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

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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

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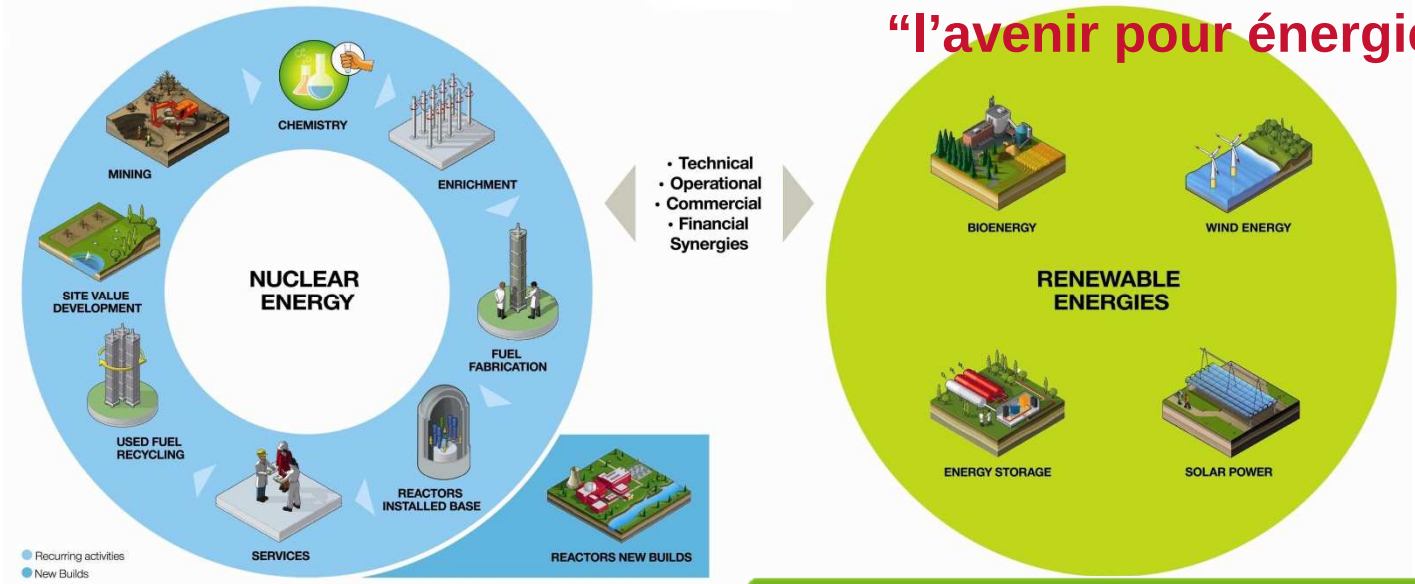
"l'avenir pour énergié"



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**
  Off-shore Wind / Bioenergy / Concentrated Solar / Energy Storage

Employees 45,340

Sales revenue €9,240M

Backlog €41,521M

TWO COMPLEMENTARY ENERGIES

To supply ever safer energy with less CO_2 to the greatest number of people.

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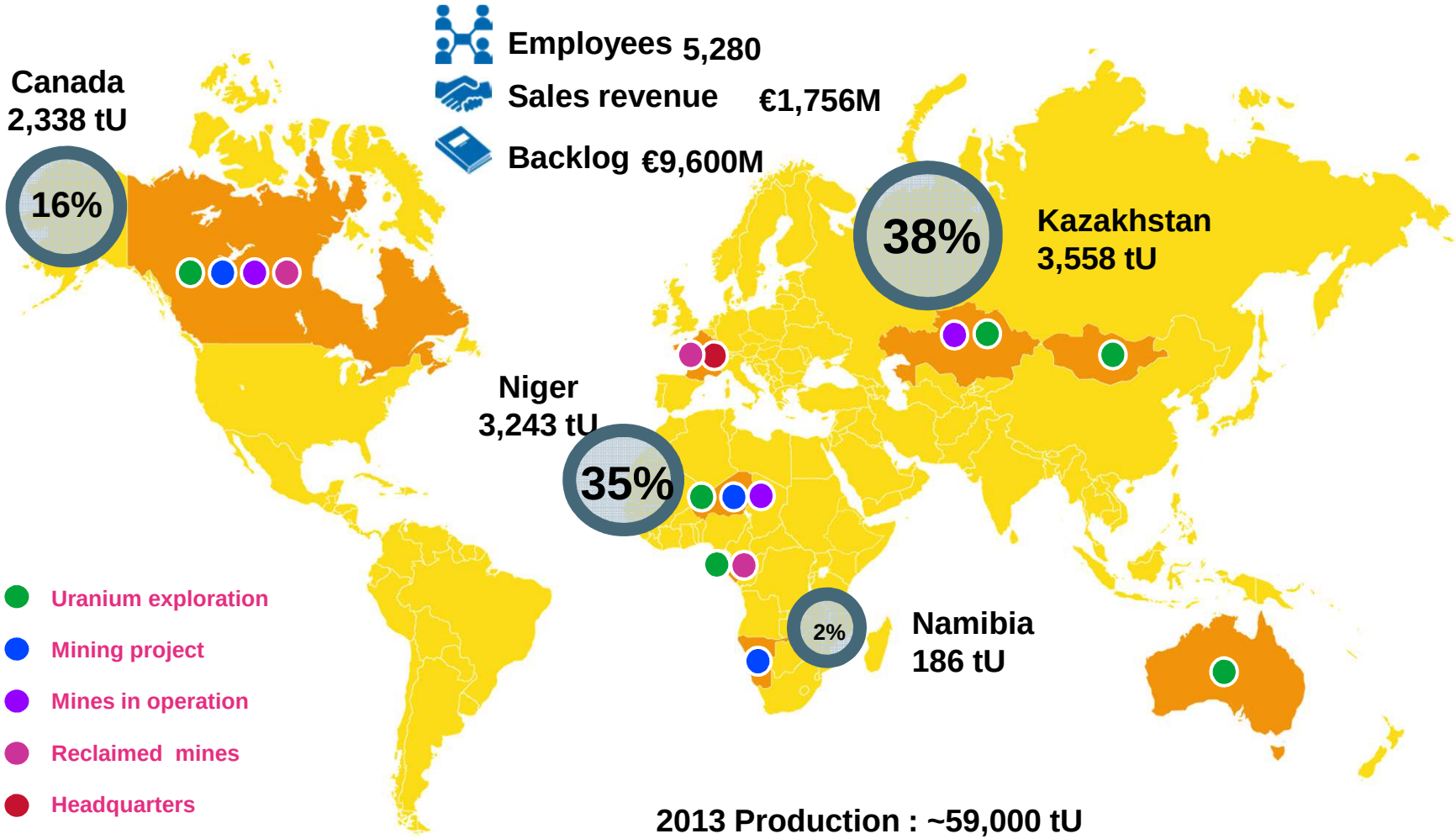
Global presence and 2013 uranium production data



2013 Production : ~59,000 tU

AREVA Mines: 9,325 tU = 15% of global production

(2nd only to KazAtomProm (19%))

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Centre d'Innovation Minière (ex SEPA)

Employees 80 | Clients | External (55%) Internal (45%)

Revenue €14M

- **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

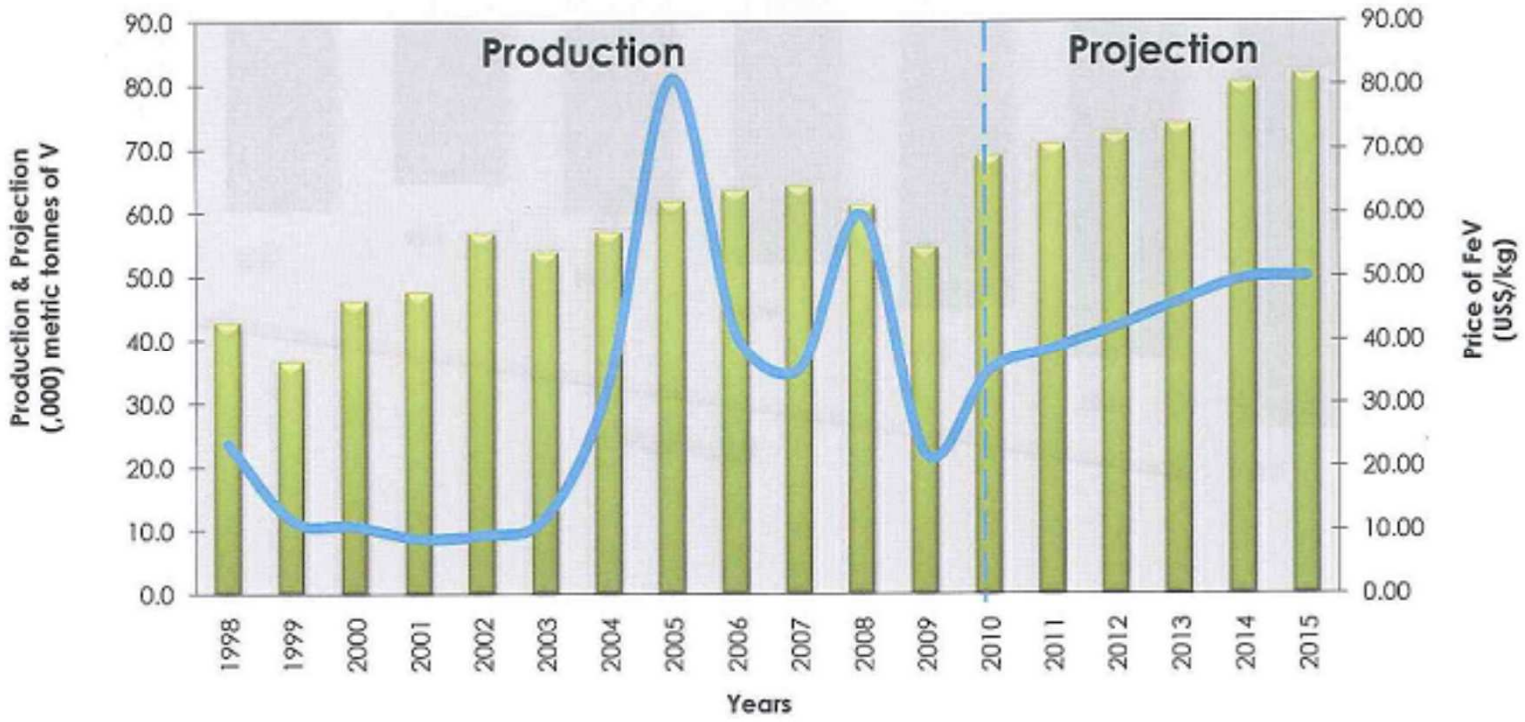
Reduce costs for existing operations (or new projects) by developing processes that can best deliver optimum values for other accompanying metals:

