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16. ABSTRACT

SRI International has developed a wireless sensor for monitoring the level of chloride ingress into concrete bridge decks. We call this device a Smart Pebble™ since it has roughly the size and weight of a typical piece of the rock aggregate that is used in such structures. It is "smart" in that it contains a chloride sensor and a radio-frequency identification (RFID) chip that can be queried remotely both to identify it and to indicate chloride concentration levels. The Smart Pebble™ is also powered remotely, thus precluding the need for any lifetime-limiting batteries. It is designed to be inserted in the bridge deck either during the initial construction (or during refurbishment) or in a back-filled core hole. The Pebble devices constructed can transpond sensor data through as much as 6 inches of concrete. We have developed stable reference electrodes in a laboratory environment, with 4000 hours of continuous measurement. Unfortunately, the resulting electrochemical cell in the Pebble device has limited stability over the intended design life.

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SMART PEBBLES™: Passive Embeddable Wireless Sensors for Chloride Ingress Monitoring in Bridge Decks

SRI Report No. P11071

Prepared by:

David G. Watters
Alfred J. Bahr
Palitha Jayaweera
David L. Huestis
SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025

Prepared for:

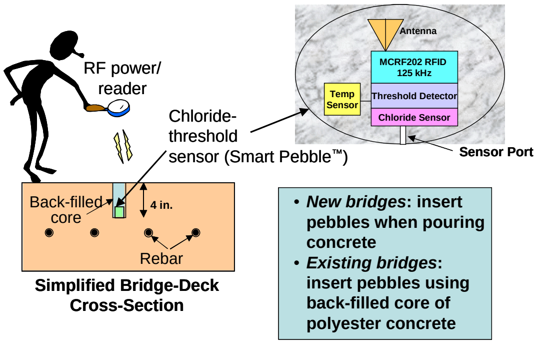
Robert Meline
Division of Research and Innovation
California Department of Transportation
5900 Folsom Blvd
Sacramento, CA 95819

SUMMARY

INTRODUCTION. SRI International is developing a wireless sensor for monitoring the level of chloride ingress into concrete bridge decks. We call this device a Smart Pebble™ since it has roughly the size and weight of a typical piece of the rock aggregate that is used in such structures. It is "smart" in that it contains a chloride sensor and radio-frequency identification (RFID) chip that can be queried remotely both to identify it and to indicate chloride concentration levels. The Smart Pebble™ is also powered remotely, thus precluding the need for any lifetime-limiting batteries. It is designed to be inserted in a bridge deck either during the initial construction (or during refurbishment) or in a back-filled core hole. A number of other inspection applications can be envisioned for this enabling technology. Development of the Smart Pebble™ has required innovation in several areas: chloride sensing, integration of sensor and RFID electronics, and packaging. This report details these developments as well as the performance of the prototype Pebble.

THE PROBLEM. A recurring maintenance problem encountered in bridge decks is that these structures contain reinforcing steel (rebar) that will corrode in the presence of chloride ions. These ions diffuse into the concrete from the surface because of the presence of salt water from various sources such as seawater spray in coastal zones or deicing salts in cold climates. The diffusion rate is slow, but finite. The resulting corrosion products expand the rebar volume and cause subsequent cracking and spalling of the concrete. There is a critical chloride concentration level where such corrosion initiates (depending on the type of concrete) and it would be desirable to determine quickly and reliably when this level has been reached so that remediation can be undertaken. Having the ability to measure this chloride threshold at a known depth above the rebar would enable prioritization of maintenance schedules before critical chloride levels reach rebar depth. Presently, concrete core samples have to be extracted and then analyzed in the laboratory, which includes logging of core number, sectioning the samples, crushing the individual layers, and making titration measurements to quantify the chloride concentration. Moreover, it typically takes several years for the critical chloride concentration to be reached, so many tests may be required. Hence, one would like to test often, but inexpensively.

OUR SOLUTION. The Smart Pebble™ concept is illustrated in Fig. S-1. The reader can be either hand-held or vehicle-mounted. For now, the Smart Pebbles™ are envisioned as being inserted in a back-filled non-concrete core for evaluation, but ultimately they would become part of the initial concrete pour.



Simplified Bridge-Deck Cross-Section

- ***New bridges*: insert pebbles when pouring concrete**
- ***Existing bridges*: insert pebbles using back-filled core of polyester concrete**

Figure S-1. Smart Pebble™ concept

A prime sensor candidate for this application is an electrochemical sensor that generates an electric potential dependent on the concentration of chloride ions. This circuit includes an RFID chip, which not only indicates when a threshold level has been exceeded by inverting the ID-code bit stream, but which also is able to power the external electronics. The reader converts this ID-code bit stream into a unique ID code. The reader can also indicate under- or over-threshold chloride-concentration conditions with a green or red light, respectively. Thus the reader can be used either for a quick visual inspection or to provide a digital output that can be recorded in a historical database.

The electrochemical sensor consists of two electrodes: a chloride-selective electrode and a reference electrode. The measured quantity in this case is the potential difference between these two electrodes. Thus, the potential of the reference electrode must remain fairly constant (say, ±5 mV) over the life of the Smart Pebble™. This requirement represents a major design challenge. Our chloride sensor concept is illustrated in Fig. S-2.

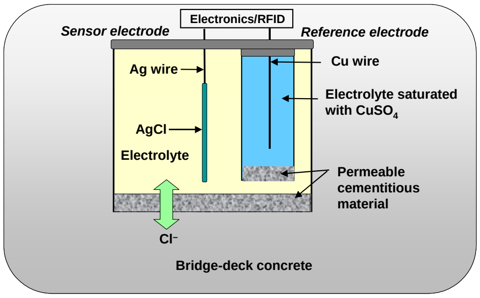


Figure S-2. Chloride sensor concept

The measured output voltage of our electrode couple when immersed in a liquid solution containing chloride ions is 44 mV/pH, which is slightly below the room-temperature response of 59 mV/pH predicted by the Nernst equation. Note that, for a chloride concentration calibration threshold of 30 mM, a concentration change of ±10 mM produces a voltage change of about ±10 mV. Thus, if the uncertainty in observed sensor voltage because of manufacturing tolerances, temperature effects, etc., is ±5 mV, we can expect to detect the concentration threshold to within ±5 mM (±17%). Note also that the error sensitivity increases as chloride concentration decreases.

PACKAGE DESIGN. The Smart Pebble™ package was designed by FusionDesign. Key components of the design are the polyurethane rubber enclosure that holds the reference and ion-selective electrodes and their electrolytes and also protects the circuit board, and the rigid polyurethane cup that protects the whole unit, especially the coil. The unit is sealed with epoxy so that only the cementitious plug is exposed to the external environment. This plug permits the chloride ions to diffuse into the electrode region and thereby alter the sensed electrochemical potential in accordance with the chloride concentration. The completed Pebble is shown in Fig. S-3.

Figure S-3. A completed Smart Pebble™

AGEING AND CALIBRATION. The unit was immersed for a lengthy period of time in a saturated calcium hydroxide solution containing a 30-mM concentration of chloride ions and the sensor potential was measured aperiodically using a high-impedance electrometer. The potential starts out high and then drops as the chloride ions diffuse into the cell. The diffusion through the cementitious plug is slow and so the time for calibration equilibrium to be reached is long. A better approach would be to start out with the electrolyte inside the cell already containing chloride ions at the desired concentration level and then leach out the chloride to a below-threshold value after calibration has been completed.

PEBBLE INTERROGATION. In operation it is anticipated that the embedded Pebble(s) will be queried either with the reader in a hand-held mode as depicted in Fig. S-1, or ultimately in a drive-by mode where the reader is mounted on the underside of, say, a truck. This latter method of interrogation and data acquisition raises the question of how rapidly the vehicle can move during this process and still maintain reliable operation. It would be highly desirable to move at a reasonable speed so as not to produce traffic back-ups on the bridge. The answer to this question depends mainly on the characteristics of the reader.

The MCRF202 reader used to test the Pebble prototypes produces 125-ms-long transmit pulses of 125-kHz energy to power the RFID chip. Initially, these pulses repeat contiguously until a valid identification (ID) code has been received from the chip. This powering-up phase can take up to 1.5 sec, depending on the range. After initial ID, the transmit pulse repeats about every 1.4 sec, resulting in a repeating series of RFID responses. The second RFID response can generally be taken as a valid Pebble response.

CONCLUSIONS. This report has described the design and development status of a Smart Pebble™ for monitoring the health of bridge decks. This device is a unique combination of an electrochemical chloride-concentration sensor with a wireless RFID chip. To date, the design has been completed and all components have been fabricated, tested, and assembled into Smart Pebble™ units. However, there is room for improvement in the electrochemical sensor design, including a more uniform manufacturing process to remove variation in measured potentials. We make recommendations for reducing the temporal drift of the electrode potentials associated with the drying of the water-based electrolyte within the sensor cell, which makes sensor calibration uncertain and affects the design values of the components in the potential-conditioning circuit.

In addition to chloride concentration threshold, sensing other important bridge-deck quantities could be incorporated in a Smart Pebble™, including pH, conductivity, moisture, polarization resistance, and temperature.

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1 INTRODUCTION

Considerable resources are expended each year to rehabilitate and repair bridges (Figure 1) that undergo corrosion damage ($3.8 billion/year in the U.S. [1]). If indirect costs such as traffic delays are included, the total nation-wide economic impact of corrosion damage is substantial. In order to reduce this impact, a compelling feature of future bridge construction will be the incorporation of smart materials—materials that can sense the condition of the bridge, adapt in the presence of harsh conditions, and heal damage caused by corrosion and wear. These smart materials will increase bridge lifetime, lower inspection costs, and enable prioritized maintenance of critical structures. A step in this direction is the development of Smart Pebbles™, which are passive wireless sensors capable of monitoring chloride ingress in bridge decks.

This report describes the development of embeddable wireless devices, which are about the size of typical rock aggregate used in concrete. Called Smart Pebbles, these devices integrate the features of radio-frequency identification (RFID) tags with sensors. They are powered remotely, so there is no need for lifetime limiting batteries. Devices each have a unique ID number. They reach equilibrium with their surroundings and report these conditions when powered by an external reader. The reader can update a database to register and track changes in bridge deck conditions. Smart Pebbles can be inserted in a bridge deck either during the initial construction (or during refurbishment) or in a back-filled core hole.

Figure 1. Bixby Bridge repairs near Big Sur, CA

1.1. Design Overview

Smart Pebbles use an electrochemical cell to measure chloride concentration [2-5]. When this concentration is above a pre-determined threshold the RFID transponds an inverted bit stream to the interrogating reader to indicate the presence of elevated chloride levels. The current device operates at 125 kHz and occupies a volume of approximately 1 cu. in. Smart Pebbles can be interrogated from a distance of 6 in., when embedded in concrete.

During the course of the project, we found that RFID communications operated as expected according to well-established theory. Development of the interface circuitry that connects the RFID with the electrochemical cell was straightforward, but required a number of design iterations. Design of a stable chloride sensor was our most challenging undertaking. Eventually, we constructed a small batch of Smart Pebbles that indicated chloride threshold changes when immersed in aqueous solutions in the laboratory. These devices were sent to Caltrans for further evaluation in more realistic environments. Progress to date indicates that *in situ* health monitoring is indeed a promising possibility for future bridge-deck designs. In this report we recommend a number of design improvements for second-generation chloride-sensing Smart Pebbles.

1.2. Outline

The outline of the report is as follows. Section 2 provides background on the motivation for measuring *in situ* chloride concentration. Section 3 describes the objectives of the effort and some design goals. Section 4 presents the theory of operation. Section 5 details the RF and electronics portion of the Pebble design. Section 6 describes the final electrochemical cell design as well as early embodiments. Section 7 describes the package design. Section 8 discusses Pebble fabrication and calibration. Section 9 describes communications between the reader and the Smart Pebbles. Section 10 considers bridge deck installation methods. Section 11 discusses design improvements and alternative sensor configurations, and Section 12 presents our conclusions.

2 BACKGROUND

This section reviews the chloride-ingress problem, the current inspection process, and corrosion mitigation strategies. We review available chloride measurement techniques and their suitability for the long-term corrosion monitoring application.

2.1. Chloride-Ingress Problem

A recurring maintenance problem encountered in bridge decks is that these structures contain reinforcing steel (rebar) that will corrode in the presence of chloride ions. These ions diffuse into the concrete from the surface because of the presence of salt water from various sources such as seawater spray in coastal zones or deicing salts in cold climates. The diffusion rate is slow, but finite. The resulting corrosion products expand the rebar volume and cause subsequent cracking and spalling of the concrete, as illustrated in Figure 2. There is a critical chloride concentration level where such corrosion initiates (depending on the type of concrete) and it would be desirable to determine quickly and reliably when this level has been reached so that remediation can be undertaken. Presently, concrete core samples have to be extracted and then analyzed for chloride content in the laboratory. Moreover, it typically takes several years for the critical chloride concentration to be reached, so many tests may be required. Hence, one would like to test often, but inexpensively.

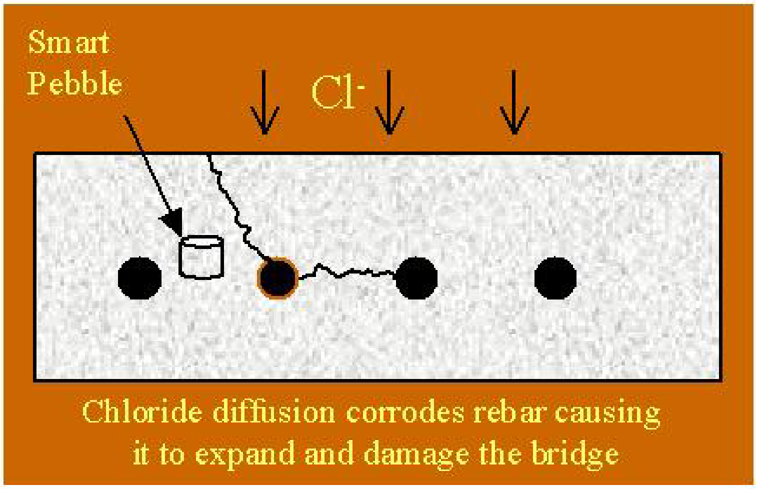


Figure 2. Effect of chloride ingress on bridge decks

2.2. Inspection Process

There are approximately 600,000 bridges in the United States [1]. Many of these bridges are subject to chloride attack due to de-icing salts, coastal spray, or soil runoff. In California every bridge is inspected every two years. Usual bridge inspection techniques include visual inspection and acoustic delamination inspection. Figure 3 shows a maintenance worker performing an acoustic chain-drag delamination test.

Figure 3. Caltrans worker inspects a bridge deck for delaminations

Chloride ingress is only measured if warranted by visual inspection. To measure chloride concentration, a maintenance engineer requests the extraction of core samples from the bridge. The samples are delivered to the laboratory for analysis. The sample is sliced into 1-in. sections (more precise profile grinding can be used to measure the depth dependence more finely). Crushed and pulverized sectionalized samples are passed through a 150-micron mesh grid. Chloride concentration measurement is performed by titration and follows either ASTM C114 or California test CT404. A test report documents the findings of the laboratory measurements.

Some of the disadvantages associated with current bridge deck chloride-ingress inspection techniques include the safety risk caused by lane closure, the time-consuming nature of the analysis, the need for manual data entry into a database, and the limited number of core samples available from a selected bridge.

2.3. Mitigation Strategies

In parallel with the bridge inspection and maintenance activity, efforts are underway to construct better bridges that are less susceptible to chloride attack. Methods of controlling corrosion include:

- Choosing a low water-cement ratio in the cement mix to reduce chloride diffusion
- Selecting admixtures that increase the corrosion initiation threshold, such as the use of fly ash.
- Using coated rebar (e.g., epoxy-coated or stainless-steel cladding) instead of traditional black steel rebar
- Using a protective cover layer that is impermeable to moisture (e.g., polyester concrete or various overlay sealants)
- Using electrochemical methods to extract the chloride or for cathodic protection

Figure 4 shows the effect of water-cement ratio on chloride diffusion rates into concrete. The plot shows that low water-cement ratios inhibit chloride ingress. Table 1 shows the higher chloride initiation threshold of admixture concrete compared with conventional concrete.

