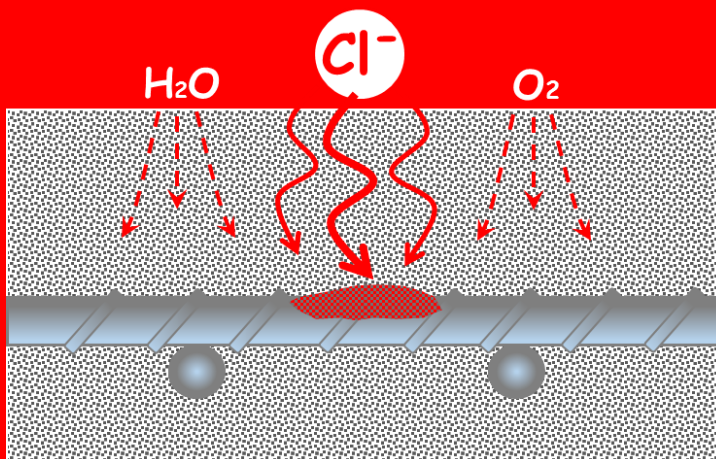


# CHLORIDE PENETRATION IN CONCRETE



## SHORT OVERVIEW AND AVAILABLE INSTRUMENTS

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## Overview

Reinforced concrete structures are exposed to harsh environments and they are often expected to last with little maintenance for long periods of time (often 100 years or more). To do this, durable structures need to be produced. One of the major forms of environmental attack is chloride ingress, which leads to corrosion of the reinforcing steel and a subsequent reduction in the strength, serviceability, and aesthetics of the structure. This may lead to early repair or premature replacement of the structure. A common method of preventing such deterioration is to prevent chlorides from penetrating the structure to the level of the reinforcing steel by using relatively impenetrable concrete. Therefore, the resistance to penetration of chloride ions into concrete must be known for design as well as quality control purposes and, in order to assess this resistance to chloride penetration, test methods are needed to allow the determination of representative values in a reasonable time.

There are different driving forces for chloride penetration in concrete: surface tension (absorption), pressure (permeation) and diffusion (movement of ions under a concentration gradient). From those, chloride ion ingress by diffusion is the dominant long-term mechanism for structures exposed to marine environments and deicing salts.

For concrete service-life calculations, the error function solution to Fick's Second Law of diffusion is the preferred approach:

$$C(x) = C_s - (C_s - C_i) \operatorname{erf}\left(\frac{x}{2\sqrt{D_a t_{ex}}}\right) \quad (1)$$

$C(x)$ : Chloride content versus depth ( $x$ ) at time  $t$

$C_s$  : Surface chloride content

$C_i$  : Initial chloride content in mixture

$\operatorname{erf}$ : Error function

$t_{ex}$  : Exposure time

$D_a$  : Apparent chloride diffusion coefficient

For **new concrete mixes**, either laboratory specimens or drilled out cores from a newly cast structure can be tested in accordance with ASTM C 1556 or NT BUILD 443 for evaluating the diffusion coefficient.

### **ASTM C 1556<sup>[1]</sup> and NT BUILD 443<sup>[2]</sup>**

1. Soak saturated specimen in a NaCl solution (165 gram NaCl per liter) for at least 35 days. For high quality concretes, this period may need to be extended to 90 days.
2. Profile grind to obtain powder samples at exact small depth increments.
3. Measure acid soluble chloride content of each powder sample (e.g. by using GI Rapid Chloride Test).
4. From the measured chloride profile, estimate the apparent diffusion coefficient by fitting Eq. (1) to the data.

The measured diffusion coefficient can be used to estimate the structures service-life for a given cover layer thickness and exposure condition, assuming the quality of the concrete cover layer is the same as of the specimen.

On **existing structures** with known exposure conditions to chlorides, profile grind followed by testing for chlorides (RCT) to obtain the chloride profile at a given exposure time. Assuming the diffusion coefficient is constant, an estimate of the remaining service life can be made for a given cover layer, all other factors being constant, using the solution to Fick's Second Law, and assuming a critical chloride content to initiate corrosion. It is expected that the diffusion coefficient obtained on site may be different from the one obtained in the laboratory because of the assumptions made and because, in a real structure, the other mechanisms of permeation and absorption are present.

Alternatives to using the time consuming ASTM C 1556 or NT BUILD 443 are the quicker **electrical methods** described below, which, however, do not determine the apparent chloride diffusion coefficient directly.

#### ASTM C 1202<sup>[3]</sup>

1. Specimen: 100 mm dia., 50 mm thick, water saturated
2. Specimen ends seated in cells
3. 3% NaCl and 0.3 N NaOH solutions in the cell chambers
4. Measure current over 6 h under a 60 V power supply instrument
5. Compute total charge passed across specimen (Coulombs) as the area below the current-time curve

ASTM C 1202 is often called “The Rapid Chloride Permeability Test” (RCPT):

- However, it does not actually measure “permeability” to chlorides. It measures only the Coulombs (charge passed or electrical conductance), which in fact, are not a material property and depends on the specimen size.
- Yet, the value obtained has been traditionally used to classify concrete samples as an indicator of their resistant to chloride penetration because conductivity is related fundamentally to the diffusion coefficient since both are affected by:
  - Type of cement and content of other binders (fly ash, slag, silica fume)
  - Porosity of cement paste
  - Connectivity and tortuosity of pores in cement paste

Some attempts have been made to correlate RCPT values with the diffusion coefficient but an accepted relationship does not exist.

