Validating a Method for Estimating Specific Conductance in Mining Wastewater

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Outline

- Regulatory Framework
- Review of Previous Work
- Current Work
  - Objectives
  - Procedure
  - Analysis and Results
  - Conclusions

Regulatory Framework

Regulatory Framework

EPA and Army Corps of Engineers issued interim memorandum in April 2010 related to Appalachian mining

- Not legally binding
- Framework for approval of all pending and future permits through CWA
- Effluent conductivity between 300-500 µS/cm

Regulatory Framework

Final Guidance was issued by EPA in July 2011

- Conductivity limit of 300-500 µS/cm maintained
- Individual ions should be regulated when overall conductivity limit cannot be attained
- States are ultimately responsible for issuing permits and can choose whether or not to follow guidance

Previous Work

Conductivity Modeling

- Knowledge gap: How ions contribute to overall conductivity at low to medium concentrations
- Theoretical models have been developed for higher ionic strength waters (i.e. Industrial waste, brine waters)
- Empirical model was developed in 2011 by R. B. McCleskey

McCleskey Model

- Empirical model for contribution of cations and anions, trace metals, and ion pairs
- Constituents were included in this study based on their presence in natural waters
- WATEQ4F was used to determine speciated concentrations of each chemical at a given pH and temperature

McCleskey Model

Model may be used for the following conditions:

- Ionic strength: 0.0004-0.7 mol/kg
- Temperature: 0-95^{o}C
- pH: 1-10
- Conductivity: 30-70,000 µS/cm

McCleskey Model

To find $\boldsymbol{\lambda_i}$, the specific conductance of an ion at 25^{o}C, need:

- **I**, the Ionic Strength
- $\boldsymbol{\lambda^o(T)}$, specific conductance at a given temperature
- **A(T)**, an empirical constant
- **B**, a second empirical constant

Each ion has a unique $\boldsymbol{\lambda_i}$, $\boldsymbol{\lambda^o(T)}$**, A(T), and B**

Ionic Strength

$$I = 1/2 \sum m_i z_i^2$$

McCleskey Model

$\lambda^o(T)$ for K^+

$$\lambda^o(T) = 0.00304\ T^2 + 1.261\ T + 40.70$$

$\lambda^o(T)$ for H^+

$$\lambda^o(T) = -0.01414\ T^2 + 5.355\ T + 224.2$$

McCleskey Model

A(T) for K^+

$$A(T) = 0.00535\ T^2 + 0.9316\ T + 22.59$$

B for K^+

$$B = 1.5$$

Ion	A	B
K^+	$0.00535T^2 + 0.9316T + 22.59$	1.5
Na^+	$0.00027T^2 + 1.141T + 32.07$	1.7
H^+	$-0.00918T^2 + 1.842T + 39.23$	0.3
Li^+	$0.00412T^2 + 0.4632T + 13.71$	0.2

McCleskey Model

McCleskey's Empirical Specific Conductance Equation:

$$\lambda_i = \lambda^\circ(T) - \frac{A(T)\mathrm{I}^{1/2}}{1 + B\mathrm{I}^{1/2}}$$

McCleskey Model

Predicted SC for the entire solution:

$$\text{Predicted Specific Conductance} = \Sigma\, \lambda_i\, m_i$$

m_i is the concentration of the i^{th} ion in solution

McCleskey Model

Results of model were excellent, with 98% of the R^2 values for predicted vs measured conductivity above 0.92

Software used to find m_i was WATEQ4F

Current Work

Objectives

Goal: Determine if MINEQL+ is an acceptable speciation software to use with McCleskey’s equations

Exploratory study to determine if MINEQL+ and WATEQ4F yield similar results for m_i values

