# Solvent Extraction Of Uranium

# Towards Good Practice In Design, Operation And Management.

**International Symposium on Uranium Raw Material for the Nuclear Fuel Cycle**
**Vienna, June 2014**

# Good Practice in Uranium Solvent Extraction

- Historical Origins
- Foundation Chemistry
  - Extractants
- SX Feed Control
- Process Stages
  - Extraction Stage
  - Downstream Stages
- Exchange Equipment
- Solvent Condition
  - Phase Disengagement
  - Crud Formation and Handling
- Towards the Future

# Historical Origins

- Originated from nuclear industry uranium concentrates
  - Based on TBP extractant from nitric acid solutions
  - Extractant screening by Oak Ridge National laboratories
- Pilot investigations with acid leach slurries
- Development through commercial application
  - Organic phosphoric acids; Dapex e.g. Shiprock
  - Secondary amine; e.g. Mexican Hat
  - Tertiary amine; Amex, e.g. Grants
- Equipment design evolved with each installation

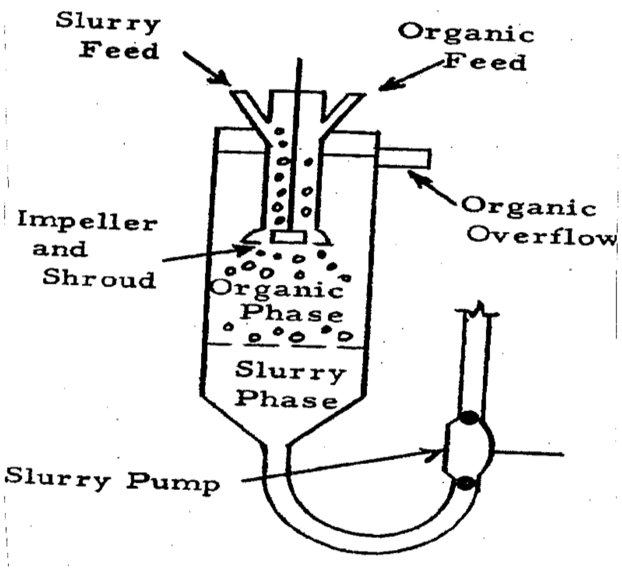


Figure 8. Internal mixer-settler

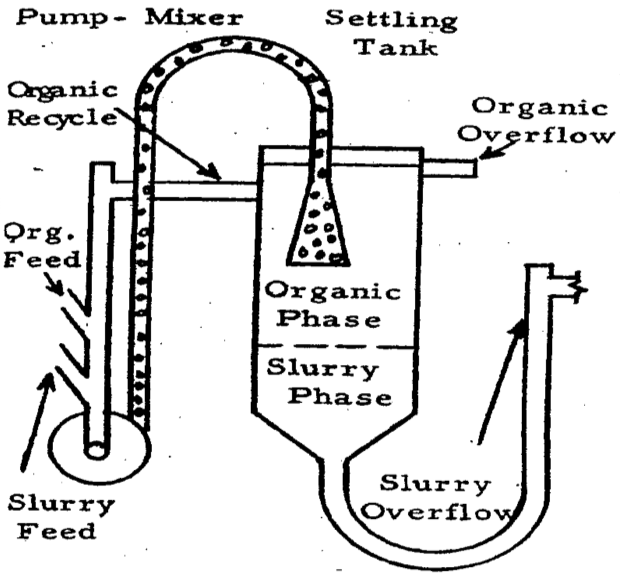


Figure 7. Pump-mixer

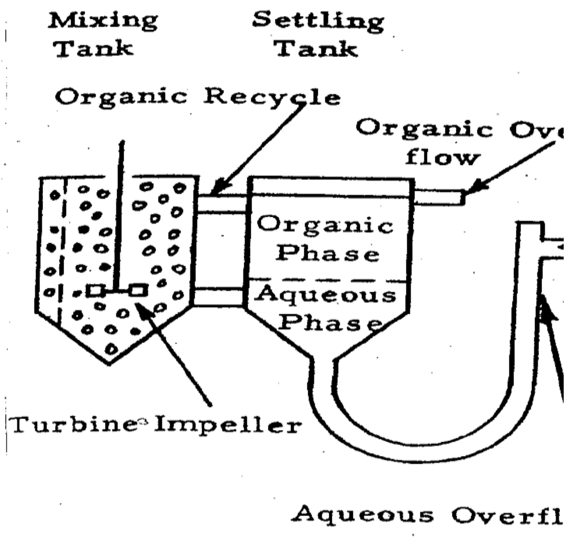
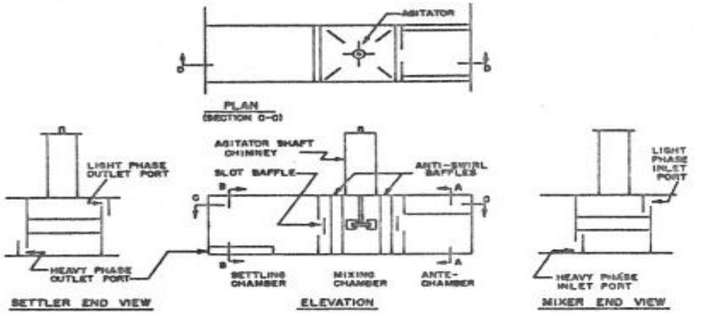


