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# Early age electrical resistivity behaviour of various concrete mixtures subject to low temperature cycling



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#### ABSTRACT

The effect of thermal cycling between -24 and + 24 °C on the electrical resistivity of five concrete mixtures was investigated at early-ages. Each mixture was subjected to two thermal cycles (initiated either 1 or 14 days after casting) wherein temperatures were changed by 1 °C/h. Electrical resistivity increased as temperature decreased. This relationship followed the Arrhenius equation until the phase transition temperature (i.e. initial freezing of the pore solution), at which point electrical resistivity increased greatly. A method of determining the phase transition temperature is presented that could be used in place of existing methods using mortar cubes. The phase transition temperature was higher during thawing cycles compared to freezing cycles for all mixtures. Mixtures with ground slag replacing cement had higher resistivity and lower phase transition temperatures than mixtures using only cement due to the change in the ionic combination of the concrete pore solution. The phase transition temperature decreases as concrete ages.

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# 1. Introduction

The construction industry desires a simple and effective means of estimating concrete strength as it cures to minimize construction delays while waiting for the concrete to reach specified strength to allow for form stripping, post-tensioning, allowing traffic on concrete pavement, or surface finishing.

The strength gain in concrete cured at various temperatures is often estimated using the maturity method presented in ASTM C1074-11. This method relates the temperature history of a concrete mixture to a reference strength-time curve for a particular concrete mixture at a reference temperature, typically 20 °C, in order to predict its strength [1]. This relation is based on the Nurse-Saul function (Equation (1)) and is popular as it is simple to calculate [2]. Alternatively, the effective age of a concrete mixture can be calculated using Arrhenius relationships (Equation (2)).

 $M = \Sigma (T - T_0) \Delta t \tag{1}$ 

$$t_e = \Sigma e^{-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_s}\right)} \Delta t \tag{2}$$

Where *M* is the maturity factor, *T* is the average curing temperature (°C in Equation (1) and K in Equation (2)) over a time-step  $\Delta t$ ,  $T_0$  is the datum temperature where concrete strength gain is assumed to halt,  $T_s$  is the specified reference temperature (K),  $E_a$  is the mix activation energy (kJ/mol), and *R* is the gas constant (8.314 J/K mol).  $T_0$  varies based on mix design and ASTM C1074 presents a method of determining this experimentally using mortar cubes. For mixtures with General Use (GU) cement and no admixtures, a  $T_0$  of 0 °C is currently recommended [1]. It has been found that powdered slag and retarding admixtures reduce the datum temperature [3]. Though this method works well for typical mix designs, it is limited as it requires concrete to remain hydrated and it does not factor in the effects of concrete curing temperature on long-term strength [4]. It is also not recommended to be used for concrete cured at low (<0 °C) temperatures [5].

More recently, concrete performance has been estimated by monitoring its electrical resistivity. Ions (such as OH<sup>-</sup>, SO<sup>2</sup><sub>4</sub><sup>-</sup>, Na<sup>+</sup>, K<sup>+</sup>,



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and  $Ca^{2+}$ ) in the concrete pore solution allow it to carry a current [6]; as it cures, pore water reacts with cementitious materials which cause electrical resistivity to increase as ion mobility is hindered by developing concrete microstructure. Electrical resistivity is also used to evaluate structural health as it also can detect chloride penetration and crack formation [7]. Though resistivity has been shown to be proportional to concrete strength gain, it is also dependent on factors such as the mix design, surface saturation, and concrete temperature [4]. For mix designs, it has been shown that the paste composition has a larger effect than aggregate choice with respect to resistivity [8], particularly for concrete 28 days and younger [9]. Younger (i.e. less than 28 days old) pastes have been shown to be more dependent on the change in pore structure than the change in pore-fluid conductivity [10]. Slower-reacting cement-slag mix designs are shown to have higher resistivities and activation energy than mixtures with no supplementary cementitious materials [9–12]. Supplementary cementitious materials delay the dissolution of released ions in the pore solution. This is attributed to them retarding the chemical reactions between the solid and liquid phase and causes an increase in the pore solution resistivity [12]. This delay is greatest for slag, followed by fly ash, then silica fume [12]. Generally, higher strength concrete has higher resistivity than lower strength concrete of the same age and temperature [8,13]. Increasing concrete temperature increases ion mobility and decreases its resistivity and vice versa. This relationship has been shown to fit Arrhenius equations between 10 and 45 °C and can be used to predict resistivity using the maturity method in ASTM C1074 [13]. However, the effect of freezing on resistivity is less studied. Olson et al. investigated the response of cement paste at temperatures ranging from 20 to  $-50 \degree C$  [14]. They found that initial ice formation in the paste macropores occurred around -8 °C. This temperature is lower than 0 °C due to pore pressures limiting ice formations in addition to the presence of ions in the pore solution. Ice is an insulator and reduces ion mobility in pore water as ice formation propagates through the liquid/solid interface [15]. This generally starts within large voids or the exterior of the concrete before propagating to smaller pores as the temperature continues to decrease [16,17]. The initial freezing and melting points of the pore water differ and the difference between these two points can be used to infer properties about the pore geometry and if the pore geometry is spherical, cylindrical, or forms a more complex shape [18]. Sato and Beaudoin studied the microscale properties of cement paste subject to freeze-thaw using electrical impedance and were able to define cement paste's susceptibility to frost action [19]. Farnam et al. investigated the effects of freezing and thawing on the resistivity of mortar specimens cured at various saturation levels and NaCl concentrations [20]. They found that Arrhenius relationships fail to predict resistivity once ice formation begins. Wang et al. showed that the resistivity of pastes decreases as moisture content increases but that resistivity increases as the number of freeze-thaw cycles increase [21].

