Applications of a Wireless Chloride Sensor in Environmental Monitoring

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Introduction

Wireless Sensor Networks have a great deal of potential for application in environmental monitoring.

It is necessary that sensors are available that are

• low cost
• robust
• low power
• measure useful things

Here we introduce a low-cost chloride sensor that potentially meets all these requirements, and we report on its initial performance

• In a soil column
• In a fluvarium
• In a greenhouse
Within the environment there are many things that could be monitored, for different stakeholders and at different scales. In this case we are proposing a chloride sensor that can be used for applications such as:

- chloride tracer for hydrology
- water quality control for irrigation
The Sensor

The sensor is made using a thick-film process. Multiple layers are built up to create a structure. The process consists of:

- Printing
- Drying
- Firing

The sensor is low cost, robust and self-generating, so low power.
The Sensor

The redox reaction between silver (Ag) and its salt – silver chloride (AgCl) has a characteristic potential that is related to the activities (a) of the reactants and products, as given by the Nernst equation:

\[
E = E^0' + \left(\frac{RT}{nF}\right) \cdot \ln \left[\frac{a_{AgCl}}{a_{Ag} \cdot a_{Cl^-}}\right]
\]

Through substitution of the various physical constants at \(T = 25^\circ C\), conversion of activities to concentrations and by conversion of the natural logarithm term to base 10, the equation takes the form

\[
E = E_0 - 0.0592 \log(C_{Cl^-})
\]

This says that there is a 59mV change for every decade change in chloride concentration.

It has to be measured against something, and this is a reference electrode.
**Reference Electrode**

The reference electrode gives a fixed potential related to a known concentration. For the experiments described here a commercial electrode was used. However recent work has resulted in an integrated reference electrode.
Sensor Performance

Sensor performance shows good repeatability from device to device.

<table>
<thead>
<tr>
<th>Chloride sensors</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>Comm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity (mv/pCl)</td>
<td>-50.7</td>
<td>-48.3</td>
<td>-49.6</td>
<td>-50.1</td>
</tr>
<tr>
<td>Offset potential (mV)</td>
<td>11.0</td>
<td>12.6</td>
<td>7.6</td>
<td>7.0</td>
</tr>
</tbody>
</table>

The table shows typical values obtained. Calibration against temperature is still required. Below we see the performance of the integrated system, showing that performance across a useful range of concentrations is available.
But can it provide useful data?

We designed a radio data logger to allow testing of the sensor. This was based on a Waspmote platform, from Libellium. Some experiments logged to an SD card, and some allowed radio telemetry for real-time monitoring, with data being displayed in a custom Matlab application.
Soil Column Experiment

This experiment was designed to show the value of making real-time measurements to validate conventional modeling predictions, which then allows other situations to be modelled with confidence. It was designed to illustrate the transport of chloride though a repacked soil column under steady state saturated flow. Sensor potentials were logged at a rate of one reading per sensor every 3 seconds, with each reading being the average of 10 successive samples. The background solution was designed to be 10mM, and a pulse of 100mM added. The progress of the pulse can be seen, although we can see preferential paths.
The preferential paths were verified by a similar experiment using a transparent column, where dye was added with the chloride. Even in carefully packed columns, it was apparent that preferential paths would be unavoidable.

As can be seen from the photo, the blue dye shows fingers spreading downwards, with blue dye already appearing at the bottom.

However, modelling for sensors near the top of the column shows good agreement with classical modelling, indicating that the sensor is giving good data.
A fluvarium is a form of river simulator, and in this case consists of a long channel (20 m) which had previously been filled with stream sediment. This was used as a representative stream environment. The slope of the fluvarium was adjustable, and the water flow rate could be controlled by a valved pump and measured at the outflow by the use of a flume.

The sensor were spread out at 30cm intervals with one sensor in the inlet pool to sample the source. Other sensors were embedded in the sediment or measured surface flow.

The fluvarium was prepared by flushing it overnight with a low concentration solution and then 100ml of 100mM solution was added to the inlet pool, with no flow.
The fluvarium was then gently tilted to allow flow, and periodically, tap water was added to the inlet pool to provide some impetus. These events are detailed in the table:

<table>
<thead>
<tr>
<th>Event</th>
<th>Time (mins)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>54</td>
<td>Fluvarium tilted</td>
</tr>
<tr>
<td>2</td>
<td>107</td>
<td>200 mL water added</td>
</tr>
<tr>
<td>3</td>
<td>114</td>
<td>200 mL water added</td>
</tr>
<tr>
<td>4</td>
<td>129</td>
<td>200 mL water added</td>
</tr>
<tr>
<td>5</td>
<td>139</td>
<td>400 mL water added</td>
</tr>
<tr>
<td>6</td>
<td>164</td>
<td>600 mL water added</td>
</tr>
<tr>
<td>7</td>
<td>185</td>
<td>1,000 mL water added</td>
</tr>
<tr>
<td>8</td>
<td>204</td>
<td>Flume turned on</td>
</tr>
</tbody>
</table>

The graph below shows the results for the embedded sensors, with only the inlet sampling sensors showing significant movement. Sensor 1 is in the inlet pool but embedded but is responding slowly to the changes in chloride.
If we look at the surface sensors we see more variation in response

There are difference between the responses, and this was due to preferential paths again forming in the surface flow. These looked like small meanders, and the responsive sensors were in the flow, and the less responsive ones were not. When the flume was turned on, so that more water was introduced continuously, the sensors all reverted to being in a flow, and all responded quickly to the reduced chloride.

Such an experiment shows how these sensors may be applied to chloride tracing.
Greenhouse Experiment - Evaporative-induced changes to soil salinity

This experiment was located in a glasshouse and temperature compensated. Six sensors were buried at a depth of 1 cm and a 7th was buried at a depth of 10 cm in a tub of freely-drained sand. The sand was wetted uniformly using a solution of 100 mM NaCl, and the sensor potentials were then logged for several days.
The experiment ran for 14 days. These are the results for the last 4 days. Note the diurnal variation. These results are compensated for temperature variations. At this point the soil is drying out and salt concentration is increasing near the surface, but things are equalising at night, presumably due to condensation. What is apparent is that there are significant variations depending on the time of day.

In-situ measurement of chloride movement in soils and evaporative-induced changes to soil salinity using a new low-cost screen printed potentiometric sensor
K Smettem, E Barrett-Lennard, NR Harris, A Cranny EGU General Assembly 2013
A typical environment, showing salt crystallisation (Western Australia)
Conclusions

These initial trials of chloride sensors in both these environments allow some interesting observations to be noted.

• The sensors are very promising and are allowing interesting data to be generated
• The sensors, being low cost, low power and robust are suitable for distributed wireless sensor networks
• The sensors are useable in real environments and allow accurate, real time measurements of chloride concentration in both fluid environments and also wet soil environments.
• The simple experiments reported here illustrate the care needed in interpreting spot measurements in a distributed environment. Even sensors positioned a few centimetres away from a preferred flow path will give results significantly different from those in the preferred flow.

Acknowledgments

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