Chloride resisting concrete containing rice husk ash and bagasse ash

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In this paper, the effects of rice husk ash (RHA) and bagasse ash (BA) as cement replacement materials on the chloride resisting properties, important to durability of concrete structures have been studied. RHA and BA have been used up to 30% replacement by weight of cement with fixed water to binder ratio of 0.55. The properties of concrete investigated include water absorption, permeability, sorptivity, resistance to chloride ion penetration in terms of total charge passed in coulombs and chloride diffusion coefficient. The compressive strength of concretes containing RHA and BA were also supplemented. The specimens incorporating RHA or BA, when exposed to chloride solution exhibit significantly lower charge passed value and lesser chloride diffusion for all cement replacement levels (CRL). Overall results indicate that RHA (25-30% CRL) and BA (15-20% CRL) blended concretes showed superior durability properties.

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Reinforced concrete structures are expected to serve with little or no repair and maintenance for long periods of time even exposed to aggressive environments. One of the major forms of environmental attack to durable concrete structures is chloride ingress. Premature deterioration due to chloride-induced corrosion of reinforcing steel in concrete structures currently constitutes a major global concern for construction industry. Reinforcement corrosion results in cracking and spalling of concrete, causing a serious loss of serviceability and structural integrity of structures. Various standard specifications limit the permissible chloride content, resistance to chloride ion penetration in terms of total charge passed and chloride diffusion coefficient. In spite of the above specifications, damage due to chloride-induced reinforcement corrosion is one of the biggest threats to the life of structures. Capillary absorption, hydrostatic pressure and diffusion are the means by which chloride ion can penetrate into concrete. The most familiar method is diffusion, movement of chloride ion under a concentration gradient. A common method of preventing the premature deterioration of concrete is the development of high performance concrete which has fine pore structure, low porosity, less permeability and prevents chloride penetration to the level of steel.

Mineral admixtures such as natural pozzolan, fly ash (FA), silica fume (SF), ground granulated blast furnace slag (GGBFS), pulverized fuel ash (PFA), and rice husk ash (RHA) are increasingly used to produce dense and impermeable cement concrete. Several researchers have studied the mode of action of these mineral admixtures responsible for enhancing concrete properties. It has been observed that concrete mixes with 25% of fly ash content as cement replacement material showed the lowest value of saturated water absorption, sorptivity and chloride diffusion when compared with that of control concrete mixes. It was also concluded that replacement of cement with fly ash up to 25% would render the concrete more durable and corrosion-resistant besides meeting the strength requirements.

The filler and pozzolanic effect of SF with increase in cohesiveness also reduced the porosity of the transition zone with aggregate. Four time reduction in chloride ion permeability is reported for the specimens containing approximately 363 kg/m³ of cement with 7.5% of SF. Studies on the effect of curing on durability properties of concrete containing slag replacement showed that chloride permeability significantly decreased with increasing slag replacement. Series of studies were undertaken to determine the effect of PFA on the durability of concrete. The result of the above studies showed conclusively that the use of PFA in concrete contributes significantly to its resistance to chloride diffusion. Very few studies were conducted to determine the effect of RHA on the durability of concrete and reported that RHA concrete with 10%
Casting of specimens
The RHA or BA was initially blended with OPC thoroughly in dry condition, subsequently with sand and then coarse aggregate. Finally, water was added and mixed evenly to obtain uniform mix. The concrete was mixed for five minutes in a laboratory drum mixer. Six, 100 mm x 100 mm x 100 mm cubes were cast from each mix for compressive strength testing. Thirty, 100 mm diameter x 50 mm thick cylindrical specimens were cast from each mix for water and chloride penetration tests. After casting, all the specimens were kept covered in the casting room for 24 h. The specimens were then demoulded and transferred to moist curing room until 28 and 90 days of testing.

Test detail

Water absorption and permeable voids
Water absorption value of control concrete, RHA concretes and BA concretes were measured at the age of 28 days and 90 days as per ASTM C 642. The difference between the 48 h immersed weight and the oven-dried weight at a temperature of 110°C for 24 h is expressed as the percentage of oven dried weight and measured as water absorption of the specimen.