The current study evaluates five typical concrete mixtures that are used by contractors in the Ottawa, Canada area. Each mixture is subjected to two thermal cycles ranging between +24 °C and -24 °C during early-age hydration periods (either after 1 or 14 days of curing) in order to investigate the effect of temperature change and concrete age on resistivity. This temperature range represents the temperature ranges experienced in spring or fall construction in Ottawa. Added focus is placed on the change in resistivity as the concrete pore water freezes and thaws, and using experimental data to evaluate this point.

Although many studies investigate the resistivity of concrete and/or cement paste, there are relatively few that investigate resistivity of these materials at temperatures below 0 °C; these studies focus on concrete or cement paste that has reached its 28-

day strength [14—18,20,21]. To the authors' knowledge, there are no currently available studies that focus on the resistivity of concrete subject to early age thermal cycling. This study closes this gap by addressing the resistivity response of concrete under low temperature thermal cycling at its early age. The mix designs, temperature range, and curing process are also meant to simulate techniques used in construction where early-age freeze thaw cycling is a concern.

# 2. Experimental program

## 2.1. Concrete mixtures

The five concrete mixtures shown in Table 1 were used. These mixtures are normal-strength mixtures that are currently used in construction in the Ottawa, Canada area. Type GU (General Use) Portland Cement and ground granulated blast furnace slag were used as cementitious materials. The coarse aggregate comprised rounded limestone with a 12 mm maximum nominal aggregate size. Sand was used as fine aggregate. Two admixtures were considered, a high range water reducer (BASF MasterGlenium 7500) and a retarder (BASF MasterSet R100).

## 2.2. Mixing process

Each mixture was batched using a 0.1 m<sup>3</sup> capacity, 21 rpm electric drum mixer. Enough concrete was mixed to make 10 cylinders. To mix the concrete, ~10% of the total water was added, followed by half the coarse aggregate, fine aggregate, and cementitious materials respectively. Once this was well mixed, the remaining materials were added in the same order aside from the remaining 10% of water, which was added slowly until the desired consistency was reached. Admixtures were mixed into the water before concrete batching.

Each mixture was used to fill 5 plastic  $102 \times 200$  mm cylinders. Concrete was added in three lifts and rodded to work out voids as per ASTM C39. Once filled, the cylinders were capped; these caps were removed after one day of curing at room temperature. The concrete cylinders were kept in their molds until the end of the trials in order to better simulate field conditions in the lab. Three cylinders were used for strength tests while the remaining two were fitted with the electrical resistivity sensor described in the following section.

#### 2.3. Resistivity sensor

Experimental data were collected from two cylinders in each mixture using a commercially available sensor that measures concrete electrical resistance, R, and internal temperature, T. The normal operating temperature range of the sensor is -25 to 45 °C and reports resistance up to 3000  $\Omega$  with an accuracy of  $\pm 2\%$ . This sensor comprised three components: the sensing unit (data acquisition system), two electrodes, and a thermocouple (Fig. 1). The sensor was mounted onto the cylinder mold cap in order to ensure that the electrodes were properly placed in the concrete. The electrodes were placed into the cylinders after concrete was placed and rodded. The thermocouple was then inserted such that it measures the temperature at the centre of each cylinder. The mixture was agitated by hand to ensure that the electrodes and thermocouple were firmly embedded in concrete and not in a void. The sensors were activated immediately after casting and recorded the concrete electrical resistance and internal temperature at a rate of once every 15 min over the curing period. Data were collected from the sensors using a tablet computer and a commercially available downloaded application written specifically for the used

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Concrete	mixtures	considered	in	study.

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Material	Mixture 1	Mixture 2	Mixture 3	Mixture 4	Mixture 5
Cement (kg/m <sup>3</sup> )	365	333	265	280	298
Slag (kg/m <sup>3</sup> )	-	77	_	-	117
Coarse Aggregate (kg/m <sup>3</sup> )	1075	1080	1055	1055	1070
Sand (kg/m <sup>3</sup> )	750	680	940	860	815
Water (L/m <sup>3</sup> )	150	153	165	150	155
Retarder (mL/100 kg)	-	200	_	-	200
High Range Water Reducer (mL/100 kg)	-	_	_	-	150
Air Entrainment (%)	6.0	6.0	_	5.5	_
w/cm ratio	0.41	0.37	0.62	0.54	0.37
Supplementary Cementitious Material (%)	0	19	0	0	28



Fig. 1. Sensor system (a) schematic illustrating electric circuit (b) photo of installed sensor.

sensors.

In order to process data, the recorded electrical resistance values needed to be converted to resistivity. Electrical resistivity,  $\rho$ , is related to resistance, *R*, using Equation (3)

$$\rho = R/k \tag{3}$$

Where *k* is the geometry factor of the sensor, typically evaluated by a calibration routine in which sensors are placed in a solution of known resistance [12]. In this case, the sensors were calibrated with a NaCl solution which was placed into a cylinder mold equivalent to the ones used in this experimental program; the calibration resulted in a *k* of 9.13 m<sup>-1</sup>.

