Chemistry 30: Equilibria

Lesson: Uranium Processing - Removing Heavy Metals from the Water (Raffinate)

Overview

Students will utilize an understanding of equilibrium to remove Fe^{3+} and Ni^{2+} from Raffinate.

Source: This activity was developed for the Saskatchewan Mining Association by A. Lafontaine (Teacher, Kenaston School). Uranium Processing information provided by B. Bharadwaj (Metallurgist, Cameco) and the Mill staff at Rabbit Lake Mine (Cameco Corporation).

Duration: 2-60 minute periods

Materials:

- pH meters (1 per group)
- Filter paper (2 per group)
- Funnels (1 per group)
- Raffinate Solution ($Ni(NO_3)_2$ and $Fe(NO_3)_3$)
- 250mL beakers (3 per group)
- 100 mL beaker (1 per group)
- 1.0 M $Ca(OH)_2$ slurry
- Disposable pipette (1 per group)
- Stir rod (1 per group)
- 10 mL graduated cylinder (1 per group)
- Sharpie
- Wash bottle
- Uranium Processing PowerPoint: **The Rabbit Lake Mill Power Point**

Notes to Teacher:

1. Raffinate is a product which has had a component or components removed; in this activity, raffinate is what is left after Uranium has been removed through the milling process.
2. The raffinate solution will need to be prepared in advance for students. To prepare, combine 50mL of 0.100M $Ni(NO_3)_2$ solution and 50mL of 0.100M solution $Fe(NO_3)_3$
3. The ~1.00M solution of calcium hydroxide will need to be prepared in advance.
4. Calcium hydroxide has a low solubility and will form a slurry rather than a precipitate. For this reason, students need to wait at least 1 minute between their 1mL additions to the raffinate solution.
5. The calcium hydroxide slurry will begin to separate; remind students to stir their slurry solution before adding any to the raffinate.

Prior Knowledge:

Before attempting these activities students should have some understanding of the following:

1. Solubility
2. Solubility Product Constant (Ksp)
3. Equilibrium
4. The Common Ion Effect
5. pH and pOH

Instructional Methods:

- Interactive Instruction
- Experiential Learning

Advanced water treatment systems and rigorous testing protects the environment (Cameco, Uranium 101)

Learning Outcomes and Indicators

Chemistry 30 Equilibria:

CH30-EQ1 Consider the characteristics and applications of equilibrium systems in chemical reactions

a. Discuss the criteria that characterize an equilibrium system (e.g., closed system, constancy of properties, equal rates of forward and reverse reactions)
c. Write the equilibrium constant (K_{eq}) expression for a variety of chemical reactions.

CH30-EQ2 Analyze aqueous solution equilibria including solubility-product constants

a. Discuss conditions necessary for the establishment of equilibrium in aqueous solutions.
b. Analyze how temperature and the common ion effect influence the solubility of substances in aqueous solution.
g. Calculate the solubility of a solution, given K_{sp}.

CH30-EQ3 Investigate phenomena related to acid-base reactions

a. Identify examples of acid-base reactions in the manufacture and use of consumer products, industrial and agricultural processes.
g. Solve problems involving pH, pOH, $[H^+]$/$[H3O^+]$, $[OH^-]$, K_w, K_a and K_b.

Grade 10 Chemical Reactions:

SC10-CR1 Explore the characteristics of a variety of chemical reactions, including the role of energy

c. Observe and describe a variety of chemical reactions, including synthesis, decomposition, combustion, single replacement, double replacement and acid base neutralization
g. Research practical examples of chemical reactions involving acids and bases, including neutralization reactions such as those involved in chemical spills, soda-acid fire extinguishers, and antacids

SC10-CR2 Name and write common formulas for common ionic and molecular chemical compounds, including acids and bases

k. Describe how the pH scale is used to classify substances as acidic, basic or neutral

Physical Science 20: Foundations of Chemistry

PS20-FC1 Predict products of the five basic types of chemical reactions and evaluate the impact of these reactions on society

a. Observe and analyze synthesis, decomposition, combustion, single replacement and double replacement (including acid base neutralization) reactions
k. Research examples of the uses of the five types of reactions relevant to industry, mining, and/or agriculture in Saskatchewan

PS20-FC2 Construct an understanding of the mole as a unit for measuring the amount of substance

h. Prepare solutions of known concentration using molarity and dilution calculations *(applicable if students make their own solutions)*
i. Research the application of solutions in industry, mining, and agriculture.