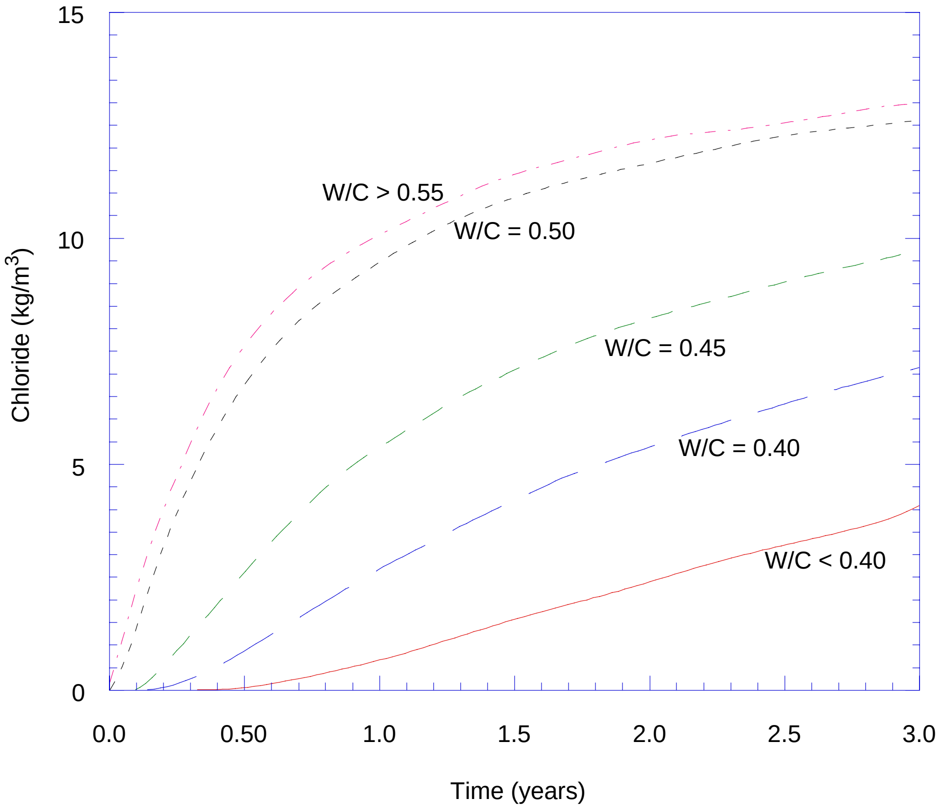


Figure 4. Affect of water-cement ratio on chloride diffusion

Table 1
Chloride Concentrations

Material or Value	Chloride Mass (lbs/yd^3)	Chloride Mass (kg/m^3)	Chloride Concentration (milliMolar)
Tap water (typical)			5 mM
Corrosion initiation threshold (Conventional Concrete)	1.44	0.86	24 mM
Corrosion initiation threshold (Admixture Concrete)	1.95	1.16	33 mM
Concrete damage (removal recommended)	3.0	1.79	50 mM
Seawater			600 mM

2.4. *In Situ* Chloride Measurement

The Smart Pebble effort seeks to measure chloride concentration (threshold) *in situ* to provide rapid indication of bridge deck conditions to maintenance engineers. There are important differences between laboratory and *in situ* measurements. Laboratory techniques have a high degree of precision, take hours to complete, and have readily available calibration standards. The instrumentation occupies a laboratory bench. This lab equipment draws watts of power and requires an engineer to interpret the results. An *in situ* sensor provides a coarse (threshold) measurement, transponds its data in a few seconds, and does not have the benefit of local calibration. It operates on a few microwatts of power harvested from the interrogating RF signal. It occupies a cubic inch of volume, and indicates bridge health as a red or green light.

In the discussion that follows, we review existing chloride inspection techniques and their suitability for the bridge deck environment.

2.4.1 Conductivity

Chloride concentration can be inferred from conductivity measurements in aqueous solution. This technique is commonly used in monitoring water quality, especially seawater. In the bridge deck environment, many ionic species may be present that do not cause corrosion (e.g., nitrates from agricultural runoff). Consequently, a measurement of conductivity does not provide a direct indication of chloride concentration. In the bridge environment a conductivity sensor may be most useful for determining whether the bridge is wet or dry.

2.4.2 Titration

Titration is the common method used in laboratory quantitative analysis for determining chloride concentration precisely. It does not lend itself easily to miniaturized, low-power, rapid-readout, long-term monitoring applications, but there has been some research performed on this topic by P. Bergveld at University of Twente in the Netherlands [6].

2.4.3 Ion Mobility Spectroscopy

IMS is seeing increased use in airport security environments for the detection of explosive compounds. The usual approach is to ionize vapors or particles and allow them to drift through a chamber at a velocity determined primarily by their molecular weight. Subsequent mass spectroscopy can be used to provide a more exact determination of the particular molecular compound. Similarly to the titration technique, this approach is difficult to miniaturize. Also, because chloride ions and hydroxide ions are approximately the same size, it may be difficult to separate the small number of chloride ions from the large number of hydroxide ions in the high-pH bridge deck environment.

2.4.4 Colorimetry

The University of Vermont built a fiber-optic chloride sensor and embedded it into a test bridge in Vermont [7]. The sensor relies on colorimetric changes produced in a fluorescent dye, causing the reflected optical signal to become redder. The fluorescent detection method determines the existence of chloride, but it does not indicate concentration and it is not a reversible reaction.

2.4.5 Fluorescence Spectroscopy

Chloride concentration is measured in biological systems using fluorescence techniques [8]. Typically, a UV light illuminates a fluorophore, thereby producing visible fluorescence. According to the Sterm-Volmer relation, chloride ions can cause collisional quenching in certain fluorophores, resulting in a reduced fluorescence intensity that is proportional to the log of the chloride concentration. Commonly used chloride-sensitive fluorophores include SPQ (6-methoxy-N-(3-sulfoproxyl)quinolinium), SPA (N-sulfopropylacridinium), Lucigenin (N,N'-dimethyl-9-9'-bisacridinium nitrate), MACA (N-methylacridinium-9-carboxamides), and MAMC (N-methylacridinium-9-methylcarboxylate). Difficulties associated with *in situ* fluorescence spectroscopy include design of a power-efficient UV light source, design of an efficient circuit to measure the short-lifetime signals (SPQ lifetime is 26 ns), and the identification of a fluorophore that is not collisionally quenched in a high pH environment.

2.4.6 Chemiresistor

Molecularly imprinted polymers (MIP) have been used for trace detection of specific compounds at the part-per-billion and even part-per-trillion level. Typically, polymers are synthesized with the trace compound present. After polymer cross-linking, the trace compound is dissolved leaving voids that retain the shape of the trace compound to be detected. When a trace compound is present in the environment, it binds to the polymer changing one or more of its properties. This technique is a chemical analogue to the antibody detection methods used in microbiology. The transduction mechanism for conveying the presence of the trace compound can be tailored for the levels of trace compounds to be detected, as well as the operating environment. A chemiresistor design provides a conductivity change proportional to the log of the concentration of the trace compound and is suitable for part-per-million detection levels. MIP sensors have been developed at SRI using surface acoustic wave and quartz crystal microbalance transduction mechanisms for sensitive detection applications such as the detection of chemical or biological warfare agents [9].

Researchers at Johns Hopkins University's Applied Physics Lab [10] are investigating methylated polypyrrole as a hydrophobic imprinted polymer that is sensitized to chloride concentration, but which is insensitive to hydroxide. SRI research in MIP devices indicates that a sensor lifetime of 6-12 months is typical, primarily due to polymer degradation and electrode delamination. However, with some effort, this lifetime can be extended. Additionally, sensor drift may be an issue. Ideally, it would be useful to include a reference polymer that is insensitive to chloride concentration for calibrating the sensor. Unfortunately, because of large batch-to-batch variation in polymer molecular weight, it is difficult to construct a sensor and reference with similar long-term properties. Chloride sensing using imprinted polymers is an area of continuing research. [5]

2.4.7 Electrochemical Cells

Potentiometric measurement of ionic concentration is a time-honored technique for detecting chloride concentration in the field. Ion-selective electrodes are commercially available to sense both anions and cations including pH, calcium, sodium, potassium, fluoride, and chloride, among others. A calibrated reference electrode (such as $Cu/CuSO_4$, Ag/AgCl, or SCE—Saturated Calomel Electrode) provides a stable reference. These electrodes and associated handheld instruments are used for environmental monitoring of soil and water quality. Short-term accuracy of the electrodes is of the order of ±2 mV. These electrodes are typically an inch in diameter and nearly a foot in length. Miniaturization of such electrodes is a possible approach for chloride sensing in bridge deck environments. Cathodic protection systems make use of the above electrodes for long-term use. However, mV-level stability is not a requirement for these devices.

2.4.8 Chloride Voltage Measurement

Researchers at the University of Virginia [11] and subsequently at Virginia Technologies (http://www.vatechnologies.com/eci.htm) have developed a powered corrosion micro-instrument for monitoring of a variety of bridge deck conditions, including conductivity, corrosion potential, temperature, polarization resistance, and chloride voltage. The chloride voltage measurement is a potentiometric measurement using a Ag/AgCl ion-selective electrode and a Mn/MnO_2 reference electrode. This uncalibrated measurement can provide an indication of chloride activity on a bridge deck. This product development follows considerable research at the University of Virginia to identify stable (especially reference) electrodes for bridge deck environments. They selected the Mn/MnO_2 electrode because of its long-term stability. However, oxide-based electrodes are universally sensitive to changes in hydroxide concentration and are commonly used as pH electrodes (e.g., Ir/Ir_2O_3, Ni/NiO, Cu/CuO). However, bridge deck pH changes from an initial value of 13.6 (saturated calcium hydroxide pore solution) to a value of 9-10 for an older bridge [12]. Carbonation effects due to acid rain—H_2CO_3—can result in even lower pH values. Consequently, a reference electrode that varies with pH may provide misleading readings. For example, for a constant pH, a chloride-sensitive electrode will in theory show a 59 mV decrease in voltage for every decade increase in chloride concentration (activity). However, a unit change in pH (from 13 to 12, for example) will result in a 59 mV increase in reference electrode potential, resulting in a factor-of-10 over-estimate of chloride concentration.

2.4.9 Microfabricated ISFET

Microsensors have been fabricated using an ion-selective membrane or coating on the gate of a field-effect transistor. Configured as a transconductance amplifier, the device consumes minimal power and provides potentiometric indication of specific ionic activity in a manner similar to a standard electrochemical cell. The advantage of this method is that the sensor can be microfabricated along with the associated interface electronics to produce a miniaturized device. For the bridge deck environment, this approach has several disadvantages, for example, (1) to prevent erosion of the small-volume electrodes over the lifetime of the bridge deck requires very high impedance circuitry (teraohms), and (2), to date, diffusion of ionic species into the gate of the semiconductor results in long-term sensor drift, which is currently an unsolved problem subject to ongoing research [13,14].

2.4.10 Summary

We conclude from this summary that none of the above methods are ideally suited for long-term chloride-concentration monitoring in bridge deck environments. Initially, we chose to use a potentiometric measurement approach with $Cu/CuSO_4$ as the reference electrode and Ag/AgCl as the chloride-sensitive electrode. As part of our investigation, we also evaluated other reference-electrode materials. We concluded that the above electrode choices were the best suited for potentiometric chloride measurement in bridge decks, but that they have significant limitations. Highway engineers are familiar with the limitations of these electrodes. The field life of a Ag/AgCl electrode is a maximum of 3-4 years [15]. The potential of Cu/CuSO4 electrodes is known to drift. Miniaturization does not improve the performance of these devices. We review the performance of specific electrode alternatives in Section 5 and make recommendations for sensor improvements in Section 11.

3 OBJECTIVES

The primary objective of this effort was to develop prototype passive Smart Pebble devices capable of measuring chloride threshold concentrations in bridge deck environments. Evaluation of these devices under realistic conditions will enable Caltrans engineers determine their suitability for long-term health monitoring applications.

Given the above main objective, secondary design goals follow. Ideally, Smart Pebbles should have the following characteristics:

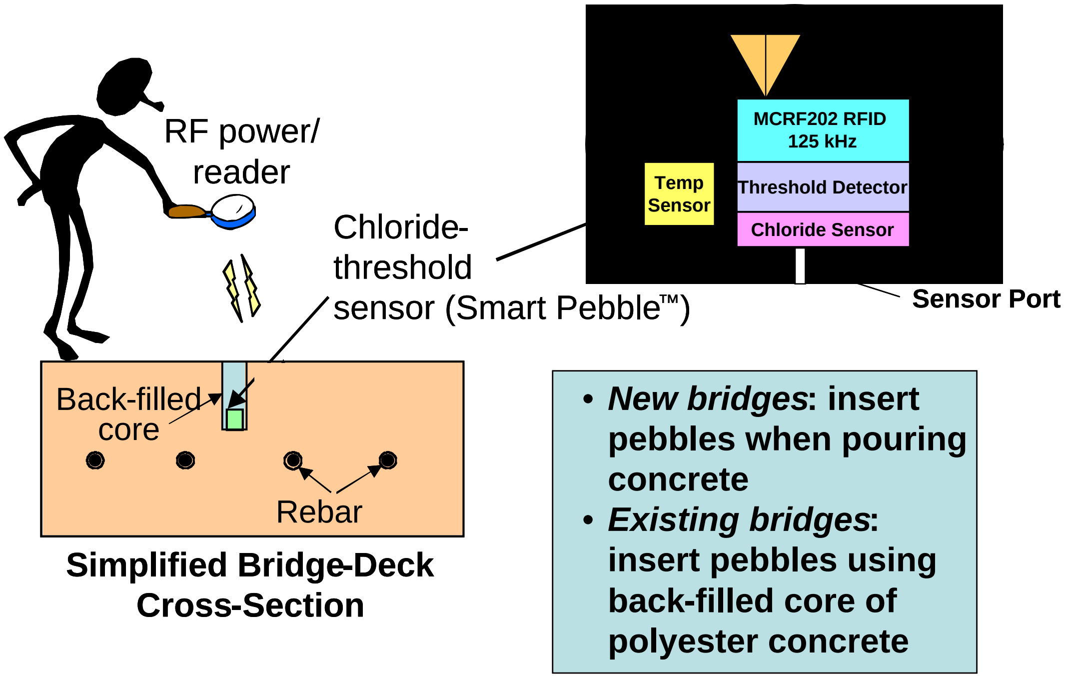
- Have the size of ordinary aggregate—approximately 1 cubic inch in volume
- Last for 20 years or more—a passive device that uses no batteries
- Survive high-pH bridge environment (pH = 13)
- Survive temperature extremes (-10° to 50° C)
- Operate over an extended temperature range (10° to 40° C)
- Have a read range of at least 6 inches (2.5 inches of concrete cover, possibly 2 inches of asphalt concrete overlay, and 1.5 inches for reader clearance above the bridge deck surface)
- Have a response time on the order of 1 second
- Be capable of detecting a chloride-concentration threshold event (the preferred threshold depends on concrete characteristics, but 30 mM is a nominal choice)
- Use a reader that supports RS-232 communication for database integration of Smart Pebble data

4 THEORY OF OPERATION

In this section, we present the theory of operation for the Smart Pebble. First we provide an overview of the major components. Then, we describe the principles that guide the design of the antenna, RFID, sensor electronics, and electrochemical cell.

4.1. Overview

Figure 5 illustrates the Smart Pebble concept. The figure shows a bridge inspector with a handheld reader polling a Smart Pebble embedded in a bridge deck. One installation method for old bridges is to insert them in core holes and back fill these holes with grout and polyester or epoxy concrete that is impervious to moisture. The core could be taken from the deck surface or from the deck soffit up to the desired location below the deck surface. The core and pebble installation from the underside of the deck would not interfere with the chloride diffusion path. In this method, the Pebble achieves equilibrium with the old bridge deck environment. Laboratory measurements of the depth-dependent chloride concentration can provide a baseline for long-term monitoring. The Smart Pebble device contains an antenna (for reader communications), an RFID device that provides a unique identifying code, and temperature-compensated electronic circuitry that interfaces with a potentiometric chloride sensor. The Pebble is open to the bridge deck environment on one side and the location of this sense port determines the depth at which the chloride concentration is monitored.



- ***New bridges*: insert pebbles when pouring concrete**
- ***Existing bridges*: insert pebbles using back-filled core of polyester concrete**

Figure 5. Smart Pebble concept of operation

Figure 6 is a functional block diagram for the Smart Pebble system. On the left-hand side, a 125-kHz transceiver (the Reader) provides power to the Smart Pebble device and receives the unique ID code and sensor status that each Smart Pebble transponds. A serial data connection (RS-232) enables the reader to upload Smart Pebble data to a bridge deck database. On the right-hand side, a Smart Pebble receives a 125-kHz radio frequency transmission from the reader. The Pebble rectifies this signal to provide a DC voltage (nominally 3-4 V) to power the RFID (serial EEPROM memory) and the sensor interface circuitry. When charged, the RFID transponds its data by modulating the impedance of the resonant antenna coil (backscatter modulation). Typically, the first response from a Smart Pebble does not contain valid sensor data, but the second and subsequent responses do accurately represent the sensor state.