# 2.4. Testing program

Once concrete was cast, it was cured for a day at laboratory conditions to ensure that initial setting occurs. After one day, one sensor from each mixture was placed into a climate controlled chamber (Fig. 2 (a)). The temperature in the chamber was cycled twice from +24 °C to -24 °C at a rate of 1 °C/h (Fig. 3). At +24 °C and -24 °C, the temperature was maintained constant for 1 h. The relatively low thermal cycling rate was selected to minimize thermal gradients in the concrete.

After the two cycles were completed, the cylinders were cured at room temperature  $(23-26 \ ^{\circ}C)$ . The second sensor from each mixture was placed into a separate chamber after 14 days of curing at room temperature and subjected to the same two thermal cycles

as the first sensors. Each sensor was given a specific identity, shown Table 2. The first value of the sensor ID corresponds to the mix design (same as Table 1) while the second corresponds to the start of the thermal cycling period ('A' mixtures were cycled after 1 day of curing while 'B' mixtures were cycled after 14 days of curing).

After 28 days, the remaining three cylinders in each mixture (cured at room temperature for the entire period) were tested in compression according to ASTM C39 (Fig. 2 (b)).

## 3. Results

#### 3.1. Concrete resistance over time

The resistivity over time for the monitored cylinders are shown in Fig. 4. The 'A' and 'B' sensors gave similar readings over the first day; this was expected as they were cured under the same conditions. These readings diverge after the 'A' cylinders were placed into the climate chamber. As temperature decreased, resistivity increased as expected. This is represented in Fig. 4 by the two spikes in resistivity for each mix. Observations during these cycles are discussed in more detail later.

Researchers have observed temperature jumps due to the heat of fusion (i.e. the onset of ice formation) [20]. This temperature jump was not observed in this program as the data sample rate (once per 15 min) was too low.

After the cylinders were cycled, they were cured for the remaining period at the baseline room temperature (23-26 °C). The resistivity of the 'A' cylinders after cycling (beyond 9 days) is



Fig. 2. (a) cylinders in climate chamber (b) cylinder after compression test.



Fig. 3. Thermal cycling program for 'A' cylinders. 'B' cylinders followed the same process but cycling started 14 days after casting.

 Table 2

 Sensor identity (related to mixture number and thermal cycling age).

Sensor ID	Mixture	Thermal Cycling Age
1A	1	1-9 days
1B	1	14-22 days
2A	2	1-9 days
2B	2	14-22 days
3A	3	1-9 days
3B	3	14-22 days
4A	4	1-9 days
4B	4	14-22 days
5A	5	1-9 days
5B	5	14-22 days

lower than those of the 'B' cylinders before cycling in all of the mixtures. This is attributed to the thermal cycles delaying curing of the concrete (i.e. more pore water is available to conduct electricity).

Notably, after the 'B' mixtures were thermally cycled (22 days after casting), the resistivity readings of those and the 'A' cylinders show similar results for Mixtures 1, 3, and 4 (Fig. 4). This is similar

to what would be expected in ASTM C1074 (i.e. the value for maturity (Equation (1)) is the same in both mixtures). However, Mixtures 2 and 5 saw lower resistivity in the 'B' cylinders after cycling than the 'A' cylinders.

As the cylinders aged, it was noticed that Mixtures 1, 3, and 4 were close to a 'leveling off' point for resistivity, indicating that the bulk of strength gain was reached. This was not the case for Mixtures 2 and 5 as the slag in these mixtures reacts at a much slower rate than cement and continues to gain strength over a longer time [22].

#### 3.2. Temperature effect on resistivity

The effect of temperature on resistivity for the first thermal cycle of each mixture is shown in Fig. 5. Similar results were observed in the second thermal cycle but not shown in Fig. 5 for clarity for reference, the results (including those from the second thermal cycle) are shown in Table 3. Several temperatures are chosen for reference in Table 3, particularly 23 °C (room temperature) and 5 °C increments from +10 °C to -15 °C. These temperatures were selected in order to illustrate the changes in resistance with particular attention to the change in resistivity when the mix water freezes or thaws.

The sensing unit is capable of reading resistance values up to 3000  $\Omega$ , corresponding to a resistivity of 328  $\Omega$ m, but goes offscale after this point. This point occurred between -15 and -18 °C for each mixture so readings below -15 °C are not presented in Table 3. Temperature readings were recorded over the entire temperature range (-24 to +24 °C).

The concrete was exposed to ambient air after removal of the cylinder caps. This means that the concrete lost moisture from diffusion to the surface as well as self-desiccation. Self-desiccation is more of a concern in high strength concrete [23]; for the concrete used in this study (w/c ratio ranging between 0.37 and 0.62), the effect of self-desiccation is expected to be low [23]. Moisture loss will create air voids in the concrete, increasing its resistivity relative to a saturated mix. These voids would also lead to a decrease in the initial ice formation temperature as the largest saturated pore size would also decrease.