- **Operations**
  - Cominak (Niger): V
  - Katco (Kazakhstan): Re
- **Projects**
  - Imouraren (Niger): V
  - Midwest (Canada): Cu, Ni and Co

Motivation

Vanadium

(used principally for steel, specialty steels and recently for energy storage applications)



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Motivation

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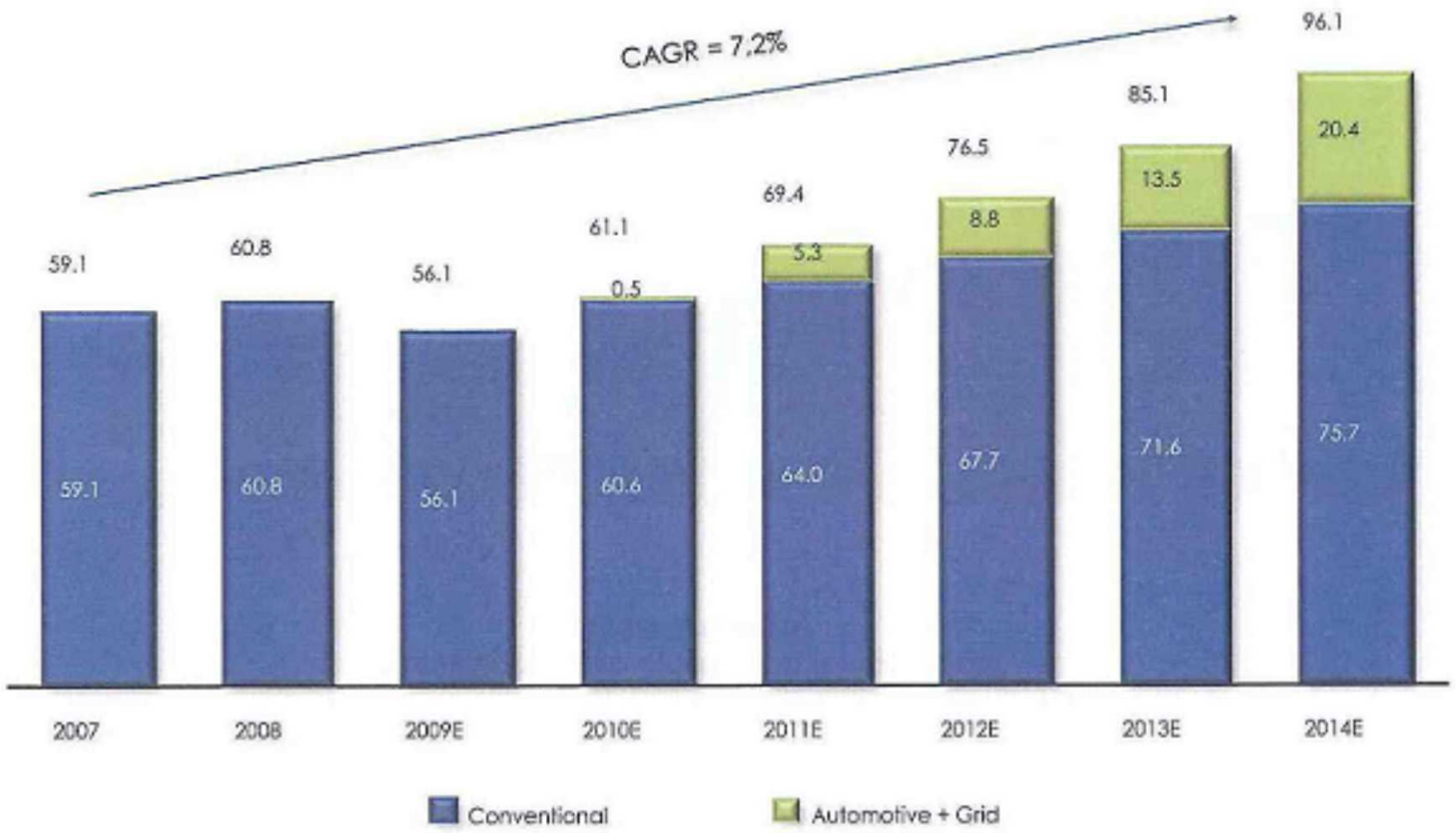
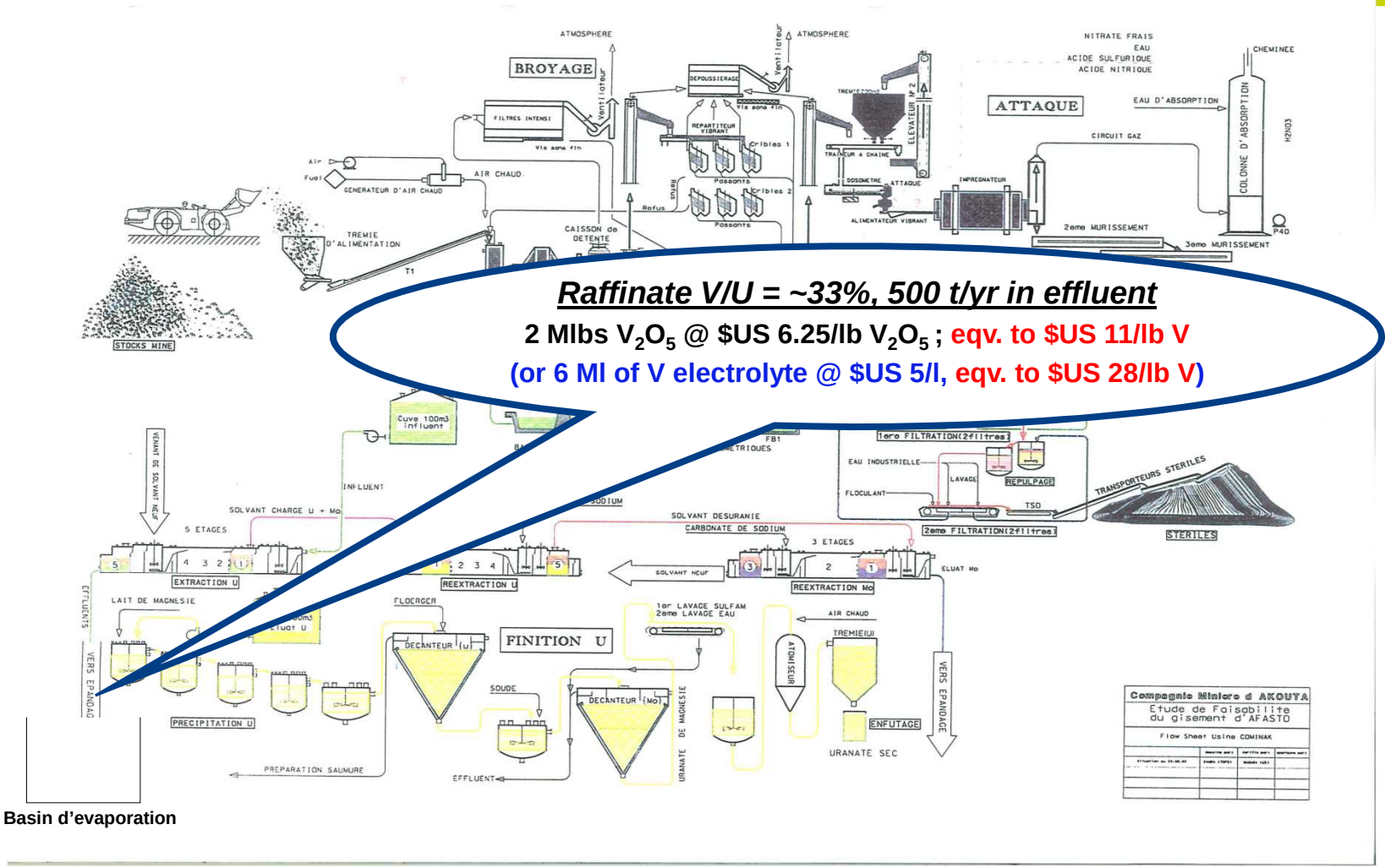
(used principally for steel, specialty steels and recently for energy storage applications)