Figure 6. Mixer-settler

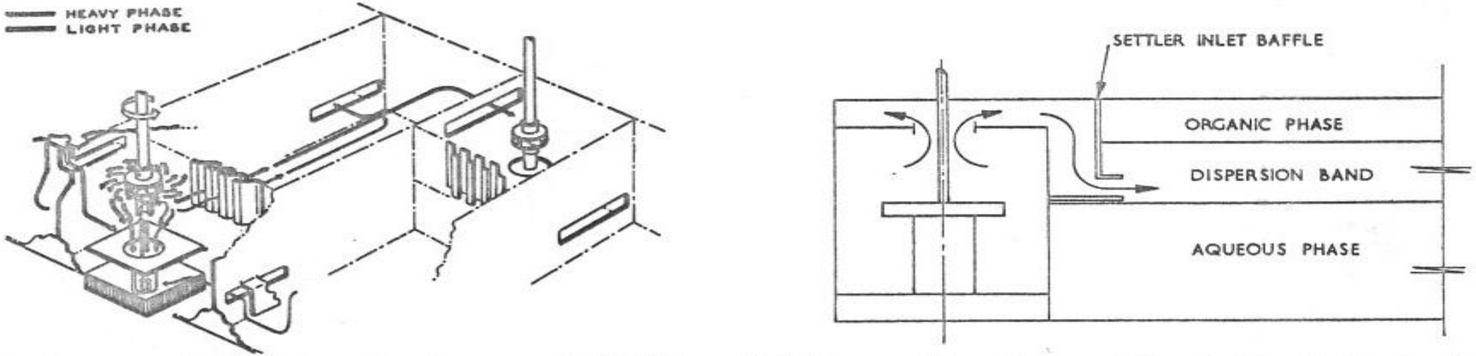
**Grinstead et. al. Peaceful Uses of Atomic Energy 1955**

# The Design and Performance of Pump-Mix and Gravity Flow Mixer-Settlers

## Royston & Burwell AAEC 1972



(e) Standard Oil Development Co. (1949)



(f) KAPL 'Pump-Mix' Unit - Coplan et al (1951)

(g) Power-Gas Pump-Mix Unit - Lott et al (1971)