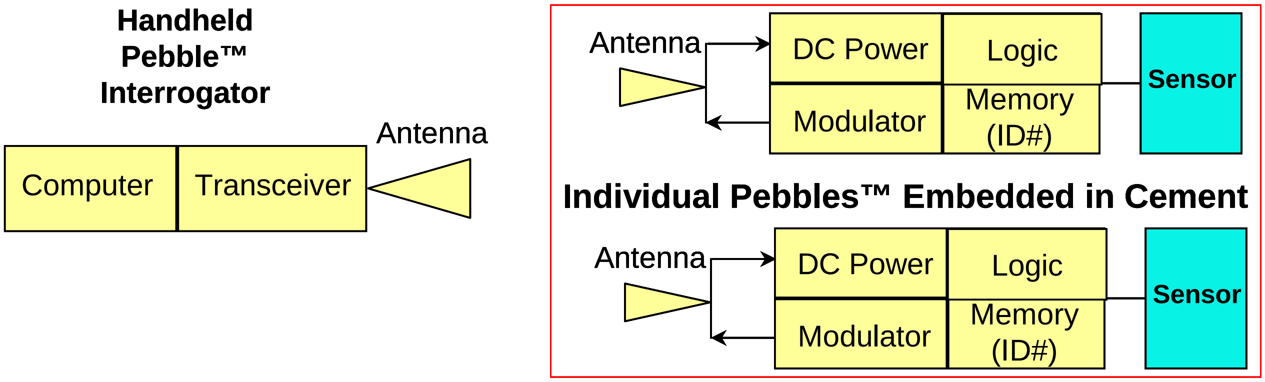


Figure 6. Smart Pebble system block diagram

4.2. Antenna Design

The design of the antennas for a Smart Pebble system [16] is subject to exactly the same considerations and constraints encountered in the design of the antennas for RFID tags. Thus, we may borrow directly from the existing knowledge base for these devices[1]. Specifically, for operating frequencies between 100 kHz and 30 MHz, small RFID tags use small coils as antennas. Since these small coils are much smaller than a wavelength at these frequencies, they do not radiate to any significant degree; rather, coupling between reader and tag coils takes place through the quasi-static magnetic near field generated by currents in the coils. Thus, these coils should not be called antennas per se because they really behave like a pair of mutually coupled coils in a transformer.

An important characteristic of these near fields is that they decay inversely as the cube of the distance from the coil. This behavior limits the read range of the tag. This limit is determined primarily by the need to power the passive Smart Pebble using the interrogating signal from the reader. Thus, depending on the voltage requirements of the electronic circuits in the tag, a requirement is established for the minimum voltage that must be induced in the tag coil by the reader. Because Reader-Pebble coupling is primarily based on the interaction of magnetic

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[1] *MicroID™ 125 kHz RFID System Design Guide*, Microchip Technologies, Inc., Sept 1998.

fields, the presence of wet or dry concrete (dielectric material) does not have a significant effect on read range.

The mutual coupling between two coils depends on their relative orientation. It is clear that the mutual coupling can be zero if the coils are oriented orthogonally to one another. Hence, for simplicity, we consider only the cases where the coil planes are parallel and the coils are either coaxial or side-by-side. For coaxially oriented coils, the mutual coupling is given by:

$$M_{ca} = \frac{\mu N_1 N_2 \pi R_1^2 \pi R_2^2}{2\pi} \left(\frac{jk}{r^2} + \frac{1}{r^3} \right) e^{-jkr} \quad . \qquad (1)$$

For side-by-side coils, the mutual coupling is given by:

$$M_{ss} = \frac{\mu N_1 N_2 \pi R_1^2 \pi R_2^2}{4\pi} \left(\frac{k^2}{r} - \frac{jk}{r^2} - \frac{1}{r^3} \right) e^{-jkr} \quad , \qquad (2)$$

where μ is the effective permeability of the Pebble ferrite, N is the number of turns in the coil, R is the radius of the coil, r is the range, and k is the free-space wave number. The subscript 1 denotes the Reader coil and the subscript 2 denotes the Pebble coil.

In this case, the coaxial orientation provides the strongest mutual coupling interaction. The induced open-circuit voltage in the Pebble coil, $V_{21} = -j\omega M I_1$, is proportional to (1) the frequency, (2) the current in the reader coil, (3) the product of the number of turns in both coils, (4) the product of the coil cross-sectional areas, and (5) the permeability of any ferrite core present in the tag coil. The design problem is to make these factors as large as possible while keeping the overall size of the Smart Pebble small. The RF voltage available at the input to the RFID is also proportional to the quality factor, Q, of the resonant circuit. Accordingly, $V_{in} = QV_{21}$.

4.3. RFID Response

Figure 7 details the function of the RFID portion of the Smart Pebble. The figure includes the RF resonant circuit and a simplified sensor. The RFID device chosen for the Smart Pebble design is the MCRF202, manufactured by Microchip Technologies. This chip provides a DC voltage for external circuitry and switch port for indicating the status of attached sensors. Under normal conditions, the RFID responds to reader queries with its 32-bit identification code. This is the uninverted state (sensor HI state) represented by the upper right portion of the figure. If a threshold event occurs (e.g., the chloride concentration is above a pre-determined threshold), the sensor changes state and the RFID responds to reader queries with is 32-bit identification code inverted. This response is illustrated in the lower right portion of the figure.

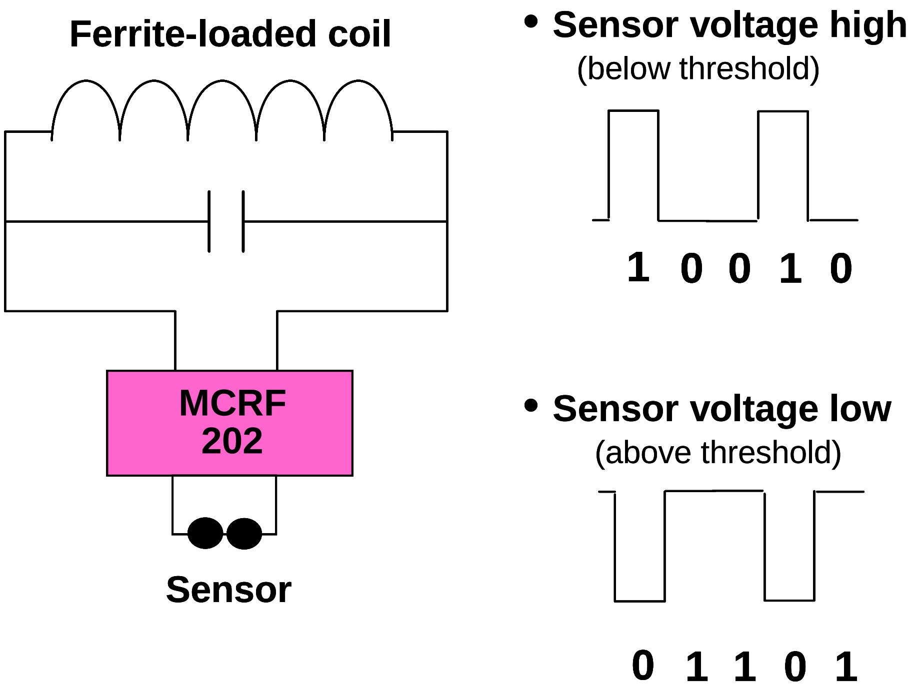


Figure 7. Bit inversion of RFID response to indicate sensor state

In general, it is possible for a reader to communicate with multiple RFID devices simultaneously. Such devices use anti-collision technology to randomize the timing of the RFID response, thereby preventing mutual interference when tags respond simultaneously. Using these proprietary algorithms, it is possible to communicate with as many as 50-100 tags per second. The MCRF202 device chosen for the Smart Pebble design supports such anticollision technology. However, anticollision technology was not included in the present version of the Smart Pebble Reader. A future Reader could easily incorporate this feature.

4.4. Sensor Interface

Figure 8 is a detailed block diagram of the Smart Pebble showing the resonant antenna, the RFID chip, the sensor-interface circuitry, and the reference and ion-selective electrodes that are part of the electrochemical cell. The RFID chip can provide as much as 10 microwatts to power the sensor electronics. This power is sufficient to operate the micropower operational amplifier and nanowatt comparator. The electrochemical cell produces a voltage that is proportional to the log of the chloride concentration. The operational amplifier amplifies this signal by approximately a factor of ten and compensates for temperature. If this signal is above the 1.2-V threshold of the comparator, the comparator output changes from HI to LO, changing the state of the switch port on the RFID. The electrochemical cell is open to the bridge deck environment, but the RFID and sensor electronics are sealed within the Pebble enclosure.

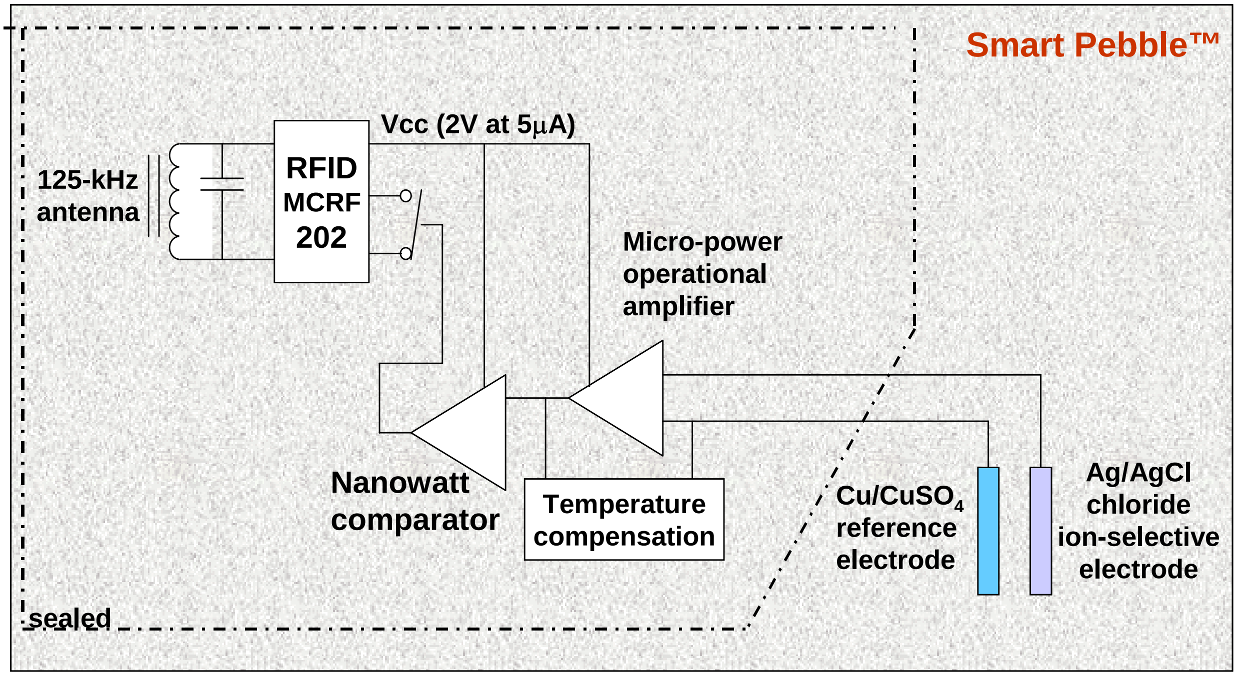


Figure 8. Detailed Pebble block diagram

4.5. Electrochemical Cell

Figure 9 is a cross-sectional sketch of the electrochemical cell geometry. The electrochemical cell is enclosed is an interior compartment with a cementitious (grout) plug acting as the salt bridge that separates the two half-cells. The ion-selective electrode is in the outer compartment. An external cementitious plug is open to the bridge deck environment to enable the electrochemical cell to reach equilibrium with the chloride concentration in the bridge deck. This equilibrium process occurs under wet bridge conditions (and is independent of whether or not the Pebble is receiving power from the reader). When the Reader queries a Pebble it transponds the current equilibrium chloride status that has been reached in the electrochemical cell.

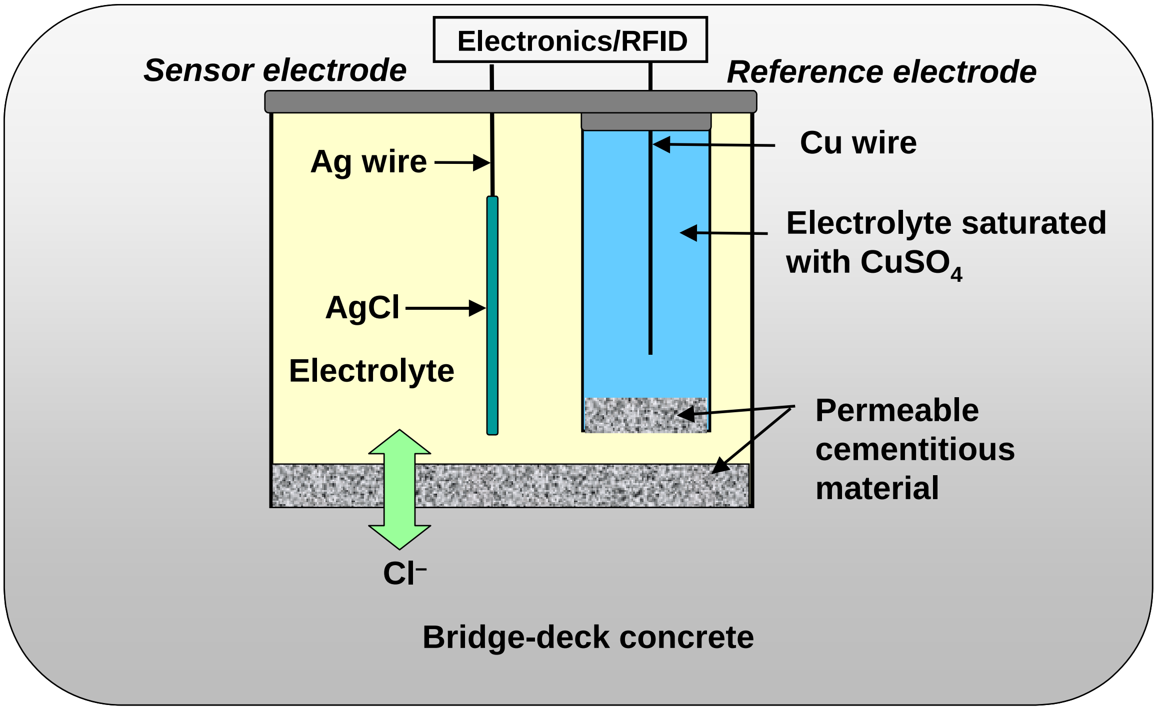


Figure 9. Electrochemical cell geometry

Ideally, the response of a potentiometric sensor follows the Nernst equation [17]. That is, $E = E^0 - (2.303RT/z_iF)\log(a_i)$, where R is the universal gas constant (8.134 J/K/mol), T is temperature in degrees Kelvin, F = 96,487 coulombs is the Faraday constant, z_i is the valence of the ionic species (chloride = -1), and a_i is the activity of the ion. E^0 is a constant that depends on the geometry and the difference in standard half-cell potentials (e.g., $E^0_{AgCl} - E^0_{CuSO4}$). Accordingly, at room temperature, an ideally Nernstian response results in a 59.1 mV change in electrode potential for every decade of change in ionic activity (concentration). For dilute solutions, the activity is essentially equal to the concentration. For higher concentrations, the relationship between concentration and activity is given by $a_i = c_i \exp(0.51z_i^2\mu^{1/2}/(1+\mu^{1/2}))$, where c is concentration and μ is ionic strength.

Another factor affecting the response of an electrochemical cell is the presence of interfering ions. An ion-selective (e.g., chloride) electrode should only respond to the ionic species of interest and not to any other ions. The revised Nernst equation becomes $E = E^0 - (2.303RT/z_iF)\log(a_i + k_{ij}a_j^{zi/zj})$, where k is the selectivity coefficient for the interfering ion, which is denoted by the subscript j. In practice, electrodes that are selective to chloride ions may also respond to other halide ions (bromides, iodides, etc.) Since these halide ions are not common in bridge deck environments, interference from these sources is not a major factor in the design of the Smart Pebble electrochemical cell. However, we have noticed that the $Cu/CuSO_4$ electrode responds to changes in pH (hydroxide ion), and the literature indicates that Ag/AgCl electrode is also OH^- sensitive (particularly at high values of pH). Figure 10 is a linear plot of theoretical cell voltage (in millivolts) as a function of chloride concentration. The logarithmic relationship between measured voltage and chloride concentration implies that precise chloride concentration measurements will be difficult to achieve. A factor-of-two change in chloride concentration results in an 18 mV change in cell potential. For electrodes with a design stability goal of ±5 mV, an 50% accuracy in chloride concentration is a realistic value.