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

Cominak operation



Basin d'evaporation

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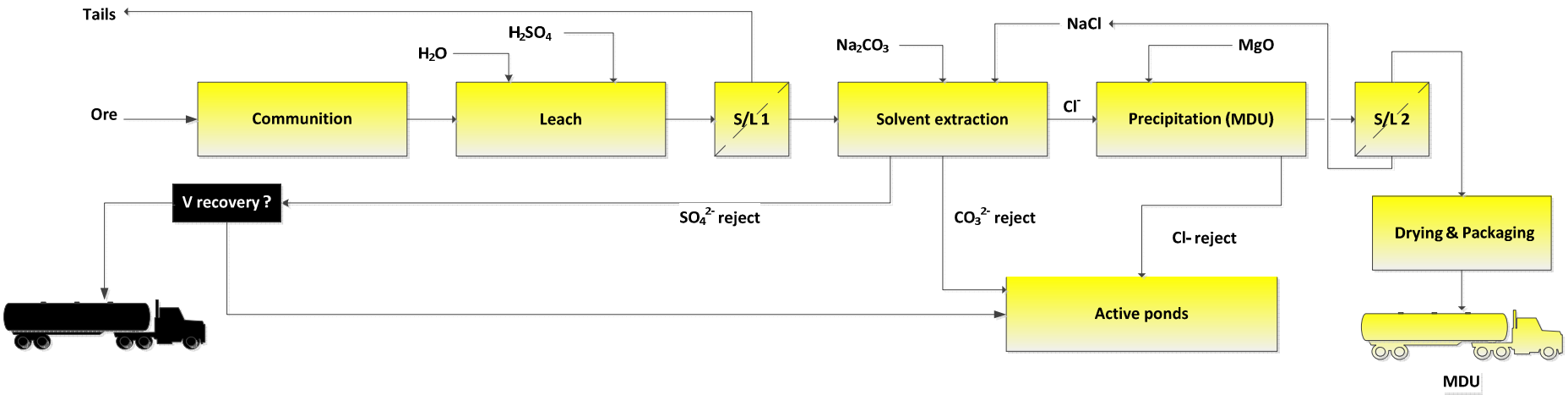
V recovery from U process raffinate . . .

Questions to consider:



- **Product type ?**
  - Metal oxides and/or Metal salts
- **Quality of product ?**
  - Grade and radioactivity
- **Process ?**
  - CAPEX and OPEX

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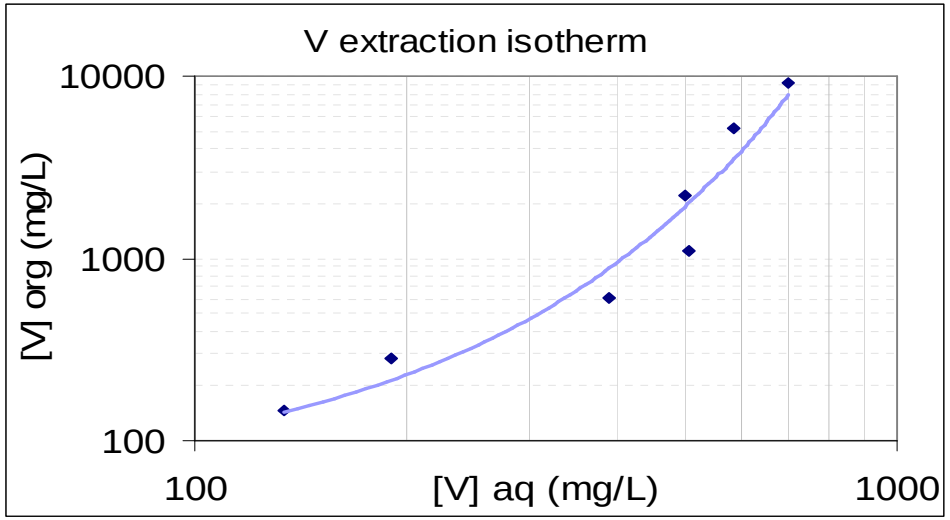
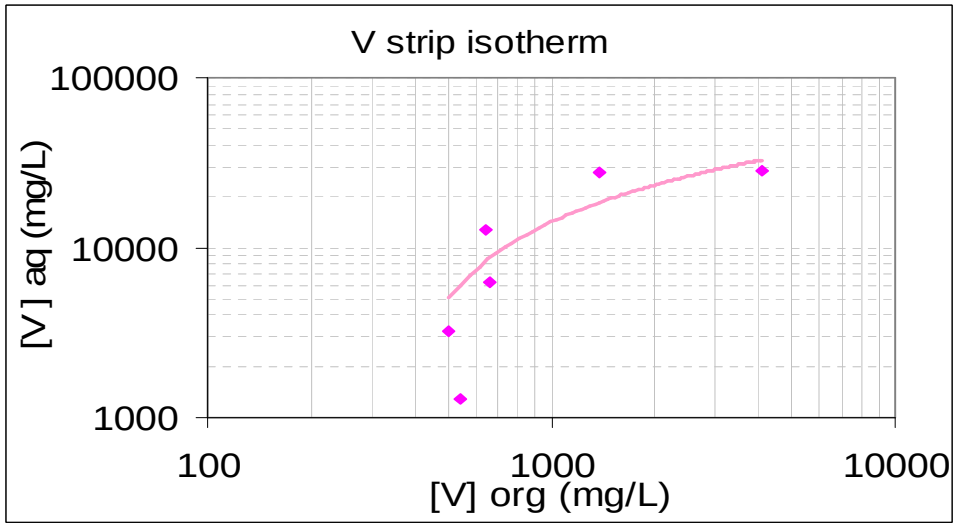
V recovery from U process raffinate





AMEX SX Process

- **Advantages**
  - ☑ **No Fe^{3+} co-extraction**
  - ☑ **High solvent charge**
  - ☑ **Fast kinetics (30s)**
- **Disadvantages**
  - ☒ **Solvent degradation**
  - ☒ **Selective strip inefficient**

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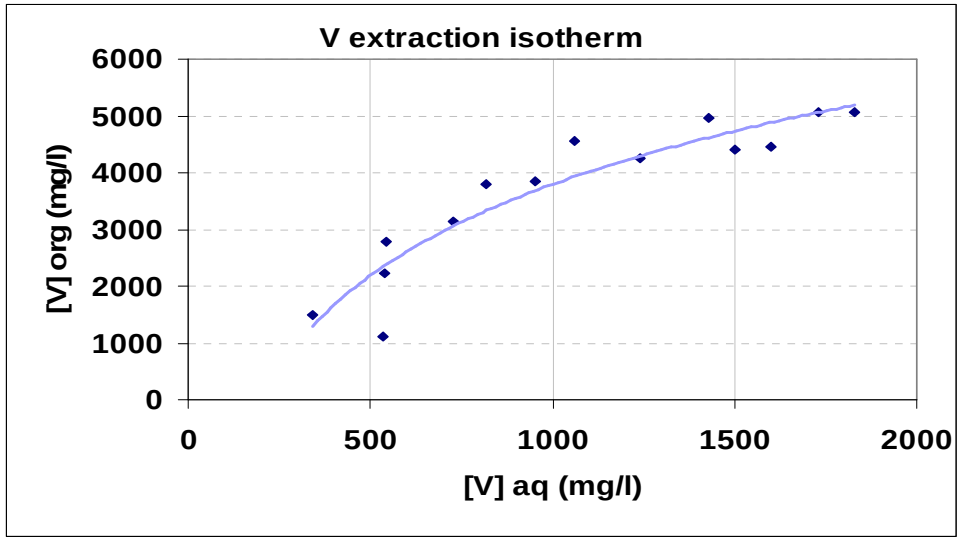
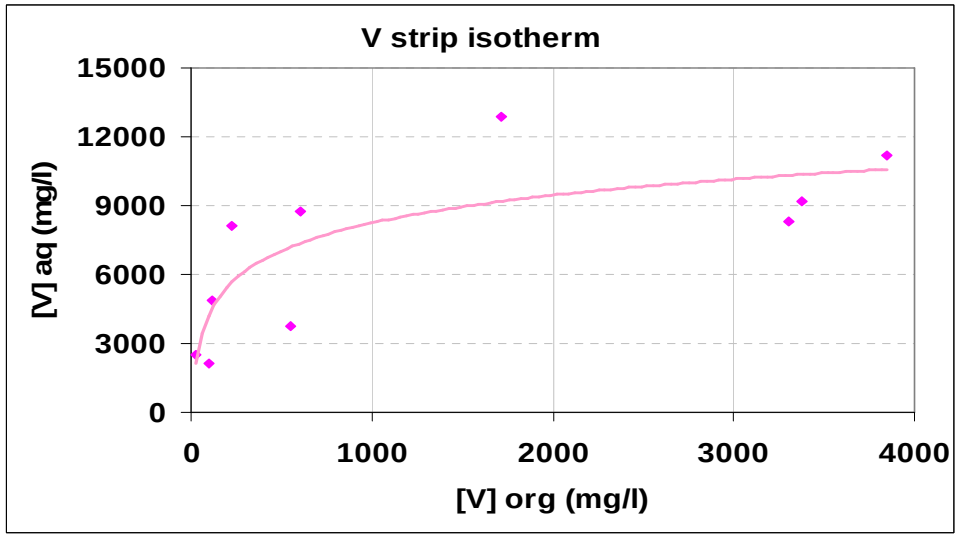
V recovery from U process raffinate . . .





