this repeatability to the minimal ion leaching from the sensors. The study demonstrates the feasibility of moisture sensing using geopolymers, and furthers our current understanding of the role of moisture in the ionic conductivity of alkali-activated materials. This work is anticipated to be the first stage in developing 2D, distributed sensor-repairs for concrete structures, and other chemical sensors that support concrete structural health monitoring and

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prognostics.

Keywords: alkali-activated materials, multifunctional materials, smart cements, electrochemical impedance spectroscopy, electrolytic sensors, water sensors, structural health monitoring

1. Introduction

The global economic cost of reinforced concrete corrosion is currently estimated to be some \$350 bn per year [1, 2]. This growing sum must be added to the significant social and environmental costs of continually maintaining a material that underpins most public services and utilities. Sensors for locating and quantifying moisture in concrete are key because water plays a leading role in reinforced concrete corrosion, accelerating the infiltration of carbonation, chloride attack and freeze-thaw damage [3, 4, 5]. As moisture data can support degradation models and proactive asset management strategies [6, 7], moisture sensors are naturally a topic of prime interest within concrete health monitoring [8, 9, 10, 11, 12, 13, 14, 15, 16, 17]. The level of interest is particularly keen within industries with significant inventories of safety-critical coastal, marine and riverside concrete assets, such as nuclear, transport, and off-shore energy generation sectors.

In this paper, we outline the first-time demonstration of moisture sensors based on geopolymers, a class of cementitious electrolytes. Geopolymers, often also referred to as alkali-activated materials [18], exhibit similar thermal and mechanical properties to ordinary Portland cement and adhere strongly to concrete substrates. They are chemically stable and have electrical conductivities in the range 10^{-6} S/cm to 10^{-3} S/cm depending on mix design [19, 20]. This makes geopolymers highly suited to concrete monitoring and maintenance applications: they have already been developed as sensors for strain and temperature [7, 21, 22, 23, 24] and as concrete repair materials [25, 24, 26].

Numerous methods for continuous moisture monitoring in concrete have already been proposed, including: fibre-optic sensors [27, 28]; concrete electrical

impedance measurements [29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40]; dielectric permittivity and capacitive sensors [29, 41, 42, 43, 44, 45]; and NEMS/MEMS (nano-/micro- electro-mechanical systems) sensors [46]. We will not adopt the cliché of criticizing these other approaches for their cost or performance, as each can be viable in the face of a specific application. The low calcium fly ash geopolymer sensors we propose in this work do, however, offer two unique benefits: i) they are multi-functional, offering both sensing and repair capability; and ii) they can be applied as 2-dimensional skin sensors, and so could support the distributed sensing of global structural health [47]. Before this latter benefit is explored further, our aim is to first demonstrate that moisture sensing using geopolymers is feasible. The work outlined here achieves this aim by developing a sensor prototype and characterising its response and performance under temperature and moisture cycling.

The remainder of this paper begins with a description of the theoretical framework that supports the link between the electrical response of geopolymers and moisture content or temperature. Following this, we describe the methods used to manufacture and interrogate the sensors, and finally discuss the sensors' responses and repeatability.

2. Theory and background

2.1. *Geopolymers material overview*

Geopolymers are a class of cementitious, aluminosilicate binders with diverse and tuneable material properties [48, 18]. They are synthesized by adding an alkali solution, called an activator, (often comprised of sodium hydroxide, NaOH, and sodium silicate, Na₂SiO₃) to raw materials which are rich in aluminium and silicon. Examples of such materials include blast furnace slag; metakaolin; or fly ash, a by-product of coal combustion [49]. While geopolymers are often cured at elevated temperatures above 30 °C, we have already demonstrated ambient-temperature curable fly ash geopolymer mix designs in previous work

[25]. Fly ash geopolymers can also offer other beneficial properties such as a
55 high workability, durability and strength [50, 51].

