Utilization of Geochemical Parameters in Developing a Conceptual Site Model

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Introduction

Early days:

- US Geological Survey
- Academic Organizations

Conducted most subsurface investigations directed at understanding the inorganic aspects of natural surface and ground water.

These investigations directed more attention at the field parameters: Temp., pH, D.O., Cond., & ORP
Contamination Assessment

Current environmental investigations:

- Organic contamination
  - Petroleum Sites
  - Non-chlorinated solvent Sites
  - Chlorinated solvent Sites

- Specific metals (or mixtures)
  - Hexavalent Chromium
  - Lead
  - Arsenic
  - Other metals
Contamination Assessment

Many of the current ground water studies are more focused on evaluation of the presence and spread of contaminants, some of the studies do not conduct the normal field parameters...

Or if they do, there is often a lack of comprehension leading to poor data validity or failure to understand the date relevance.
Field Parameters

**Temperature**
- Degrees Celsius

**Specific Electrical Conductance**
- Micromhos per centimeter

**Dissolved Oxygen (DO)**
- mg/L

**Oxidation-Reduction Potential (ORP)**
- millivolts

**pH**
- pH

**Acidity & Alkalinity**
- Eh
Temperature seems like a simple parameter to measure and to understand... stick a thermometer in the water and read the resulting temperature.

But what is the value of this reading?

1. Low flow sampling, consistent formation water.
2. Temperature of the water will dictate whether the contaminant is present.
Temperature

Case Study:
Surface spill of light kerosene fuel over a fairly course grained, exposed soil, construction area.

Ground water temperature was measured at 95 °C

Two new 12” diameter steam condensate pipelines were buried in the saturated soil.

Was there any residual fuel oil present in the ground water?
Specific Electrical Conductance

Specific Electrical Conductance (EC) measures the ability of water to conduct electrical current due to the presence of dissolved elements or ions.

We use EC as an approximation of Total Dissolved Solids (TDS) – the specific ratio depends on the type of material dissolved in the water.

In general – EC (µmhos/cm) will be in the range of 0.55 to 0.75 of the TDS in mg/L. Approximating the TDS is very important for remediation design.
Specific Electrical Conductance

EC is often used by remediation system designers to evaluate separation technologies.

Reverse Osmosis – high conductivity means higher osmotic pressures. The higher the pressure, the more costly the remedy.

Ultrafiltration – high conductivity means more cleaning cycles.

Ion Exchange – high conductivity produces shorter operating cycles between regeneration.
Dissolved Oxygen

Under ideal conditions:

• 1 bar of atmospheric pressure
• 20 degrees Celsius
• Fresh water with no salinity
• Neutral pH

What is the maximum solubility of oxygen? (express your answer in mg/L)
Dissolved Oxygen

Oxygen Solubility in Fresh Water
Salinity \sim 0

Temperature (deg C)

Oxygen Solubility (mg/l)

Pressure (bar)

\begin{enumerate}
\item 4
\item 2
\item 1
\end{enumerate}
Dissolved Oxygen

Thus, from the previous slide we now know that if the DO meter exceeds 10 mg/L... stop work and recalibrate your equipment.

Aerobic bacterial action generally is capable of decreasing the DO content to approximately 1 mg/L, so even anaerobic ground water commonly will contain detectable DO levels.

Oh ... just one more thing!
Dissolved Oxygen

Thus, from the previous slide we now know that if the DO meter exceeds 10 mg/L… stop work and recalibrate your equipment.

Aerobic bacterial action generally is capable of decreasing the DO content to approximately 1 mg/L, so even anaerobic ground water commonly will contain detectable DO levels.

Please don’t report negative DO levels… it will just tick off and embarrass your Project Manager.
Oxidation – Reduction Potential

ORP is a measurement of the electrical potential of ground water – reported in millivolts.

Positive ORP values are indicative of oxidizing conditions that are present when:

- DO is generally high
- pH is relatively low (acidic <7)
- Aquifer is aerobic
- Positive ORP is often observed at sites where mobile hexavalent chromium is detected.
Oxidation – Reduction Potential

Negative ORP values are indicative of reducing conditions that are present when:

- DO is generally low
- pH is relatively high (caustic > 7)
- Aquifer is anaerobic
- Negative ORP is usually produces a good condition for reductive dechlorination treatment of chlorinated compounds.
pH is often depicted on a graphical color scale as shown above. The pH value is related to the ratio of positively charged hydrogen ions \([H^+]\) and negatively charged hydroxyl ions \([OH^-]\).
When do you sample?

During well purging, monitor the indicator field parameters (turbidity, temperature, specific conductance, pH, Eh, DO) every three to five minutes. Note: during the early phase of purging emphasis should be put on minimizing and stabilizing pumping stress, and recording those adjustments. Purging is considered complete and sampling may begin when the above indicator field parameters have stabilized. Stabilization is considered to be achieved when three consecutive readings, taken at three (3) to five (5) minute intervals, are within the following limits:

- Turbidity (10% for values greater than 1 NTU),
- DO (10%),
- Specific Conductance (3%),
- Temperature (3%),
- pH (± 0.1 unit),
- ORP/Eh (± 10 millivolts).
When do you sample?