Volume of permeable voids of each specimen was calculated from the ratio of volume of voids to the bulk volume of the specimen. Volume of voids was obtained from the volume of water absorbed by an oven-dried specimen.

Coefficient of water absorption test
The use of coefficient of water absorption is considered as a measure of permeability to water\(^1\). This measures the rate of uptake of water by dry concrete specimen in a period of 60 min. The coefficient of water absorption value of concrete specimens was measured using the following expression at the age of 28 and 90 days.

\[
K_w = \left( \frac{Q}{A_t} \right) \times \frac{1}{t}
\]

where \(K_w\) is coefficient of water absorption, \(Q\) is quantity of water absorbed by the oven dry specimen in time, \(t\) is 60 min and \(A_t\) is total surface area of concrete specimen through which water penetrates.

Sorptivity test
Sorptivity is a measure of the capillary forces exerted by the pore structure causing fluids to be drawn into the body of the material. For one dimensional flow, it is stated that

\[
i = S t^{1/2}
\]

where \(i\) is cumulative water absorption per unit area of inflow surface, \(S\) is sorptivity and \(t\) is time elapsed. The sorptivity values of concrete specimens were measured at the age of 28 and 90 days according to the method developed\(^1\) at the University of Toronto, Canada.

Rapid chloride permeability test (RCPT)
The concrete specimens, on completion of moist curing period of 28 and 90 days were used for RCPT as per ASTM C 1202. The positive reservoir of the cell was filled with 0.30 M NaOH solution while the negative reservoir was filled with 3.0% NaCl solution as shown in Fig. 1. Two identical titanium substrate insoluble anode (TSIA) meshes were used as anode and cathode. A direct current (DC) of 60 ± 0.10 V was applied across the specimen faces, and the current across the specimen was recorded at every 30 min interval, covering a total period of 6 h. By knowing the current and time history, the total charge passed (CP) through the specimen was computed by Simpson's rule as given in the ASTM 1202

\[
CP = 900\left[ I_0 + 2I_{30} + 2I_{60} + 2I_{90} + \cdots + 2I_{180} + I_{210} \right]
\]

where CP is total charge passed in coulombs, \(I_0\) is initial current in ampere and \(I_t\) is current in ampere at time \(t\) min.

Chloride diffusivity test
The RCPT was introduced in USA in the early 1980's and has been increasingly used in several countries. This method is based on the measurement of total charge passed through the concrete over a short period of 6 h. In Norway, therefore, a similar
method was introduced\textsuperscript{13}, where the rate of chloride penetration is determined with the same test setup shown in Fig. 1. The chloride diffusivity was calculated as per the following expression

\[ D = \beta_0 \frac{k TLV (dc/dt)}{Ze_v EC_o A} \text{(cm}^2\text{s})\]

where \( D \) is diffusion coefficient (cm\(^2\)/s); \( \beta_0 \) is correction factor for ionic interaction, varies from 1.22 to 1.70 based on the chloride concentration from 0.1M to 0.5M NaCl; \( k \) is Boltzman constant (1.38x10\(^{-16}\) ergs/k/ion); \( T \) is temperature (K); \( Z \) is chloride valence (\( Z = 1 \) for NaCl); \( e_v \) is charge of proton (4.8x10\(^{-10}\) e.s.u); \( E \) is applied electrical potential (V); \( L \) is specimen thickness (cm); \( V \) is volume of chloride collecting tank (cm\(^3\)); \( C_o \) is initial chloride concentration in chloride source solution (mol/cm\(^3\)); \( A \) is cross-sectional area of specimen (cm\(^2\)); and \( (dc/dt) \) is steady state migration rate of chloride ion (mol/cm\(^3\)/s).

The diffusion coefficient for all the concrete specimens cured for 28 days and 90 days were measured by placing the specimens in the diffusion cell between two components containing solutions of 3% NaCl and 0.3 M NaOH. A potential of 12 V was applied and chloride ion migration through the specimens were monitored until steady state is reached.

**Compressive strength**

Soon after the moist curing of 28 and 90 days, the concrete cube specimens were withdrawn from the curing tank and subjected to compressive strength test as per IS 9013-1997.