#### NT BUILD 492<sup>[4]</sup>

This electrical method estimates the so-called “Chloride migration coefficient from non-steady-state migration experiments”  $D_{nssm}$  (**NOT** the Apparent chloride diffusion coefficient,  $D_a$ ) by means of:

1. 100 mm dia. x 50 mm water-saturated specimen
2. Cell with 10% NaCl as the catholyte solution and 0.3 N NaOH as the anolyte solution
3. Apply voltage (10 to 60 V) for specified time (6 to 96 h) depending on the initial current
4. Split specimen to get access to the cross section
5. Apply AgNO<sub>3</sub> on the concrete surface. AgCl precipitates as white powder as the indicator of the chlorides presence.
6. Measure the average depth of chloride ion penetration
7. Calculate the non-steady-state migration coefficient  $D_{nssm}$  from the equation stated in NT BUILD 492 standard.

Available data show a good correlation between  $D_{nssm}$  and  $D_a$  but the values are not equal to each other.

With some differences, a similar procedure using 20-30 V is stated in the French standard **XP P 18-462**, “Essai accéléré de migration des ions chlorure en régime non-stationnaire” [9]

In addition, another method to obtain a migration coefficient is through steady (or permanent) state tests such as the procedure in the French standard **XP P 18-461**, “Essai accéléré de migration des ions chlorure en régime stationnaire” [10], where calculations to obtain the coefficient are derived from the Fick’s first law of diffusion. However, because “steady state” means that a constant flux of chlorides through the concrete specimen must be achieved, this test is usually carried on thinner specimens (e.g. 20 mm thick) and the procedure requires a longer time.

### **ASTM C 1760<sup>[5]</sup>**

Measures the bulk electrical conductivity of hardened concrete:

1. 100 mm dia x 200 mm long specimens (molded or cores), water saturated
2. Uses the same ASTM C1202 apparatus
3. 3% NaCl solution in the cell chambers
4. Apply voltage 60 V across the specimen end faces
5. Record the current at 1 min.
6. Calculate the bulk conductivity in mS/m

Bulk conductivity is a material property and has theoretical relationship to the diffusion coefficient of chloride ions. Limited experimental data confirm that there is a correlation between the apparent chloride diffusion coefficient and the bulk conductivity.

### **MERLIN BULK CONDUCTIVITY or EXCALIBUR SURFACE CONDUCTIVITY**

These methods are faster options than ASTM C 1760 and ASTM C 1202. **Merlin** measures the bulk conductivity (or the inverse, resistivity) of laboratory cast or core specimens while **Excalibur** measures the surface conductivity (or the inverse, surface resistivity) of laboratory cast or core specimens. Although there is no standard method for bulk resistivity, **AASHTO TP 95** [6] is an

available standard method for surface resistivity. ASTM standards are currently under development.

Both methods are very well correlated provided that the obtained surface resistivity value is affected by the correct geometric factor which depends on concrete specimen size. The general procedure is as follows:

1. Water-saturated specimen, 100 mm diameter and a length up to 200 mm (other specimen sizes are possible)
2. Check the system with a verification kit with known conductivities (or resistivities)
3. Enter the dimensions of the specimen into the software
4. Mount the specimen, blotted dry on the circumferential surface, in the instrument bench
5. Measure the conductivity (or the resistivity) until stable value is achieved (within 2-3 seconds)

The bulk conductivity measured with **Merlin** or the surface conductivity measured with **Excalibur** are related directly to the charge passed through a specimen as measured by ASTM C 1202 providing the current remains constant during the 6 h test duration.

Furthermore, concrete conductivity (or its inverse, resistivity) has been shown to have good correlation with key durability parameters such as permeability or diffusivity to deleterious ions (e.g. chlorides and sulphates) and fundamentally, concrete resistivity is related with the micro-structural characteristics of concrete, therefore, it can be used in research to develop and understanding of the relationships between electrical conductivity and other mechanisms and characteristics (e.g. corrosion activity, w/cm ratio, setting time, etc.).

For service life calculations regarding reinforcement steel corrosion, the diffusion coefficient  $D$  of ions ( $D_a$  for our case with chloride ions) can be related to the electrical conductivity through the Nernst-Einstein relation:

$$\frac{\sigma}{\sigma_p} = \frac{D}{D_w}$$

Where:

- $\sigma$  = bulk electrical conductivity of the saturated porous material
- $\sigma_p$  = electrical conductivity of the pore fluid
- $D$  = bulk diffusion coefficient of the ionic species through the porous material
- $D_w$  = diffusion coefficient of the ionic species through water (values for chloride ions are published, for example,  $D_w = 1.8 \times 10^{-9} \text{ m}^2/\text{s}$  at  $20^\circ\text{C}$ ) [7].