Source: **Saskatchewan Evergreen Curriculum**

Big Picture Questions

1. Why do heavy metals need to be removed from raffinate before it can be released?
2. How is an understanding of chemical equilibria applied in the purification of raffinate (waste water) left over from the uranium milling process?

Background Information

Saskatchewan is a world leader in uranium production. In 2013 Saskatchewan produced 100% of Canada's primary uranium, representing 16% of the world's production, from 3 operating mines – McArthur River, Eagle Point and Cigar Lake (Saskatchewan Mining Association).

Uranium ore is rock with elevated amounts of uranium in it. Once the rock has been removed by open pit and/or underground mining, it must be milled to separate the uranium from the other constituents. The milling process for uranium is similar to that used for other metals, such as copper, gold or nickel (Cameco Uranium 101). (See PowerPoint: **The Rabbit Lake Mill Power Point).**

All water used in mining and milling processes is treated to remove contaminants before it is released to the environment.

Some of the by-products of the uranium milling process are heavy metals which remain in the "raffinate" (the solution remaining after the uranium has been removed.)

Cameco's uranium mining operations use a combination of conventional water treatment systems and reverse osmosis to remove heavy metals and other contaminants. Conventional water treatment systems employ a series of chemicals that are mixed with the raffinate and systematically bind themselves to the undesired elements and then are passed through fine sized paper or cloth filters, trapping the contaminants. The contaminants captured by these systems are typically placed in a tailings facility. Treated water, released to the environment, is tested on an ongoing basis to ensure stringent regulatory limits are met and the environment is protected. (Cameco, Uranium 101).

The conventional system is a low pH treatment circuit designed to remove metals. The pH is adjusted by addition of sulphuric acid (to lower pH) and lime (to raise pH). After the solution has passed through four treatment tanks, it is sent to the Low pH Clarifier where the metals precipitate and settle out. The precipitates are recycled back to treatment tanks, or are sent to the tailings facility. Clear liquid overflows the clarifier and is further treated in a High pH Treatment circuit (Cameco Rabbit Lake Mill).

The activity presented in this lesson plan simulates the conventional water treatment system.

The Saskatchewan uranium mining industry is committed to responsible environmental stewardship. The industry directly employs 83 people whose full-time responsibility is to ensure that all operations meet strict environmental standards set out by both the federal and provincial governments. Twenty-four hours a day, 365 days a year, comprehensive sampling, monitoring and assessment programs are in operation to ensure that the physical environment is protected. All sites are subject to compliance-based monitoring; water and air emissions from the mine and mills are tested on a regular basis to ensure that contaminants, if any, remain within regulatory limits. The industry's long-term goal is to return all operations, as closely as possible, to a natural state suitable for future uses (Saskatchewan Mining Association).

Safety concerns

- **Calcium hydroxide is a base; have a neutralization kit available if necessary and use caution when pipetting this slurry.**

Vocabulary	
Acid	Base
Equilibrium	Raffinate
Solubility	Solubility Product Constant

LESSON PLAN

Procedure and Timeframe (2-60 minute class periods)

Motivational Set (15-20 minutes)
Teacher can use the Uranium PowerPoint to give students an understanding of where their raffinate solution came from. In addition, students can brainstorm why the raffinate needs to be purified before it is released back into the environment and what happens with the metals that have been removed from the solution.

The Activity:
Part 1: Pre-lab Work (15-20 min.)
1. Students will need to use given ksp values to calculate at what pH $Fe(OH)_3$ and $Ni(OH)_2$ will precipitate out of the solution.