**XRD analysis**

Concrete core samples were collected from control concrete, 30% RHA blended concrete and 20% BA blended concrete specimens after 90 days of curing. Powder samples were prepared mechanically from the core samples. The powder samples were subjected to XRD analysis by X-ray diffractometer of model Expert pro (Philips, USA), using CuK\(\alpha\) radiation with nickel filter.

**Results and Discussion**

The chemical and physical properties of RHA and BA are reported in Tables 1 and 2, respectively. From Table 1, the SiO\(_2\) content of OPC, RHA and BA are found to be 19.25%, 87.32% and 64.15%, respectively. These data clearly indicate that the SiO\(_2\) content was increased by about 4 times and 3 times for RHA and BA, respectively when compared to OPC. The burning temperature selected as 650°C for one hour to prepare RHA and BA as cement replacement materials\textsuperscript{14}, enhanced the fineness and pozzolanic properties to the ashes. This burning process also brought down the carbon content. The loss on ignition (LOI) for RHA and BA are found to be 2.1% and 4.9%, respectively. The LOI value of RHA is quite less than the permissible value of cement and the LOI of BA is equivalent to maximum permissible value (5%) of cement as per IS: 8112-1989.

In this study, uniform water to binder ratio (W/B) of 0.55 was adopted for different cement replacement levels (CRL). Inclusion of more than 15% of BA and 20% of RHA in concrete caused substantial reduction in concrete workability. Maximum CRL used was 30% for both RHA and BA. Even at this CRL and in the absence of super-plasticizer in the mix, the reduced workability did not affect the casting of specimens. The reduced workability of fresh concretes containing RHA or BA was due to the absorption of water by these ashes during mixing. The addition of RHA or BA also reduced the concrete density considerably. This was basically due to lower densities of RHA and BA compared with the cement.

The results of the permeability related properties such as water absorption, volume of permeable voids, coefficient of water absorption and sorptivity are given in Table 4. The 48 h saturated water absorption value of RHA concrete for different CRLs concrete specimens were in the range of 4.97-6.58% at 28 days of curing and 2.87-4.31% at 90 days of curing. Similarly, the values for BA concretes were 4.91-6.34% for 28 days of curing and 3.12-4.35% for 90 days of curing for different CRLs. The water absorption values in the order of 4.3-6.3% have been reported for fly ash concrete specimens\textsuperscript{15}. Thus, the water absorption values of RHA concrete and BA concrete are found to be comparable with fly ash concrete.

The volume of permeable voids of RHA and BA concretes were in the range of 11.31-14.39% at 28 days of curing and 6.12-8.98% at 90 days of curing. The volume of permeable voids of control concrete was 11.85% at 28 days and 8.37% at 90 days. It is also reported\textsuperscript{16} that the volume of permeable voids for the fly ash concrete was in the range of 8.14% up to 180 days of curing. These results also showed that the volume of permeable voids for RHA and BA concrete are found to be comparable with fly ash concrete and control concrete.
The coefficient of water absorption values decreased up to 25% replacements for both RHA and BA concrete at 28 days of curing and 90 days of curing (Table 4). Maximum reduction in coefficient of water absorption of 63% compared to control concrete was obtained for 25% RHA concrete at 90 days. Similarly, maximum reduction of 41% was obtained for 15% BA concrete compared to that of control concrete at 90 days. The reduction in coefficient of water absorption up to 25% of both RHA and BA may be due partially to the high specific surface area of RHA and BA leading to number of nucleation sites for additional hydration products and partially to the refinement of capillary pores by these ashes in RHA and BA concrete. At 30% of replacement of both the RHA and BA, there is an increase; however, these values are quite less than that of control concrete at 90 days. The RHA and BA in the mixes at 30% replacement also contribute to refinement of pore size, although this contribution is nearly equal to that of replaced cement. These results may be obtained due to lower level of cement present in the system.

Cook\(^1\) has reported that highly reactive pozzolana, such as rice husk ash is able to reduce the size of voids in hydrated cement pastes, thus making them almost impermeable even at early age (7-28 days). Bhanumathidas and Mehta\(^2\) confirmed the pore-refining capacity of RHA when present in a Portland cement concrete. Singh \(et al.\)\(^3\) showed the pore refining capacity of BA when present in a Portland cement paste. Gopalakrishnan \(et al.\)\(^4\) reported 30-50% reduction in coefficient of water absorption in fly ash based mixes up to 30% of replacement and showed that capillary pore had less inter connected in fly ash based concrete. Our study also indicates that the impermeability properties of RHA and BA blended concretes are considerably improved due to pore refinement.