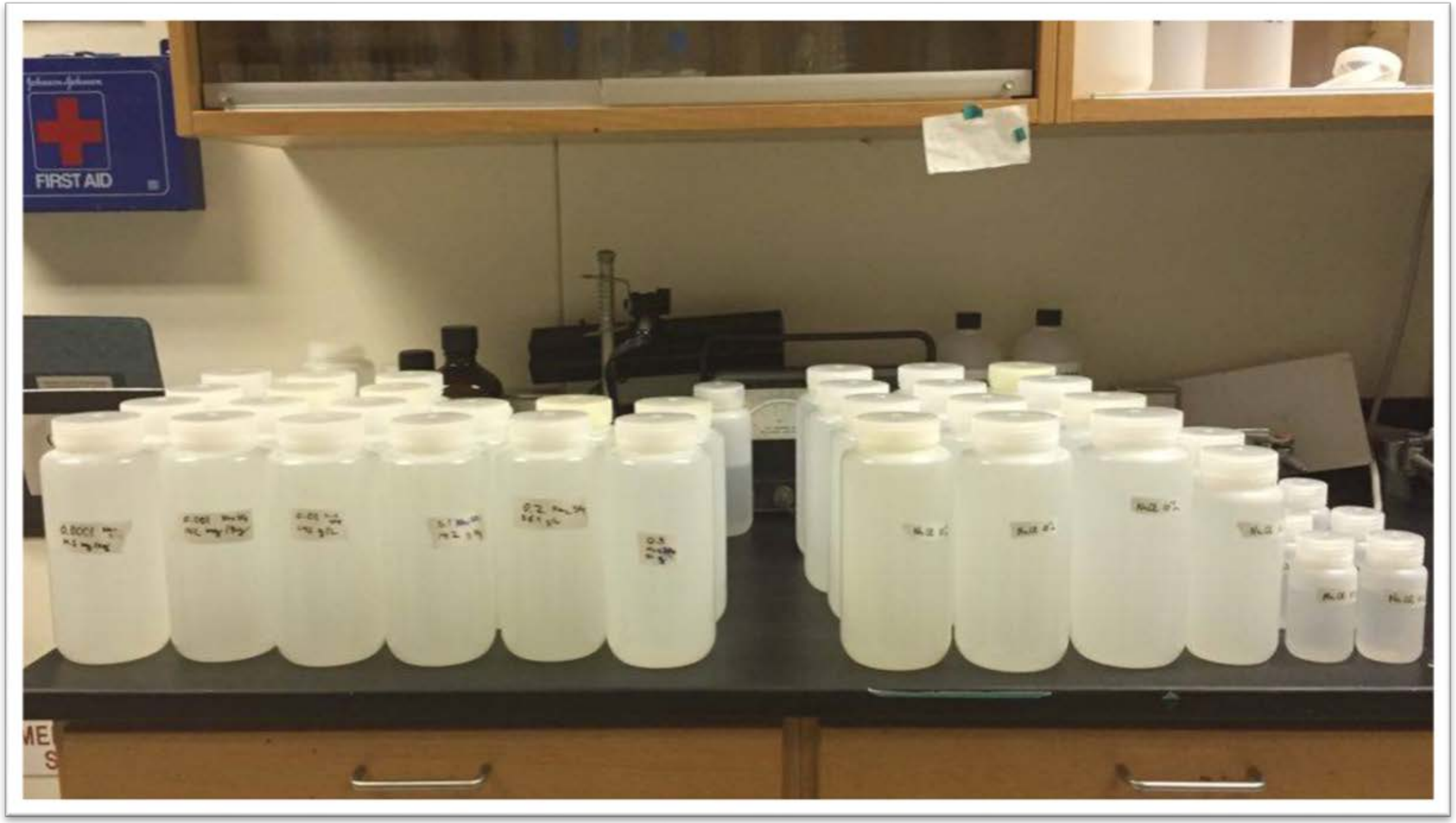
Procedure

-Solutions were created at six molalities (0.0001, 0.001, 0.01, 0.1, 0.2, and 0.5 m)

-Eight compounds were used ($NaHCO_3$, KNO_3, $MgSO_4$, K_2SO_4, $CaCl_2$*$2H_20$, Na_2SO_4, KCl, and NaCl)