## 4. Discussion

For all mixtures and cycles, resistivity increased as temperature



Fig. 4. Electrical resistivity readings over time for the monitored cylinders. Sudden increases in resistivity correspond to temperature cycling.

decreased. The change in resistivity with temperature agrees well (curves fitted in the next section) with the Arrhenius exponential curves presented in the literature at temperatures above  $0 \,^{\circ}C$  [1,13]. However, there is a distinctive change in resistivity, typically between -5 and  $0 \,^{\circ}C$ , where this curve no longer fits (see Fig. 5). This change was more sudden in the younger 'A' mixtures than it was in the older 'B' mixtures. Mixtures with blended slag (2 and 5) also had less abrupt changes, particularly during the freezing cycles; differences observed with the slag mixtures are discussed in more detail later. A method of evaluating the transition temperature, attributed to the phase change between water and ice, is presented in the next section.

At temperatures lower than the transition point, resistivity generally varied linearly with temperature. Linearity is more apparent in the thawing cycles than in the freezing cycles, which show a slight increase in slope as temperature decreased.

## 4.1. Determining activation energy

The activation energy,  $E_a$  (J/mol), for a concrete mixture can be determined by multiplying the slope of a conductivity (1/ $\Omega$ cm) versus 1000/(T+273) curve by the gas constant (8.314 J/K mol) [18]. This process is illustrated in Fig. 6 and these curves are presented for the first cooling cycle of each mixture in Fig. 7. The remaining cycles are not shown in Fig. 7 for clarity but had similar trends. The activation energy was evaluated based on the best-fit slope at temperatures ranging between 5 and 24 °C and is presented in Table 4. The effect of the testing parameters on activation energy are discussed in the following sections.

#### 4.2. Evaluating phase transition temperature

The abrupt change in resistivity that occurs (generally between  $-5 \circ C$  and  $0 \circ C$ ) represents the initial change in state of the concrete pore water to ice (or ice to water) and is known as the phase transition temperature,  $T_p$ . To facilitate comparison across parameters, a means of determining  $T_p$  is required.  $T_p$  was found by making two best-fit lines on the temperature-resistivity curves (Fig. 5) using curve-fitting software, illustrated in Fig. 8. The first line, using resistivity measured between 5 °C and 24 °C follows the form in Equation (4). This is the same general form as the Arrhenius relationship that has successfully been used to normalized concrete resistivity in the past [12]. The second line, using resistivity readings at temperatures below -5 °C, aside from the freezing cycles for Mixtures 2 and 5, follows a linear form, seen in Equation (5). For the freezing cycles in Mixtures 2 and 5, the transition temperature was found to be below  $-5 \degree C$  so Equation (5) for these two mixtures was evaluated for at temperatures below -10 °C rather than -5 °C.

$$\rho = A e^{BT} \tag{4}$$

$$\rho = CT + D \tag{5}$$

Where *T* is the mixture temperature (°C), *A* is the theoretical resistivity ( $\Omega$ m) at *T* =  $\infty$  and *B* (1/°*C*) is proportional to *E<sub>a</sub>*, (i.e. for all mixtures, *B* = -0.0121*RE<sub>a</sub>*), *C* is a constant representing the change in resistivity in concrete with frozen pore water ( $\Omega$ m/°C) and *D* is a general constant ( $\Omega$ m).

The intersection point of Equations (4) and (5) was solved for



Fig. 5. Temperature versus resistance readings for the first thermal cycle of each mixture. Results for the second cycle are not shown for clarity. The sudden change in slope in each plot represents the onset of phase change (freezing or melting) in each mixture.

during each mixture's heating and cooling cycles to determine  $T_p$ . The results of this, including the best-fit constants and R<sup>2</sup> values, are given in Table 5. The best fit lines gave strong correlations (R<sup>2</sup> > 0.99 for Equation (4) and R<sup>2</sup> > 0.94 for Equation (5)) for all mixtures.  $T_p$  is affected by the mix design, as expected. However, it also varies based on the concrete age, whether the concrete is being heated or cooled, and the cycle number. The effect of these parameters on  $T_p$  is explored in the following sections.

It is suggested that the phase transition temperature is the same as the 'datum temperature' (point where it is assumed that curing, and thus strength gain, ceases in concrete) used to evaluate concrete maturity in ASTM C1074-11. The datum temperature is generally in the -10 to 0 °C range [1,5,13], similar to the observed phase transition temperature range of -8.5-1.4 °C in this study. However, further investigation is required to confirm this. If these two values are the same, then concrete resistivity readings could be used in lieu of mortar tests to evaluate the datum temperature of concrete. This would be beneficial as resistivity sensing require less equipment than the technique presented in ASTM C1074-11. Additionally, the actual concrete mixture can be used rather than a mortar mixture.

In mature concrete (older than 28 days), the Arrhenius

Table 3 Resistivity outputs during thermal cycles at reference temperatures ranging from -15 to 23 °C.