The pore solution conductivity of concrete  $\sigma_p$  depends on the composition of the raw materials, the mixture proportions, the curing conditions, and the degree of hydration. The majority of mature concrete pore solution conductivities are in the range of 10 S/m to 20 S/m, but it is best to estimate the pore solution conductivity of a particular mixture.

A reliable web-based calculator for the pore solution conductivity of a particular mixture has been developed by Dale Bentz, NIST, USA, and can be found at:

<http://ciks.cbt.nist.gov/poresolncalc.html> [8]

To use the calculator, the following information needs to be provided:

- The mass of water and each type of cementitious material in a unit volume of the concrete.
- The sodium oxide ( $\text{Na}_2\text{O}$ ) and potassium oxide ( $\text{K}_2\text{O}$ ) content of the cementitious materials.
- The silica ( $\text{SiO}_2$ ) content of fly ash and silica fume, if used.
- The degree of hydration of the cementitious system.
- The curing condition: saturated or sealed.

The underlying assumptions for the calculations are given on the form. For example, only the alkali ions and their hydroxides are considered; other ions, such as chlorides are not considered. The following screen shot of the calculator shows the input fields and output.

### Mixture Proportions

Material	Mass (kg or lb)	$\text{Na}_2\text{O}$ content (mass %)	$\text{K}_2\text{O}$ content (mass %)	$\text{SiO}_2$ content (mass %)
Water	160.0	Not applicable	Not applicable	Not applicable
Cement	300.0	0.2	1.0	Not applicable
Silica fume	20.0	0.2	0.2	99.0
Fly ash	100	0.2	0.2	50.0
Slag	0.0	0.2	0.5	Not applicable

Estimated system degree of hydration (%): 90

Hydrodynamic viscosity of pore solution relative to water: 1.0

Curing: Saturated ☐ Sealed ☒

**Estimated pore solution composition (M):**

K+: 0.59

Na+: 0.23

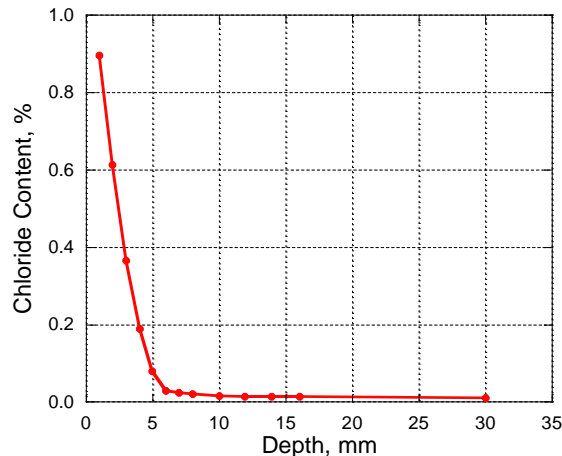
OH-: 0.83

**Estimated pore solution conductivity (S/m):** 16.04

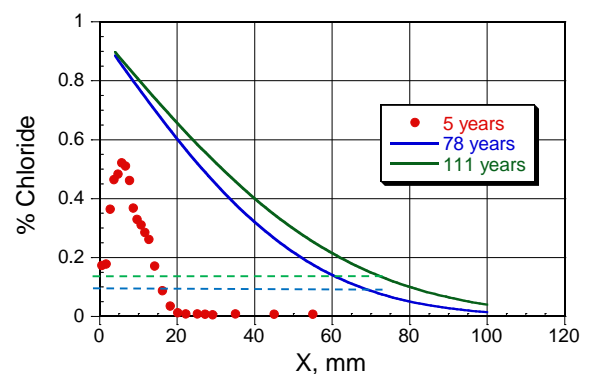
## GERMANN INSTRUMENTS Test Systems for the standards/procedures mentioned

### 1. PROFILE GRINDER and Rapid Chloride Test (RCT)

These systems can be used to perform ASTM C 1556 and NT BUILD 443 for apparent chloride diffusion coefficient  $D_a$ , which can afterwards be used for estimation of service life using the solution to Fick's Second Law of Diffusion:



**Fig.1. Laboratory testing.** Profile grinding of specimen subjected to 35 days of immersion in the laboratory. Chloride content of each sample is determined using the RCT. The profile obtained is shown in the right figure. An apparent chloride diffusion coefficient of  $29 \text{ mm}^2/\text{y}$  is estimated by fitting the solution Fick's Second Law of Diffusion in accordance with ASTM C 1556 or NT BUILD 443



**Fig.2. On-site testing.** Profile grinding in progress on a sea structure (left) and chlorides being measured with the RCT (middle) after each step of grinding. From the profile (red dots in the right figure, neglecting the values of the first 5 mm affected by carbonation) an apparent diffusion coefficient of  $10.9 \text{ mm}^2/\text{y}$  is estimated. For the cover layer of 80 mm and for a critical threshold chloride value to initiate corrosion of reinforcement of 0.05% Cl/concrete mass, the estimated remaining service life is 78 years. Similarly, for  $C_{cr} = 0.10\%$  Cl/concrete mass, the estimated remaining service life is 111 years, all other factors being constant.