DAPEX SX Process

- **Disadvantages**
  - ☒ Fe^{3+} co-extraction
  - ☒ Lower solvent charge
  - ☒ Slower kinetics (120s)
- **Advantages**
  - ☑ No solvent degradation
  - ☑ Selective strip possible

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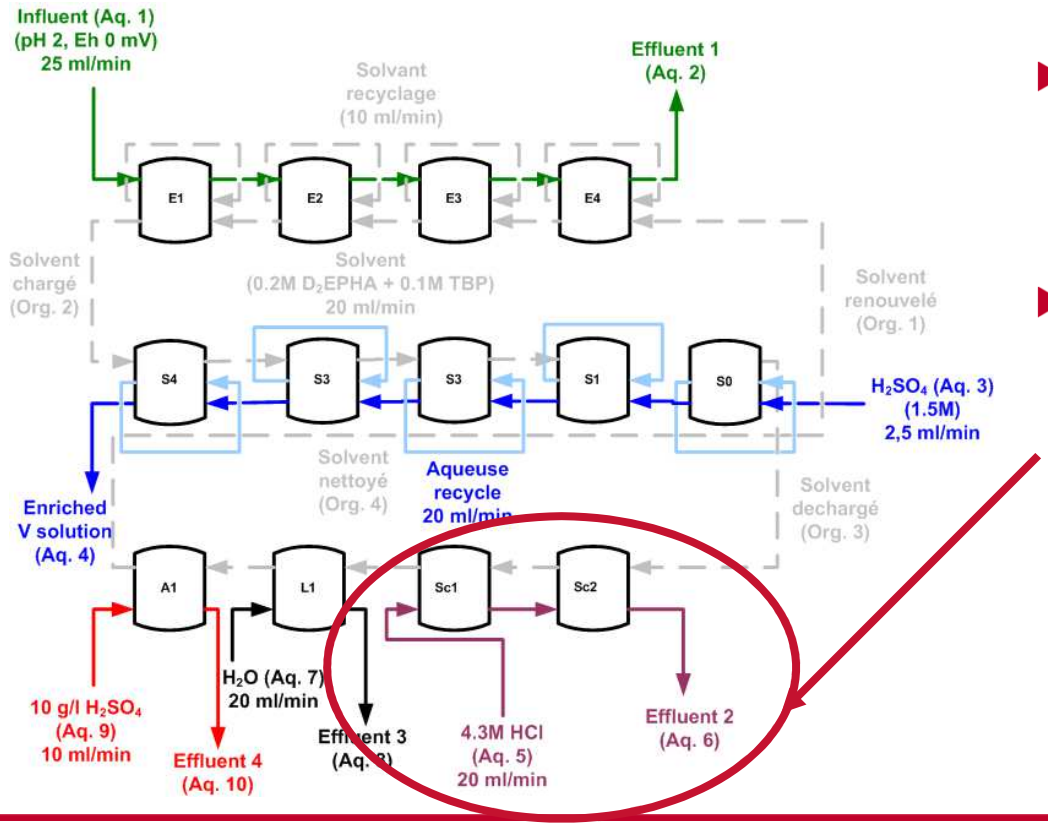
DAPEX SX pilot

PLS

Step	V (mg/l)	U (mg/l)	Th (mg/l)	Fe (g/l)
Blended raffinates	1590	9	8	7,8
Post Fe reduction	1230	14	11	12,4
Post U polish	1250	2	11	12,5
Salt dopage (head)	1500	2	11	12,4

Schema



- Batch reduction (using Fe^0) followed by standing ➲ Fe re-oxidation
- Continuous process requires bleed solvent treatment for;
  - Fe^{3+} via HCl (to leach) and
  - U via Na_2CO_3 (to U recovery)

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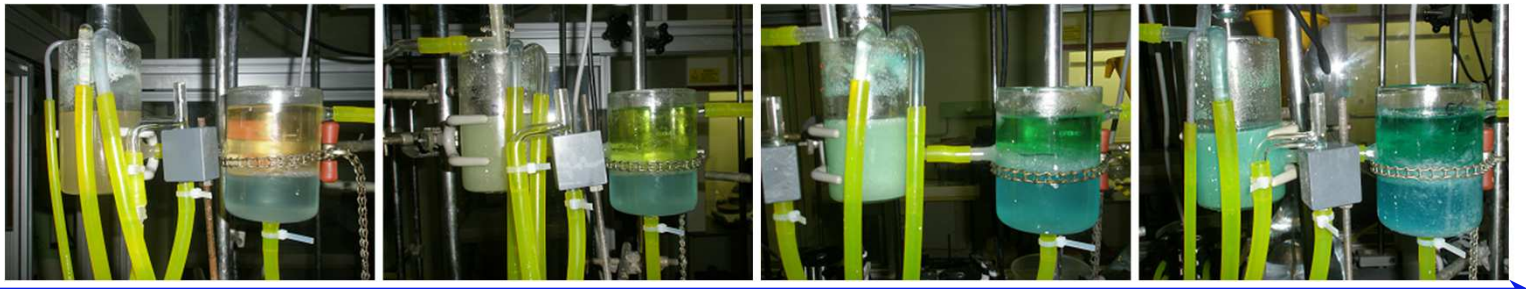
DAPEX SX pilot

Extraction



Strip

Scrub, **Wash & Acidification**

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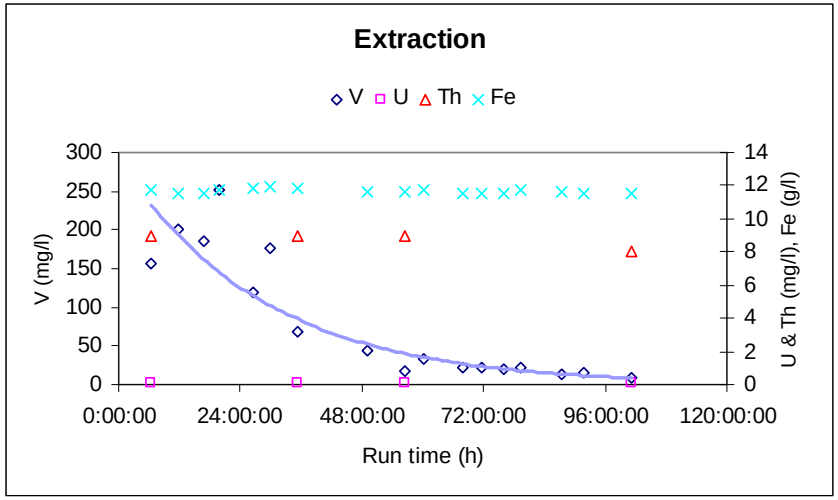
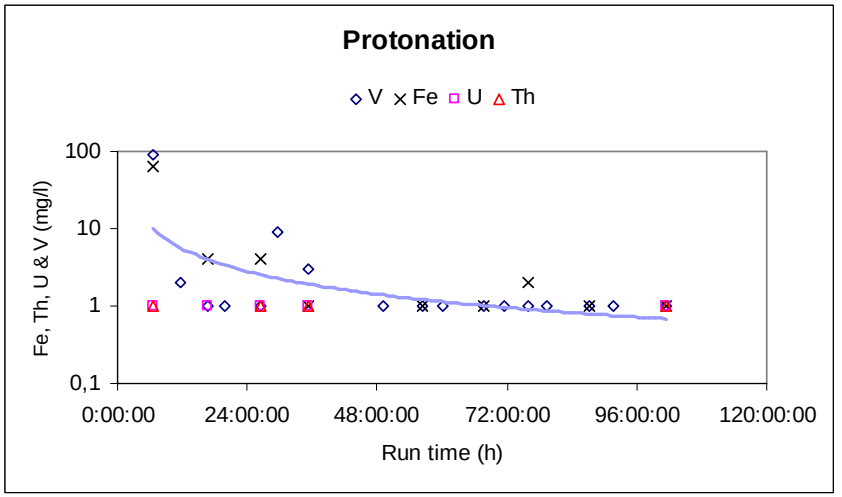
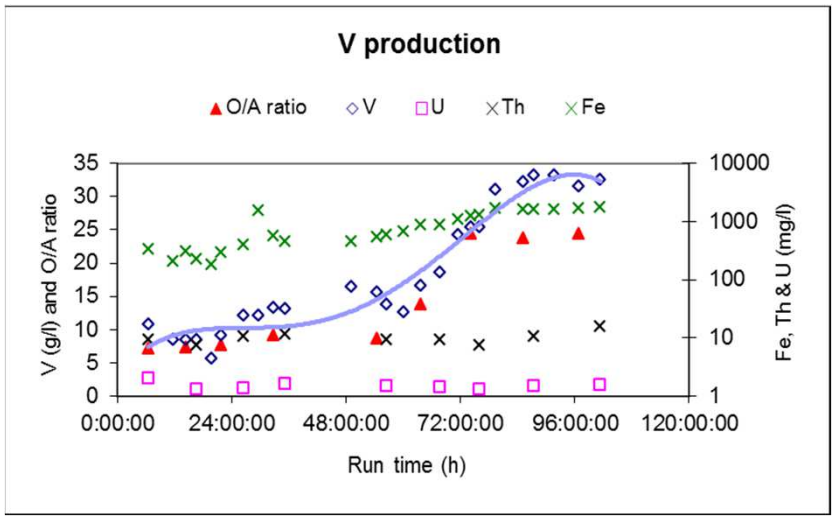
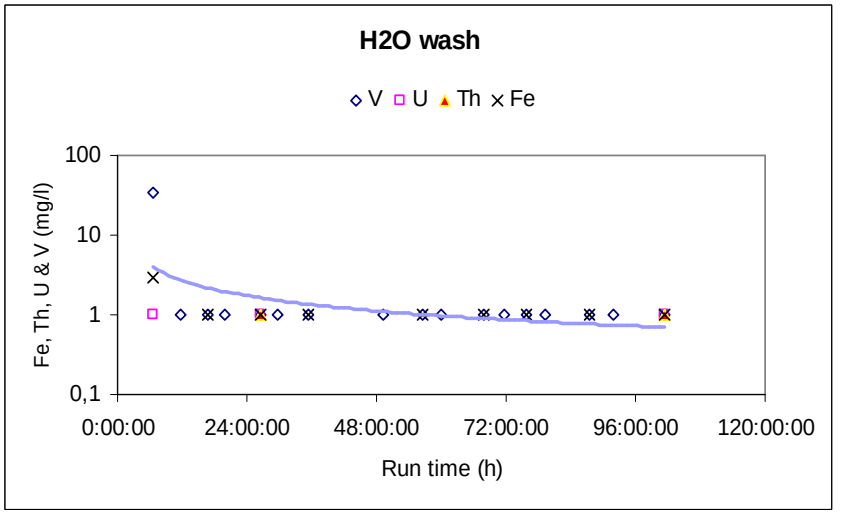
DAPEX SX pilot