The electrical conductivity of geopolymers stems from the alkali metal ions
(in our case Na^+) introduced by the activator solution [19, 26]. A proportion
of the population of these ions is actively bonded to the negatively charged
alumino-silicate matrix. The remaining ions are mobile, able to move through
60 the matrix, partly because it is disordered (rather than crystalline) [52]. They
increase the ionic content of the water inside the cured material's pores, mi-
grating along the pore network and acting as carriers of electrical current under
an applied voltage [20]. Geopolymers are therefore often referred to as solid
electrolytes, electrolytic conductors, or ionic conductors. Measured changes in
65 the electrical conductivity of geopolymers allow these materials to be employed
as sensors [7, 21, 22, 23].

2.2. Electrochemical impedance spectroscopy (EIS)

Geopolymers can be electrically interrogated using metal electrodes, which
are embedded prior to curing. This produces a sensor cell, as shown in Figure 1.
70 While standard circuits are comprised mainly of electronic conductors, geopolym-
mer sensors are a composite of electronic conductors (the metal electrodes) in
contact with an ionic conductor (the geopolymer). They are therefore classed as
an electrochemical system, and exhibit behaviors that are not present in most
standard electronic sensors.

75 Electrochemical Impedance Spectroscopy (EIS) is a non-destructive tech-
nique that can be used to analyze electrochemical systems both at rest and in re-
sponse to external measurands. In potentiostatic EIS, the frequency-dependent
current response of the sensor cell, $I(t)$, is measured during an applied, time-
varying voltage excitation, $V(t)$:

$$\begin{aligned} V(t) &= V_0 \cos(\omega t), \\ I(t) &= I_0 \cos(\omega t - \phi(\omega)). \end{aligned} \tag{1}$$

Figure 1: Photograph of geopolymer sensor cell showing electrodes used for sensor interrogation.

80 Here, V_0 and I_0 are the amplitudes of the applied voltage and measured current respectively, $\phi(\omega)$ is the frequency-dependent phase difference between $V(t)$ and $I(t)$, and $\omega = 2\pi f$ is the radial frequency of applied ac voltage. The electrical impedance of the cell, Z , can be defined using Euler notation as [53]:

$$Z = \frac{V(t)}{I(t)} = Z_{mod}(\cos(\phi) + i\sin(\phi)) = Z_{mod}e^{i\phi}, \quad (2)$$

where i is the imaginary unit, $Z_{mod}(\omega) = |Z|$ is the frequency-dependent mag-
 85 nitude or modulus of the impedance, and $\phi = \arg(Z)$ is the phase angle between real and imaginary components. The real component of the impedance, $Z_{real} = \text{Re}(Z)$, is the electrical resistance of the cell, while the imaginary component, $Z_{imag} = \text{Im}(Z)$, is its reactance. Inductive elements in a sensor cell, L , cause current changes to lag behind voltage, as $Z_{imag} = i\omega L$. Ca-
 90 pacitive elements, C , meanwhile, cause current changes to lead the voltage as $Z_{imag} = -\frac{i}{\omega C}$. Acquired EIS impedance data are typically assessed using a combination of Bode plots (plots of Z_{mod} and ϕ against swept frequency), and Nyquist plots (plots of Z_{real} against Z_{imag}).

2.3. The electrical impedance of geopolymers

95 The impedance response of electrolytic cells can be modeled using equivalent circuits comprised of resistors, capacitors and inductors in series and/or parallel. Previous studies [54, 55] have shown that electrolytic cells made using alkali-activated binders can be modeled using the equivalent circuit shown in Figure 2a. The elements in this circuit include the:

- 100 • *Resistance of the Electrolyte, R_e* : the resistance of the liquid electrolyte within the geopolymer pores. This resistance depends on the number of ions (i.e. the ion concentration and volume of the cell, both of which are often constant), and the mobility of the ions (a function of ion concentration, metal ion type, and temperature) [56].
- 105 • *Connected pore resistance, R_c , and unconnected pore resistance, R_{uc}* : the

resistance of the ion conducting pathways between the connected (percolating) and unconnected pores in the geopolymer matrix [57].