## 2. Electrical Methods, Instrument 1: **PROOVE'it**

For the test methods that involve electrical measurements, very different values may be obtained if different water content conditions of the concrete specimens are used. Therefore, prior to testing the concrete, specimens should be fully water saturated, e.g. by using a vacuum desiccator and a vacuum pump as shown in Fig. 3, and following the ASTM C 1202 procedure for water saturation.

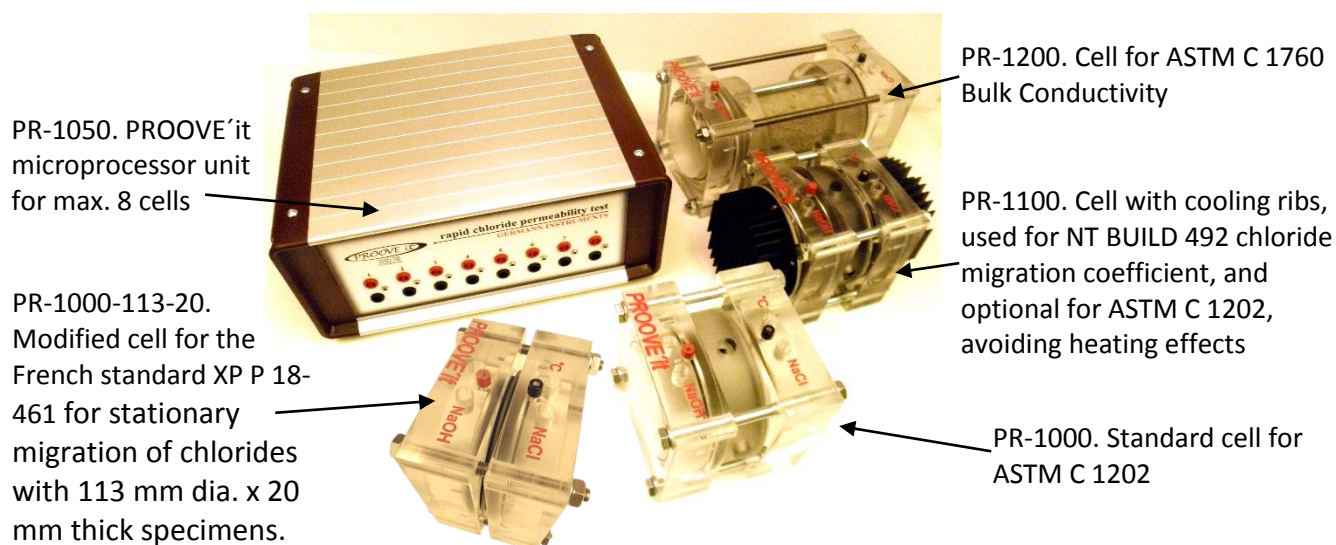


**Fig. 3.** The **PR-1070 Vacuum desiccator** for saturating max. 24 specimens (dia. 100 mm x 50 mm) and the **PR-1081 vacuum pump** with hose, <10 mm Hg vacuum.

Precision coring and slicing equipment is available for preparing test specimens. Consult the latest version of the Germann Instruments catalog or visit the website for more information.

### 2.1. **PROOVE'it PR-1050, for 8 Cells and adjustable voltage**

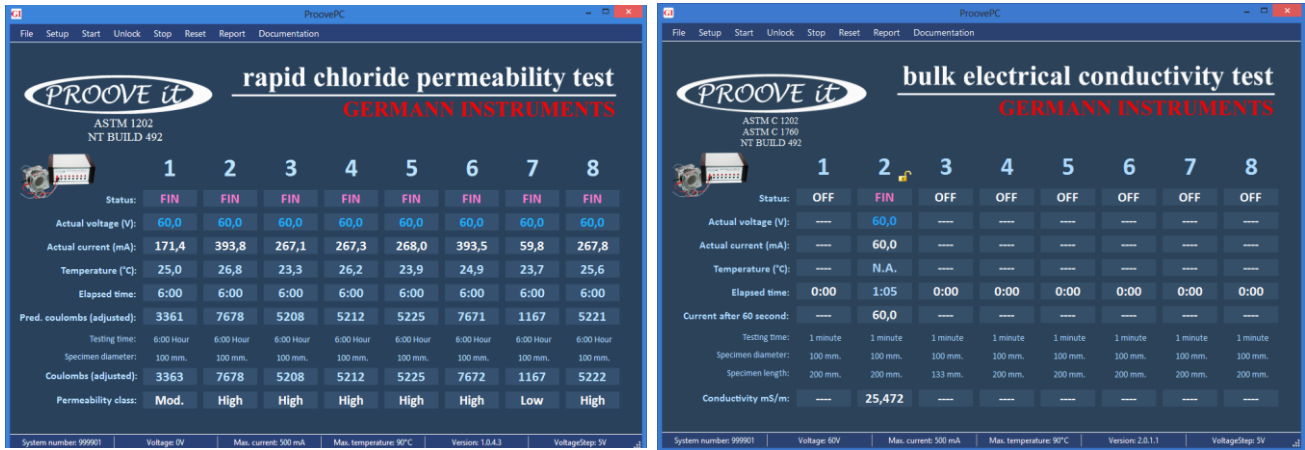
The PR-1050 eight cell PROOVE'it microprocessor unit and related software can be used to perform ASTM C 1202 (the RCPT), ASTM C 1760, NT BUILD 492, XP P 18-461 and XP P 18-462.