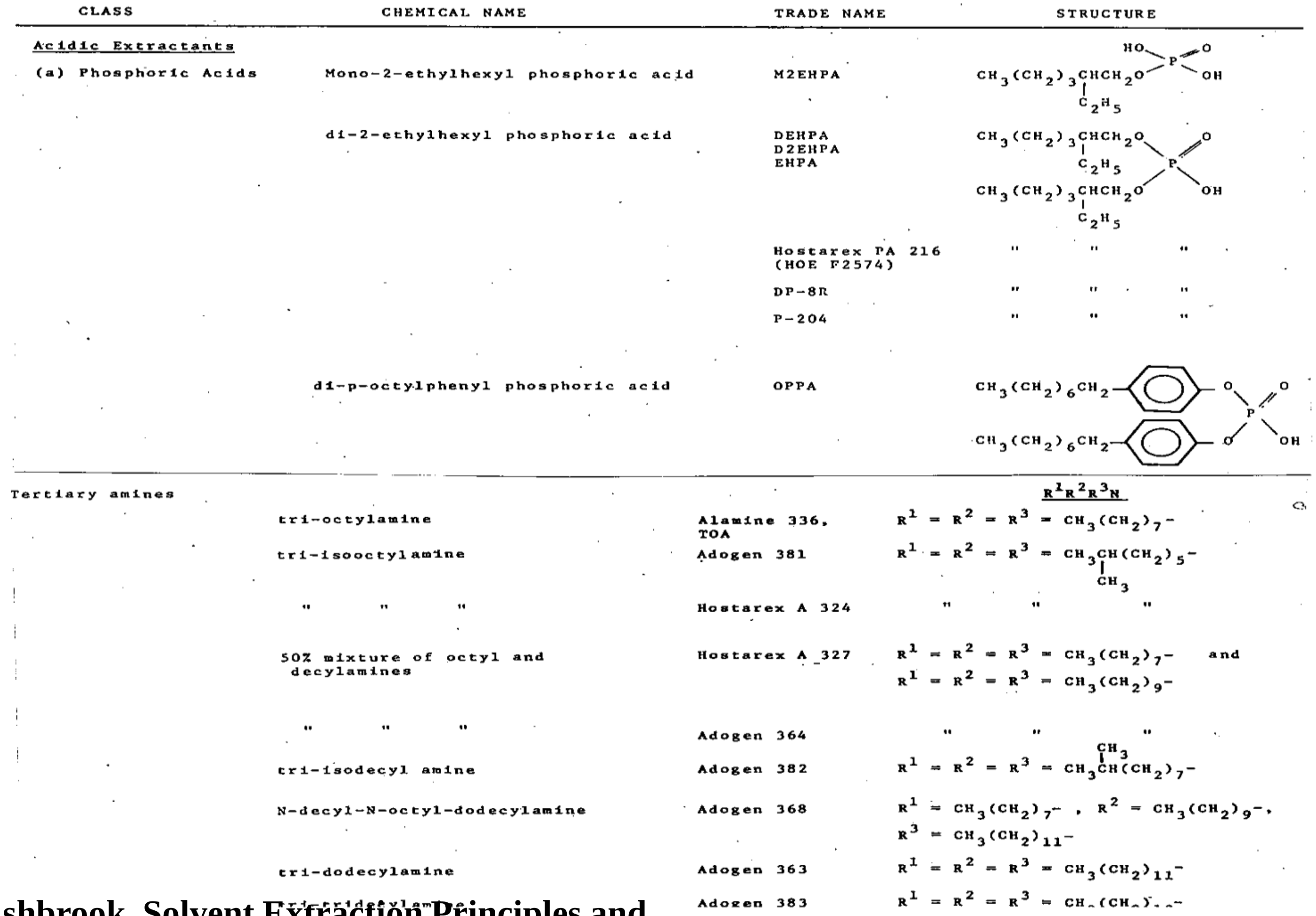
FIGURE 1(e) - (g) SKETCH OUTLINES OF HORIZONTAL MIXER-SETTLERS

# Foundation Chemistry

- Cationic extractants are less selective for $UO_2^+$
- Anionic extractants applied with acid liquors
  - Commercial extractant unproven for alkaline liquors
- Recognition of diluent and modifier choices
  - Aliphatic, narrow-cut kerosene favoured for low cost
  - Aromatic diluent favoured as biocide
  - Suppression third-phase formation
    - Isodecanol with secondary & tertiary amines
    - TBP or DBBP with organic phosphoric acid
- Scrubbing displaces impurities and entrainment
- Stripping with strong solution; Cl, SO4, CO3

# Extractants

- Cationic extractants favoured with selected impurities
  - Can mitigate high Mo, SiO2, V
  - Co-recovery of rare earths elements
- Anionic extractants dominant application
  - Olympic Dam, Ranger, Key Lake
  - Following ion exchange; Eluex/Bufflex/Purlex process
- Mixed extractant for high chloride & sulphate PLS
  - Durango, Colorado & Honeymoon, South Australia
- Brand or generic names for each chemical formula



| CLASS | CHEMICAL NAME | TRADE NAME | STRUCTURE |
|---|---|---|---|
| **Acidic Extractants** | | | |
| (a) Phosphoric Acids | Mono-2-ethylhexyl phosphoric acid | M2EHPA | $CH_3(CH_2)_3CH(C_2H_5)CH_2O-P(=O)(OH)_2$ |
| | di-2-ethylhexyl phosphoric acid | DEHPA<br>D2EHPA<br>EHPA | $[CH_3(CH_2)_3CH(C_2H_5)CH_2O]_2P(=O)OH$ |
| | | Hostarex PA 216<br>(HOE F2574) | " " " |
| | | DP-8R | " " " |
| | | P-204 | " " " |
| | di-p-octylphenyl phosphoric acid | OPPA | $[CH_3(CH_2)_6CH_2-C_6H_4-O]_2P(=O)OH$ |
| Tertiary amines | | | $R^1R^2R^3N$ |
| | tri-octylamine | Alamine 336,<br>TOA | $R^1 = R^2 = R^3 = CH_3(CH_2)_7-$ |
| | tri-isooctylamine | Adogen 381 | $R^1 = R^2 = R^3 = CH_3CH(CH_3)(CH_2)_5-$ |
| | " " " | Hostarex A 324 | " " " |
| | 50% mixture of octyl and decylamines | Hostarex A 327 | $R^1 = R^2 = R^3 = CH_3(CH_2)_7-$ and<br>$R^1 = R^2 = R^3 = CH_3(CH_2)_9-$ |
| | " " " | Adogen 364 | " " " |
| | tri-isodecyl amine | Adogen 382 | $R^1 = R^2 = R^3 = CH_3CH(CH_3)(CH_2)_7-$ |
| | N-decyl-N-octyl-dodecylamine | Adogen 368 | $R^1 = CH_3(CH_2)_7-$ , $R^2 = CH_3(CH_2)_9-$,<br>$R^3 = CH_3(CH_2)_{11}-$ |
| | tri-dodecylamine | Adogen 363 | $R^1 = R^2 = R^3 = CH_3(CH_2)_{11}-$ |
| | tri-tridecylamine | Adogen 383 | $R^1 = R^2 = R^3 = CH_3(CH_2)_{12}-$ |