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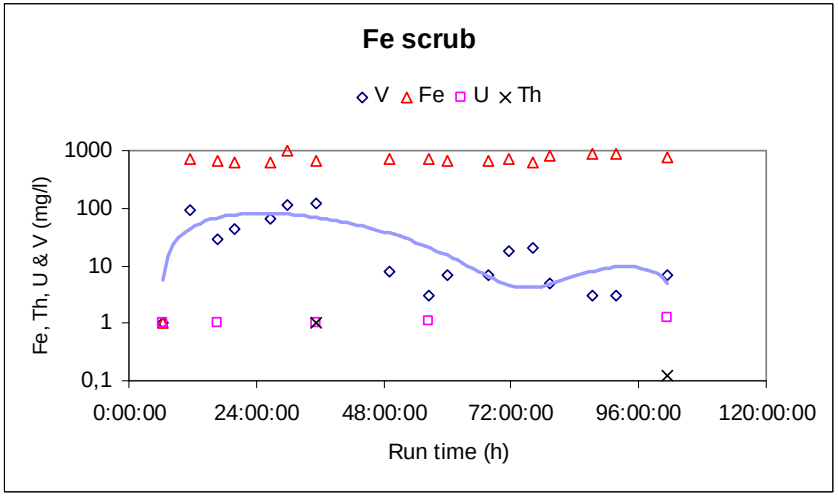
DAPEX SX pilot



Metal	Extraction	V Strip	Fe Scrub	H_2O Wash	H_2SO_4 Contact	Global
Process efficacy @ 101 h						
Th	20%	90%	< 1%	< 1%	< 1%	18%
U	95%	< 1%	8%	5%	5%	16%
Fe	7%	< 1%	95%	< 1%	8%	7%
V	> 99%	> 99%	98%	< 1%	< 1%	99%

V eluate composition

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

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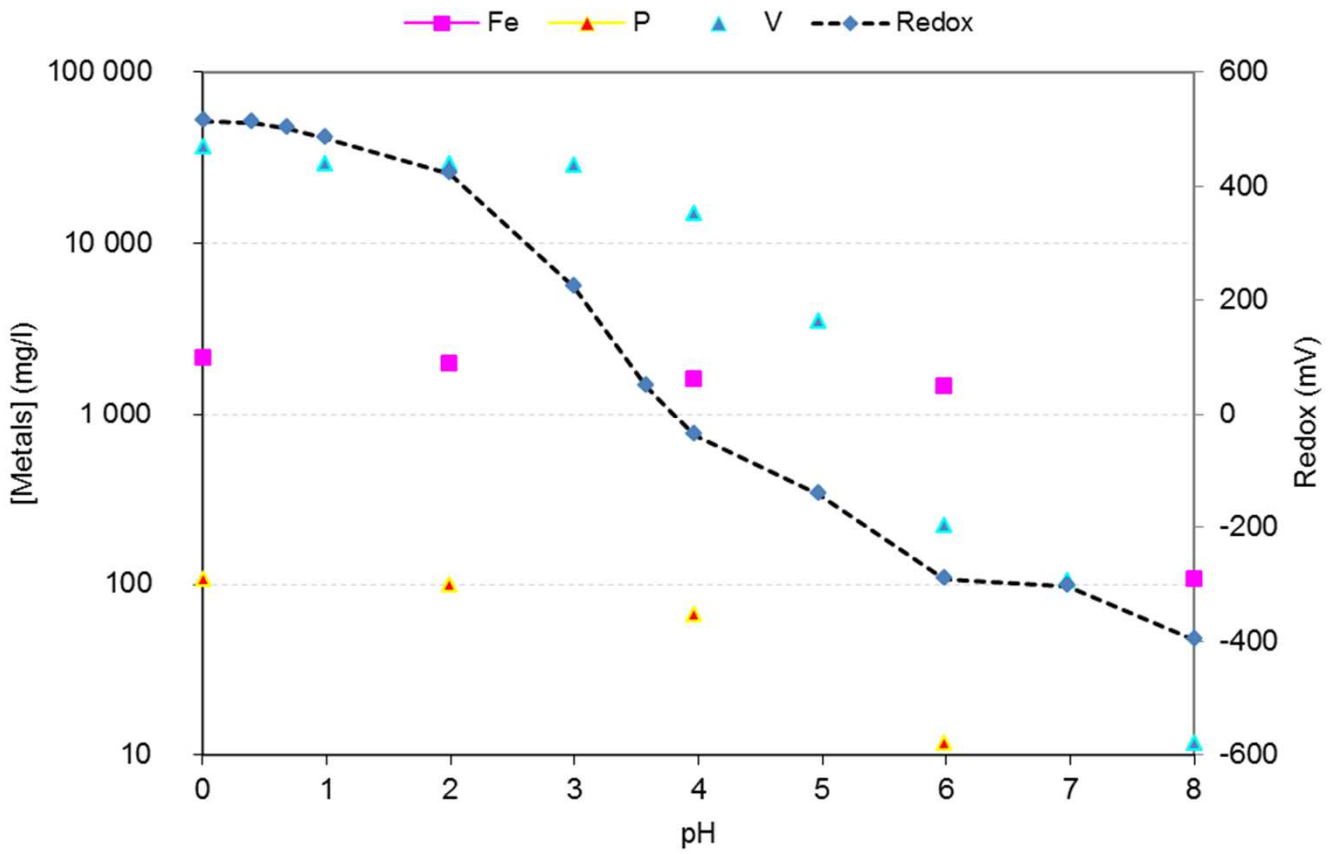
Product finishing: Option 1a – Metal oxide

