Journées Promotion
Procédés Produits (J3P):

Journée Scientifique: Procédés hydrométallurgiques pour la récupération et le recyclage des métaux

“Valorisation de Vanadium”

Neilesh SYNA
AREVA Mines / SEPA
Nancy, mardi 8 Juillet 2014
Reference: SEPA/SET-NS/EG-2014/1627
Plan

- Introduction
  - AREVA
  - AREVA Mines
  - Centre d’innovation minière (ex SEPA)
- Objective
- Motivation
- Cominak operation (Niger)
- V recovery from U process raffinate (flowsheet development)
  - Separation and purification
  - Product finishing
- Conclusions and future work
TWO COMPLEMENTARY ENERGIES

To supply ever safer energy with less CO₂ to the greatest number of people.

NUCLEAIRE ➔ A WORLD LEADER

- Integrated offer
  Covering every stage of the nuclear fuel cycle, reactor design and construction, and operating services.

RENEWABLE ENERGIES ➔ A KEY PLAYER

- High-tech solutions
  Offshore Wind / Bioenergy / Concentrated Solar / Energy Storage

Employees 45,340
Sales revenue €9,240M
Backlog €41,521M
2013 Production: ~59,000 tU
AREVA Mines: 9,325 tU = 15% of global production
(2nd only to KazAtomProm (19%))
Centre d’Innovation Minière (ex SEPA)

- Employees 80
- Revenue €14M
- Clients External (55%) Internal (45%)

4 Sections
- Section Laboratoire d’Essais (LAB)
- Section Pilotes Industriels (SPI)
- Section Analyses (SAN)
- Section Etudes (SET)

Competencies
- Mineral processing
- Hydrometallurgy
- Pyrometallurgy
- Analysis
- U, Th, Au, Mo, V, REE

Régime ICPE:
- U (10 t)
- Th (600 kg)

Certifications
- COFRAC (pgres 100-1 (eaux nat.)/ 135 (radionucléides) / 156 (boues))
- ISO 14001 and OHSAS 18001

Objective

Reduce costs for existing operations (or new projects) by developing processes that can best deliver optimum values for other accompanying metals:

◆ Operations
  - Cominak (Niger): V
  - Katco (Kazakhstan): Re

◆ Projects
  - Imouraren (Niger): V
  - Midwest (Canada): Cu, Ni and Co
Vanadium
(used principally for steel, specialty steels and recently for energy storage applications)
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(used principally for steel, specialty steels and recently for energy storage applications)

Synergy with Renewable Energies BG for Vanadium Redoxflow Battery (VRB) production

**Cominak operation**

**Raffinate V/U = ~33%, 500 t/yr in effluent**

2 Mlbs $V_2O_5$ @ $US 6.25/lb V_2O_5$; eqv. to $US 11/lb V$

(or 6 Ml of V electrolyte @ $US 5/l, eqv. to $US 28/lb V$)

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Questions to consider:

- **Product type?**
  - Metal oxides and/or Metal salts
- **Quality of product?**
  - Grade and radioactivity
- **Process?**
  - CAPEX and OPEX
V recovery from U process raffinate

**AMEX SX Process**

**Advantages**
- ✔️ No Fe\(^{3+}\) co-extraction
- ✔️ High solvent charge
- ✔️ Fast kinetics (30s)

**Disadvantages**
- ❌ Solvent degradation
- ❌ **Selective strip inefficient**
**DAPEX SX Process**

- **Disadvantages**
  - Fe$^{3+}$ co-extraction
  - Lower solvent charge
  - Slower kinetics (120s)

- **Advantages**
  - No solvent degradation
  - Selective strip possible
Batch reduction (using Fe⁰) followed by standing Fe re-oxidation

Continuous process requires bleed solvent treatment for:
- Fe³+ via HCl (to leach) and
- U via Na₂CO₃ (to U recovery)
DAPEX SX pilot

Extraction

Strip

Scrub, Wash & Acidification
DAPEX SX pilot

**Fe scrub**

![Fe scrub graph](image)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Extraction</th>
<th>V Strip</th>
<th>Fe Scrub</th>
<th>H₂O Wash</th>
<th>H₂SO₄ Contact</th>
<th>Global</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th</td>
<td>20%</td>
<td>90%</td>
<td>&lt; 1%</td>
<td>&lt; 1%</td>
<td>&lt; 1%</td>
<td>18%</td>
</tr>
<tr>
<td>U</td>
<td>95%</td>
<td>&lt; 1%</td>
<td>8%</td>
<td>5%</td>
<td>5%</td>
<td>16%</td>
</tr>
<tr>
<td>Fe</td>
<td>7%</td>
<td>&lt; 1%</td>
<td>95%</td>
<td>&lt; 1%</td>
<td>8%</td>
<td>7%</td>
</tr>
<tr>
<td>V</td>
<td>&gt; 99%</td>
<td>&gt; 99%</td>
<td>98%</td>
<td>&lt; 1%</td>
<td>&lt; 1%</td>
<td>99%</td>
</tr>
</tbody>
</table>