- *Solid phase, or bulk capacitance, C_b* : the dielectric capacitance associated with the solid phase of the geopolymer between the electrodes. This will be comprised of hardened geopolymer paste and unreacted fly ash particles.
- *Interface resistance, R_i , and double layer capacitance, C_i , at the specimen-electrode interface*: a single layer of Na^+ ions in the geopolymer will adhere to the negatively charged surface of the metal electrode. This layer acts as a dielectric, separating the electrons in the metal electrode from the Na^+ in the geopolymer.
- *Pore wall capacitance, C_p* : a double layer capacitance present between the unconnected pores of the pore solution.

In the present work, modifications have been made to this standard model to produce a new equivalent circuit shown in Figure 2b. The changes are justified as follows:

1. The solid phase capacitance is described by:

$$C_b = \varepsilon_0 \frac{A_e}{d}, \quad (3)$$

where ε_0 is the effective dielectric constant of the solid phase of the geopolymer cell, A_e is the shared area between the electrodes in the specimen, and d is the separation between the electrodes. In the present work, the electrodes embedded in the geopolymer cell are stainless steel wires of diameter 0.4 mm, embedded at a depth of 7.5 mm, and their separation $d = 55$ mm. This set up, specific to our sensor design, means that $A \ll d$, and $C_b \approx 0$ F. Capacitor C_b is therefore removed.

2. Double layer capacitances in electrolytic systems can be modeled using constant phase elements (CPEs), represented as elements Q in Figure 2b. In this work, all double-layer capacitances are modelled using CPEs which have an impedance described by:

Figure 2: a) the equivalent circuit previously used to describe alkali-activated materials. b) the equivalent circuit used to describe the geopolymer cells in this work.

$$Z_{cpe} = \frac{1}{Y_0} \frac{1}{(i\omega)^{\alpha'}}, \quad (4)$$

where Y_0 and $\alpha' = [0, 1]$ are fitting parameters. While the use of CPEs in electrochemical circuit modeling is common, it is a slightly controversial approach as Y_0 and α do not have widely accepted physical meanings. However, it is accepted that equation (4) describes the net result of ion dynamics in electrochemical systems [52, 58]. When ions make forward hops between vacant sites in the geopolymer, they make a positive contribution to conductivity. However, because ion movements within geopolymers are highly correlated, forward hops are often soon followed by backwards ionic hops which cancel out the conductivity contribution. This is why CPEs describe a low conductivity at low EIS frequencies. At high EIS frequencies, there is no time for backwards ionic hops before the polarity of the electrodes switches, so all ionic hops are forwards, and all contribute positively to conductivity.

3. Electrolytic cells often exhibit inductive loops at high frequencies. While inductances are commonly attributed to experimental artifacts such as electrode cross-talk, particularly when measured currents are small, some research has suggested that it could also stem from genuine electrochemical processes, such as relaxation of adsorbates on the electrodes [59]. Regardless of the cause, inductive effects were seen in our system, and so an inductance term, L , and corresponding resistance, R_L , was added to the equivalent circuit.

The overall impedance response of the geopolymer sensor modeled by the circuit shown in Figure 2b is:

$$Z = R_e + Z_{transport} + Z_{electrode}, \quad (5)$$

where $Z_{transport}$ and $Z_{electrode}$, found through parallel sums of components, capture the total impedance of ion transport and electrode effects respectively.

2.4. Temperature and moisture sensing principle

Bulk electrical conductivity in cementitious materials is a function of the conductivity of the pore solution, σ_0 , the volume of the pore network filled with pore solution, ϕ_{con} , and the connectivity factor of the pore network, β [39]:

$$\sigma = \sigma_0 \phi_{con} \beta. \quad (6)$$

If geopolymers follow this same principle, then their conductivities, σ , will depend on measurands which alter the three terms on the right hand side of equation (6).