Part 2: Selective Precipitation (60-80 min.)
1. Students will complete the procedure as it is laid out in the student handout.
2. Students will then complete the discussion questions and conclusion section of the lab.

Assessment Method and Evidence

Activity 1:

✓ Anecdotal notes and/or checklist
- Students will show proper lab safety and collaboration within their labs groups (if applicable).

✓ Discussion questions:
- Students will be able to answer the discussion questions provided.

✓ Calculation Sheet:
- Students will calculate the pH $Fe(OH)_3$ and $Ni(OH)_2$ will precipitate out of the solution at in the pre-lab section.

✓ Observation Chart:
- Students will describe the increase in pH they are observing with the addition of $Ca(OH)_2$ to the raffinate

Extension Activities

1. In order for raffinate to be returned to the environment, the pH must be returned to the normal pH range for the area it will be released to. Have students predict (having an understanding of

neutralization) how this can be accomplished. Students can then develop and test procedures to accomplish this task.

Resources

Cameco Corporation, 2015. **The Rabbit Lake Mill PowerPoint** . Available at: http://www.saskmininged.com/uploads/2/2/4/3/22432080/uranium_mill_tour_presentation_chem_ck_rev1.pdf

Cameco **Uranium 101 Milling.** Available at: **http://www.cameco.com/uranium_101/mining-milling/milling/**

Canadian Nuclear Safety Commission. **Uranium Mines** http://nuclearsafety.gc.ca/eng/uranium/mines-and-mills/index.cfm

Oresome Resources **The Chemistry of Uranium: Available at:** http://www.oresomeresources.com/resources_view/resource/fact_sheet_chemistry_of_uranium

Saskatchewan Mining Association **Uranium in Saskatchewan Fact Sheet.** Available at: http://www.saskmining.ca/uploads/general_files/24/final-uranium-fact-sheets-2013.pdf

For more information and lesson plans about the history, science, mining, and safety of nuclear technology go to:

Canadian Nuclear Safety Commission at: http://nuclearsafety.gc.ca/cnsconline/fl/index-eng.cfm

Teach Nuclear at: http://teachnuclear.ca/

For more information on the mining of uranium in Saskatchewan, check out the following video:
Cameco McArthur River Virtual Tour
https://www.youtube.com/watch?v=T_cYEBotDBo

For more information on the milling of uranium in Saskatchewan, check out the following video:
https://www.youtube.com/watch?v=zmlvAOSr7dw

Removal of Heavy Metals from Raffinate (Student Copy)

Introduction/Background:
Uranium is a silvery-white metal, roughly 70% denser than lead and is the only naturally occurring element on earth capable of sustaining a chain of nuclear fission. Uranium is more common than tin, silver and gold. It is found is very low concentrations almost everywhere on earth in soil, rocks, and water and Saskatchewan is a world leader in uranium production.
Source: www.cameco.com/uranium_101

For more information on the mining of uranium in Saskatchewan, check out the following video:
https://www.youtube.com/watch?v=T_cYEBotDBo

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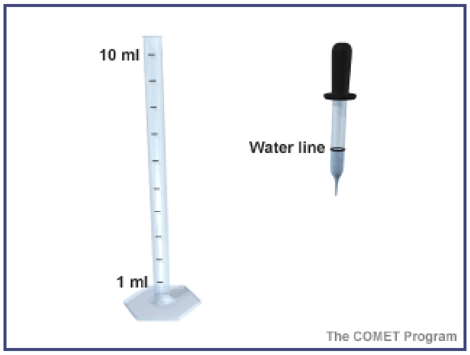
Pre-Lab Work:
$Fe(OH)_3$ has a k_{sp} of 2.79×10^{-39}.
$Ni(OH)_2$ has a k_{sp} of 5.48×10^{-16}.
Using the solubility product constants given above, calculate the pH at which iron and nickel will precipitate out of the raffinate solution. Show all of your formals, substitutions and units in this section (remember to watch for significant figures).