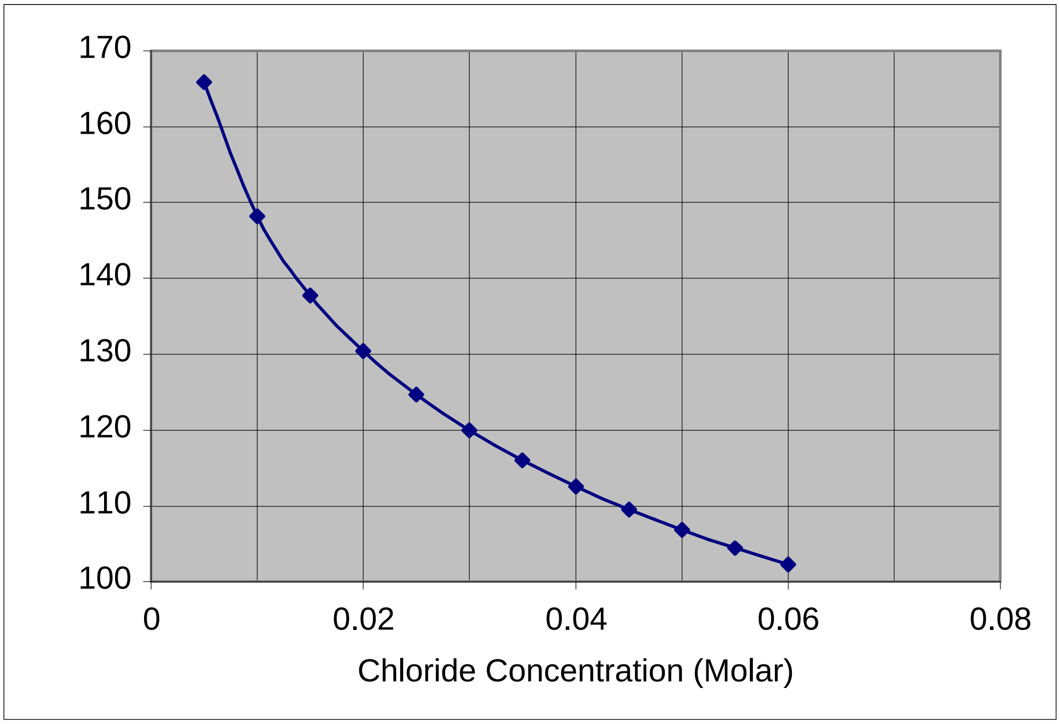


Figure 10. Ideal response of an electrochemical cell

5 ELECTROCHEMICAL CELL DESIGN

In this section we describe the electrochemical cell design. First, we describe the laboratory apparatus used to measure electrode performance. Then, we describe the design of the Ag/AgCl electrode and provide an historical account of the development process for the reference electrode. Finally, we describe the Ag/AgCl-Cu/CuSO4 couple and its response as a function of temperature.

5.1. Measurement Setup

Figure 11 shows the experimental setup for evaluating the performance of electrodes. Electrodes are inserted into a temperature-controlled bath. Experiments were conducted on Smart Pebble electrodes over a temperature range of 10°-50° C. Electrode potential is measured using a high-input-impedance Keithley electrometer. Up to 12 electrodes can be monitored simultaneously using the Keithley scanner. The computer controller scans through each of the electrode channels, periodically recording the voltage measured by the electrometer associated with each channel (e.g., every 5 minutes). The computer also records bath temperature.

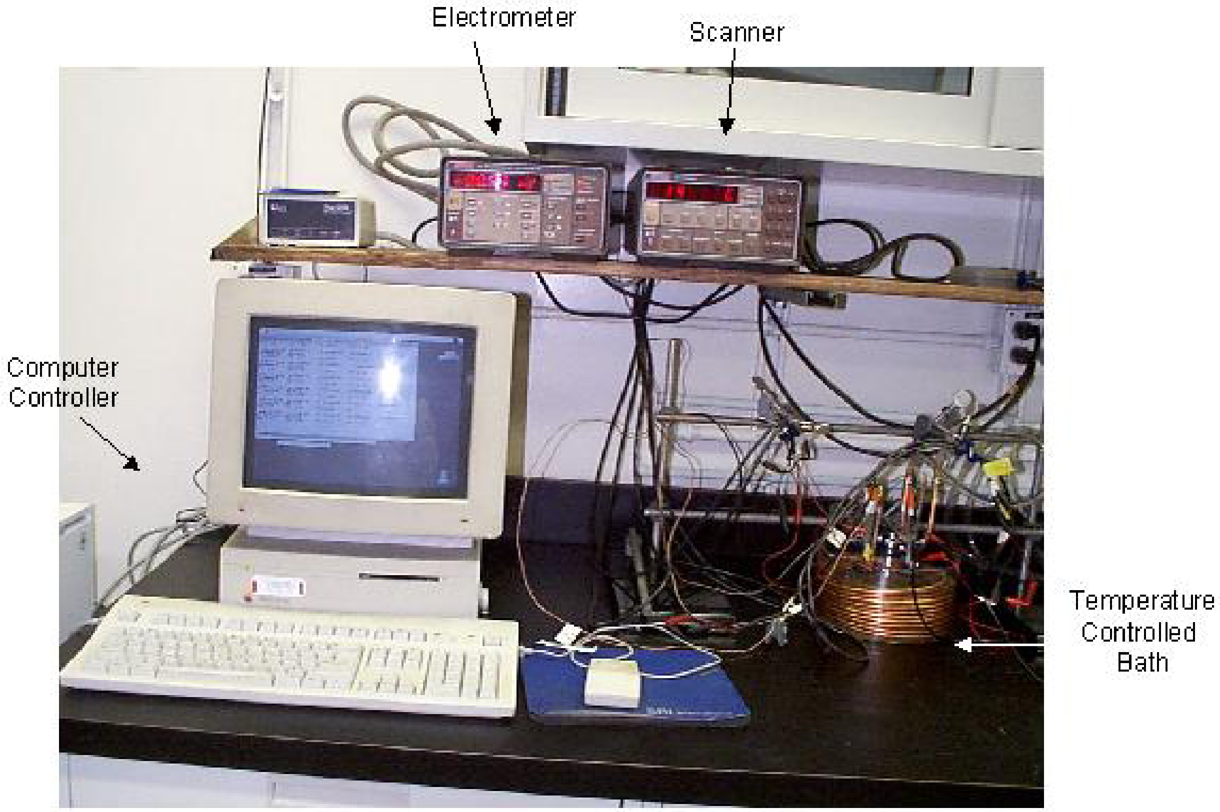


Figure 11. Electrode measurement setup

5.2. Chloride-Sensitive Electrode

We began the electrochemical cell-design process with the ion-selective electrode. Ag/AgCl is a common choice for a chloride-sensitive electrode. We constructed electrodes using a variety of techniques: (1) thermal melt process—AgCl was dip-coated onto a silver wire by repeatedly dipping a silver wire into a molten AgCl bath (450° C), (2) electroplating—a thick AgCl coating was deposited onto a silver-wire electrode in an electrolytic cell containing a 5 M HCl solution, and (3) a combination—a silver wire electrode was prepared using the electroplating process and then the tip was dip-coated in the AgCl melt. We also compared spiral-wire electrodes with straight-wire electrodes. We found that electrode preparation process was not a significant factor in the response of the Ag/AgCl electrode. Figure 12 shows a spiral-wire electrode and the measured electrode potential with respect to a saturated calomel electrode (SCE) as a function of time when immersed in an aqueous solution containing 15 mM NaCl. An ageing interval of a few hundred hours is necessary to achieve a stable potential. The theoretical value for an ideal Ag/AgCl electrode with a 15 mM chloride concentration at room temperature is 86 mV vs. SCE. The figure also illustrates the temperature dependence of the electrode potential. For the prototype Pebble units, we selected a straight-wire design for the Ag/AgCl electrode.

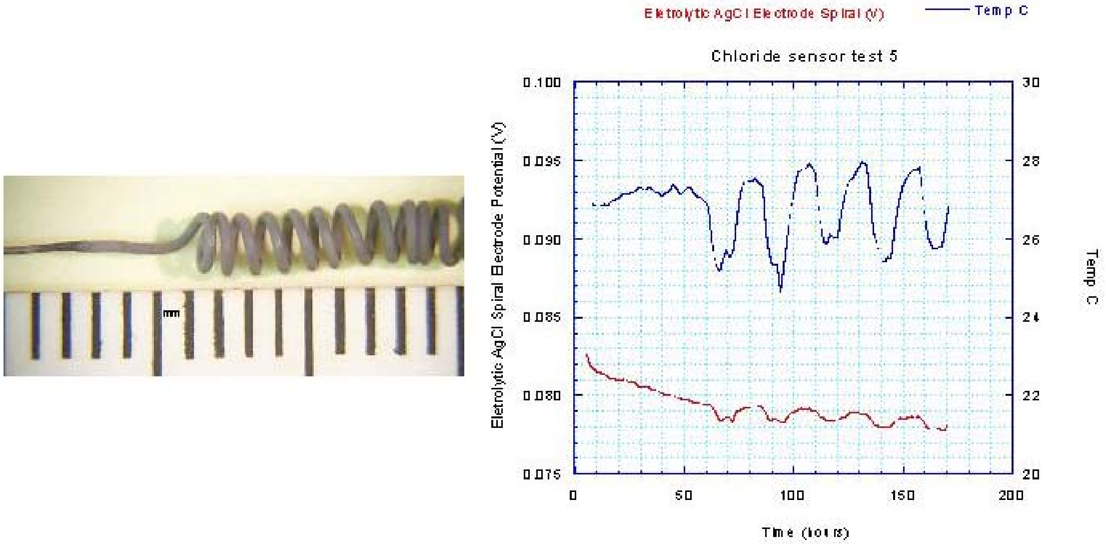


Figure 12. Early Ag/AgCl electrode and ageing curve

5.3. Reference Electrode

After completing the initial chloride-sensitive electrode design, we began the design process for the reference electrode. We considered many possible reference electrodes as candidates for the Smart Pebble design. Ultimately, we settled on a $Cu/CuSO_4$ reference electrode in a saturated $Ca(OH)_2$ solution. In this section, we review some of the possible electrode choices and compare the performance of some of the alternatives.

5.3.1 Saturated Calomel Electrode

Hg/Hg_2Cl_2 is the "gold standard" reference electrode for many electrochemistry applications. The potentials of the Ag/AgCl electrode and reference-electrode candidate designs were all measured with respect to an SCE reference electrode but we did not select an SCE for the Smart Pebble reference electrode because:

(a) Mercury compounds in bridge decks might be a potential environmental health concern,

(b) The SCE has known long-term stability difficulties in the $Ca(OH)_2$ environment because the Ca^{2+} ions replace the Na used in the glass frit of the SCE. (It might be possible to construct a Hg/Hg_2Cl_2 electrode using a calcium borosilicate glass frit instead of the sodium borosilicate glass used in commercial SCEs.)

(c) The saturated-KCl filling solution might leak out of the SCE and poison the electrochemical cell with chloride.

5.3.2 Silver/Silver Chloride

Ag/AgCl electrodes have seen wide use as reference electrodes, especially in medical applications. The primary disadvantage to using a Ag/AgCl reference electrode is that a saturated-KCl filling solution is used in the reference cell. As described above, if this KCl should leak out of the reference cell, the high chloride concentration could result in a false reading by the ion-selective electrode.

5.3.3 Metal/Metal Oxide or Metal/Metal Hydroxide

Common Me/MeO and Me/MeOH electrodes include Ni/NiO, Mn/MnO_2, Ir/Ir_2O_3, Cu/CuO and others. Ni/NiO electrodes are useful in high-temperature applications. Mn/MnO_2 has been used in concrete. Ir/Ir_2O_3 has been used in medical applications. We explored the Cu/CuO system in this work. A key advantage of these oxide-based electrodes is their long-term stability. A key disadvantage is that all of these electrodes are sensitive to pH changes and could be used as pH electrodes. In fact, in a previous effort, we sputtered Ir/Ir2O3 film onto silicon for use as a pH microelectrode vs. Ag/AgCl to monitor corrosion in aircraft compartments. For bridge deck applications it is necessary to either assume that the pH is constant (which is not true over the long term), or to somehow fix the pH within the electrochemical cell. We report Ni/NiO and Cu/CuO performance results within the $Cu/CuSO_4$ discussion that follows.

5.3.4 Copper/Copper Sulfate

Copper-copper sulfate electrodes are the traditional choice for many concrete-monitoring applications. However, they have known long-term drift and stability limitations. We constructed a variety of $Cu/CuSO_4$ electrodes as a baseline design. We found that these electrodes had a stable response in pore solution over thousands of hours. Because of the sensitivity of Me/MeO electrodes to pH changes, we selected the $Cu/CuSO_4$ for the Smart Pebble design. Figure 13 shows the reference electrode assembly.

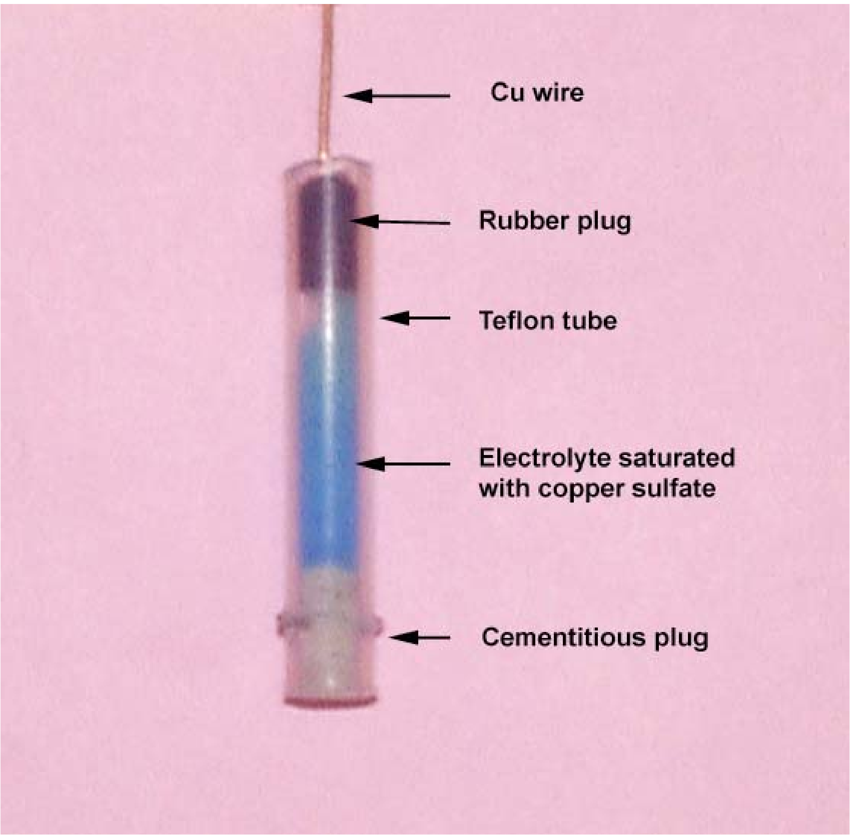


Figure 13. Reference electrode assembly

Figure 14 shows long-term stability measurements of $Cu/CuSO_4$ reference electrodes. The drift responses of five separate units were measured over a period of nearly 4000 hours. Short-term transients are due to instrumentation noise. Residual stability is approximately ±5 mV, which is the design goal. We saw similar stability performance for Cu/CuO reference electrodes. Figure 15 shows the Cu/CuO results (tested up to 2500 hours) on a plot that also includes some $Cu/CuSO_4$ data. Ni/NiO electrodes were tested up to 1500 hours, but were not as stable. Figure 16 presents the Ni/NiO data.