- Temperature, pH, and SC were measured

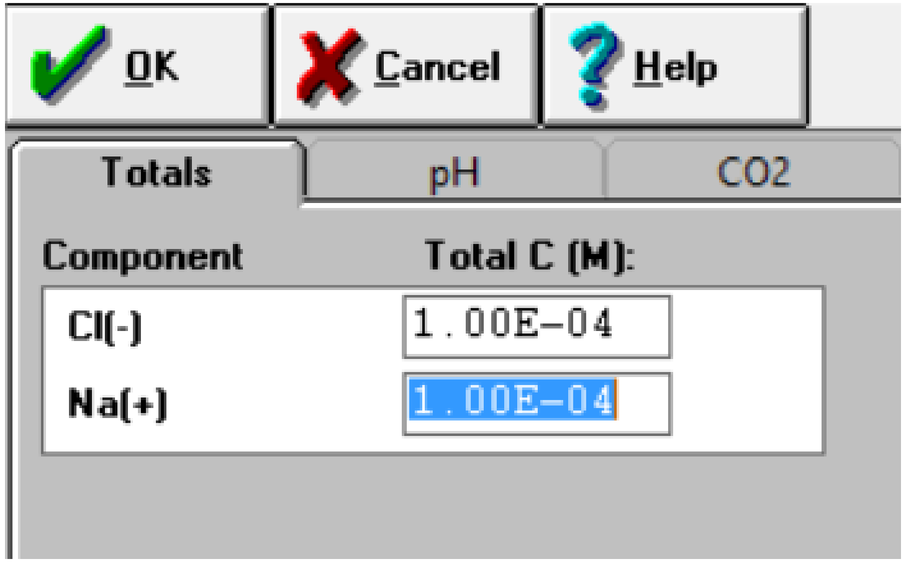
Procedure



Procedure

- Determine species formed in solution

Calculation Wizard




```
Run: 1
          ID                  Species        Conc.
------------------------------------------------------
Type I - COMPONENTS
           2 H2O                             1.000E+00
           3 H(+)                            4.900E-05
          19 Cl(-)                           1.000E-04
          45 Na(+)                           1.000E-04

Type II - COMPLEXES
        3800 OH-                      (-1)   1.640E-10

Type III - FIXED ENTITIES
        3801 H2O (Solution)
      175310 pH                       (+1)
```

Procedure

- λ^0(T) and A(T), and B determined for each species

Ion	λ^0	A	B
K^+	$0.003046T^2 + 1.261T + 40.70$	$0.00535T^2 + 0.9316T + 22.59$	1.5
Na^+	$0.003763T^2 + 0.8770T + 26.23$	$0.00027T^2 + 1.141T + 32.07$	1.7
H^+	$-0.01414T^2 + 5.355T + 224.2$	$-0.00918T^2 + 1.842T + 39.23$	0.3
Li^+	$0.002628T^2 + 0.7079T + 19.20$	$0.00412T^2 + 0.4632T + 13.71$	0.2

Source: McCleskey 2011

Procedure

Find the SC for each ion using McCleskey's equations

$$\lambda_i = \lambda^\circ(T) - \frac{A(T)\mathrm{I}^{1/2}}{1 + B\mathrm{I}^{1/2}}$$

Procedure

- For **each** concentration, find m_i for each ion in solution

```
Run: 1
        ID              Species      Conc.
______________________________________________

Type I - COMPONENTS
         2 H2O                       1.000E+00
         3 H(+)                      4.900E-05
        19 Cl(-)                     1.000E-04
        45 Na(+)                     1.000E-04

Type II - COMPLEXES
      3800 OH-                 (-1)  1.640E-10

Type III - FIXED ENTITIES
      3801 H2O (Solution)
    175310 pH                  (+1)
```

Procedure

Find predicted SC for each concentration

$$\text{Predicted SC} = \sum \lambda_i m_i$$

Procedure

- Compared calculated and measured SC

Sodium Chloride			
	Measured	Predicted	
Goal (mol/kg)	**SC (uS/cm)**	**SC (uS/cm)**	**% error**
0.0001	12.8	28.3	121.0
0.001	123.3	123.3	0.0
0.01	1,180	1,112.5	5.7
0.1	10,220	9,826.8	3.8
0.2	19,140	18,608.0	2.8
0.5	44,100	42,856.7	2.8

Results

- 27% of values differed by more than 20%

	Compound							
Molality	**Na_2SO_4**	**KNO_3**	**$CaCl_2$**	**$MgSO_4$**	**$NaHCO_3$**	**KCl**	**NaCl**	**K_2SO_4**
0.0001	13%	88%	82%	64%	16%	42%	121%	2%
0.001	7%	9%	14%	1%	12%	8%	0%	2%
0.01	2%	7%	7%	29%	11%	8%	6%	0%
0.1	18%	2%	5%	60%	12%	4%	4%	5%
0.2	23%	1%	5%	59%	15%	5%	3%	6%
0.5	68%	12%	17%	65%	23%	4%	3%	42%

Possible Explanations

- Small mass of 0.0001 m solutions
- Ionic strength below suggested range
- Unknown problem with $MgSO_4$
- Effect of temperature and pH
- Differences between ΔH Values in MINEQL and WATEQ4F

$$\log\left(\frac{K_1}{K_2}\right) = \frac{-\Delta H^O}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Low Concentration Solutions

- Poor correlations for 10^{-4} m solutions
- 0.0001 m solutions with > 20% difference were remade
- Negative percent difference implies lower than stated chemical concentration