In the same Table 3, the sorptivity values of both RHA concrete and BA concrete were decreasing with the increase of RHA or BA up to 25% replacement level at 28 days and 90 days. The sorptivity of control concrete at 28 days was 14.90x10\(^{-6}\) m/s\(^1/2\) and at 90 days was 10.86x10\(^{-6}\) m/s\(^1/2\). The least value of sorptivity of RHA concrete and BA concrete at 90 days were 6.38x10\(^{-6}\) m/s\(^1/2\) and 5.67x10\(^{-6}\) m/s\(^1/2\) respectively at 15% replacement level. It has been reported\(^5\) that good concrete will have sorptivity value of less than 12x10\(^{-6}\) m/s\(^1/2\). These results indicate the higher resistance to capillary suction of the RHA concretes or BA concretes up to 25% replacement level than control concrete.

The total charge passed (coulombs) obtained from the RCPT for the RHA concretes and BA concretes in different CRL at 28 days and 90 days of curing are reported in Fig. 2. From Fig. 2, the total charge (coulombs) passed is found to be always lower for all the concrete specimens incorporating RHA or BA with different CRL when compared to control concrete.

For example, the electrical charge passed through control specimen at 28 days and 90 days of curing were found to be 3140 and 2512 coulombs respectively. For all the replacement levels of RHA, the charge passed through the 30% of RHA cured for 90 days was found to be the least (656 coulombs) and among the BA concretes, 25% of BA replacement.

<table>
<thead>
<tr>
<th>Mix designation</th>
<th>RHA or BA (%)</th>
<th>Water absorption (%)</th>
<th>Volume of permeable voids (%)</th>
<th>Coeff. of water absorption x10(^{-6}) (m/s(^{1/2}))</th>
<th>Sorptivity x10(^{-6}) (m/s(^{1/2}))</th>
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<tbody>
<tr>
<td>Control C</td>
<td>0</td>
<td>4.88</td>
<td>11.85</td>
<td>1.68</td>
<td>14.90</td>
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<tr>
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<td>5</td>
<td>4.97</td>
<td>12.02</td>
<td>8.01</td>
<td>5.00</td>
</tr>
<tr>
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<td>10</td>
<td>4.60</td>
<td>12.30</td>
<td>7.87</td>
<td>1.255</td>
</tr>
<tr>
<td>R3</td>
<td>15</td>
<td>5.62</td>
<td>12.79</td>
<td>7.13</td>
<td>1.132</td>
</tr>
<tr>
<td>R4</td>
<td>20</td>
<td>6.15</td>
<td>13.83</td>
<td>6.73</td>
<td>1.084</td>
</tr>
<tr>
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<td>25</td>
<td>6.34</td>
<td>14.09</td>
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<td>6.58</td>
<td>14.39</td>
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<tr>
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<td>6.34</td>
<td>13.45</td>
<td>8.98</td>
<td>1.54</td>
</tr>
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</table>
cured for 90 days was found to be the least (771 coulombs). These results decreased the charge passed by 4 times and 3 times for RHA and BA concretes respectively. From the above results, it can be seen that the charge passed is decreasing with increased curing period and with increasing cement replacement level up to 30% of RHA or 25% of BA. At 30% of BA, there is an increase in charge passed value; however, the value is quite less than that of control concrete.

The transport of chloride ions through concrete depends on the pore structure of the concrete while the electrical conduction depends on both pore structure characteristics and electrical conductivity of the pore solution. The finer particles of ashes develop discontinuous and tortuous pore in concrete structure and reduce the electrical conductivity of the pore solution. Moreover, the micro and macro pores present in the concrete are completely filled up by finer particles. The addition of supplementary cementing material such as RHA or BA changes greatly the chemical composition of the pore solution, which has little to do with the pore structure itself. Chindaprasirt et al. reported that 30% fly ash concrete reduced the charge passed value to 700 coulombs due to pore refinement of fly ashes. Similarly, RHA and BA blended concretes are considerably improved due to pore refinement and change in chemical composition of the pore solution. This decrease in permeability of RHA and BA concretes in turn increases the durability of concrete even in aggressive chloride environment.