**V eluate composition**

<table>
<thead>
<tr>
<th>Element</th>
<th>As</th>
<th>COT</th>
<th>Fe</th>
<th>P</th>
<th>Si</th>
<th>Th</th>
<th>U</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc (mg/l)</td>
<td>1</td>
<td>199</td>
<td>1 560</td>
<td>108</td>
<td>1</td>
<td>11</td>
<td>4</td>
<td>39 200</td>
</tr>
<tr>
<td>[Metal]/V (ppm)</td>
<td>30</td>
<td>5 077</td>
<td>39 796</td>
<td>2 755</td>
<td>26</td>
<td>281</td>
<td>109</td>
<td>-</td>
</tr>
</tbody>
</table>

Product finishing: Option 1a – Metal oxide

**Direct (without oxidation) precipitation**

\[ 2\text{VOSO}_4 + 4\text{NH}_4\text{OH} \rightarrow \text{V}_2\text{O}_4 \downarrow + 2(\text{NH}_4)_2\text{SO}_4 + 2\text{H}_2\text{O} \]

\[ \text{V}_2\text{O}_4 + \frac{1}{2}\text{O}_2 + \Delta \rightarrow \text{V}_2\text{O}_5 \]
Product finishing: Option 1a – Metal oxide

<table>
<thead>
<tr>
<th>Parameter</th>
<th>V content</th>
<th>Fe content</th>
<th>P content</th>
<th>Si content</th>
<th>U + Th content</th>
<th>Radioactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✗</td>
<td>✔</td>
</tr>
<tr>
<td>conformity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Intensity counts

Precipitate and Oxide product

2 theta

Quality?
- Incapable of meeting grade and radioactivity (due to Th and U co-precipitation) unviable

Product and price?
- Metal oxide at conventional market price

Process?
- 4 stages (low CAPEX and OPEX)
Product finishing: **Option 1b – Metal oxide**

*Indirect (with oxidation) precipitation*

\[
\text{VOSO}_4 + \frac{1}{2} \text{O}_2 + 2\text{NH}_4\text{OH} \rightarrow \text{HVO}_3 \downarrow + (\text{NH}_4)_2\text{SO}_4
\]

\[
2\text{HVO}_3 + \text{Na}_2\text{CO}_3 \rightarrow 2\text{NaVO}_3 + \text{H}_2\text{O} + \text{CO}_2 \uparrow
\]

\[
2\text{NaVO}_3 + (\text{NH}_4)_2\text{SO}_4 \rightarrow 2\text{NH}_4\text{VO}_3 \downarrow + \text{Na}_2\text{SO}_4
\]

\[
2\text{NH}_4\text{VO}_3 + \Delta \rightarrow \text{V}_2\text{O}_5 + \text{NH}_3 \uparrow + \text{H}_2\text{O}
\]
Product finishing: **Option 1b – Metal oxide**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>V content</th>
<th>Fe content</th>
<th>P content</th>
<th>Si content</th>
<th>U + Th content</th>
<th>Radioactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial conformity</td>
<td>✔️</td>
<td>✔️</td>
<td>✔️</td>
<td>✔️</td>
<td>✔️</td>
<td>✔️</td>
</tr>
</tbody>
</table>
Quality ?
- Capable of meeting grade and radioactivity specifications

Product and price ?
- Metal oxide at conventional market price

Process ?
- 8 stages (increased CAPEX and OPEX ☑ viable)
Product finishing: **Option 2 – Metal salt**

**Crystallisation**

- V solubility function of acidity and heat
- Evaporative concentration (for V saturation) followed by seeding for nucleation

![Graph showing V solubility function of acidity and heat](image)

\[ \text{VOS}_4 + H_2O + H_2SO_4 + \Delta \rightarrow \text{VOS}_4 \downarrow + H_2O \uparrow + H_2SO_4 \]
Product finishing: **Option 2 – Metal salt**

- Fe deportment in V eluate to be managed in SX circuit

<table>
<thead>
<tr>
<th>Parameter</th>
<th>V content</th>
<th>Fe content</th>
<th>P content</th>
<th>Si content</th>
<th>U + Th content</th>
<th>Radioactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial conformity</td>
<td>✔</td>
<td>✗</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
</tr>
</tbody>
</table>
Quality?
- Capable of meeting grade and radioactivity specifications

Product and price?
- Metal salt ($\text{VOSO}_4 \cdot x\text{H}_2\text{O}$) at a premium price (compared to $\text{V}_2\text{O}_5$)

Process?
- 3 stages (low CAPEX / OPEX, preferred route)
Conclusions and future work

Conclusions

- DAPEX SX viable for V recovery from U process raffinate solution
- Product finishing ➔ metal salt preferred

<table>
<thead>
<tr>
<th>Flowsheet</th>
<th>Least n° of stages</th>
<th>Product grade and quality</th>
<th>Product value</th>
<th>Overall preference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Option 1a (metal oxide)</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Option 1b (metal oxide)</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Option 2 (metal salt)</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
</tr>
</tbody>
</table>

Future work

- Examine ion exchange (IX) resins (instead of solvents) for the same duty
- Conduct financial study to validate flowsheet(s) selection
- Economics (+) ➔ discuss the next stage with management for on-site piloting
- Technology equally applicable to Imouraren project (to verify)

Acknowledgments

- Organisers of the J3P congress
- AREVA Mines
Merci pour votre attention

Questions ?