Increasing the temperature of a geopolymer enhances ion mobility and encourages electrolytic dissociation, both of which increase σ_0 . Therefore, provided there is no evaporation of water at high temperatures, the relationship between geopolymer conductivity, σ , and temperature, T , is expected to follow [60]:

$$\ln(\sigma) = \frac{D_1}{T} + D_2 T + D_3, \quad (7)$$

where D_1 , D_2 and D_3 are constants. While the first term in equation (7) has been used on its own to describe the ‘Arrhenius dependence’ of geopolymer conductivity in previous literature [7, 21, 22], in this work we will use the full form of equation (7).

Water content within the geopolymer, meanwhile, can affect all three terms in equation (6). It reduces the conductivity of the pore solution, σ_0 , by diluting it, but meanwhile increases pore fill volume, ϕ_{con} , and connectivity, β [37]. At very low water contents, conductivity can decrease dramatically as the liquid electrolyte cannot cover the internal surfaces of the pores [37]. In previous studies of ordinary Portland cement systems, electrical conductivity was found to have an exponential dependence on water content [31]:

$$\ln(\sigma) = D_4 W + D_5, \quad (8)$$

where D_4 and D_5 are constants. Given the lack of previous literature on moisture sensors, we will adopt an equation of this form to describe geopolymer conductivity in this work.

If we define the admittance of a geopolymer sensor as the inverse of impedance:

$$\mathbf{A} = \frac{1}{\mathbf{Z}}, \quad (9)$$

185 then we can note that, for a fixed cell geometry, the modulus of admittance, $A_{mod} = |\mathbf{A}|$, will be proportional to conductivity, σ . Equations (7), (8) and (9), can then be combined to produce a characterization equation for the geopolymer sensor:

$$\ln \left(\frac{Z_{mod}}{Z_{mod,0}} \right) = \frac{G_1}{T} + G_2 T + \frac{G_3}{W} + G_4 T \frac{1}{W} + G_5, \quad (10)$$

where $G_{1,...,5}$ are constants. Equation (10) includes an additional cross-dependence
190 term between moisture and temperature. The equation considers shifts in the modulus of the impedance only, and furthermore normalizes all Z_{mod} values by $Z_{mod,0}$, where $Z_{mod,0}$ is the impedance of the sensor in ambient conditions (i.e. at a water content of 60% and at a temperature of 20 °C). This normalization makes the characterization equation independent of variations in sensor
195 geometry.

3. Materials and Methods

3.1. Sensor fabrication

The geopolymer binder used in this work was synthesized from low calcium fly ash and an alkaline solution made from sodium hydroxide (SH) and
200 sodium silicate (SS), with a liquid to solid ratio, $L/S = 0.5$, and $SH/SS = 0.4$. A detailed description of the geopolymer binder's fabrication, its mechanical properties and suitability as a repair is described in our previous work [25]. The mixed binder was poured into rectangular silicon moulds (dimensions 55 mm × 30 mm × 15 mm) with electrodes penetrating 2 mm into the corners to cast the

205 geopolymer cells shown in Figure 1. The electrodes were 7-wire braided stainless steel wires of diameter 0.4 mm. The geopolymer cells were cured for 30 days at 20 °C and 95% relative humidity in an environmental chamber prior to testing.

The four-electrode configuration shown in Figure 1 is known as *Van Der Pauw configuration*. It minimizes lead and contact resistance effects, and the
210 influence of electrode polarization at low frequencies [61, 62]. We also found in preliminary work that the configuration reduces stress and the probability of micro-cracking in our samples at the electrode-geopolymer interface as samples cure and shrink, partly because it maximizes the distance between adjacent electrodes.

215 3.2. Interrogation system

During potentiostatic EIS a 10 mV voltage was applied to geopolymer cells. The low magnitude of the voltage produces a pseudo-linear current response, allowing impedance to be calculated more conveniently [53, 63]. The frequency of the applied voltage was swept over the range 10 Hz – 100 kHz during impedance
220 characterization.