The chloride diffusion coefficients calculated for OPC, RHA and BA blended concretes are presented in Fig. 3. The chloride diffusion coefficient decreased with increasing RHA or BA replacements up to 20-25%. Beyond this level, any increase in replacement level increased the diffusion coefficient.

The range of diffusion coefficient of RHA concrete varies from 2.32 to $3.65 \times 10^{-8}$ cm$^2$/s at 28 days and 1.50 to $2.61 \times 10^{-8}$ cm$^2$/s at 90 days of curing. Similarly, the chloride diffusion coefficient of BA concrete varies from 1.34 to $3.27 \times 10^{-8}$ cm$^2$/s and 1.26 to $2.63 \times 10^{-8}$ cm$^2$/s at 28 days and 90 days of curing, respectively. Control concrete showed 3.90 $\times 10^{-8}$ and 3.36 $\times 10^{-8}$ cm$^2$/s at 28 days and 90 days of curing. These results also indicated that reduction of diffusion coefficient value observed by 2.24 times for RHA concrete at 20% replacement, and 2.67 times for BA concrete at 25% replacement respectively. Thus, the replacement of OPC with RHA or BA have reduced the chloride permeability values in terms of diffusion coefficient and also the extension of moisture curing period from 28 days to 90 days resulted in reduction in magnitude of diffusion coefficient of chloride ion. These lower diffusion coefficients play a major role in enhancing the service life of concrete structures even in aggressive chloride environments.

The compressive strength data collected at 28 days and 90 days of curing for RHA and BA blended concrete are reported in Fig. 4. The compressive strength of RHA concrete increased with the increase of RHA content up to 30% replacement at 28 and 90 days of curing. In the case of BA concrete, the
Compressive strength increased up to 20% replacement at 28 days and 90 days of curing. When the BA content was increased beyond 20% replacement, the compressive strength values were lower in both 28 days and 90 days of curing. The results also showed maximum increase in compressive strength values of 18.62% for RHA concrete at 20% of replacement and 15.68% for BA concrete at 15% of replacement. The increase in strength up to 30% of RHA and 20% of BA may be due partially to high specific surface area and the presence of reactive silica in RHA and BA and partially to the pozzolanic reaction as reported by many researchers. At 25% and 30% of replacements, BA also contributes to the compressive strength, although this contribution is less than that of replaced cement. Moayad et al. showed that the compressive strength development in 1:3 RHA blended cement mortars of same consistency with 30% cement replacement was equivalent to that of control mortar. Zhang and Malhotra also reported that the compressive strength of concrete containing up to 30% of RHA was higher than that of control concrete at 7, 14, 28, and 90 days. Bhanumathidas and Mehta also confirmed in their study, that the 90 days compressive strength with RHA up to 40% was somewhat higher than the corresponding concrete mixtures without RHA. Singh et al. revealed that increase in compressive strength in BA blended cement up to 20% may be due to pozzolanic reaction between calcium hydroxide and reactive silica in BA in the alkaline environment. Chindaprasirt et al. showed that the strength development of 30% fly ash concrete was rather good especially when the fine fly ash was dominant in comparison to that of control concrete. The good dispersing and filling effect of the fly ash has been reported as the reasons for the relatively good strength development of the fly ash concrete. The effect of RHA up to 30% and BA up to 20% replacements on the chloride penetration and strength are highly recognized in this study for blended cement concretes, although chloride penetration decrease with an increase in the strength of concrete.