Mixture	ture Cycle		23 °C	10 °C	5 °C	0 °C	$-5 \ ^{\circ}C$	$-10\ ^{\circ}C$	−15 °C
1A	1	Cooling	13.8	21.9	26.1	30.8	92.3	177	295
		Heating	16.5	21.9	25.1	29.8	120	225	_a
	2	Cooling	17.7	26.2	30.9	37.5	94.1	168	271
		Heating	20.5	26.5	31.1	36.9	128	208	318
1B	1	Cooling	24.9	36.8	43.1	52.1	77.0	149	249
		Heating	23.6	34.0	39.5	46.5	117	193	282
	2	Cooling	24.2	35.4	42.0	50.6	77.9	152	236
		Heating	23.9	35.0	41.3	50.0	125	198	293
2A	1	Cooling	16.6	27.3	32.5	39.6	70.9	135	224
		Heating	20.9	27.4	31.3	36.9	107	181	272
	2	Cooling	23.2	35.9	42.5	52.4	70.3	130	218
		Heating	29.6	35.9	41.5	50.3	114	179	258
2B	1	Cooling	46.3	72.0	86.3	106	136	175	253
		Heating	40.9	62.2	72.9	90.1	145	210	293
	2	Cooling	42.3	65.6	79.0	97.9	126	168	256
		Heating	42.4	64.1	76.4	93.9	150	210	291
3A	1	Cooling	10.1	15.7	18.4	21.9	107	205	327
		Heating	11.7	15.4	17.5	21.1	145	253	_a
	2	Cooling	12.9	18.9	22.0	26.0	116	199	312
		Heating	14.3	18.9	21.6	26.1	147	243	_a
3B	1	Cooling	20.2	29.0	34.1	40.6	87.2	157	253
		Heating	18.8	26.1	29.8	35.7	119	198	282
	2	Cooling	19.2	27.9	32.8	39.3	91.9	165	272
		Heating	19.2	27.3	31.9	38.9	130	206	305
4A	1	Cooling	11.6	18.4	21.6	26.1	94.1	180	311
		Heating	13.4	18.1	20.6	24.9	133	232	_a
	2	Cooling	14.9	22.0	25.9	30.8	103	174	282
		Heating	15.9	22.3	25.7	30.6	136	223	321
4B	1	Cooling	22.4	32.4	37.8	45.2	81.8	154	248
		Heating	21.2	30.2	35.0	45.4	119	191	284
	2	Cooling	21.4	31.2	36.9	44.4	87.7	154	258
		Heating	21.4	31.5	36.9	43.9	122	201	301
5A	1	Cooling	14.5	23.6	27.2	33.1	84.3	150	264
		Heating	17.9	23.1	26.3	30.1	104	196	312
	2	Cooling	19.9	30.8	36.3	43.7	87.8	153	247
		Heating	26.2	31.0	35.5	42.2	128	204	290
5B	1	Cooling	59.9	94.8	113	142	181	237	_a
		Heating	50.6	74.7	89.2	108	192	292	_ <sup>a</sup>
	2	Cooling	52.2	83.2	99.2	124	160	212	_ <sup>a</sup>
		Heating	52.2	79.2	93.8	116	200	290	_a

<sup>a</sup> Resistivity readings offscale (>328  $\Omega$ m).



**Fig. 6.** Illustration of the method used to determine activation energy (found using the slope of the line) at temperatures above the phase transition temperature. Below the phase transition temperature, activation energy increases suddenly before stabilizing once much of the phase change has occurred.

relationship has been shown to apply over a large temperature range (-30 to 70 °C) with a sudden change in slope at  $T_p$  [18]. However, this behaviour was not observed in this study. As seen in

Fig. 7, there are two regions where the Arrhenius relationship applied (1) at temperatures above  $T_p$ , where the activation energy was calculated (2) at temperatures well below  $T_p$  (between  $-10 \degree C$ and -15 °C for the tested mixtures). Between these two regions, the bulk of the phase change from water to ice occurs and this transition leads to a rapid change in slope (i.e. activation energy) at temperatures just below  $T_p$ . As the concrete cures further, the slope decreases until it stabilizes at around -10 to -15 °C. The transition region became less prominent as the concrete matured and, given time, is expected to reach the state where the Arrhenius relationship applies over the entire temperature range. Similar trends were observed when monitoring resistivity in cement pastes with high moisture content [20]. This indicates that younger (i.e more saturated) concrete is less likely to follow the Arrhenius relationship at temperatures just below  $T_p$  relative to an older (i.e. less saturated) concrete.

Due to this, the approach from Equations (4) and (5) to determine the phase transition temperature is recommended for young (i.e. less than 28 day) mixtures since the Arrhenius relationship does not apply at temperatures just below phase transition for young (or saturated) mixtures, as seen in Fig. 7 and Farnam et al. [20]. However, the approach using the Arrhenius relationship shown by McCarter et al. should be used in place of Equation (5) for older, drier (28-day and beyond) mixtures where the Arrhenius relationship applies over the entire temperature range [18].

## 4.3. Effect of heating or cooling

As observed in Fig. 5, there is a difference in resistivity for the same mixture when cooled or heated past the phase transition temperature. This is further illustrated in Fig. 9 for the first thermal cycles of Mixture 1B and 5B. The 'B' mixtures were used in this comparison as the 'A' mixtures are less mature and thus are more affected by strength development occurring during heating and cooling cycles. Generally, Mixtures 1, 3, and 4 (all using only Portland cement as a binder) followed the trends seen with Mixture 1B while the remaining mixtures (2 and 5 – using blended cement and slag) followed the trends seen in Mixture 5B.