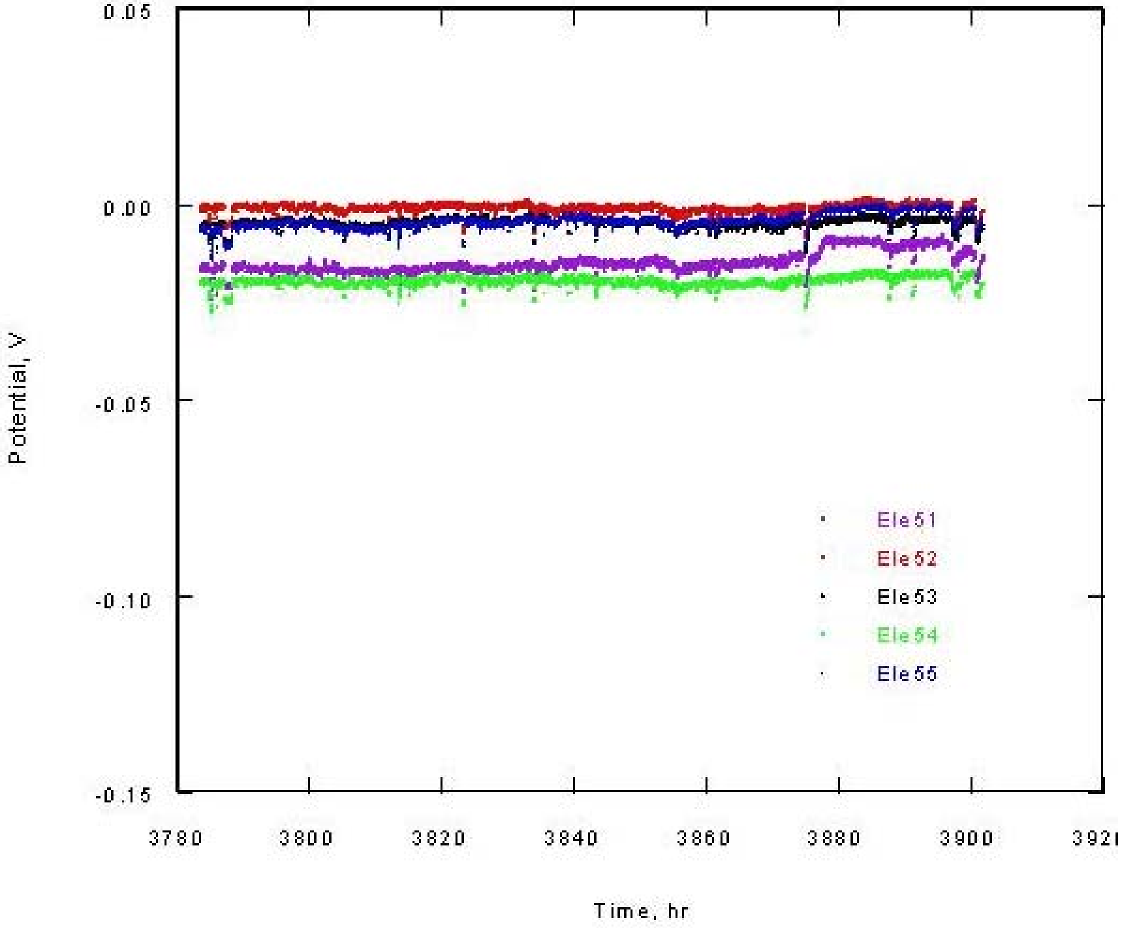


Figure 14. Long-term stability of Cu/CuSO$_4$ electrodes in pore solution

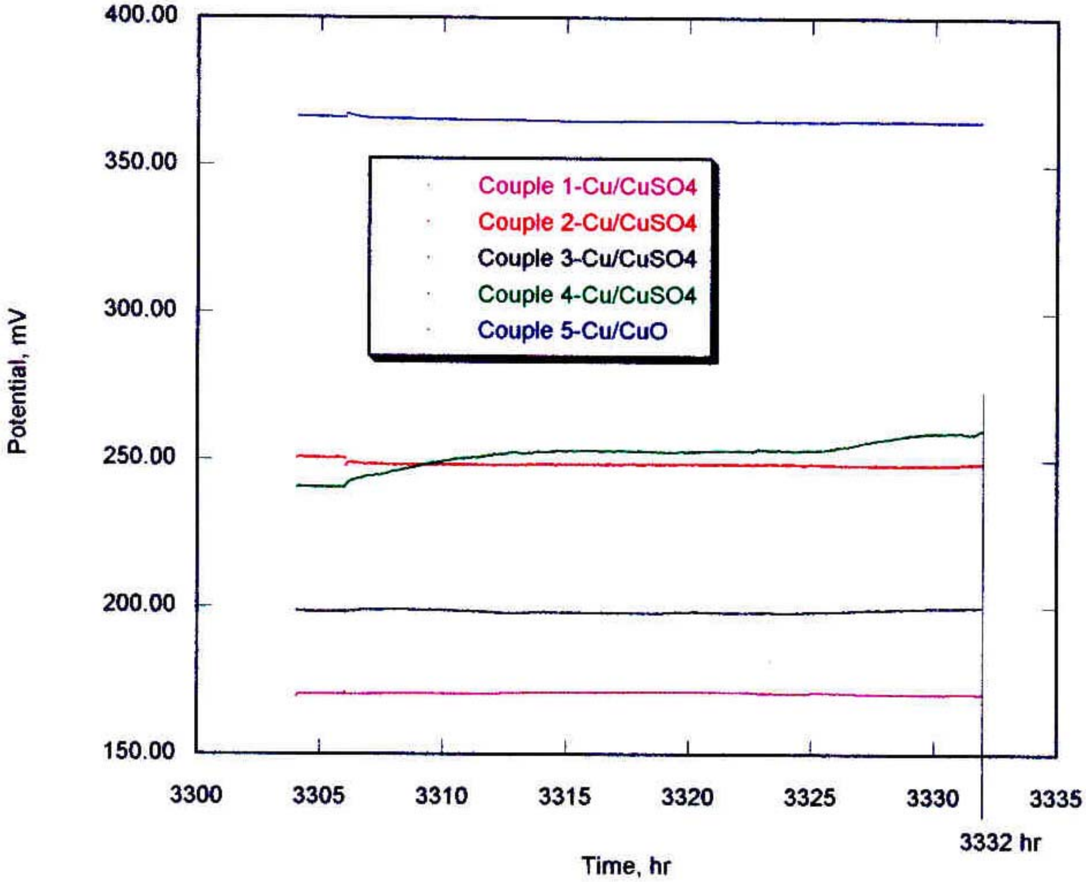


Figure 15. Long-term stability of Cu/CuO electrode (upper trace—couple 5)

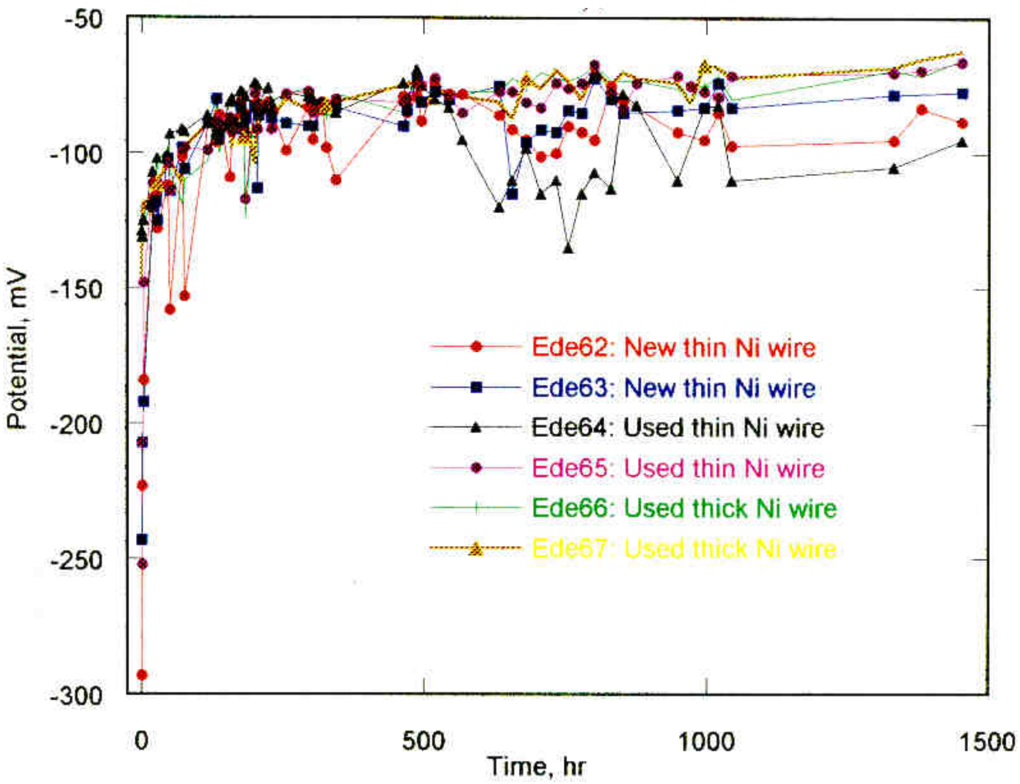


Figure 16. Long-term stability of Ni/NiO electrodes in pore solution

5.4. Freezing-Point Suppression

The most important feature of a Smart Pebble is its ability to reside *in situ* in a bridge deck and report on chloride ingress when polled by an external reader. This implies that the Pebble must survive harsh temperature extremes, such as freezing temperatures. Although it might not be necessary to query Pebbles when they are extremely cold, the Pebbles need only be designed to *withstand* the freezing temperatures. Accordingly, we investigated the use of polyethylene glycol (PEG) having various molecular weights as a means of depressing the freezing point of the cell electrolyte. We found that the initial stability of reference electrodes containing PEG was good, but gradually the electrodes failed. Initially, we attributed this failure to electrode preparation. We thoroughly cleaned the electrodes and anodized them in a H_2SO_4 bath. Using these electrodes, we again saw good initial stability (after ageing), but eventually the color changed from the characteristic copper sulfate blue to a purple. This indicated that the PEG was reacting with the copper wire. Ordinarily, this reaction might be expected under low pH conditions, but the copper wire should be passive under high pH conditions. This problem occurs in car radiators where ethylene glycol antifreeze can attack the copper tubing. The usual solution is to use a corrosion inhibitor to prevent this reaction from taking place. Unfortunately, this approach lowers the activity of the electrode, and consequently would reduce the responsiveness of an electrochemical cell. We eventually abandoned the PEG approach.

High-temperature (50° C) tests were performed on aged Cu/$CuSO_4$ (with and without PEG) and Ni/NiO/MeOH electrodes. The high-temperature tests clearly reveal instability in the PEG formulation. Both the Cu/$CuSO_4$ electrode without PEG and the Ni/NiO/MeOH electrode are stable. Figure 17 is a plot of these results.

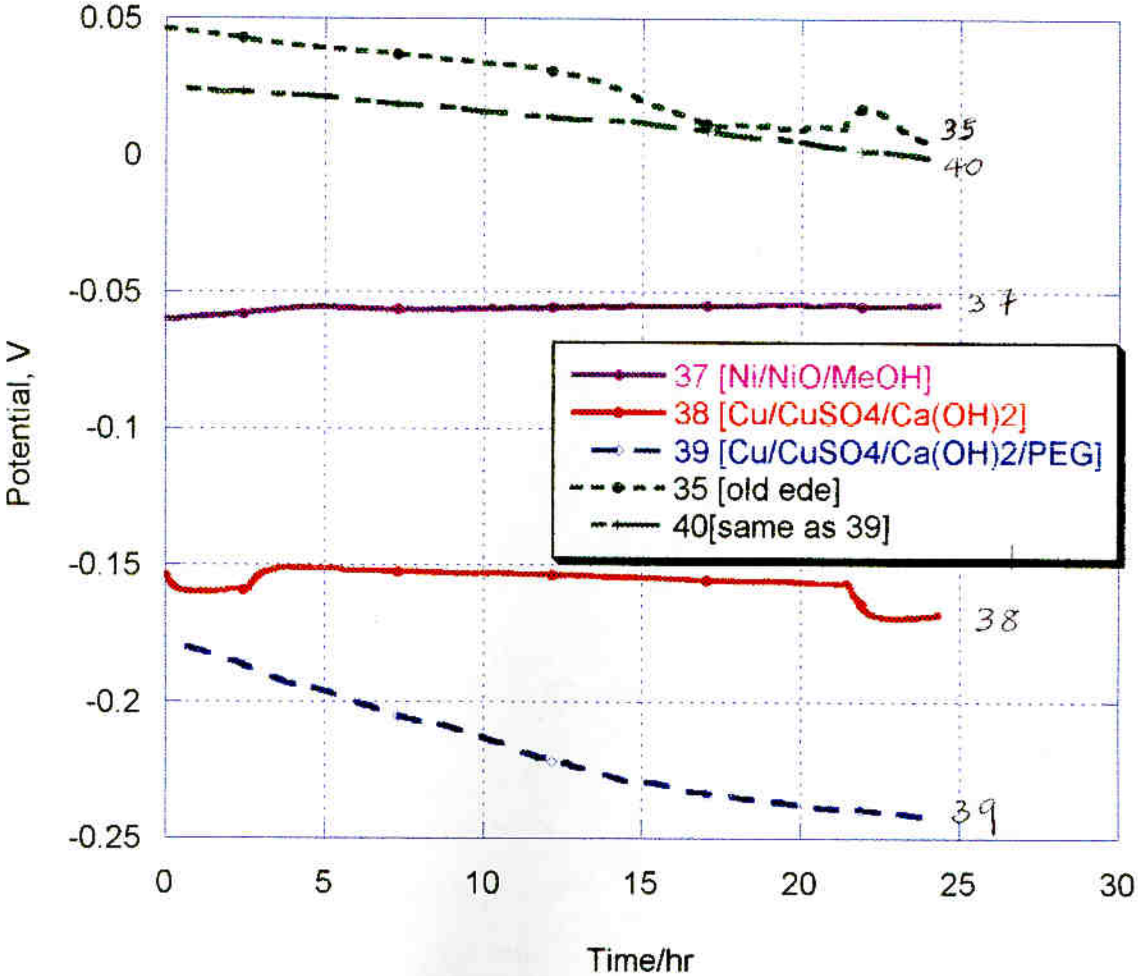


Figure 17. High-temperature (50° C) tests of aged electrodes showing instability in the PEG formulation (trace 39 and trace 40)

5.5. Moisture Retention

Another challenge associated with the electrochemical design is the need to retain moisture under dry bridge deck conditions. If the electrolyte evaporates from the cell, the chloride concentration in the cell will rise, yielding a misleading result. High molecular weight PEG is hygroscopic. However, this absorbed water will evaporate in dry air. Relative humidity data on bridge decks is needed to assess the moisture retention capability of PEG. The working conservative assumption is that the humidity of the bridge will approach the humidity of the air. Therefore materials that dry out in air might be expected to dry out in bridge decks as well. In addition to PEG, we tested carboxymethylcellulose, silica gel, and calcium hydroxide. We found that calcium hydroxide retained moisture in dry air better than most hygroscopic materials. Unfortunately, the calcium hydroxide eventually dries out as well. Also, carbonation products produced by carbon dioxide absorption can plug the cell port.

5.6. Electrochemical Cell Performance

We paired sequentially each reference electrode with the same Ag/AgCl electrode and measured its ability to detect changes in chloride concentration. Table 2 compares measured cell potential vs. chloride concentration. The trend shows how close the response is to the desired 59-mV-per-decade Nernstian response. We observe that the Cu/$CuSO_4$ system with PEG provides the best response. The Cu/$CuSO_4$ without PEG and the Ni/NiO electrodes have a similar response near 45 mV/pCl. The Ni/$Ni(OH)_2$ electrodes with a response near 40 mV/pCl are inferior. We conclude that our electrochemical cell design has a slightly sub-Nernstian response of approximately 45 mV/pCl.

Table 2
Ag/AgCl vs. Reference Electrode cell potential (in Volts) as a function of chloride concentration

Reference Electrode Type	10 mM NaCl	15 mM NaCl	20 mM NaCl	25 mM NaCl	30 mM NaCl	Trend (mV/pCl)
Cu/$CuSO_4$/$Ca(OH)_2$/PEG/H_2O	0.2454	0.2415	0.2359	0.2308	0.2226	61
Cu/$CuSO_4$/$Ca(OH)_2$/H_2O #06	0.1223	0.1140	0.1087	0.1042	0.1006	45
Cu/$CuSO_4$/$Ca(OH)_2$/H_2O #07	0.1095	0.1031	0.0981	0.0944	0.0887	46
Ni/NiO/$Ca(OH)_2$ #10	0.2237	0.2200	0.2131	0.2090	0.2056	46
Ni/$Ni(OH)_2$/$Ca(OH)_2$ #11	0.1620	0.1525	0.1450	0.1395	0.1320	39
Ni/$Ni(OH)_2$/$Ca(OH)_2$ #1	0.1547	0.1460	0.1405	0.1370	0.1330	42

5.7. Temperature Dependence

Figure 18 shows the measured temperature response of a Ag/AgCl-Cu/CuSO4 couple for different chloride concentrations (30 mM, 10 mM, and background) in saturated calcium hydroxide solution. The measurements show that the temperature dependence is linear, to first order, which is consistent with the theoretical model (Nernst equation). From these measurements, we can estimate the residual background chloride concentration to be approximately 0.3 mM.