Mineralogical analysis carried out by XRD for control concrete, 30% RHA blended concrete and 20% BA blended concrete cured for 90 days are shown in Figures 5a, 5b, and 5c, respectively. All of them show a prominent peak around d-spacing of 3.327 Å (26.850 20 value), where calcium silicate hydrate, [Ca$_3$(Si$_2$O$_5$)(H$_2$O)$_7$, C-S-H] in nekoite phase...
is known to be one of the major products of hydration\(^{16}\). Similarly, another common product, namely calcium aluminium silicate hydrate (C\(_{3}\)A\(_{2}\)Si\(_{4}\)O\(_{13}\).4H\(_{2}\)O) is also found in all the three figures. In addition, XRD show a different pattern from those of control concrete (Fig. 5a); and a new phase (additional phase) has been formed in the RHA concrete and BA concrete (Fig. 5b and Fig. 5c). In comparison to the PDF\(^{29}\) (00-33-306), the new phase is proved to be C\(_{3}\)A\(_{2}\)Si\(_{4}\)O\(_{13}\).6H\(_{2}\)O (d-spacing 3.04\(\AA\), 2.79\(\AA\), 1.82\(\AA\)), also known as calcium silicate hydrate [C-S-H (I)] gel\(^{16,28}\) (hydration product).

These results reveal that the reaction between the reactive silica present in RHA or SA and the extra lime in cement in the presence of water, can take place and yields C-S-H (I) gel\(^{29,30}\). Primarily, the strength of the concrete is attributed to the C-S-H component. Therefore, in comparison to the concrete without RHA or BA addition, there will be more C-H-S (I) gel and less portlandite in the concrete with RHA or BA addition. This contributes to improvement in the strength and its resistance to chloride penetration due to reaction between RHA or BA and Ca(OH)\(_{2}\) in hydrating cement.

**Conclusions**

From this study conducted, the following conclusions are drawn:

(i) The water absorption and permeable void values of RHA and BA blended concrete showed comparable results with fly ash blended concrete and control concrete.

(ii) The coefficient of water absorption results indicated that RHA (25% CRL) and BA (15% CRL) blended concrete showed a maximum reduction of 63% and 41% when compared to control concrete.

(iii) The sorptivity values obtained for RHA (25% CRL) and BA (25% CRL) blended concrete showed excellent resistance to capillary suction compared to control concrete.

(iv) The total charge passed (coulombs) from the RCPT results revealed that the charge passed decreased by 4 times and 3 times for RHA (30% CRL) and BA (25% CRL) blended concrete compared to control concrete after 90 days of curing.

(v) The chloride diffusion coefficient (\(D\) values) showed a reduction of 2 times and 3 times for RHA (20% CRL) and BA (25% CRL) blended concrete compared to control concrete.

(vi) Compressive strength increased by 18% and 15% for RHA (20% CRL) and BA (15% CRL) blended concrete compared to control concrete after 90 days of curing.

(vii) The results obtained from RCPT test and chloride diffusion coefficient test confirmed the pore refinement and improvement in micro structural aspects of RHA and BA blended concretes.

(viii) The XRD analysis data showed the formation of new phase such as calcium silicate hydrate [C-S-H (I)] gel in RHA concrete and BA concrete. The enhanced strength and resistance to penetration in RHA blended concretes up to 30% or BA blended concretes up to 20% possibly may be attributed to the formation of more C-S-H (I) gel in hydrating cement.

(ix) From the test conducted, RHA (25-30% CRL) and BA (15-20% CRL) blended concrete showed a proven track record of improving mechanical as well as permeability characteristics of concrete. Hence, RHA and BA blended concrete may be considered as a better substitute for chloride resisting concrete formulations.

**Nomenclature**

\(A\) = cross-sectional area
\(A_s\) = surface area
\(C_0\) = initial chloride concentration
\(D\) = diffusion coefficient
\(E\) = potential, V
\(e_o\) = charge of protons (4.8x10\(^{-10}\) e.s.u)
\(I_0\) = initial current in ampere
\(I\) = current in ampere at time \(t\) min
\(I_c\) = cumulative water absorption per unit area
\(k\) = Boltzmann constant (1.38x10\(^{-16}\) ergs /K / ion)
\(K_w\) = coefficient of water absorption
\(L\) = length
\(Q\) = quantity of water absorbed
\(S\) = sorptivity
\(T\) = temperature, K
\(t\) = time
\(V\) = volume
\(Z\) = chloride valence (\(z=1\) for NaCl)
\(dc/dt\) = steady state rate of chloride ion
\(\beta_0\) = correction factor (varies from 1.22 for 0.1 M to 0.5 M NaCl)

**References**