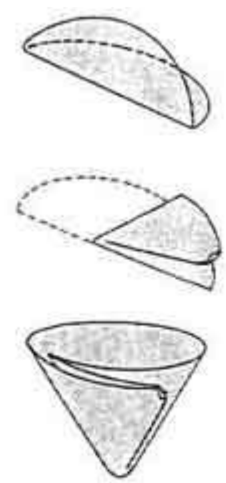
Materials: (per group)
- pH meter
- Filter paper (2 coffee filters)
- Funnel
- 100mL Raffinate Solution
- 3-250mL beakers
- 100mL beaker
- Wash bottle
- ~25mL 1.00 M $Ca(OH)_2$ slurry
- Disposable pipette
- Stir rod
- 10 mL Graduated Cylinder
- Sharpie Marker
- Paper Towel

Procedure:
1. Fill the 10mL graduated cylinder with 1mL of tap water.
2. Use the disposable pipette to remove the 1mL of tap water from the graduated cylinder. Mark on the disposable pipette, using the sharpie, the water line (see the image to the right). This will tell you when you have 1mL of solution in your pipette for the rest of the procedure.



3. Empty the water into the sink. Set your pipette aside to be used later.
4. In one of your 250mL beakers, obtain 100mL of the raffinate solution from your teacher.
5. Using your 100mL beaker, obtain approximately 25.0 mL $Ca(OH)_2$ slurry from your teacher.

6. Using the pH mater, record the pH of your raffinate in Table 1 (next to the 0mL $Ca(OH)_2$ added).
7. Using your pipette, add 1mL of the $Ca(OH)_2$ slurry to the raffinate solution (stir the solution as you add the 1mL $Ca(OH)_2$).
8. Continue to stir the solution for 1 minute. Then, using your pH meter, measure the pH of the solution. Record this in the table below. The pH meter can remain in the solution until step 11.
9. Repeat steps 7 and 8 *until* you are within 1 of the desired pH for your first precipitate to form (you should start to see a precipitate forming here). At this point, lower the amount of $Ca(OH)_2$ slurry you are adding to approximately 0.5mL at a time (continue waiting/stirring for 1 minute and recording the pH between additions).
10. Continue step 9 *until* you reach a pH of 0.5-1 higher than the desired pH for your first precipitate to form.
11. Stop adding $Ca(OH)_2$ slurry. Use your wash bottle to rinse off the pH meter and set aside.
12. Obtain one 250mL beaker, one coffee filter and a funnel. Fold the filter paper (or coffee filter) as shown in the image to the right and place inside the funnel. Slowly pour the raffinate solution into the filter paper. Continue this step until all of the raffinate solution has been filtered.



13. Remove the filter paper and set aside on paper towel to dry.
14. Repeat steps 6-13 to remove your second precipitate. Record the pH and amount of $Ca(OH)_2$ slurry added at each step in Table 2.
15. Clean up your materials/equipment as instructed by your teacher.

Observations:
Table 1:

Total $Ca(OH)_2$ added (mL)	**Measured pH**
0	

Table 2:

Total $Ca(OH)_2$ added (mL)	Measured pH

Discussion/Analysis Questions:

1. Write out the dissociation equations for the two precipitates formed above. Remember to include states and charges.
2. What effect does adding $Ca(OH)_2$ have on the equilibrium systems shown in question 1.
3. In terms of ion concentration, why does the pH increase as you continue to add $Ca(OH)_2$ to the raffinate solution?

Conclusion:

Write a paragraph summarizing your results and comparing it to other groups in the class. Be sure to extend your ideas outside of the classroom.

Removal of Heavy Metals from Raffinate (Teacher Copy)

See answers to questions and helpful hints in red italics.

Introduction/Background:

Uranium is a silvery-white metal, roughly 70% denser than lead and is the only naturally occurring element on earth capable of sustaining a chain of nuclear fission. Uranium is more common tin, silver and gold. It is found is very low concentrations almost everywhere on earth in soil, rocks, and water and Saskatchewan is a world leader in uranium production.