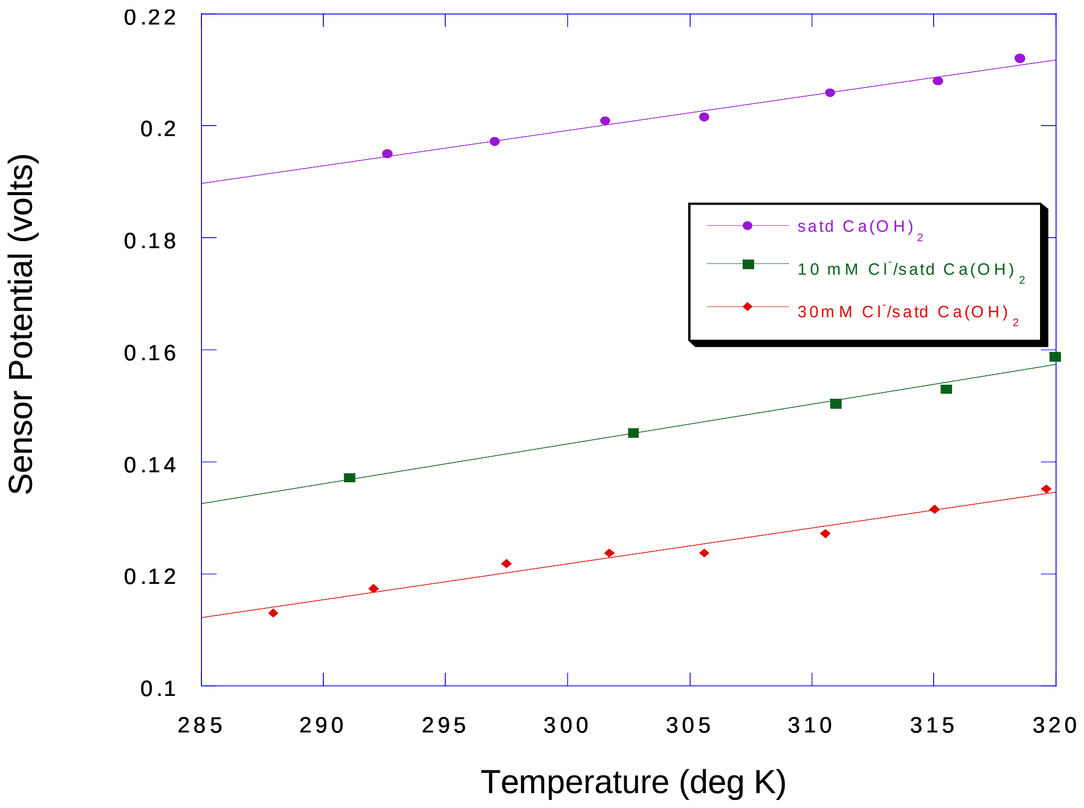


Figure 18. Temperature dependence of electrochemical cell as a function of chloride concentration

6 ELECTRONIC DESIGN

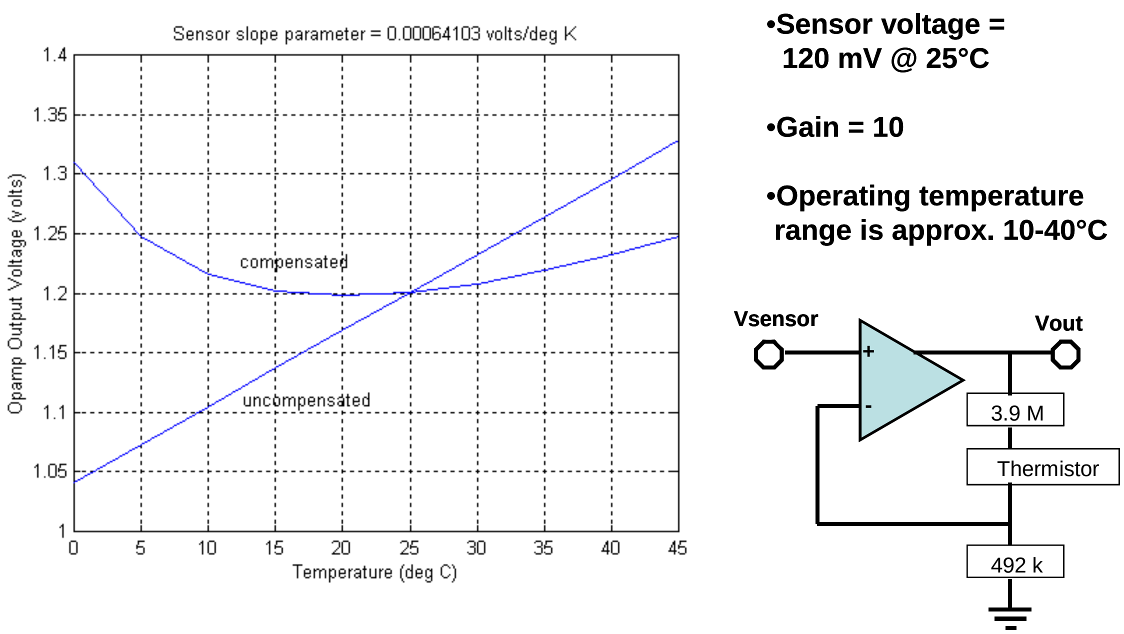
In this section, we describe details of the sensor-interface electronics design. We describe the temperature-compensation circuit and present the final circuit design used in the prototype Smart Pebbles.

6.1. Temperature-Compensation

One of the factors to be considered in designing the signal-conditioning electronics is the variation of the sensor voltage with temperature. This variation was measured in the laboratory using an unpackaged pair of electrodes (electrode couple) immersed in saturated $Ca(OH)_2$ solution containing representative concentrations of Cl^{-}. The data are shown in Fig. 18. We see that the sensor potential varies linearly with temperature and that the slope of this variation is essentially the same for different chloride concentrations. A linear fit to these data gives a slope of 0.000641 volts/°K at a chloride concentration of 30 mM. An approximate, but simple, way of introducing temperature compensation into the signal-conditioning circuit is to use a thermistor in the operational amplifier circuit. This circuit is illustrated schematically in Fig. 19. The resistance of the thermistor can be modeled using manufacturer's data. In our case, it is given by Eq. 3.

$$R_{therm} = \left[-0.8664 + \frac{81.3579}{T\left(^{\circ}C\right) + 18.59} \right] 504\ kohm\ . \tag{3}$$

Given this equation, the sensor potentials for a chloride concentration of 30 mM at temperatures of 10 and 40 °C (283 and 313 °K), and the desired output voltage (1.2 V), we arrive at the two resistor values shown in Fig. 19. The resulting compensated and uncompensated output voltages are shown plotted vs. temperature in Fig. 19. This circuit enables a measurement accuracy of ±5 mV over a 0-50° C range. Other factors that influence accuracy include sensor drift and comparator hysteresis.



•**Sensor voltage = 120 mV @ 25°C**

•**Gain = 10**

•**Operating temperature range is approx. 10-40°C**

Figure 19. Temperature-compensation circuit and its theoretical performance

6.2. Circuit Design Details

Figure 20 is a circuit diagram that shows the sensor interface circuitry. PSPICE, a commercial circuit-modeling tool, was used to model the circuit performance. An equivalent circuit for the electrochemical cell was derived using an electrochemical impedance spectroscopy (EIS) sweep of an Ag/AgCl electrode. The Cu/CuSO4 electrode is tied to ground. The switch port of the MCRF202 is modeled as an 800-kilohm resistor. Power from the MCRF202 is modeled as a DC voltage. PSPICE modeling enabled parametric studies of operational amplifier and comparator bias circuitry as a function of DC voltage and temperature. In an early design, we considered using a two-stage amplification circuit to enable stable gain of as much as a factor of 14. Because early electrochemical cell potentials were reasonably high (350 mV) at the 30 mM threshold (in aqueous solution), we decided that one amplification stage was sufficient. However, during the course of the electrochemical cell development we learned that the cell potential is lower in saturated calcium hydroxide solution. Hand-made electrodes resulted in a considerable spread in the threshold potentials, ranging from 80-250 mV. A two-stage amplification circuit is more appropriate for these lower potentials. Unfortunately, we had already committed the circuit to design layout when this behavior was discovered.

Key components of the sensor-interface circuit include a drain resistor that prevents charge accumulation at the output of the amplifier, and R6, a variable resistor (potentiometer) used to set the gain of the operational amplifier for each electrode pair. Potentiometers have known reliability limitations for long-term monitoring applications. Nevertheless, because of the wide variability in electrode potentials, a potentiometer was selected as the most useful component for adjusting these prototype Pebbles. In future designs, we anticipate that electrode potentials will be more repeatable and the insertion of a set of fixed-value trim resistors will be sufficient to calibrate the circuit. C4 provides an RF shunt between the input ports of the operational amplifier. We found that the electrode leads picked up 125 kHz from the reader, which subsequently confused the response of the comparator. The addition of the shunt capacitor corrected this problem.

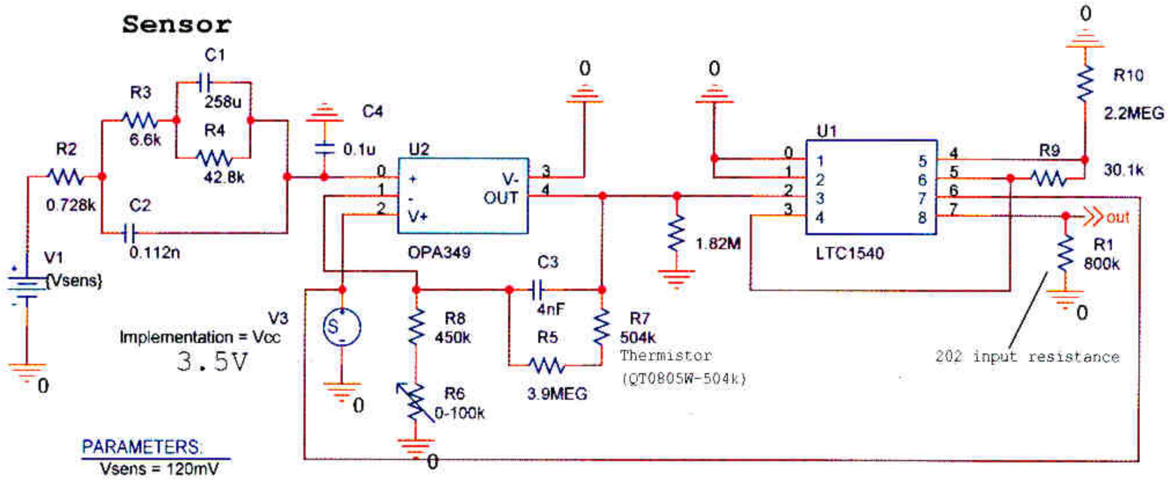


Figure 20. Sensor-interface electronics circuit schematic

7 PACKAGE DESIGN

The Smart Pebble™ package was designed by Fusion Design[2]; the details are shown in Figure 21. Key components of the design are the polyurethane rubber enclosure that holds the reference and ion-selective electrodes and their electrolytes and also protects the circuit board, and the rigid polyurethane cup that protects the whole unit, especially the coil. The unit is sealed with E. V. Roberts RF 1735 epoxy so that only the cementitious plug is exposed to the external environment. This plug permits the chloride ions to diffuse into the electrode region and thereby alter the sensed electrochemical potential in accordance with the chloride concentration.

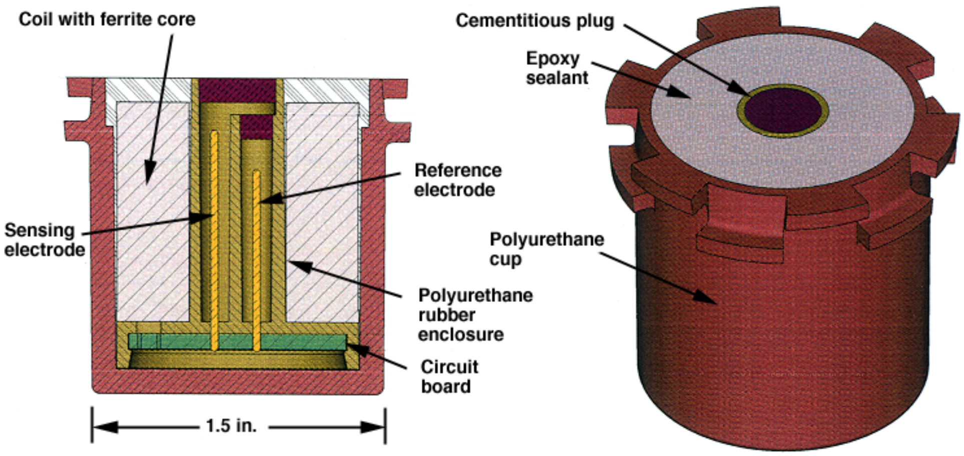


Figure 21. Package design for the Smart Pebble

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[2] FusionDesign, 591 West Hamilton Ave., Campbell, CA 95008-0521

8 FABRICATION AND CALIBRATION

8.1. Fabrication

The reference and sensor electrodes are individually aged in saturated calcium hydroxide solution until their potentials stabilize. Then they are mounted in a polyurethane rubber enclosure and the unit is immersed in a saturated calcium hydroxide solution containing 30 mM of sodium chloride which is prepared using ultrapure Milli-Q® water. This chloride concentration value was selected as a calibration point for the Smart Pebble™ and corresponds to 1.9 lbs/yd^3 (1.127 kg/m^3) of chloride in Portland cement concrete used in bridge decks. Once the sensed potential has stabilized, its value is measured and recorded for use in selecting resistors to establish the nominal gain in the electronic-interface circuit. The electrodes are then connected to the finished circuit, the unit is re-immersed in 30 mM solution, allowed to re-stabilize, and a variable resistor is adjusted to set the gain so the comparator just triggers at the 30-mM threshold level. After calibration, the antenna coil is connected to the circuit and the unit is tested with the Reader to be sure that the proper Reader response is obtained. Assuming satisfactory performance, the entire unit is then potted into a rigid polyurethane enclosure, with only the cementitious access port exposed to the external environment. At present, different electrode couples tend to exhibit slightly different sensed potentials at the chloride-concentration threshold and so each Smart Pebble™ must be custom fabricated and calibrated. Figure 22 is a photograph of the Smart Pebble™ components.

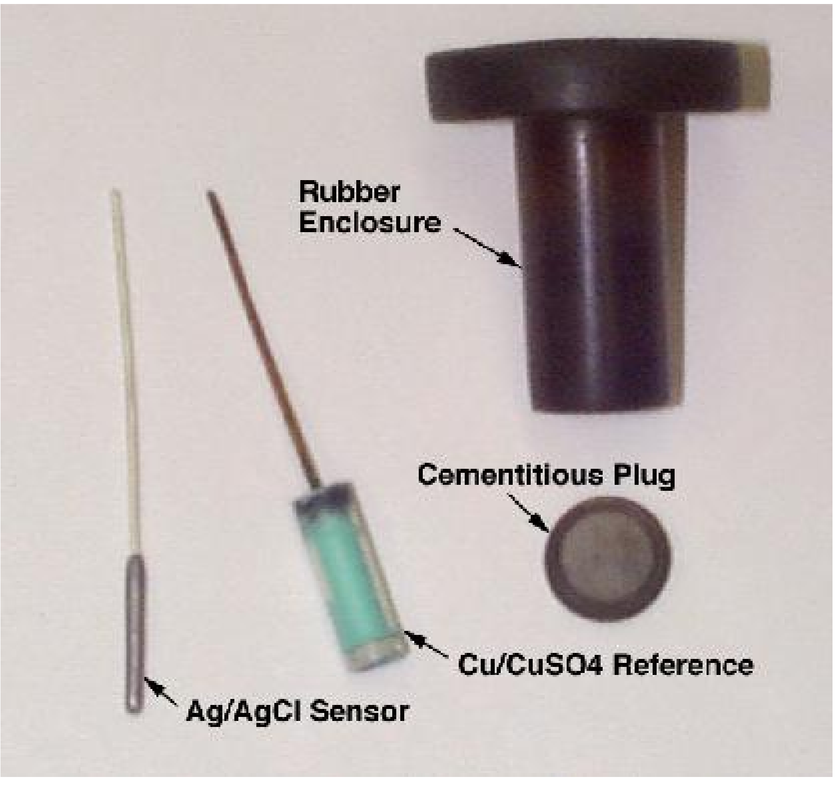

Figure 22. Photograph of electrochemical cell components

Figure 23 shows a view of the circuit board and ferrite-core coil mounted on the assembled sensor cell. The ferrite core (not visible) inside the coil is composed of two stacked Fair-Rite* one-inch-diameter toroids made of 77 material. The coil itself consists of a single layer of approximately 300 turns of AWG 42 copper wire wound on a polystyrene form. The wall of this form was made 0.1-inch thick to keep the coil windings far enough away from the ferrite core so that the self-resonance frequency of the coil occurs well above the 125-kHz operating frequency. The major electronic components are also indicated on the figure. These components were chosen on the basis of their very low power consumption so that they could be activated by the power available from the MCRF202. Figure 24 is a photograph of a fully-assembled Pebble.