3.3. Calibration methods

The procedure for the moisture and temperature calibration is summarized as a flowchart in Figure 3:

1. The geopolymer sensor cell was immersed in deionized water for 24 hours
225 to reach a high water content;
2. Surface water was removed from the cell, and its wet mass, $M_{i,1}$, was measured.
3. Geopolymer cells were sealed in a box for 24 hours to allow water within the pores to equilibrate and homogenize. This ensured that moisture mea-
230 surements were conducted in a steady state regime. The sealed sample was placed in an environmental chamber and connected to the interrogation system. A separate data logger was placed within the box to verify

Figure 3: Flowchart showing the steps in the water and temperature characterization experiment.

temperature and relative humidity measurements (resolution of 0.5 °C and 0.5% RH).

- 235 4. Temperatures within the chamber were cycled in 5 °C steps from 5 °C to 30 °C and back to 5 °C. For each temperature point, temperatures were held for 2 hours to allow the system to reach thermal equilibrium. Once thermal equilibrium was reached, impedance spectra were measured twenty times over a 20 minute duration to allow an average to be taken.
- 240 5. After temperature cycling, the geopolymer sensor was taken out of the sealed container and its wet mass, $M_{i,2}$, was weighed a second time. The wet mass M_i was then defined as the mean value of $M_{i,1}$ and $M_{i,2}$, while the variation was used to establish an error in moisture content.
- 245 6. The sensor was placed in a desiccator with silica gel to drive water out of the sample through evaporation. The sensor was regularly weighed until a new target mass (target moisture level) was reached.

This cycle was repeated for all target moisture contents. Some samples underwent several drying and wetting cycles and several temperature cycles to assess sensor repeatability. Once the characterization was complete, each sample
 250 was completely dried in an oven at 105 °C for 24 hours and its dry mass M_d was measured. This allowed the gravimetric water content w_i , of the samples to be quantified [64]:

$$w_i(\%) = \frac{M_i - M_d}{M_d} \times 100 \quad (11)$$

3.4. Post-mortem examination of ion leaching

The drying and wetting cycles could cause Na^+ , Si^+ and Cl^- ions from the
 255 geopolymer to leach from samples, reducing their ionic conductivity over time. To assess this, inductively coupled plasma optical emission spectrometry (ICP-OES) and ion chromatography (IC) were used to measure ionic leaching from geopolymer cells. Sensors were immersed three consecutive times in 1.1 L of deionized water for 24 hours. After each wash, water samples were collected
 260 and filtered with a 0.45 μm pore size filter prior to analysis of ion content.

4. Results and discussion

4.1. Geopolymer cell impedance response

Figure 4 shows a typical Bode plot of phase and Z_{mod} for a geopolymer sensor, taken at a water content of $w = 88 \text{ wt}\%$ and temperature of $T = 20^\circ \text{C}$. The fits shown use the equivalent circuit model given in Figure 2b, and the values for each component are given in Table 1.

Figure 4: Bode plot for Z_{mod} and ϕ obtained for sensor at $w = 88\%$ and $T = 20^\circ \text{C}$.

Table 1: Values of parameters used in the equivalent circuit model for impedance data shown in Figure 4

Circuit element	Re (Ω)	Rc (Ω)	Ruc (Ω)	Yp (μF)	a_p	Ri (Ω)	Yi (μF)	a_i	L (μH)	RL (Ω)
Value	108	57	33	50	0.7	63	74	0.5	0.7	5

4.2. Temperature dependence of impedance

Figure 5 shows Bode plots for sensors at temperatures ranging from 6 °C to 30 °C. In this figure, isotherms have been plotted on the y-axis by taking the product of the modulus of admittance and temperature, or $A_{mod}T$. Figure 5 demonstrates that the geopolymer sensors obey a scaling law typical of ionic conductors known as Summerfield scaling [52]: the shape of each Bode plot is independent of temperature (e.g. the $T = 11$ °C line can be shifted up or down to superimpose onto any other temperature line). This means that we can define a master curve, arbitrarily defining a baseline frequency of $f_0 = 100$ Hz, and a baseline admittance at 100 Hz of $A_{0,mod} = A_{mod}(100 \text{ Hz})$ for each line. This allows us to plot all of the data shown in Figure 5 onto a single scaled Summerfield plot, which is shown in Figure 6.