**Fig. 4.** The PR-1050 PROOVE'it up to max 8 cells shown with the various testing cells.



Examples of the computer display using the **PR-1040 software** for performing ASTM C 1202 and ASTM C 1760 are shown below.



**Fig.5.** Eight specimens tested according to ASTM C 1202, RCPT, using PR-1000 cells, (left figure); and one test completed for bulk conductivity according to ASTM C 1760 using the PR-1200 cell (right figure).

Below is shown an example of chloride penetration after testing in accordance with NT BUILD 492 using the PR-1100 cell and the PR-1040 software to evaluate the non-steady-state diffusion migration coefficient.



**Fig. 6.** Chloride penetration depth of ~8 mm on a specimen after NT BUILD 492 testing

For this example, a non-steady-state chloride migration coefficient of  $D_{nssm} = 3.37 \cdot 10^{-12} \text{ m}^2/\text{s}$  is calculated using the following parameters in equation (4) in the NT BUILD 492 standard:

1. Applied voltage  $U = 30\text{V}$
2. Test duration  $t = 24 \text{ hours}$
3. Temperature  $T = 20^\circ\text{C}$
4. Length  $L = 50 \text{ mm}$
5. Penetration depth  $x_d = 8 \text{ mm}$

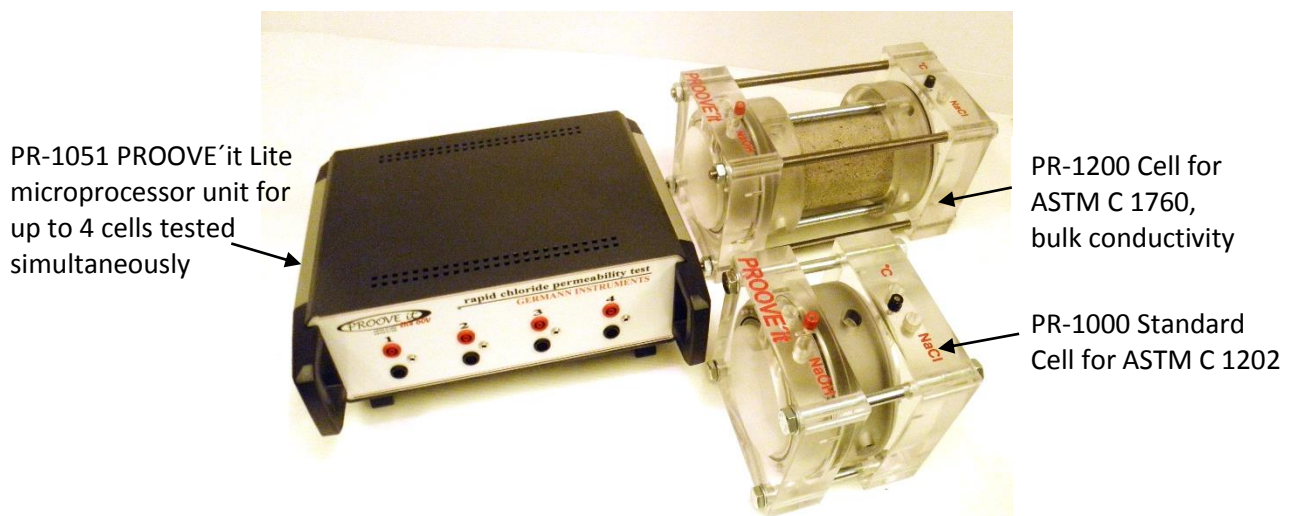
The migration coefficient  $D_{nssm}$  obtained by NT BUILD 492 is reported in units of  $10^{-12} \text{ m}^2/\text{s}$ . A more convenient unit is  $\text{mm}^2/\text{y}$ , which can be calculated multiplying by  $31.536 \times 10^{12}$ . In the example, the non-steady-state chloride migration coefficient  $D_{nssm}$  is  $106.3 \text{ mm}^2/\text{y}$ .