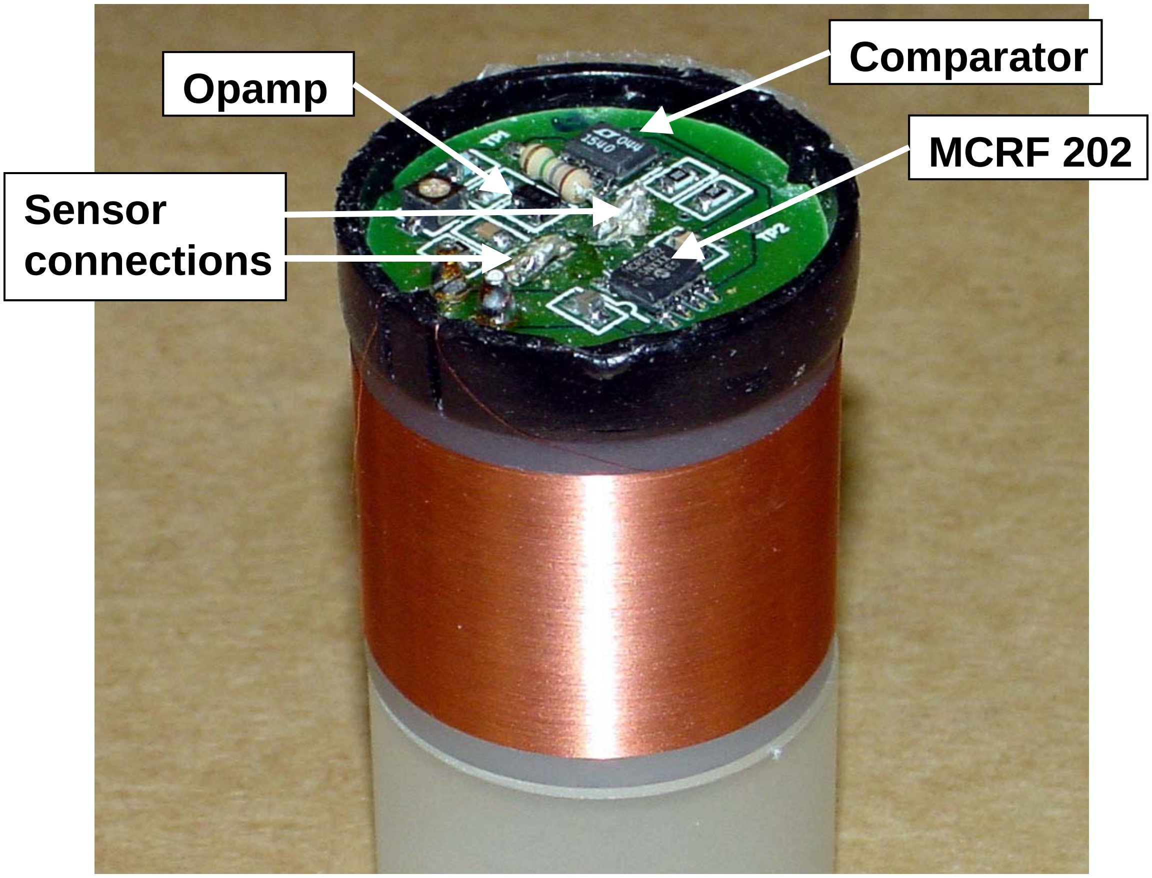

Figure 23. Photograph of sensor-interface electronics and coil antenna

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[*] Fair-Rite Products Corp., P.O. Box J, One Commercial Row, Wallkill, NY 12589-0288

Figure 24. Photograph of assembled Smart Pebble

8.2. Ageing

A typical ageing characteristic of a packaged sensor cell is shown in Fig. 25. As discussed above, the unit was immersed for a lengthy period of time in a saturated calcium hydroxide solution containing a 30-mM concentration of chloride ions and the sensor potential was measured aperiodically using a high-impedance electrometer. The figure shows that the potential (in millivolts) starts out high and then drops as the chloride ions diffuse into the cell. The diffusion through the cementitious plug is slow and so the time required to reach a calibrated equilibrium is long. A better approach would be to start with the electrolyte inside the cell already containing chloride ions at the desired concentration level and then leach out the chloride to a below-threshold value after calibration has been completed.

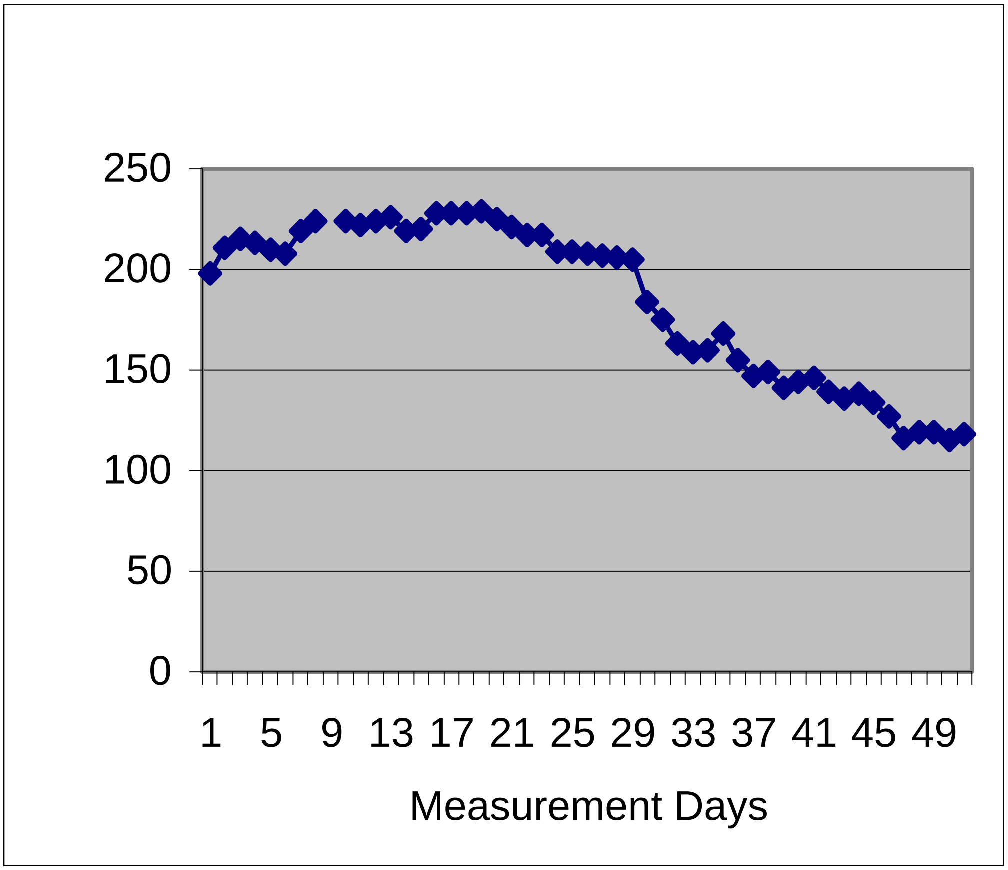


Figure 25. Ageing characteristic of a Smart Pebble

8.3. Procedure

The detailed procedure for assembling and calibrating the Smart Pebble devices is given below.

Table 3

Assembly and Calibration Procedure

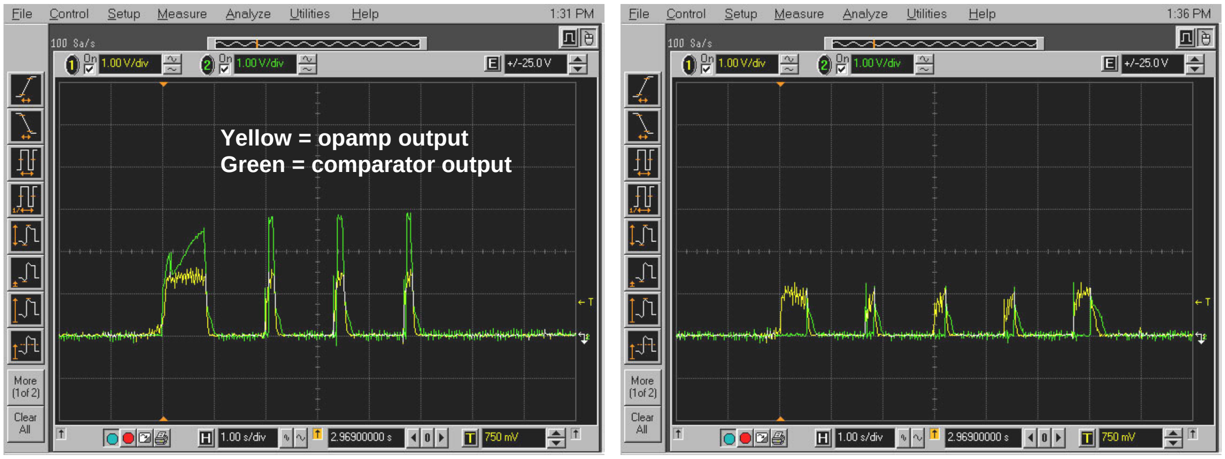
1. Make reference and silver/silver chloride electrodes.
2. Age electrodes for 30 days and select at least 15 with the closest voltage readings with respect to an SCE reference. Each electrode is tagged and numbered for tracking during the assembly process.
3. Assemble electrodes in polyurethane rubber housing.
4. Age these assemblies in 30 mM solution, monitor voltages
5. Once a steady-state value has been reached, record the final voltages. Based on early measurements the expected voltage is approximately 230 mV. We found that the spread of voltages actually was in the 80-300 mV range.
6. Measure sensor voltage vs. temperature (10-40 deg C) for a couple of sensors in 30 mM solution to determine the slope parameter to calibrate the thermistor compensation circuit.
7. Select values for a combination of fixed and variable resistors to be used in the op-amp gain control circuit to compensate for sensor voltage spread.
8. Program a MCRF 202 chip with a unique ID number.
9. Stuff the printed circuit boards with finalized components.
10. Use conductive epoxy (instead of solder) to cement the electrodes to the circuit board to avoid overheating the cell electrodes. Trim electrode wires. Make sure the board is well seated in the bottom of the rubber housing.
11. Return the Pebbles to 30 mM solution to continue the ageing process.
12. Power up each board with a DC supply (3 V) and measure the output of the comparator at test point 2. Adjust the variable resistor as needed until the comparator just triggers (at the 30 mM set point).
13. Remove Pebbles from 30 mM solution and solder RF coil wires to pins on the circuit board.
14. Return Pebbles to 30 mM solution to continue ageing for a day or two and then test performance using the 202 Reader. The ferrite toroids should be inserted in the coils for this test. The current reader should indicate a “red” condition. If necessary, re-adjust the variable resistor.
15. Place a polyester tape protective cover over the cementitious plug to retain moisture for storage and shipping. Seal Pebbles in plastic housings using an epoxy potting compound.

9 COMMUNICATION

Figure 26 is a photograph of the handheld reader used for Smart Pebble communications. It features a 12-in. diameter loop antenna in a plastic housing. The handheld allows the user to adjust the angle of the antenna head. The readout unit displays a light and an audible tone when it receives a valid ID response from a Pebble. A red light is associated with a below threshold reading (chloride concentration OK). A green light is associated with an above threshold reading (chloride concentration is too high). We plan to reverse these light indications in a future version of the reader. The handheld reader is equipped with an RS-232 port for serial data communications.

Figure 26. Photograph of handheld reader and early prototype Smart Pebble

Figure 27 is a digital oscilloscope display of the voltages within the Smart Pebble during reader query events. Charging of the unit occurs during the first pulse. Subsequent replies by the Pebble occur rapidly when a reader query is received. Figure 27(a) shows the response (at the op-amp output and at the comparator output) when the sensor is below threshold. Figure 27(b) shows the response when the sensor is above threshold.



Below concentration threshold (inverted ID)

Above concentration threshold (normal ID)

Yellow = opamp output
Green = comparator output

- **1st pulse continues until a valid ID is received**
- **Comparator triggers cleanly on each pulse**
- **Comparator output goes to 202 sensor port**
- **Comparator output level depends on range**

- **Opamp output is too low to cleanly trigger comparator**

(a) **(b)**

Figure 27. Pebble response to reader (a) inverted ID, and (b) uninverted ID

10 BRIDGE DECK INSTALLATION AND TESTING CONSIDERATIONS

One of the challenges associated with Smart Pebble testing is to replicate the long time scales associated with chloride ingress in actual bridge decks. Chloride ingress occurs over a period of tens of years, depending on bridge deck and environmental characteristics. It would be desirable to test the Smart Pebble design and make recommendations for design improvements in a shorter time interval. We review several approaches to Smart Pebble testing in the section below.

10.1 Old Bridge Decks

One approach to the measurement of bridge deck chloride concentration is to insert a Smart Pebble into an old bridge deck that is undergoing chloride ingress. A core sample can be extracted from the bridge deck. Chloride concentration measurements of this core sample can be used as a baseline for Smart Pebble response. One approach is to drill the core from the top surface of the bridge, insert the Pebble, and refill the core with a polyester concrete (impermeable to moisture). In this design, the Pebble sense port is in contact with the old bridge material. Chloride ions (and moisture) would follow a path through the old bridge deck material rather than the back-filled core material. There is some question in this technique about how to ensure that moisture does not flow along the boundary between the back-filled core and the bridge deck material.

An alternative old-bridge approach is to drill the core sample from the bottom (underside) of the bridge. This would leave the top-surface of the bridge deck unaltered, but would require access to the bridge deck from the underside. This approach may be useful for early tests of the Smart Pebble (a few locations). For larger-scale testing, it may be more convenient to insert the Pebbles from the top side.

10.2 New Bridges

Although Smart Pebbles could be included in the concrete pour, their random distribution within the mix may not provide the best data on bridge health. Although it would be possible to geo-locate Pebble position and orientation with a modified Pebble and reader design, Pebbles located too close to the top surface may not provide useful chloride-ingress data, and Pebbles located beneath the rebar may be difficult to query and again may not provide useful chloride-ingress data. A preferred approach would be to tie Smart Pebbles to the rebar matrix prior to the concrete pour. Caltrans fabricated a frame to hold the pebble at the desired depth when attached to the top mat of rebar, as shown in Figure 28.

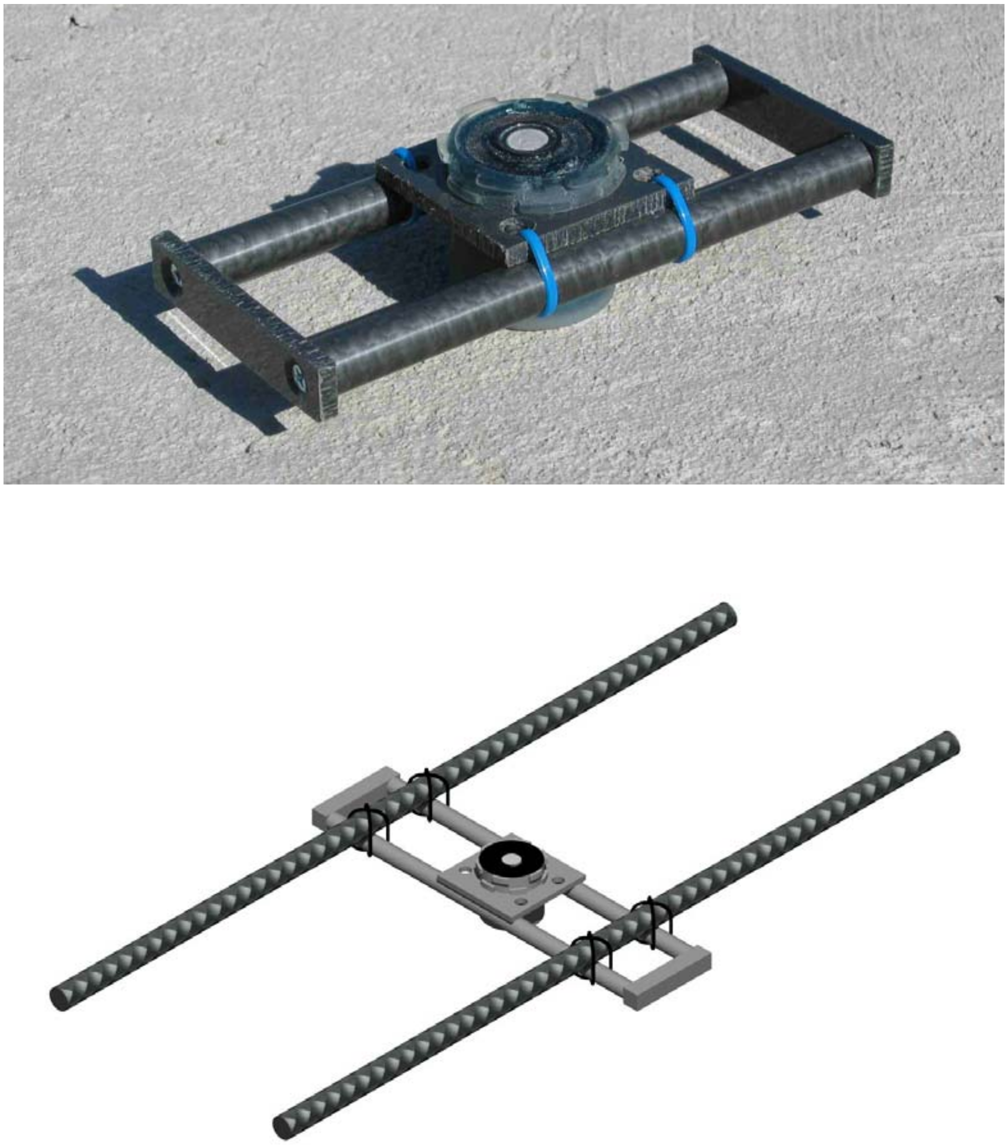


Figure 28. Frame for mounting Pebble to rebar

10.3 Laboratory Tests

Testing of Smart Pebble devices under laboratory conditions can include ponding tests for long-term performance, repetition of freeze-thaw cycles, and using electrochemically driven chloride profiles—where a surplus of chloride resides on the top surface of a concrete slab and an applied potential causes across the slab causes the chloride ions to drift into the concrete. Alternatively, batches of concrete can be made with known chloride composition to verify the threshold level at which the Reader indicates that the Smart Pebble changes state.

11 ADVANCED DESIGNS

In this section, we describe (a) design improvements for the chloride-sensing Smart Pebble, (b) reader improvements that enable vehicle-mounted polling of embedded Pebbles, and (c) other sensors that are compatible with the Smart Pebble architecture.

11.1 Chloride Sensor Design Improvements

One of the challenges associated with long-term chloride-sensor operation is to keep the electrochemical cell from drying out. During the Smart Pebble development effort, we experimented with a variety of hydrophilic compounds to retain moisture within the cell. Early experiments with polyethylene glycol (PEG) showed some reactivity with the copper reference electrode. Silica gel and carboxymethylcellulose readily absorb moisture, but will dry out quickly in dry air. Calcium hydroxide had the best water retention characteristics of the substances we tried and is compatible with the bridge deck pore solution. Consequently, we filled the electrochemical cell with saturated calcium hydroxide. An excess of calcium hydroxide allowed the cell to maintain a high pH. Unfortunately, experiments in air showed that carbon dioxide ingress into the cell resulted in carbonation (production of calcium carbonate) and subsequent drying of the cell. Consequently, the measures we have taken to date have been ineffective in keeping the cell moist under dry atmosphere conditions. A partially dry cell gives a misleadingly high chloride concentration measurement because chloride does not evaporate. Tests were not performed in concrete.