Direct (without oxidation) precipitation

$$2VOSO_4 + 4NH_4OH \rightarrow V_2O_4 \downarrow + 2(NH_4)_2SO_4 + 2H_2O$$

$$V_2O_4 + ½O_2 + \Delta \rightarrow V_2O_5$$



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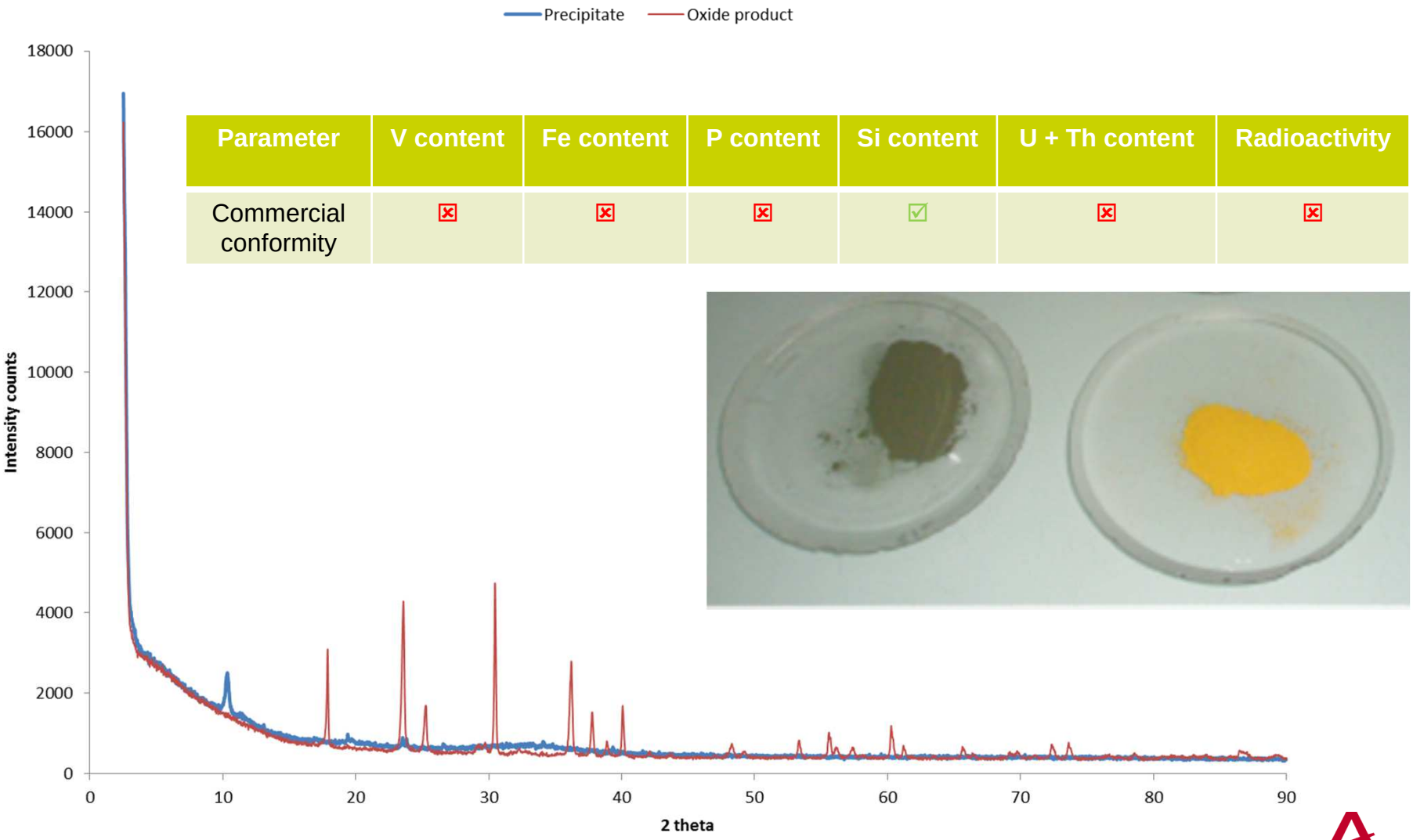
Product finishing: Option 1a – Metal oxide

Parameter	V content	Fe content	P content	Si content	U + Th content	Radioactivity
Commercial conformity	☒	☒	☒	☑	☒	☒



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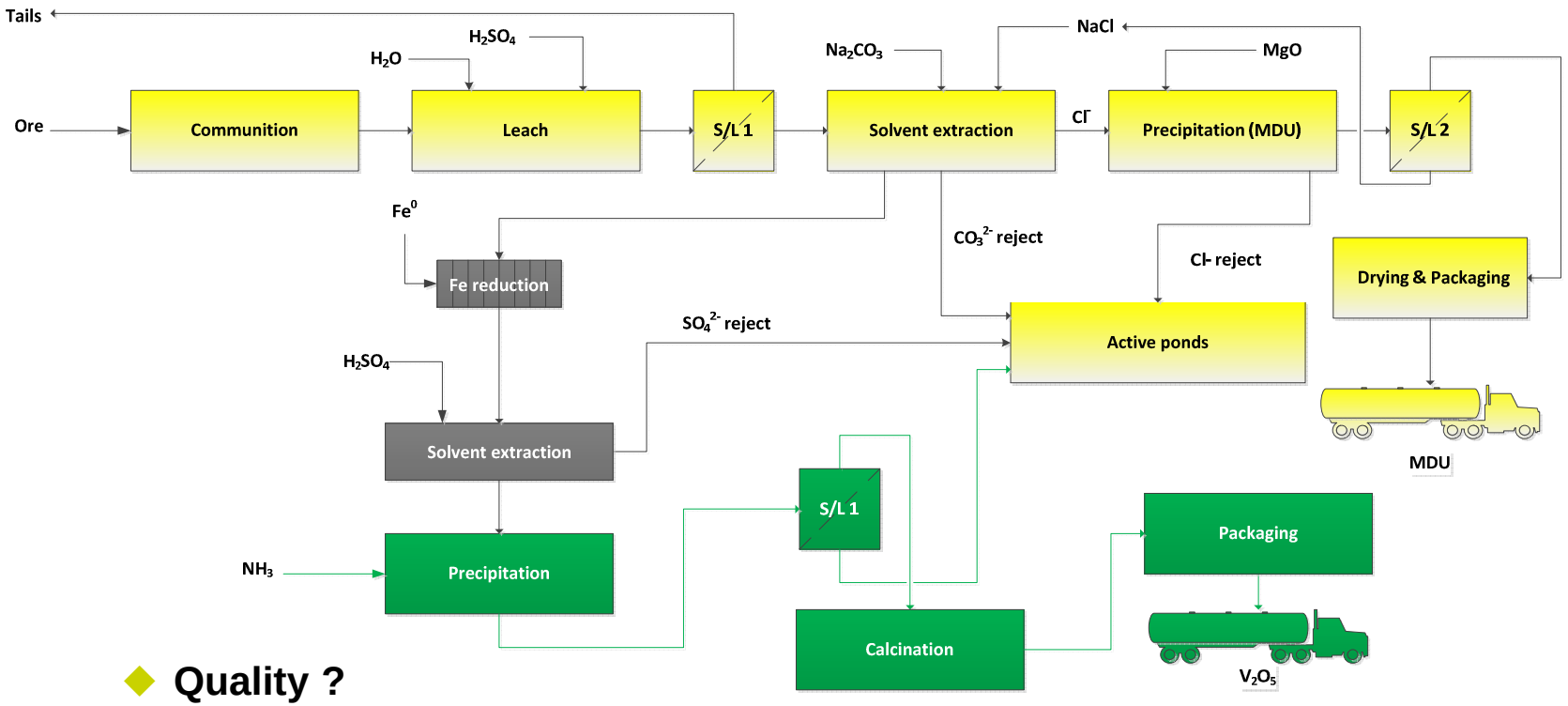
Product finishing: Option 1a flowsheet



- **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)

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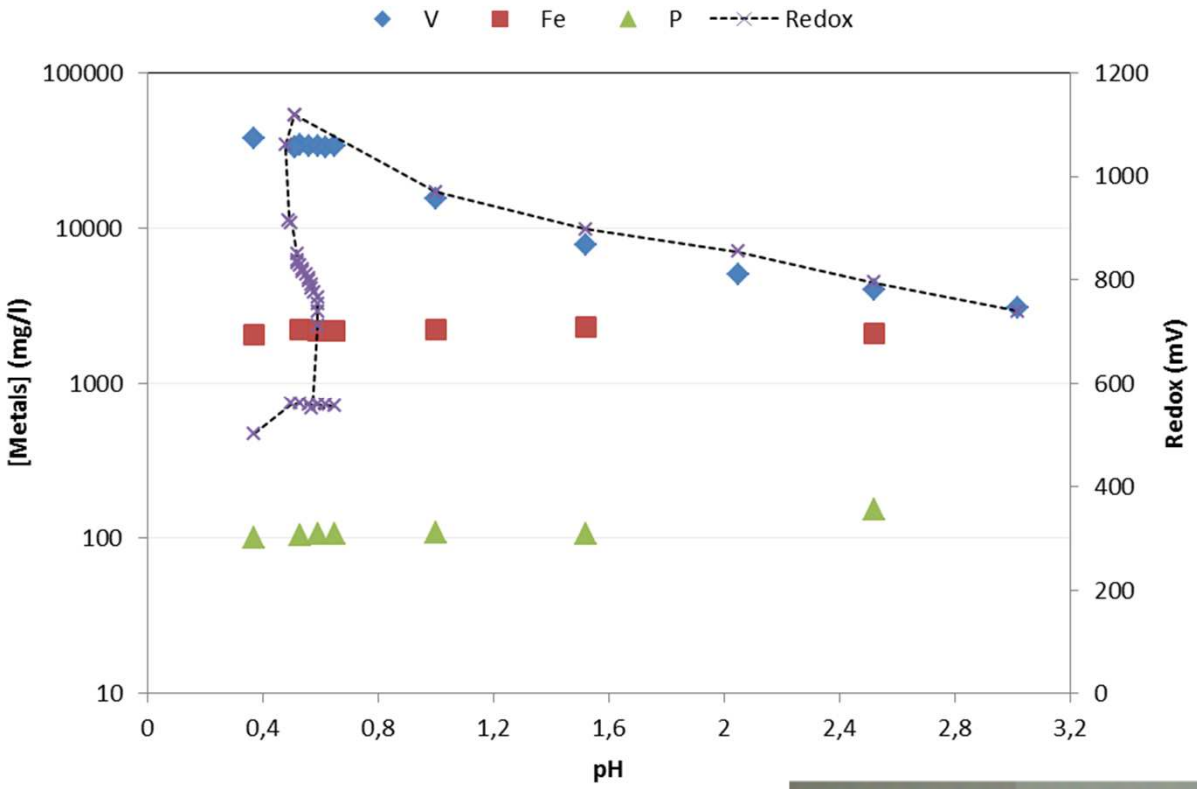
Product finishing: Option 1b – Metal oxide