$D_{nssm}$  is not equivalent to the apparent chloride diffusion coefficient  $D_a$  obtained from ASTM C1556 or NT BUILD 443, and should not be used directly for calculation of service life. Data show that there is correlation between both coefficients, but an accepted relation has yet to be established. The same goes for the steady-state chloride migration coefficient obtained and calculated by means of the French standard XP P 18-461.

## 2.2. PROOVE'it Lite PR-1051, for 4 Cells

The PR-1051 PROOVE'it Lite, four cell system version, can be used to perform ASTM C 1202 (the RCPT) and ASTM C 1760 (bulk conductivity) but it cannot be used to perform NT BUILD 492, XP P 18-461 or XP P 18-462 because it only works with a fixed 60 V current.

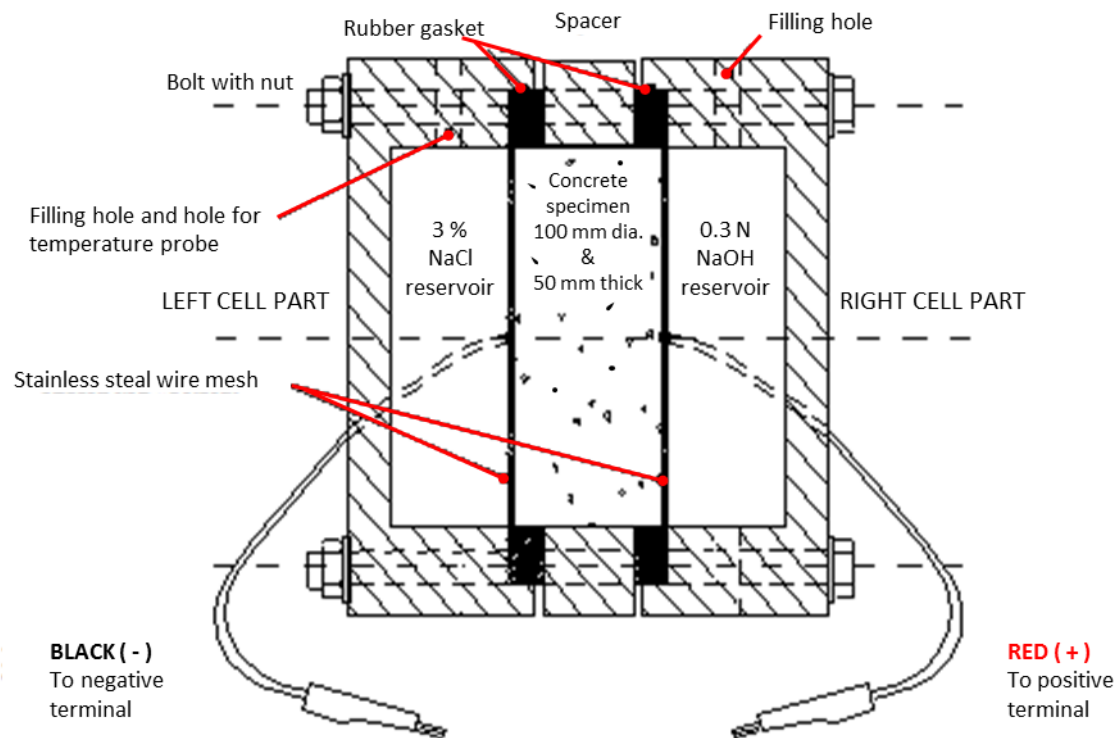
The PR-1041 software for the PROOVE'it Lite model has the same functionality as shown in Fig. 5, but is limited to using only 4 channels.



**Fig. 7.** The PR-1051 PROOVE'it Lite model for with the PR-1000 and the PR-1200 cells

## 2.3. PROOVE'it Cells

The schematic of the cells is illustrated in Fig. 8. To avoid applying epoxy (to eliminate stray currents) on the circumferential face of the specimen, the cell is designed in such a manner that the gaskets are compressed against the specimen to achieve water tightness. This is done, after choosing the proper gasket size, by tightening the nuts on the four bolts. The spacer will squeeze the gaskets positioned in the grooves of the cell parts, the gaskets will expand and push against the specimen to finally obtain a watertight seal.



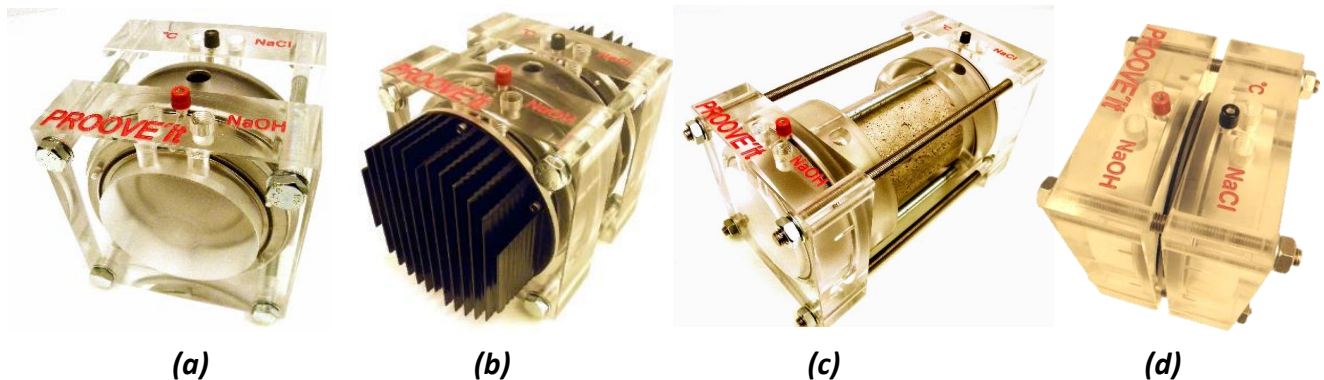
**Fig. 8.** The schematic of a PROOVE'it cell