As expected, as mixtures are cooled from room temperature to  $T_p$  the resistivity follows the Arrhenius relationship. However, resistivity increases sharply once  $T_p$  is passed due to the onset of ice formation. Ice severely limits the flow of ions through the mix solution relative to water and causes an increase in resistivity. Additional ice formation, caused by propagation of the ice front to smaller pores as temperature is lowered further [15], caused further increases in resistivity. Once the temperature begins increasing from -24 °C back to  $T_p$ , resistivity is seen to be higher than at the same temperature during the cooling cycle for all mixtures. Ice formation during is controlled by the pore entry size while ice thawing is controlled by the maximum pore radius [14]. This means that there is more ice (i.e. higher resistivity) in concrete at the same temperature during thawing than there is during freezing. After heating passing  $T_p$ , it is seen that resistivity is slightly lower (by 8  $\pm$  2% for Mixtures 1, 3 and 4 and 16  $\pm$  4% for Mixtures 2 and 5) than it was during the first cooling cycle which was unexpected. This is believed to be due to ice formation (and expansion) creating more efficient routes for water to redistribute in the mixture, increasing ion flow and decreasing resistivity. This behaviour is discussed further in the next sections as it is also affected by mixture age and cycle number.

 $T_p$  was found to be lower (ranging between  $-2.6 \degree C$  and  $-8.5 \degree C$ ) than the freezing point of water in all mixtures during cooling. This lower freezing point is attributed to ions in the pore water solution reducing the freezing point of water from 0 °C (i.e. the freezing point depression). For all mixtures,  $T_p$  was lower by between 1.7 °C



Fig. 7. Arrhenius plots for the tested mixtures comparing the 'A' and 'B' cylinder results for the first cooling cycle. Results from the other cycles are similar and not shown for clarity. Sudden slope changes in each plot represent the onset of ice formation in each mixture.

#### Table 4

Activation energies for each mixture and cooling cycle. Activation energy evaluated as per the process illustrated in Fig. 6.

Mixture	Cycle 1	Cycle 1			
	Cooling	Heating	Cooling	Heating	
1A	22.4	17.2	21.5	18.5	
1B	20.6	19.1	20.9	20.6	
2A	24.0	16.6	22.5	19.8	
2B	23.3	22.2	23.9	23.2	
3A	21.6	15.6	20.3	16.8	
3B	20.5	18.1	19.8	19.1	
4A	23.8	15.8	21.1	19.2	
4B	19.9	19.6	20.8	20.6	
5A	23.7	15.2	21.9	17.7	
5B	24.0	21.7	25.3	21.5	

and 4.9 °C during cooling than heating. When melting, the ice melts at temperatures closer to 0 °C. This is attributed to the ions being trapped in ice and unable to mobilize (and cause a reduction in the melting point) until a  $T_p$  closer to the melting point of water is

reached.

## 4.4. Effect of concrete cycling age

The effect of the concrete age when it is first cycled on resistivity is shown for Mixtures 1 and 5 in Fig. 10. Results for the other mixtures are presented in Table 3. The resistivity-temperature response of the slag-blended mixtures was very similar to that of the mixtures with only Portland cement binders for the 'A' mixtures the early age behaviour of the slag-blended mixtures is dominated by hydration of the easily accessible cement. In the older 'B' mixtures, the increase in resistivity is considerably higher in Mixtures 2 and 5 than in Mixes 1, 3, and 4. The slower reacting slag and retarder admixture in Mixtures 2 and 5 delay reactions and cause a corresponding increase in resistivity. However, though resistivity is higher for slag-blended mixtures this increase has been shown not to significantly affect the 28-day compressive strength [11].

At temperatures above  $T_{p_i}$  the older 'B' mixtures had higher resistivity at the same temperature than the younger 'A' mixtures



Fig. 8. Illustration of the method used to determine the phase transition temperature for each mixture and cycle.

as they had longer time to cure. Interestingly, at temperatures lower than  $T_p$  in Mixtures 1, 3 and 4, the resistivity was lower in the 'B' Mixtures than the 'A' mixtures. Less ice forms in the older

mixtures (as more water has reacted or evaporated) and ions are more freely able to flow through the aggregates and binders (i.e. fewer are trapped in ice). This relationship was not observed in Mixtures 2 and 5 as the slag and retarder react considerably slower than cement, causing large increases in resistivity at all temperatures (relative to the cement only mixtures).

 $T_p$  was found to be lower during cooling in the 'B' mixtures than the 'A' mixtures. This difference averaged 1.7  $\pm$  0.3 °C for the cement-only mixtures and 3.4  $\pm$  0.9 °C for the slag blended mixtures. This is believed to be due to the older mixtures having higher concentrations of ions preventing ice formation as less water is available in the pore network of older concretes. Concrete age did not appear to have an effect on  $T_p$  during heating.

For all mixtures, the activation energy was lower during heating cycles than during cooling cycles with the difference between the two being dependent on concrete age. For instance, the ratio  $(E_{a,cooling}/E_{a,heating})$  was lower in the younger 'A' mixtures  $(0.77 \pm 0.03)$  compared to the older 'B' mixtures  $(0.94 \pm 0.04)$ . This trend agrees with values in the literature that show that fully cured mixtures have essentially equal activation energies during cooling and heating cycles [18].