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$Fe(OH)_3$ has a k_{sp} of 2.79×10^{-39}.
$Ni(OH)_2$ has a k_{sp} of 5.48×10^{-16}.
Using the solubility product constants given above, calculate the pH at which iron and nickel will precipitate out of the raffinate solution. Show all of your formals, substitutions and units in this section (remember to watch for significant figures).

Students should determine $Fe(OH)_3$ will precipitate out at a pH of 4.48 and $Ni(OH)_2$ will precipitate out at a pH of 9.01 (see calculations below)

Nickel Hydroxide

$Ksp = [Ni^{2+}][OH^-]^2$
$5.48 \times 10^{-16} = (x)\,(2x)^2$
$5.48 \times 10^{-16} = 4x^3$
$5.16 \times 10^{-6} = x$
Therefore, $[Ni^{2+}] = 5.16 \times 10^{-6}$ M *and* $[OH^-] = 2x = 1.03 \times 10^{-5}$ M

$pOH = -\log [OH^-]$
$pOH = -\log (1.03 \times 10^{-5})$
$pOH = 4.99$

Therefore, $pH = 14 - pOH = 14 - 4.99 = 9.01$

Iron Hydroxide

$Ksp = [Fe^{3+}][OH^-]^3$
$2.79 \times 10^{-39} = (x)\,(3x)^3$
$2.79 \times 10^{-39} = 27x^4$
$1.01 \times 10^{-10} = x$
Therefore, $[Fe^{3+}] = 1.01 \times 10^{-10}$ M *and* $[OH^-] = 3x = 3.02 \times 10^{-10}$ M

$pOH = -\log [OH^-]$
$pOH = -\log (3.02 \times 10^{-10})$
$pOH = 9.52$

Therefore, $pH = 14 - pOH = 14 - 9.52 = 4.48$

Materials: (per group)

- pH meter
- Filter paper (2 coffee filters)
- Funnel
- 100mL Raffinate Solution
- 3-250mL beakers
- 100mL beaker
- Wash bottle
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- Disposable pipette
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Procedure:

1. Fill the 10mL graduated cylinder with 1mL of tap water.
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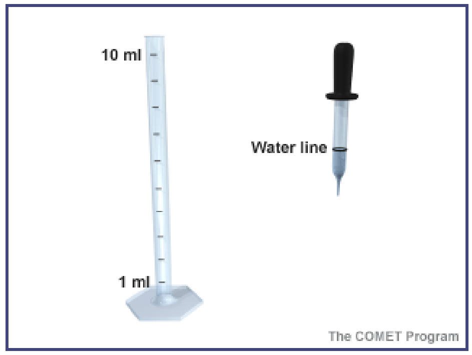


3. Empty the water into the sink. Set your pipette aside to be used later.
4. In one of your 250mL beakers, obtain 100mL of the raffinate solution from your teacher.
   To make the raffiante solution, use the formula: wt = CmmV.
   Where,
   C= concentration of solution in Molarity
   mm= molar mass of compound in g/mol
   V= volume of solution needed in Liters

   For a 500mL solution of raffinate:

   Iron Nitrate calculation (mm of 404.00g/mol)
   wt = CmmV = (0.1M)(404.00g/mol)(0.250L) = 10.1g of $Fe(NO_3)_3$

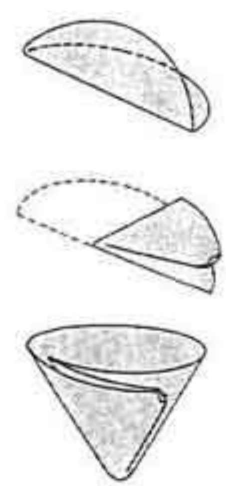
   Nickel Nitrate calculation (mm of 290.81g/mol)
   wt = CmmV = (0.1M)(290.81g/mol)(0.250L) = 7.3g of $Ni(NO_3)_2$

   *****make the solutions separate then combine***
5. Using your 100mL beaker, obtain approximately 25.0 mL $Ca(OH)_2$ slurry from your teacher.
   To make the calcium hydroxide solution, use the formula: wt = CmmV.
   Where,
   C= concentration of solution in Molarity
   mm= molar mass of compound in g/mol
   V= volume of solution needed in Liters