An alternative solution is to include a valve in the design of the Smart Pebble interface with the concrete. Figure 29 illustrates this concept. A cementitious plug provides a compatible interface with the bridge deck. A moisture-absorbing sponge-like foam material expands when moisture is present. A seal provides a vapor barrier to prevent moisture from escaping from the cell. The electrochemical cell is partially filled with a moisture-absorbing sponge-like material as well. The reference electrode and chloride-sensing electrode have the same geometry as in the original design.

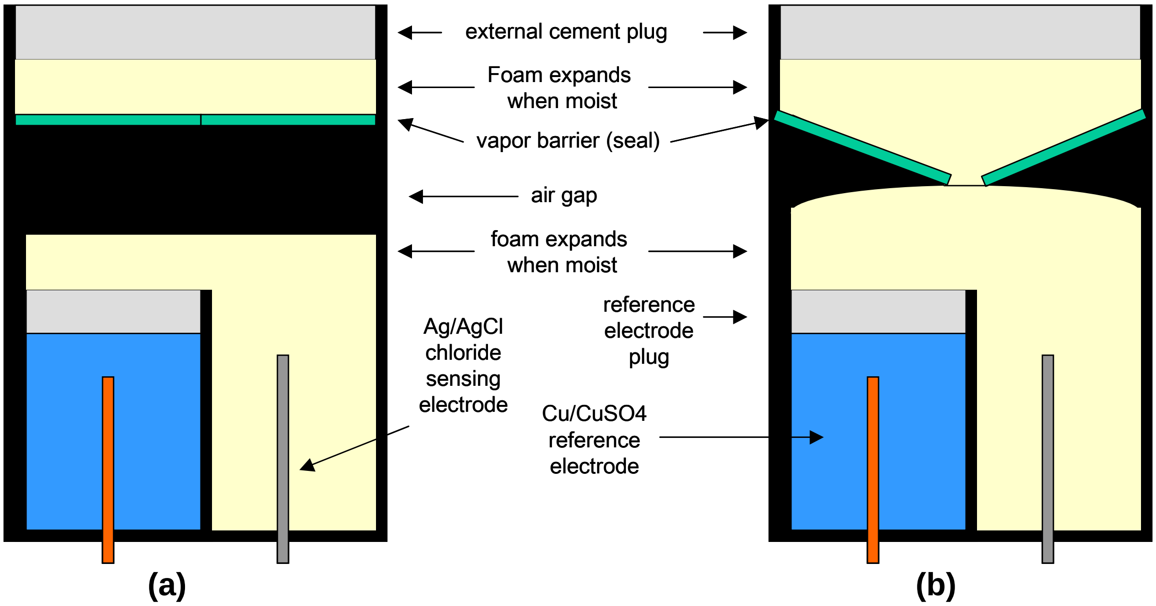


Figure 29. Smart Pebble with valve to seal in moisture under dry bridge deck conditions: (a) valve sealed, and (b) valve open

Under dry bridge deck conditions, Figure 29(a), the electrochemical cell is sealed from the environment. This enables the cell to retain moisture. The sealed cell enables the Smart Pebble to produce a reliable reading of chloride threshold concentration when polled by an external reader under dry bridge-deck conditions. Chloride ion transport only occurs during wet conditions, so the sealed state of the electrochemical cell does not affect its equilibrium with the bridge-deck chloride concentration.

Under wet bridge deck conditions, Figure 29(b), moisture absorbed by the foam layer beneath the cementitious plug expands, pushing open the seal. Expansion continues until contact is made with the foam material in the electrochemical cell. This internal foam will also expand as additional moisture from the bridge is absorbed by the electrochemical cell. Because liquid-phase transport between the bridge environment and the electrochemical cell is now possible, chloride ions are transported from the bridge into the cell and equilibrium is reached. Foam materials must be carefully engineered so that the foam within the electrochemical cell does not expand as much as the foam in contact with the top plug. This will prevent the expanding interior foam from forcing the seal closed.

As the bridge deck dries out, capillary action will allow some of the moisture from the cell to wick into the bridge environment. Slowly the foam materials will contract as moisture is removed from the system. Eventually, the force associated with contraction will overcome the stiction force between the two foam materials and an air gap will appear. As the bridge deck continues to dry out, contraction will continue and the seal closes, isolating the electrochemical cell from the environment. Because the cell will retain some moisture, measurement of chloride concentration will be possible under dry bridge deck conditions. Designs that reduce capillary action and stiction forces should be explored as a part of the development of this valve assembly.

A wide range of material choices are available for the seal and expanding foams associated with this valve assembly. The current cell design relies on flexible polyurethane as the housing material. This material is compatible with the high pH bridgedeck environment. Consequently, open-cell polyurethane foam is a logical first choice. Other sponge-like materials of interest include other open-cell polymer foams, bentonite clays, and methylcellulose compounds. Similarly, a polyurethane rubber film material is a logical first choice as a seal material.

11.2 Vehicle-mounted Reader Design

According to the present design, a handheld reader queries embedded Pebbles. It would be desirable to mount a reader onto a vehicle to enable data collection on the move. Mobile read-out enables more rapid inspection of bridge decks and protects personnel from traffic hazards. The response characteristics of the current Pebble design are such that approximately 2 s is required to obtain a valid reading. This communication process is described in detail in Section 9. Using the existing reader design, it would be possible to mount a ski beneath a Caltrans pickup truck. This ski would have a standoff above the bridge deck surface of an inch or two. In this configuration, the reader would begin transmissions near the front of the vehicle to energize the Smart Pebbles. Valid readings from the Pebbles would be received near the rear of the vehicle as it passes over the Pebble location 2 s later. For a 15-ft long ski, the rate of travel would be 7.5 ft/s, or approximately 5 mph. A reader designed to query Pebbles at a faster rate should allow vehicle operation up to 10 mph. Even faster speeds are possible using a longer ski (larger vehicle). Alternatively, a future Pebble could be designed using a 13.56 MHz RFID chip. Faster communications are possible with such a device, but at the date of this writing, no commercial 13.56 MHz RFIDs are available with a sensor interface.

Figure 30 shows the vehicle-mounted-reader concept. In practice, the reader location may depend on the optimum placement of Pebbles. That is, if Pebbles are located near the center of the bridge deck, then a centered reader ski is the logical choice. On the other hand, Pebbles located near the shoulder of the bridge deck (where drainage may aggravate chloride ingress) should be polled using a side-mounted reader ski. Polling Pebbles that are evenly distributed within a lane could be accomplished using multiple reader skis beneath the vehicle.

Figure 30. Vehicle-Mounted Reader Concept

11.3 Other Sensor Configurations

The Smart Pebble design architecture is compatible with other sensors that could be used to monitor other bridge deck parameters. Figure 31 shows a sample of some of the quantities that could be measured. Both threshold and concentration measurements are possible.

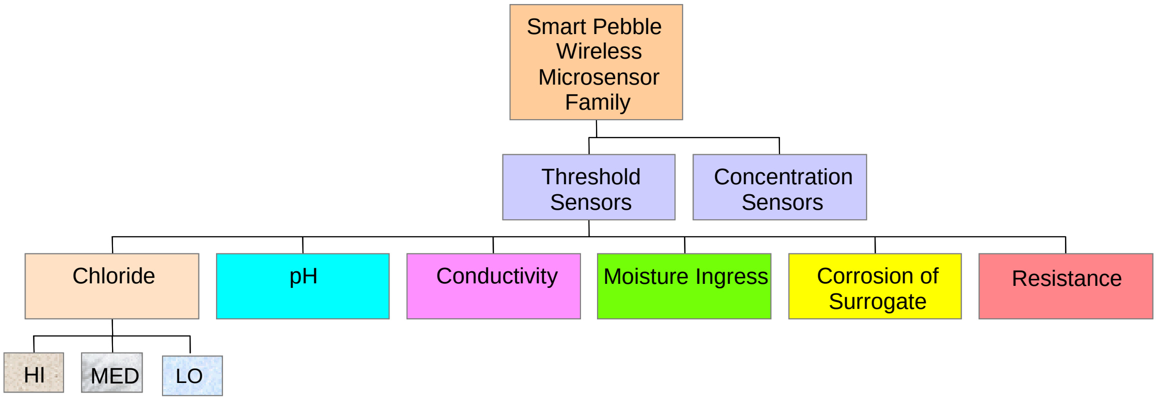


Figure 31. Taxonomy of Smart Pebble compatible sensors

11.3.1 Chloride Sensors

A variety of chloride sensor configurations can be implemented using the Smart Pebble design. The simplest approach is to fabricate sensors having a variety of pre-determined threshold values. In a region of interest, one could disperse sensors with a low, medium, or high-valued chloride threshold. Alternatively, and using anti-collision RFID technology, a single Smart Pebble could be constructed using two RFID chips and two sensor circuits, but a single electrochemical cell. The first circuit would be set to a low-valued chloride threshold concentration. The second circuit would be set to indicate a high-valued chloride threshold concentration. The logic of the response would follow, where 0 = concentration below threshold, and 1 = concentration above threshold: 00 = LO—chloride concentration is below the lowest setting, 10 = MED—chloride concentration is above the threshold of the first RFID and below the setting of the second one. 11 = HI—chloride concentration is above both threshold values. 01—ERROR—chloride concentration is below the low setting and above the high setting, a false reading.

Lastly, it would be possible to construct a chloride concentration sensor using a serial A-to-D converter in place of the comparator. A clock circuit is needed for timing circuitry associated with the micropower ADC. Although this could be constructed from micropower components, an application specific integrated circuit (ASIC) design would provide the greatest cost advantage for production units. It is worth noting that the potentiometric chloride sensor provides a coarse indication of chloride concentration. It is doubtful that more than 2 bits of chloride data will be accurately represented by the measurement (over the range that is useful for bridge deck inspection). That is, with a background concentration typically near 5 mM, and a damage threshold near 50 mM, the chloride sensor will operate over a room temperature range of approximately 45 mV. Given a design uncertainty of ±5 mV, a 2-bit quantization is sufficient to represent the useful range of values.

11.3.2 pH Sensors

An electrochemical cell that monitors pH would follow a similar design as the Smart Pebble sensor. In this case, it might be desirable to use Ag/AgCl as the reference electrode (in a saturated KCl solution) and a Me/MeO electrode as the pH-sensitive electrode (e.g., Ni/NiO or Cu/CuO). The range of implementations available for the chloride sensor above applies to the pH sensor design as well.

11.3.3 Conductivity and Moisture Content

A circuit designed to measure DC conductivity is shown in Figure 32 (4-probe method). An AC-coupled design would enable a bipolar measurement. The frequency of the measurement is nominally the inverse of the reader pulse width once the circuit is fully charged. This measurement would be useful in determining whether the bridge is wet or dry. For epoxy-coated rebar, a sample of the epoxy batch used to make the rebar could be included in the Pebble. Moisture ingress beneath the epoxy layer would indicate that the protective coating surrounding the rebar might be compromised.

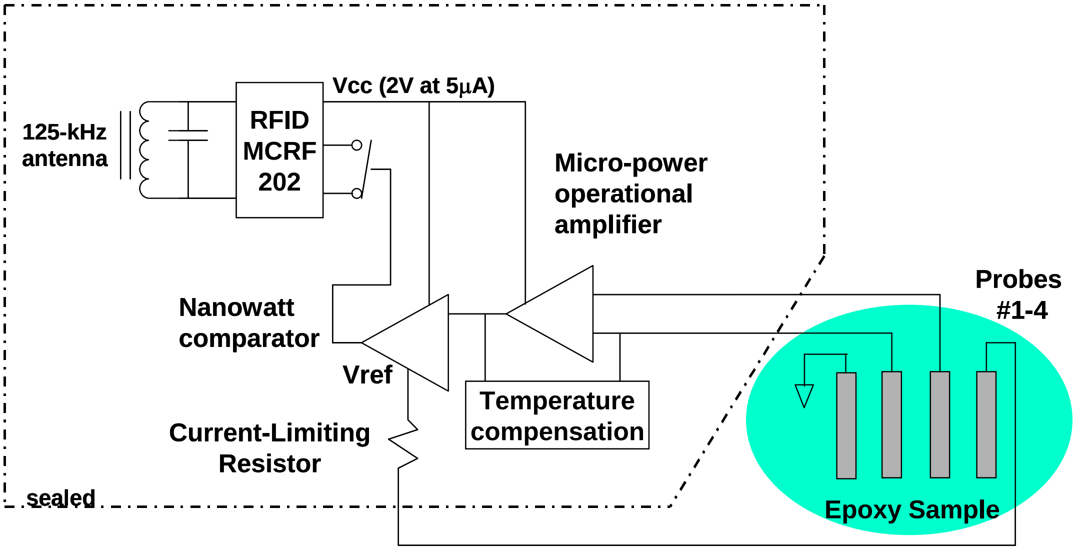


Figure 32. Measurement of Moisture ingress beneath an Epoxy coating

11.3.4 *Corrosion of a Surrogate*

Finally, thin black-steel wires can be incorporated into a Smart Pebble to indicate actual corrosion rate of steel in the bridge deck. This may be indicative of material loss on the actual rebar. In Figure 33, sufficient loss of material will break the first steel wire, opening the circuit. A second, larger-diameter wire would break as corrosion continued. On the other hand, if corrosion mitigation strategies were applied to the bridge, the treatment would extend the time constant associated with the breaking of the second wire. In this way, the Smart Pebble could monitor both the occurrence of initial corrosion and the progress of rehabilitation. Hybrid designs are possible as well. For example, a Smart Pebble could be constructed with two RFIDs—one with a chloride sensor and the other with a corroding surrogate wire. If the chloride sensor fails, breaking of the wire would provide a backup warning.

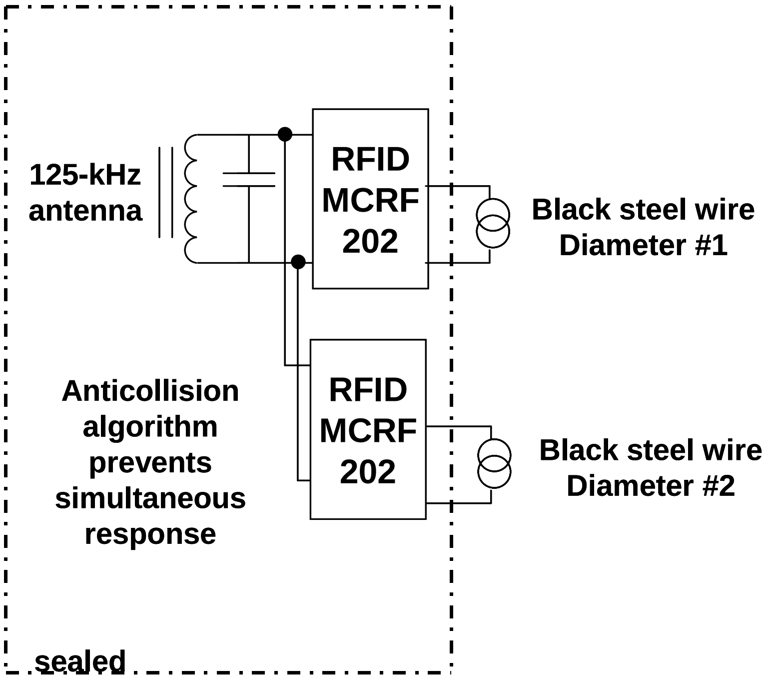


Figure 33. Surrogate Rebar Material corrodes indicating the presence of corrosive bridge deck conditions

12 CONCLUSIONS

This report describes the theory and development of Smart Pebbles, passive wireless sensors that can be embedded in bridge decks to detect chloride ingress and other quantities for long-term monitoring and health assessment. The Smart Pebbles technology offers the possibility of reducing the cost associated with bridge deck inspection. Prioritized maintenance may enable modest rehabilitation of structures rather than costly repair of structural damage.

The development work to date has focused on RFID communications, sensor-RFID integration, and sensor development. The Pebble devices we have constructed can transpond sensor data through as much as 6 inches of concrete. We have developed stable reference electrodes in a laboratory environment, with 4000 hours of continuous measurement. Unfortunately, the resulting electrochemical cell in the Pebble device has limited stability. This is due to evaporation of the electrolyte in air environments, subsequent carbonation of the calcium hydroxide solution, and drift of the Ag/AgCl electrode due to mixed potential interaction of Ag/Ag_2O under changing pH conditions. We recommend modifications to the Pebble design to include a simple valve that opens under wet bridge conditions and closes to seal in the electrolyte when the bridge is dry.

A small batch of Pebbles was prepared for Caltrans for evaluation and testing. Recommendations from these tests along with the above concepts can be incorporated into a second-generation Smart Pebble device.

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