Some standards suggest large reservoirs for the solutions, partly to keep the chloride concentration in the catholyte chamber constant and partly to reduce temperature rise. The PROOVE'it cells have 0.5 liter reservoirs, however, the 3 % NaCl solution used for ASTM C 1202 and ASTM C 1760 will not experience a significant change in concentration during testing and consequently, the effect is negligible on the results. For NT BUILD 492, a 10% NaCl solution is used and during testing, experience also shows that this concentration will also be maintained. Yet, in cases where highly permeable concrete is tested and a potential concentration decrease is suspected, the cells can be connected through their threaded filling holes to an external reservoir with NaCl solution and circulated with a small pump in the external reservoir.

The heating effect is evident if poor concrete quality is tested using the PR-1000 cell conforming to ASTM 1202. The temperature rise increases electrical conductivity and this will increase the Coulombs measured. The software turns off the system if the temperature in the NaCl reservoir reaches 90°C.

To avoid specimen heating, the PR-1100 cell with cooling ribs has been developed. The cooling ribs are optional for conducting RCPT measurements but are highly recommended for conducting NT BUILD 492, XP P 18-461 or XP P 18-462 because temperature must be kept constant. Should an increase in temperature be recorded during testing, a fan can be used to enhance the heat transmission through the cooling ribs.

Each of the cells are illustrated below.



**Fig. 9.** The PROOVE'it cells: the **standard PR-1000 cell (a)** for ASTM C 1202; the **PR-1100 cell with cooling ribs (b)** for NT BUILD 492, and RCPT with optional heat reduction; the **PR-1200 cell (c)** adapted for ASTM C 1760 and the **PR-1000-113-20 (d)** modified for the French standard XP P 18-461 for 113 mm dia. and 20 mm thick specimens (cooling ribs can also be mounted here).

### 3. Electrical Methods, Instrument 2: **MERLIN**

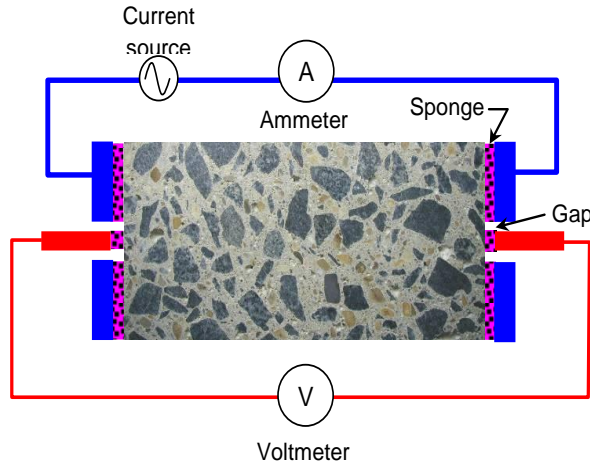
**Merlin** is used to measure the bulk electrical conductivity, or its inverse, the bulk electrical resistivity, of saturated 100 mm diameter concrete cylinders or cores with lengths up to 200 mm. The test is simple to perform and a measurement is obtained within two seconds.

The term **bulk** is used to indicate that the measurement is made through the specimen as opposed to a **surface-based** measurement.



**Fig. 10.** **Merlin** being used on a water-saturated cylinder. A conductivity of 9.675 mS/m is measured after 2 seconds, the usual time taken to obtain a stable reading.





**Fig. 11.** The Merlin method of operation

An alternating current source with a specific square wave is used to apply current through the saturated cylinder or core. A voltmeter measures the voltage drop across the specimen, and an ammeter measures the current through the specimen. A particular advantage with the Merlin is that the disturbing specimen impedance is eliminated during measurement, providing a quick and accurate reading.

From the measured current  $I$  and voltage  $V$ , the bulk conductivity is calculated as follows:

$$\sigma = \frac{I}{V} \frac{L}{A}$$

Where  $L$  is the specimen length and  $A$  is the specimen cross-sectional area.

The bulk resistivity is the inverse of the bulk conductivity, that is,  $\rho = 1/\sigma$

As discussed in pages 4 to 6, the bulk conductivity may be used to estimate the apparent chloride diffusion coefficient, which can be later used in service life calculations.