The overlap of the isotherms in Figure 6 shows that the number of mobile ions is unchanged between temperature cycles. The linear relationship, meanwhile, supports the notion of time-temperature superposition in geopolymers [52]. To conduct an electrical current, an ion within the geopolymer must hop from its existing site to an adjacent site, and this adjacent site must relax to accommodate the ion. The longer it takes for an ion to be accommodated, the higher the probability for a backwards hop. Increasing temperature speeds up relaxation, and so essentially speeds up the ion hopping process (hence time-temperature superposition).

Figures 5 and 6 have consequences for temperature sensing. If we want to monitor temperatures using geopolymers, we are essentially free to choose almost any excitation frequency in the linear region of Figure 6 that we wish. It is

Figure 5: Bode plots of isotherms of $A_{\text{mod}} T$. Data shown is for samples at a constant water content of $w = 77\%$.

Figure 6: Scaled Summerfield plot representing all data in Figure 5 as a single data series.

not prudent to use frequencies that are too low, as this can encourage electrolysis, driving gradual ion migration to one electrode causing corrosive chemical reactions (and, as might be expected given the theory above, corrosion at low interrogation frequencies is particularly pronounced at higher temperatures).

Figure 7: Nyquist plots from 10 Hz to 100 kHz, for a geopolymer sample system at 20 °C for different water contents. Fits are obtained using the equivalent circuit model shown in Figure 2b.

295 4.3. Moisture dependence of impedance

Figure 7 shows Nyquist plots for the geopolymer cell at water contents ranging from $w = 51\%$ to $w = 88\%$, and at a constant temperature of $T = 20\text{ }^{\circ}\text{C}$.

Figure 8: Scaled Summerfield plots for water as a colorized set of series for each water content value.

As the water content decreases, impedance increases as expected. Resistive and inductive circuit elements in the modeled system all increase in magnitude as the water content decreases.

Repeating the scaled Summerfield plot process for water contents produces the plot shown in Figure 8. The trend is similar to Figure 6 but there is more scatter in the results. It is clear that water, like temperature, speeds up the ion hopping process. This makes physical sense: as described by equation (8), water increases the connectivity of the pore network and the volume of the pore network filled with electrolyte solution. We hypothesise that the added scatter in the Summerfield plot could be due to an added non-linear effect: the dilution of the pore solution. The colorization of the data points for each water content, shown in Figure 8, supports this hypothesis, as it demonstrates that high water contents have a lower admittance than expected. This result may warrant further investigation in future work, along with the source of the inductive effects at high frequency seen for drier samples.

From the perspective of sensing, the increased scatter in results at higher frequencies suggests that this could be a more sensitive region for sensing moisture contents and distinguishing them from temperature shifts. We have therefore opted to select a single frequency of 10 kHz for the remainder of the sensor characterization described in this paper. As shown by Figure 4, this frequency also corresponds to the region where phase angles tend to be at their highest values, but the frequencies are not so high that we see the influence of the inductance that we are currently unable to fully explain.

4.4. Sensor response

Figure 9 shows plots of sensor response at 10 kHz to temperature and moisture contents. Here we have defined the sensor response as $Z_{mod}/Z_{mod,0}$, where $Z_{mod,0}$ is the modulus of impedance of the sensor in ambient conditions (i.e. at a water content of 60% and at a temperature of 20 °C). As shown, equations (7) and (8) provide good non-linear fits to the data.

Figure 9: a) Plots of $Z_{mod}/Z_{mod,0}$ versus temperature for each water content. Non-linear fits use equation (7). b) Plots of $Z_{mod}/Z_{mod,0}$ versus water content for each temperature. Non-linear fits use equation (8).

Figure 10: 3D plot of calibration curve for sensor as a function of both moisture and temperature. The surface of best fit shown is described by (10).

Table 2: Parameters and their 95% confidence bounds for the plane of best fit, equation (10), shown in Figure 10.