Indirect (with oxidation) precipitation

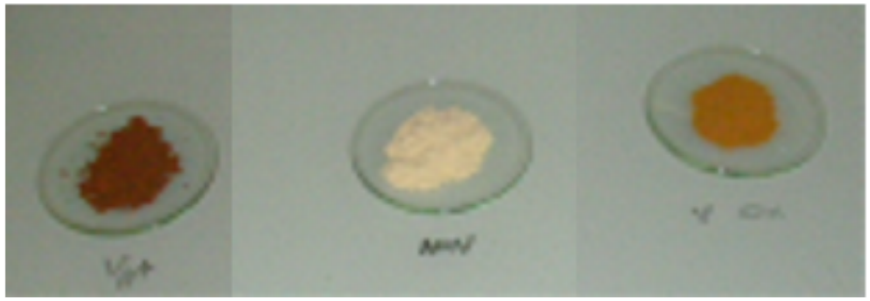


$$VOSO_4 + \tfrac{1}{2}O_2 + 2NH_4OH \rightarrow HVO_3 \downarrow + (NH_4)_2SO_4$$

$$2HVO_3 + Na_2CO_3 \rightarrow 2NaVO_3 + H_2O + CO_2 \uparrow$$

$$2NaVO_3 + (NH_4)_2SO_4 \rightarrow 2NH_4VO_3 \downarrow + Na_2SO_4$$

$$2NH_4VO_3 + \Delta \rightarrow V_2O_5 + NH_3 \uparrow + H_2O$$



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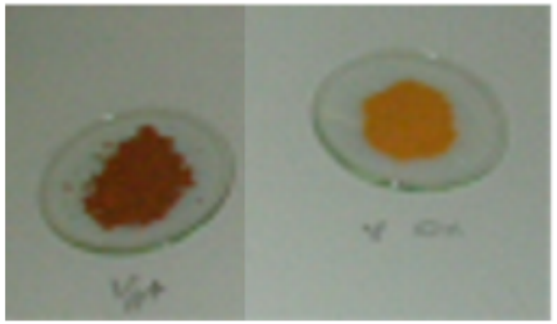
Product finishing: Option 1b – Metal oxide

Parameter	V content	Fe content	P content	Si content	U + Th content	Radioactivity
Commercial conformity	☑	☑	☑	☑	☑	☑



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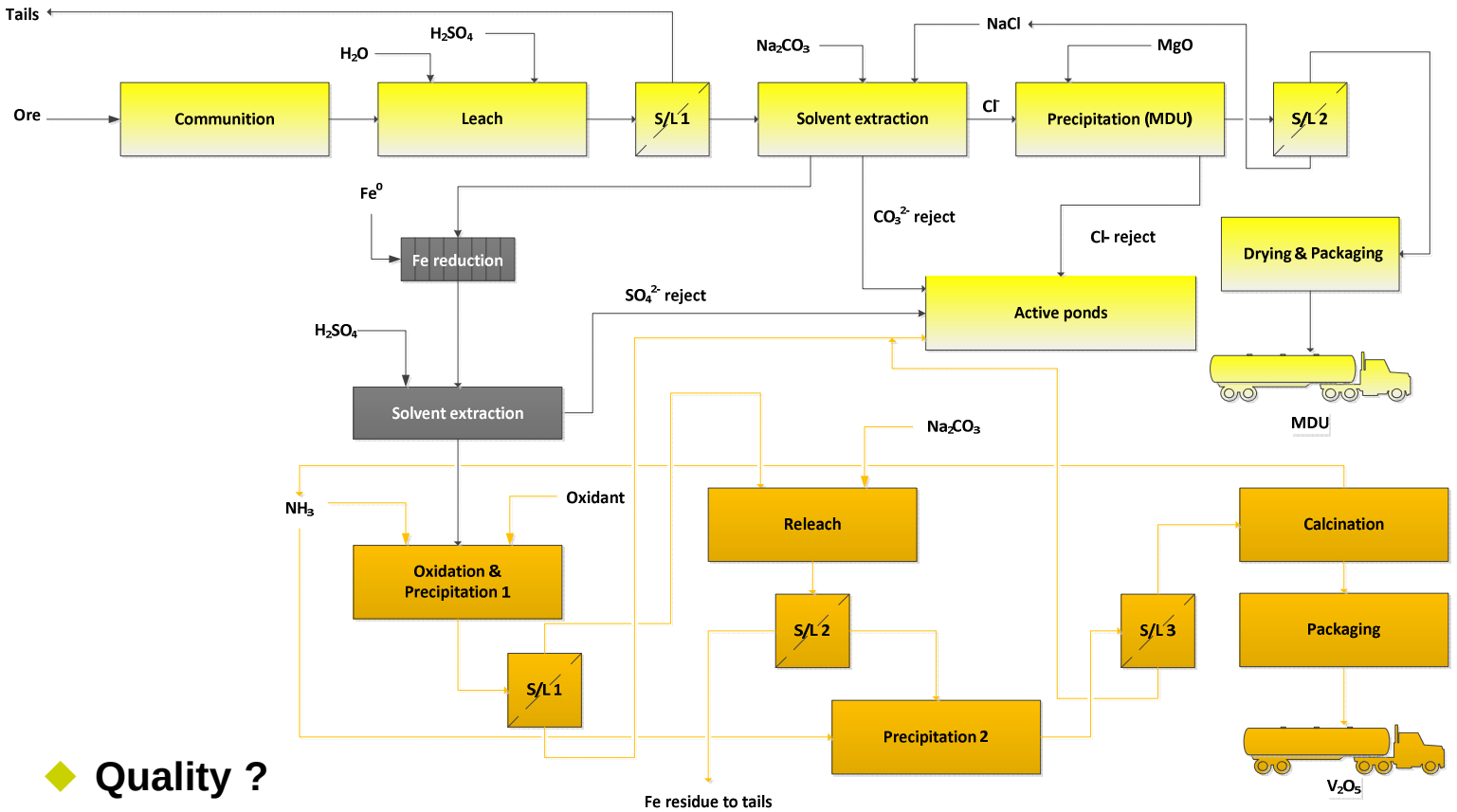
Product finishing: Option 1b flowsheet



- **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**)

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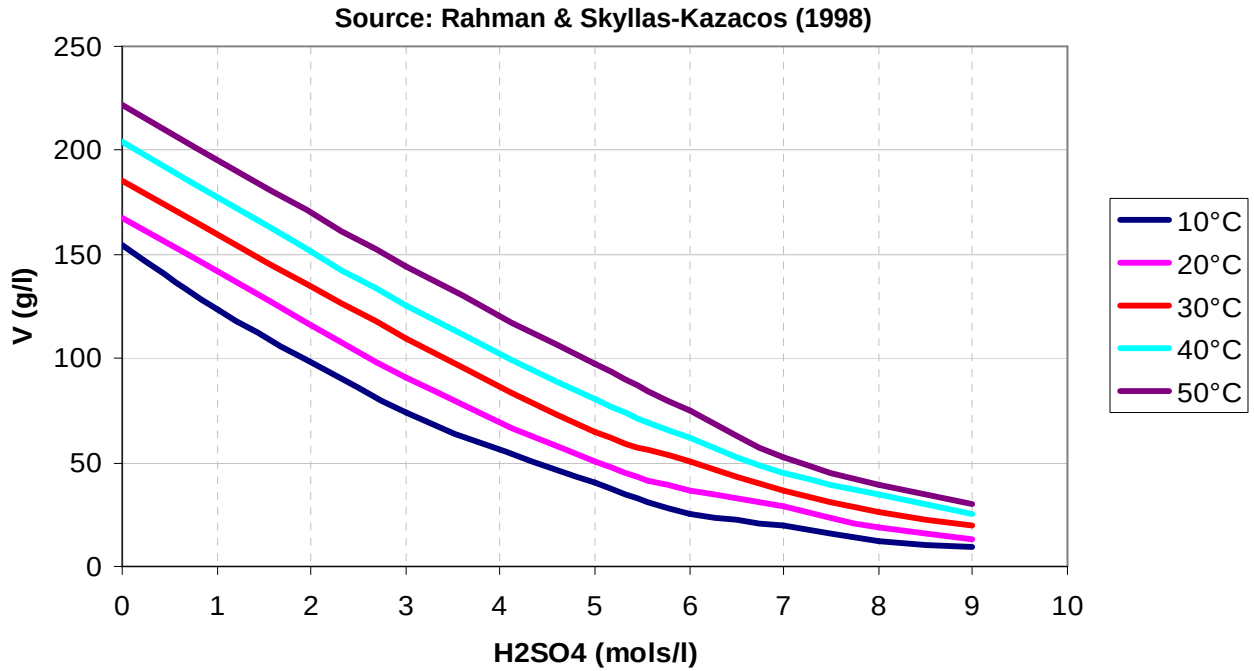
Product finishing: Option 2 – Metal salt