Original Solutions			
Compound	**SC Measured**	**SC Calculated**	**% Difference**
KNO_3	13.8	25.9	-87.7%
$CaCl_2$	19	34.5	-81.6%
$MgSO_4$	14.7	24.1	-64.0%
KCl	15.9	22.6	-41.9%
NaCl	12.8	28.3	-121.0%

Low Concentration Solutions

- Chemicals adhere to measuring dish
  - Solution water poured over dish to ensure complete transfer

	Original			Remade		
Compound	**SC Measured**	**SC Calculated**	**% Difference**	**SC Measured**	**SC Calculated**	**% Difference**
KNO_3	13.8	25.9	-87.7%	20.5	27.1	-32.2%
$CaCl_2$	19	34.5	-81.6%	38.1	34.8	8.7%
$MgSO_4$	14.7	24.1	-64.0%	28.5	24.4	14.4%
KCl	15.9	22.6	-41.9%	15.4	23.8	-54.5%
NaCl	12.8	28.3	-121.0%	14.9	28.6	-91.9%

Low Concentration Solutions

- Percent differences reduced but still fairly large
- Determined **low ionic strength** was the cause of errors
  - I = 0.0001, lower threshold for use is 0.0004

	Original			Remade		
Compound	**SC Measured**	**SC Calculated**	**% Difference**	**SC Measured**	**SC Calculated**	**% Difference**
KNO_3	13.8	25.9	-87.7%	20.5	27.1	-32.2%
$CaCl_2$	19	34.5	-81.6%	38.1	34.8	8.7%
$MgSO_4$	14.7	24.1	-64.0%	28.5	24.4	14.4%
KCl	15.9	22.6	-41.9%	15.4	23.8	-54.5%
NaCl	12.8	28.3	-121.0%	14.9	28.6	-91.9%

Results

- Half of remaining errors due to $MgSO_4$

	Compound							
Molality	**Na_2SO_4**	**KNO_3**	**$CaCl_2$**	**$MgSO_4$**	**$NaHCO_3$**	**KCl**	**NaCl**	**K_2SO_4**
0.0001	13%	88%	82%	64%	16%	42%	121%	2%
0.001	7%	9%	14%	1%	12%	8%	0%	2%
0.01	2%	7%	7%	29%	11%	8%	6%	0%
0.1	18%	2%	5%	60%	12%	4%	4%	5%
0.2	23%	1%	5%	59%	15%	5%	3%	6%
0.5	68%	12%	17%	65%	23%	4%	3%	42%

Magnesium Sulfate

- Positive percent error
  - Solution has higher than predicted concentration

Molality	SC Measured	SC Calculated	Percent Error
0.0001	28.5	24.4	14.4
0.001	194.8	197.5	-1.4
0.01	1,463	1,045.5	28.5
0.1	8,940	3,599.7	59.7
0.2	15,300	6,307.1	58.8
0.5	30,500	10,570.8	65.3

Magnesium Sulfate

- High measured concentration is counterintuitive
  - Magnesium sulfate is hygroscopic
  - Pure $MgSO_4$ mass typically less than measured chemical mass
- Corrective measures:
  - Confirm solution concentration using ICP
  - Measure conductivity and pH at 25^{o}C
  - Replicates

Sensitivity Analysis

The effect of temperature and pH on predicted conductivity values was explored

- Greater understanding of effect on percent error values
- Potential for simplification of inputs to both MINEQL and empirical equations

Sensitivity Analysis

Changes explored:

- pH alone
- Temperature in MINEQL+ alone
- Temperature in empirical equations alone
- Temperature in both empirical equations and MINEQL+

Sensitivity Analysis : Results

- Changes to pH and temperature within MINEQL+ had minimal effect on predicted SC
- Temperature changes in empirical equations had much greater effect on predicted SC

λ^0	A
$0.003046T^2 + 1.261T + 40.70$	$0.00535T^2 + 0.9316T + 22.59$
$0.003763T^2 + 0.8770T + 26.23$	$0.00027T^2 + 1.141T + 32.07$

Conclusions

- Further work includes:
  - Replicates and expansion of tested compounds
  - Confirmation of chemicals in solution (ICP)
  - Comparing MINEQL+ and WATEQ4F for differences in constants and assumptions

Conclusions

- Sensitivity analysis
  - Changes in MINEQL+ affect predicted SC far less than changes to empirical equation temperature input
- Additional work needed before MINEQL+ may be used in place of WATEQ4F with McCleskey's equations

Acknowledgements

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1872

Invent the Future

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Questions