**ORP millivolts vs. Time**

![Graph showing ORP millivolts over time with a red arrow pointing to a Cr^6+ concentration of <0.01 mg/l at a certain time point.](image_url)
Oops... a distraction
Did you sample too soon?

![Graph of ORP millivolts vs. Time]

- **Cr^{+6} = 11 mg/l**
- **Cr^{+6} = <0.01 mg/l**

**dig deeper**

**ACUITY ENVIRONMENTAL SOLUTIONS**
How can the aquifer do that?

This investigation was related to an environmental release of chromic acid from a sump. The initial release breached a containment sump, entered the storm sewer and impacted the pipe bedding materials.

Ground water was impacted with low pH, high ORP chromic acid. However, after some time, the monitoring well started to show signs of neutral pH and low ORP... and coincidentally... low hexavalent chrome values as well.

Can an aquifer shift from -100 millivolts up to +150 millivolts just by withdrawing water for 5,000 seconds?
How can the aquifer do that?

Obviously the answer to that last question has to be: YES!

Otherwise this would be an idiotic case study... did anybody in here get that question wrong?

So, what did create the conditions that would allow the field parameters to behave as presented in the graph?

- Equipment calibration?
How can the aquifer do that?

Obviously the answer to that last question has to be: **YES !**

Otherwise this would be an idiotic case study... did anybody in here get that question wrong?

So, what did create the conditions that would allow the field parameters to behave as presented in the graph?

- Equipment calibration?
  - **NOPE!**
How can the aquifer do that?

Obviously the answer to that last question has to be: **YES !**

Otherwise this would be an idiotic case study... did anybody in here get that question wrong?

So, what did create the conditions that would allow the field parameters to behave as presented in the graph?

- Equipment calibration? **NOPE!**

- What about the presence of a strong reducing agent?
How can the aquifer do that?

Obviously the answer to that last question has to be:  
YES!

Otherwise this would be an idiotic case study... did anybody in here get that question wrong?

So, what did create the conditions that would allow the field parameters to behave as presented in the graph?

- Equipment calibration?  
  NOPE!

- What about the presence of a strong reducing agent?  
  YES!  There was a second sump leaking soap.
Acidity and Alkalinity

Acidity and Alkalinity are obviously closely related to the pH of the aquifer.

These parameters are usually measured in the analytical laboratory.

Acidity is the ability of the ground water to react with hydroxyl ions, and is operationally defined as the amount of base required to raise the pH to 8.2.

It is usually reported as meq/L or mg/L of CaCO$_3$.
Acidity and Alkalinity

Why is this information important?

How will the remediation system designer use this information?

Will it impact the cost evaluation of the final remedy?
Acidity and Alkalinity

Why is this information important?
Many of the *in situ* remedies rely on relatively neutral (pH ~ 7) environments in order for the biological activity to work effectively.

How will the remediation system designer use this information?
This information will be used to calculate the mass of buffering agent that must be injected to adjust the aquifer pH. Cost of injection/mixing as well.

Will it impact the cost evaluation of the final remedy? ABSOLUTELY!!!! It can double the $$$$.
Major Cations and Anions

Cations
• Positive Charge
• Calcium
• Magnesium
• Sodium
• Potassium

Anions
• Negative Charge
• Chloride
• Sulfate
• Carbonate
• Bicarbonate
RedOx Controlled Ions

- Sulfate
- Carbonate
- Bicarbonate
- Nitrogen Series
  - Ammonia
  - Nitrite
  - Nitrate
- Arsenate – Arsenite pair
- Selenium
- Iron
  - Ferrous
  - Ferric
- Hexavalent Chromium (Chromate)
- Trivalent Chromium
Graphical Methods

Chromium

\[ \text{pH} \quad \text{pe} \quad \text{Eh(V)} \]

- \( P_{O_2} = 1 \text{ atm} \)
- \( P_{H_2} = 1 \text{ atm} \)

- \( \text{Cr}^{3+} \)
- \( \text{HCrO}_4^- \)
- \( \text{CrO}_4^{2-} \)
- \( \text{Cr}_2\text{O}_3 \)
- \( \text{Cr(OH)}_2 \)
Graphical Methods
Graphical Methods
Graphical Methods
Graphical Methods
Graphical Methods

Trilinear Plot of Ions vs. Time – Ions are stable
Graphical Methods

Trilinear Plot of Ions vs. Time – Ions are shifting
Development of Valid Site Conceptual Models

Start Conceptual Site Models by validating the data:

• Compare the pH, DO and ORP values to each other. If the relationships are not in place – challenge the data, challenge the sampling method, or challenge your Conceptual Site Model.

• Next understand the ion chemistry of the Site. If you are creating reducing conditions – then are the ions responding accordingly?
Development of Valid Site Conceptual Models

• Don’t proceed to report data that does not make sense, unless you can repeat the data and understand what physical and chemical conditions produced the result that you measured.

• Remember – we are working in a dynamic field where a chemical was released into the environment in a manner that has altered the environment. So don’t automatically conclude that the contaminant you think is present, is the only contaminant.
Thank you.

Please enjoy the rest of the conference.