	Parameter	G_1	G_2	G_3	G_4	G_5
	Value	0.82	-0.012	163.2	-1.09	-2.24
95% confidence bounds	Lower	0.44	-0.016	161.1	-1.20	-2.32
	Upper	1.20	-0.001	165.4	-0.97	-2.16

The overall response of the sensor for any general water/temperature combination is better characterized by fitting temperature and moisture simultaneously, using equation (10). Figure 10 shows the data from Figure 9 on a 3D scatterplot. Here we have defined the “dryness” of the sample as the inverse of its moisture content, or $1/w$. This allows us to fit a surface described by equation (10), where the parameters of the fit and their standard errors are given in Table 2.

Using these parameterization constants, the water content of a sample can be ascertained if a second reference sensor (a nearby thermocouple) is used for temperature compensation as:

$$w = \frac{G_3 + G_4 T}{\ln\left(\frac{Z_{mod}}{Z_{mod,0}}\right) - \frac{G_1}{T} - G_2 T - G_5} \quad (12)$$

4.5. Sensor precision

The non-linear dependence of the sensor means that the precision is not fixed for all water contents and temperatures. In general, precision is higher when the changes in impedance are large, i.e. when the conductivity of the sample is high, at high temperatures and moisture contents.

Nevertheless, the precision can be calculated by mapping the impedance fluctuations of the EIS interrogator onto the moisture and temperature axes, using the calibration surface shown in Figure 10. The fractional errors in the impedance values measured using our interrogator are typically 0.1 – 0.8 %. As such, the results of this exercise, shown in Table 3, demonstrate that, even in worse case conditions, the precision of the sensor is acceptable, at $\delta w = 0.3 \text{ wt}\%$ and $\delta T = 0.2 \text{ }^\circ\text{C}$. In typical conditions, precisions of $\delta w = 0.1 \text{ wt}\%$ and $\delta T = 0.1 \text{ }^\circ\text{C}$ are achievable.

4.6. Sensor repeatability

Figures 11 and 12 demonstrate the excellent repeatability of the sensors in response to temperature and wetting cycles. For the two temperature cycles shown, the response is repeatable to within a maximum deviation of 1-2%. For

Table 3: Worst case, best case and typical precisions for moisture and temperature sensing.

	Moisture precision	Temperature precision
	δw , wt%	δT , °C
Worst case	0.26	0.18
Typical case	0.09	0.10
Best case	0.02	0.06

Table 4: Critical comparison of sensor developed in this work with other common moisture monitoring techniques from [65].

	Precision	Repeatability	Continuous
	(vol%)	(vol%)	measurement?
Neutron scattering	0.01-4	0.02	no
Time-domain reflectometry	1-3	0.2	yes
Frequency domain reflectometry	1-3	0.2	yes
Geopolymer sensor	0.03-0.5	0.2-2	yes

moisture, sensor repeatability between all three wetting cycles is 3-4%. This
 355 corresponds to a repeatability in moisture measurement of 0.2-1.5 wt%.

4.7. Critical comparison with other sensors

The moisture content values quoted as wt% in this paper can be converted
 to vol% by multiplying by the relative bulk density of the geopolymer matrix
 (measured to be $R_D = 1.535$). This allows the precision and repeatability
 360 of our sensor to be compared to other common moisture sensors reviewed in
 [65]. As shown in Table 4 The precision of our sensor compares favourably with
 competing methods, with a comparable or lower repeatability.

4.8. Ion leaching

The good repeatability of the impedance response with moisture shown in
 365 Figure 12 suggests that ion leaching is minimal. However, ICP and IC analyses

Figure 11: Sensor response for increasing and decreasing temperature cycles for $w = 89 \text{ wt\%}$. Non-linear fits use equation (7).

Figure 12: Sensor response for three consecutive wetting-drying cycles. Non-linear fits use equation (8).

were conducted to assess long-term moisture sensing performance. The results, shown in Table 5, suggest that Na^+ ions do leach in small quantities from the geopolymer when it is submerged in water, along with silicon and chloride ions. Despite this, their percentages are thought to be a small fraction of the sodium
370 that the geopolymer binder contains. Whether Na^+ exists in the pore solution or adsorbed onto the pore walls is unknown and beyond the scope of this work but the very low levels of Na^+ being leached during the wash cycles (15 — 51 mg/L) shown in Table 5 is an encouraging sign for the long term performance of the sensor.