## 4.5. Variations from cycle 1 to cycle 2

Generally, the first and second thermal cycle showed similar

Table 5

Values used to determine Phase	Transition T	emperature, 1	1
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Mixture Cycle			Equation (4) Values (>5 °C)			Equation	(5) Values (<-	5 °C)	Transition Temp	Transition Resistivity	
			A	В	R <sup>2</sup>	С	D	R <sup>2</sup>	T <sub>p</sub> ,°C	<i>ρ</i> . Ωm	
1A	1	Cooling	31.0	-0.035	0.995	-20.1	-17.3	0.973	-2.55	33.9	
		Heating	27.6	-0.023	0.993	-21.5	10.6	0.985	-0.81	28.1	
	2	Cooling	35.9	-0.031	0.997	-19.1	-17.7	0.979	-2.98	39.4	
		Heating	35.4	-0.028	0.995	-18.1	32.0	0.977	-0.20	35.6	
1B	1	Cooling	49.6	-0.030	0.996	-18.4	-28.3	0.980	-4.64	57.0	
		Heating	44.7	-0.028	0.995	-16.6	28.7	0.989	-1.04	46.0	
	2	Cooling	48.3	-0.030	0.996	-18.5	-25.3	0.977	-4.36	55.1	
		Heating	47.5	-0.030	0.996	-17.2	30.4	0.982	-1.09	49.0	
2A	1	Cooling	39.7	-0.038	0.995	-18.3	-40.1	0.970	-4.79	47.5	
		Heating	34.1	-0.022	0.993	-17.2	12.3	0.983	-1.33	35.1	
	2	Cooling	50.5	-0.034	0.997	-16.9	-29.1	0.973	-5.29	60.5	
		Heating	47.3	-0.028	0.995	-14.7	35.1	0.987	-0.91	48.5	
2B	1	Cooling	101	-0.035	0.996	-18.3	-18.7	0.963	-8.51	137	
		Heating	84.9	-0.031	0.997	-14.9	65.2	0.983	-1.62	89.3	
	2	Cooling	93.3	-0.035	0.997	-17.4	-7.8	0.967	-7.39	120	
		Heating	89.3	-0.033	0.996	-14.8	67.0	0.982	-1.90	95.1	
3A	1	Cooling	21.8	-0.033	0.996	-22.3	-14.3	0.984	-1.67	23.0	
		Heating	19.1	-0.021	0.992	-23.1	24.8	0.983	0.25	19.0	
	2	Cooling	25.5	-0.030	0.996	-20.1	6.3	0.983	-1.00	26.3	
		Heating	24.5	-0.026	0.994	-19.5	50.0	0.980	1.36	23.6	
3B	1	Cooling	38.5	-0.028	0.996	-18.4	-20.8	0.979	-3.44	42.4	
		Heating	33.4	-0.025	0.996	-17.4	26.2	0.985	-0.44	33.8	
	2	Cooling	37.4	-0.029	0.997	-19.0	-19.2	0.982	-3.16	41.0	
		Heating	36.1	-0.028	0.997	-17.5	35.9	0.984	-0.01	36.1	
4A	1	Cooling	26.5	-0.037	0.989	-21.9	-30.0	0.972	-2.71	29.3	
		Heating	22.8	-0.023	0.994	-21.6	19.9	0.980	-0.14	22.9	
	2	Cooling	30.1	-0.031	0.997	-18.7	-3.7	0.972	-1.90	31.9	
		Heating	28.6	-0.025	0.965	-18.1	40.8	0.978	0.71	28.1	
4B	1	Cooling	42.9	-0.028	0.997	-18.5	-27.0	0.980	-4.07	48.1	
		Heating	39.9	-0.028	0.993	-17.0	26.3	0.987	-0.85	40.8	
	2	Cooling	42.1	-0.029	0.997	-18.4	-18.7	0.984	-3.56	46.8	
		Heating	42.6	-0.031	0.993	-17.0	36.3	0.987	-0.40	43.2	
5A	1	Cooling	33.3	-0.035	0.993	-19.3	-31.0	0.969	-3.57	37.8	
		Heating	27.8	-0.019	0.970	-19.1	12.4	0.983	-0.83	28.3	
	2	Cooling	42.8	-0.033	0.997	-18.1	-16.7	0.970	-3.59	48.3	
		Heating	40.4	-0.026	0.995	-16.6	41.0	0.986	0.03	40.4	
5B	1	Cooling	135	-0.035	0.997	-23.7	-2.5	0.940	-7.50	175	
		Heating	103	-0.031	0.996	-19.8	91.2	0.964	-0.67	105	
	2	Cooling	119	-0.036	0.997	-25.7	-39.9	0.942	-7.61	156	
		Heating	109	-0.032	0.996	-18.6	103.7	0.966	-0.33	110	



Fig. 9. Resistivity versus temperature plots illustrating the effect of heating or cooling on resistivity readings for the first thermal cycle of Mixtures 1B and 5B. These plots show that the freezing and melting points for the mixtures differ by several degrees.



Fig. 10. Difference between 'A' and 'B' cylinders during cooling and heating cycles for Mixtures 1 and 5. The increase in resistivity caused by the used of blended slag in Mixture 5, particularly in the older 'B' cylinders is noticeable.

trends for each mixture but some changes were observed. The largest change was noticed for the 'A' mixtures between the first and second cycle at temperatures above  $T_p$ . The ratio of the resistivity of the second to the first cycle in the 'A' mixtures averaged 1.22  $\pm$  0.04 for Mixtures 1, 3, and 4 and 1.35  $\pm$  0.03 for Mixtures 2

and 5. This large difference is attributed to maturity developed over the course of the first thermal cycle. Considerably lower gains were seen in the 'B' mixtures (1.04  $\pm$  0.02) as curing is further along during their thermal cycles.