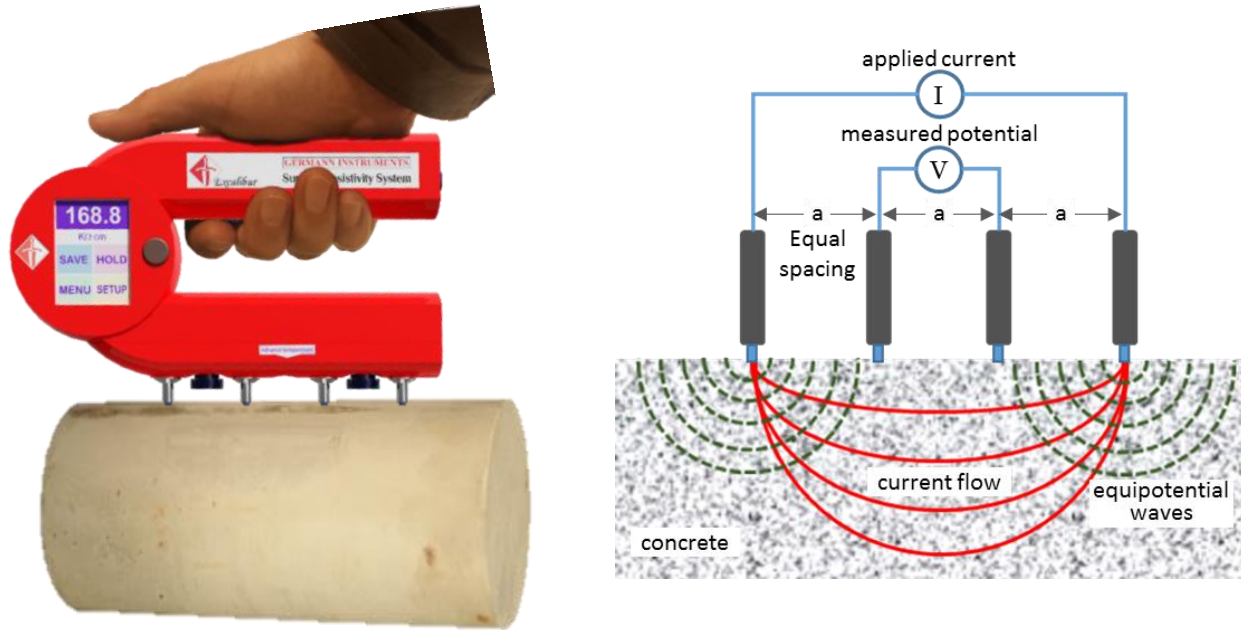
A 100 by 200 mm verification cylinder is provided to check that the **Merlin** system is operating correctly. The cylinder includes a push button switch that can be used to select a precision resistor from 10  $\Omega$  to 1 M $\Omega$ . For example, if the 1000  $\Omega$  resistor is selected and the system is functioning correctly, the conductivity reading of the verification cylinder should be 25.46 mS/m and the resistivity should be 0.039 k $\Omega$ ·m.



**Fig. 12.** The verification cylinder is used to make sure the system is working properly before performing a measurement.

#### 4. Electrical Methods, Instrument 3: EXCALIBUR

**Excalibur** is a hand held device that also measures quickly the electrical resistivity, however, unlike Merlin, Excalibur is placed on the concrete surface. This surface resistivity measurement is based on the four-probe, Wenner array, technique. A current is applied to the two outer probes and the voltage measured by the two inner probes.



**Fig. 13.** The Excalibur method of operation

The surface resistivity is then calculated from:

$$\rho = \frac{1}{\sigma} \quad \& \quad \sigma = \frac{I}{V} 2 \pi a k$$

Where  $a$  is the electrode spacing and  $k$  is the geometric correction factor which depends on the shape and dimensions of the specimen. The standard spacing of the device is 38.1 mm (1.5 in) for concrete with up to 25 mm (1 in) maximum aggregate size. If the appropriate correction factor is applied and the same storage and curing conditions are followed, the correlation between bulk resistivity and surface resistivity has proved to be very close to 1:1. Small differences can be found depending on the irregularities of the concrete surface.

Because of its size and light weight, **Excalibur** is a fast, easy-to-use and cost-effective method for quality control and quality assurance for potential durability of concrete in construction works, for example, by means of concrete resistance to chloride penetration according to the classification provided by AASHTO TP 95 standard. It provides highly accurate readings by eliminating the error due to electrical impedance.



Two extension probes are available to connect to this instrument and increase its extent:

**Excalibur Accordion:** Extension probe with adjustable electrode spacing for testing concrete with larger maximum size aggregate or specimen shapes different from those considered in AASHTO TP 95.

**Excalibur Submergible:** Extension probe for making measurements in fresh concrete. The electrical resistivity of fresh concrete has been shown to provide good indicators of water content, w/cm ratio, setting time, etc.

## 5. References

Visit our web page at [www.germann.org](http://www.germann.org) where more information can be obtained.

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