Table 5: Percentage of Na^+ , Si^+ and Cl^- ions leached from the geopolymer sample into deionized water.

Wash cycle	Na+ [%]	Si+ [%]	Cl- [%]
1st wash	0.06496	0.00393	0.00062
2nd wash	0.03716	0.00262	0.00018
3rd wash	0.12294	0.01382	0.00031

375 4.9. Sensor drift

Another important parameter to investigate is the long-term stability of the sensor’s response. Low frequency changes in the sensor response (sensor drift) were extracted independently of high frequency changes (noise), using a low-pass filter: the signal was smoothed with a 20 sample (20 minute) period
380 moving average. We then define the drift as the maximum fractional shift in this smoothed signal. Using this approach allowed us to extract a drift indicator for all temperature and moisture points over a total sampling period of 28 days. The result, shown in Figure 13, show that sensor drift is usually negative, and worst at high temperatures and low moisture contents, but is always <3% over
385 each 20 minute period.

Figure 13: Sensor drift as a function of time, temperature and moisture. Data labels show each moisture content as samples were dried over 28 days. Meanwhile, each temperature is plotted as a new series. The data shown here cover the same data points plotted in Figure 10.

5. Conclusions and future work

This paper has demonstrated the viability of monitoring moisture in concrete using low calcium fly ash geopolymer, a class of multi-functional materials historically used for concrete repair.

390 In this work, we have developed a sensor prototype consisting of a geopolymer block with stainless steel electrodes in a Van Der Pauw configuration, coupled with an electrical interrogation system to measure electrical impedance. A laboratory experimental campaign of impedance measurements was conducted in order to characterise the sensor and assess its performance (precision, repeatability, and drift) at varying moisture contents and temperatures. Ion leaching
395 analyses showed that a high sensor repeatability stemmed from the fact that relatively low levels of Na^+ (the main ionic charge carrier in the sensor) are leached during wetting/washing cycles. It was found that, in general, sensor performance is lower at low moisture contents (25 wt%). Electrical conductivity (and so sensitivity) decrease as the sensor is dried, and this leads to a
400 lower achievable precision. Low moisture combined with high temperature (30 °C) was meanwhile found to lead to a higher sensor drift. This may partly be due to some change in the physical mechanisms behind geopolymer electrical conductivity when pore connectivity is low and ion mobility is high.

405 The affordability of the technique outlined in this work is on par with direct measurements of concrete impedance, but the higher electrical conductivity of geopolymers could allow for monitoring over a broader range of moisture contents with affordable electronics. The sensor prototype outlined constitutes a solution for structural health monitoring applications in damp, critical environments, such as nuclear repositories, where the sensors could be deployed and
410 either routinely monitored or continuously interrogated with a wireless system.

Future work will investigate the impedance response of geopolymer patches on concrete substrates, characterise the response time of the sensor, and investigate field deployment methods. We will also seek to explicitly demonstrate
415 that moisture can be ascertained independently of temperature when a second

reference sensor (a nearby thermocouple) is used for temperature compensation.

Acknowledgements

Thank you to Dr Tatyana Peshkur for technical support during analysis of ion leaching, to Prof. Alessandro Tarantino for experimental design support
420 to target and measure water contents, to Dr John Douglas for assistance with defining non-linear surface fits, and to Dr Carmelo Mineo for assistance with programming for data analysis.

Declarations

The author(s) declare no potential conflicts of interest with respect to the
425 research, authorship, and/or publication of this article.

Funding

This work was funded in part by the National Nuclear Laboratory ICASE award (NNL/UA/022), EPSRC (EP/L014041/1), the Royal Society (RG160748) and the Scottish Funding Council's Oil & Gas Innovation Centre.

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