The decrease in resistivity at temperatures above  $T_p$  during the

heating cycle relative to the cooling cycle discussed earlier was not observed during the second thermal cycle, indicating that the redistribution of pore water in the mixture only occurs during the first freeze-thaw cycle.

The  $T_p$  during the second cycle averaged slightly higher (by < 0.5 °C) than during the first cycle. However, the standard deviation in  $T_p$  between cycles is larger than the average gain so, unless further investigated, this change is insignificant.

## 4.6. Effect of mix design on resistivity

As mentioned, the five mixtures fit into two general categories: slag-blended mixtures (2 and 5) and normal portland cement mixtures (1, 3, and 4). Considering Mixture 1 as a baseline, the ratio of  $\rho$  for a mixture against Mixture 1's  $\rho$  for the same cycle is shown for the first cycle in Fig. 11.

For the 'A' mixtures, each mixture had a consistent ratio of  $\rho$  to Mixture 1 at temperatures above  $T_p$ . The lower ratios for Mixtures 3 (0.71 ± 0.01) and 4 (0.83 ± 0.02) were expected as these mixtures have higher water cement ratios (0.62 and 0.54 respectively) that allow for increased ion mobility through the mixture. The higher values for Mixtures 2 and 5 (1.30 ± 0.07 and 1.11 ± 0.07) were also expected due to the slag and retarding admixture reducing ion flow. In the 'B' mixtures above  $T_p$ , Mixtures 3 and 4 had similar  $\rho_{mix1}$   $\rho_{mix1}$  values (0.79 ± 0.01 and 0.89 ± 0.01 respectively) as in the 'A' mixtures which are expected. The ratio for the slag blended mixtures increased greatly (up to 1.85 ± 0.08 in Mixture 2 and 2.31 ± 0.16 in Mixture 5) in the 'B' mixture. Similar trends were seen with

the slag-blended mixtures' activation energies.

At temperatures below  $T_p$  for the 'A' mixtures the ratios inverted (to 0.81 ± 0.05 for Mixture 2, 1.16 ± 0.04 for Mixture 3, 1.05 ± 0.03 for Mixture 4, and 0.91 ± 0.04 for Mix 5). This inversion is believed to be related to the amount of ice forming in the mixture (increases with w/c ratio).  $T_p$  is lower in the slag-blended mixtures and thus, at the same temperature, would have less ice formation (i.e. more water is available) than the other mixtures, accounting for why Mixtures 2 and 5 have higher resistivity than Mixture 1 despite having similar w/cm ratios.

In the 'B' mixtures below  $T_p$ , the Portland cement mixtures all had very similar resistivity values (the  $\rho_{mix}/\rho_{mix1}$  is 1.07 + 0.06 for Mixture 3 and 1.03 + 0.04 for Mixture 4). After 14 days, the amount of ice formation in the mixtures is lower and current would be carried moreso through the binding material and aggregates, which are similar in each mixture. Different responses were seen in the blended-slag mixtures as their lower  $T_p$  offsets the sudden increase in resistivity relative to the other mixtures, causing a gradual shift towards the resistivity of Mixture 1 as temperatures decrease further.

#### 5. Conclusions and recommendations

Five concrete mixtures were subjected to two thermal cycles from +24 to -24 °C at either 1 or 14 days after casting. The electrical resistance of the mixtures was monitored, as was the internal concrete temperature. The following was ascertained from this study:



Fig. 11. Ratio of resistivity for Mixtures 2 through 5 against that of Mixture 1 during thermal cycling. Slag-blended mixtures (2 and 5) show significantly different behaviours than the ordinary portland cement mixtures across all investigated temperature ranges.

- 1. For all mixtures and cycles, resistivity changed with temperature and followed the Arrhenius relationship at temperatures above the phase transition temperature,  $T_p$ . This relationship did not hold at temperatures below  $T_p$  where, for the tested cylinders, resistivity increases linearly and at a more rapid rate.
- 2. The phase transition temperature,  $T_p$ , is readily found during thermal cycling as there is a sudden change in resistivity at the onset of ice formation or melting. It is believed that this point corresponds with the datum temperature used in maturity calculations (i.e. concrete no longer gains strength at temperatures below  $T_p$ ). Future work should investigate this further as the method presented here requires less work than the method presented in ASTM C1074 for evaluating the datum temperature.
- 3. Mixtures that use slag as a supplementary cementitious material show considerably higher resistivity than those using ordinary Portland cement. Slag reduces the phase transition temperature as well.
- 4.  $T_p$  is affected not only by mix design but also concrete age ( $T_p$  decreased as concrete aged for all mixtures being cooled).  $T_p$  is lower for concrete being cooler than concrete being thawed.

The results show that though various mixtures have different temperature-resistivity relationships, they follow similar trends with regards to age and phase transition temperature. This is promising as it shows that electrical resistivity could be used to estimate performance of young concrete mixtures at temperatures at or below freezing. It is recommended that additional work investigate the response of mixtures with other supplementary cementitious materials (e.g. fly ash, silica fume) and admixtures (e.g. accelerators) to better understand how they affect the resistivity-temperature relationship, particularly the effect on the phase transition temperatures.

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