Crystallisation

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



$$VOSO_4 + H_2O + H_2SO_4 + \Delta \rightarrow VOSO_4\downarrow + H_2O\uparrow + H_2SO_4$$

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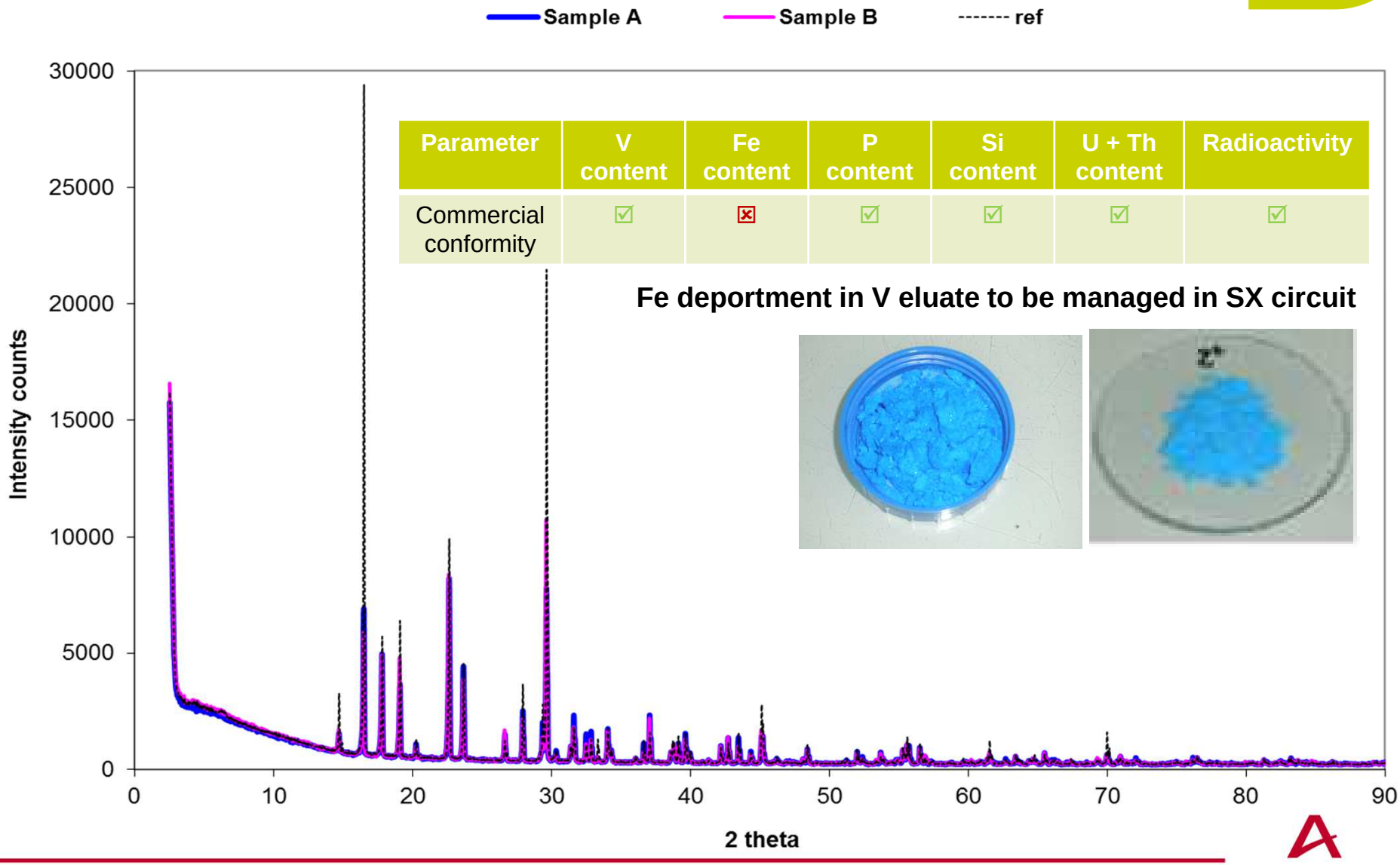
Product finishing: Option 2 – Metal salt



Parameter	V content	Fe content	P content	Si content	U + Th content	Radioactivity
Commercial conformity	☑	☒	☑	☑	☑	☑

Fe deportment in V eluate to be managed in SX circuit

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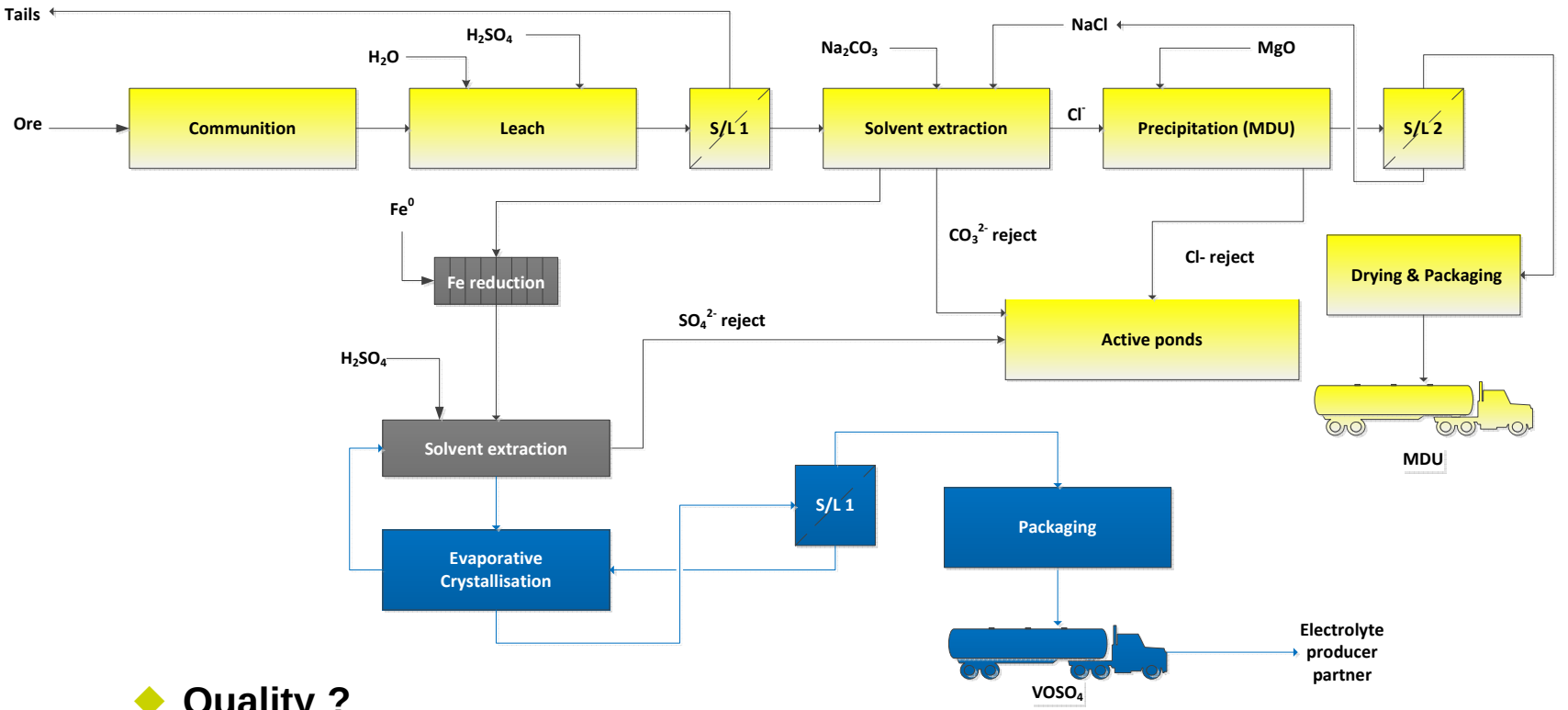
Product finishing: Option 2 flowsheet



- **Quality ?**
  - Capable of meeting grade and radioactivity specifications
- **Product and price ?**
  - Metal salt ($VOSO_4.xH_2O$) at a premium price (compared to V_2O_5)
- **Process ?**
  - 3 stages (low CAPEX / OPEX, ➲ **preferred route**)

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Conclusions and future work

Conclusions

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

Flowsheet	Least n° of stages	Product grade and quality	Product value	Overall preference
Option 1a (metal oxide)	++	+	+	+
Option 1b (metal oxide)	+	++	++	++
Option 2 (metal salt)	+++	+++	+++	+++

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

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Merci pour votre attention

Questions ?

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