For a 125mL solution of calcium hydroxide:

Calcium Hydroxide calculation (mm of 74.10g/mol)
wt = CmmV = (1.0M)(74.10g/mol)(0.125L) = 9.3g of $Ca(OH)_2$

6. Using the pH meter, record the pH of your raffinate in Table 1 (next to the 0mL $Ca(OH)_2$ added).
7. Using your pipette, add 1mL of the $Ca(OH)_2$ slurry to the raffinate solution (stir the solution as you add the 1mL $Ca(OH)_2$).
8. Continue to stir the solution for 1 minute. Then, using your pH meter, measure the pH of the solution. Record this in the table below.
9. Repeat steps 7 and 8 *until* you are within 1 of the desired pH for your first precipitate to form (you should start to see a precipitate forming here). At this point, lower the amount of $Ca(OH)_2$ slurry you are adding to approximately 0.5mL at a time (continue waiting/stirring for 1 minute and recording the pH between additions).
10. Continue step 9 *until* you reach a pH of 0.5-1 higher than the desired pH for your first precipitate to form.
11. Stop adding $Ca(OH)_2$ slurry.
12. Obtain one 250mL beaker, one coffee filter and a funnel. Fold the filter paper (or coffee filter) as shown in the image to the right and place inside the funnel. Slowly pour the raffinate solution into the filter paper. Continue this step until all of the raffinate solution has been filtered.
13. Remove the filter paper and set aside on paper towel to dry.
14. Repeat steps 6-13 to remove your second precipitate. Record the pH and amount of $Ca(OH)_2$ slurry added at each step in Table 2.
15. Clean up your materials/equipment as instructed by your teacher.



Observations:
Table 1:

<table>
<tr><th>Total Ca(OH)₂ added (mL)</th><th>Measured pH</th></tr>
<tr><td>0</td><td>1.0-2.00</td></tr>
<tr><td>1</td><td rowspan="7">pH will continue to rise</td></tr>
<tr><td>2</td></tr>
<tr><td>3</td></tr>
<tr><td>4</td></tr>
<tr><td>5</td></tr>
<tr><td>6</td></tr>
<tr><td>7</td></tr>
<tr><td>7.5-8</td><td>5.0-6.0</td></tr>
<tr><td></td><td></td></tr>
</table>

*****Initially the pH will drop slightly then continue to rise as more calcium hydroxide is added. More calcium hydroxide will be needed if you start with a lower pH value***

Table 2:

Total $Ca(OH)_2$ added (mL)	Measured pH
0	***6.5-7.0***
1	***pH will continue to rise***
2	
3-3.5	***10-10.5***

*****Students will only need 3-4mL of $Ca(OH)_2$ at this point to reach their desired pH. Advise students to add 0.5mL of $Ca(OH)_2$ at a time once the pH reaches 7.5.***

Discussion/Analysis Questions:

1. Write out the dissociation equations for the two precipitates formed above. Remember to include states and charges.

   $Fe(OH)_{3(s)} \leftrightarrow Fe^{3+}_{(aq)} + 3OH^{-}_{(aq)}$

   $Ni(OH)_{2(s)} \leftrightarrow Ni^{2+}_{(aq)} + 2OH^{-}_{(aq)}$

2. What effect does adding $Ca(OH)_2$ have on the equilibrium systems shown in question 1.
   Adding calcium hydroxide increased the [OH-] in solution. Referring to the common ion effect, this causes the equilibrium to shift to the left (towards the reactants) which causes a precipitate to form.

3. In terms of ion concentration, why does the pH increase as you continue to add $Ca(OH)_2$ to the raffinate solution?
   Adding calcium hydroxide to the raffinate solution increased the [OH-] in solution thus increasing the pH of the solution (making it more basic as calcium hydroxide is a base).

Conclusion:

Write a paragraph summarizing your results and comparing it to other groups in the class. Be sure to extend your ideas outside of the classroom. ***Answers will vary***