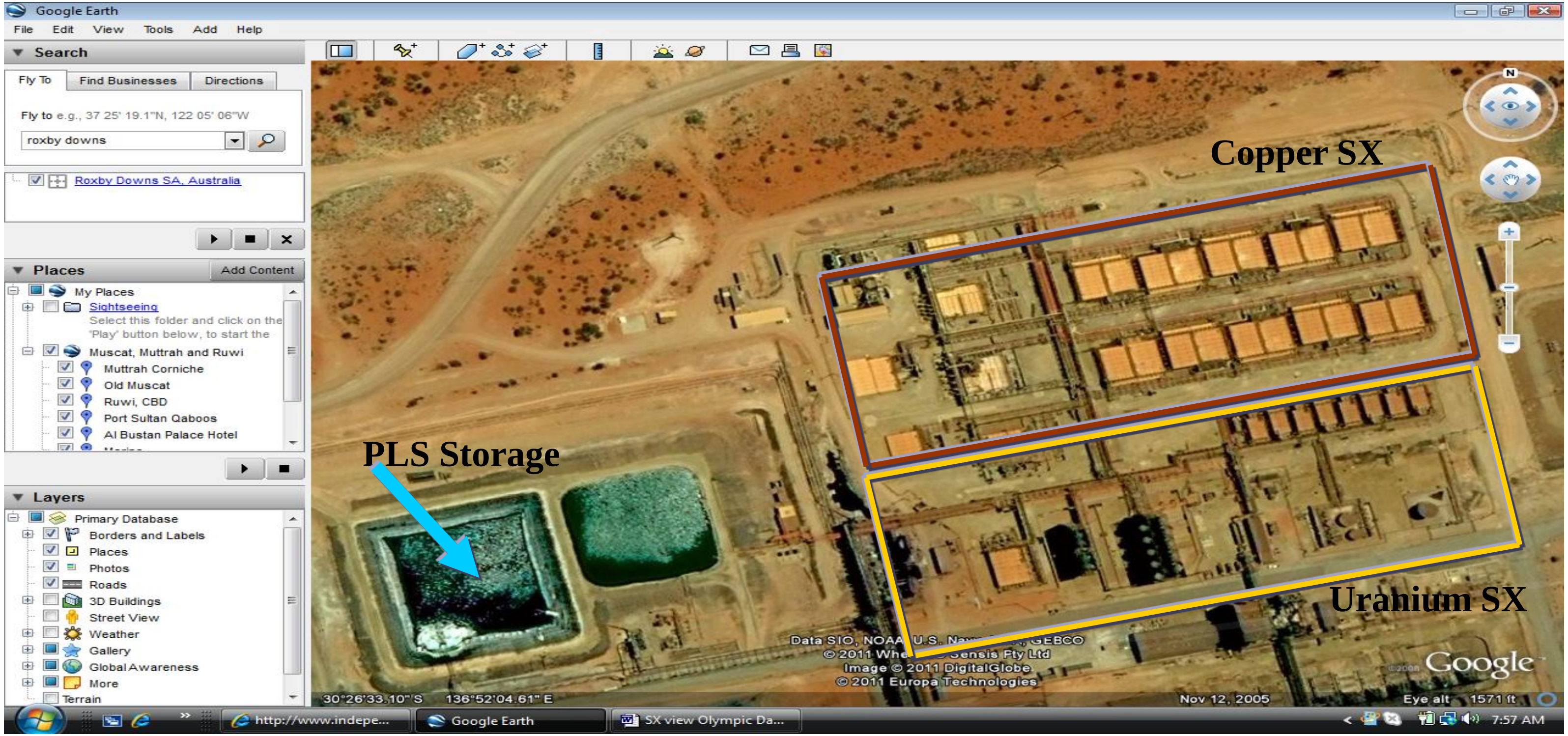
**Ritcey and Ashbrook, Solvent Extraction Principles and Application. Part1, Table 1, page 91, Elsevier 1984**

# Feed Control

- Stable feed flow and chemistry improves performance
  - PLS storage or surge volume allows attenuation of variability
- Minimizing surge volume lowers project returns
- Simulation and trade-off study can specify optimum surge
  - 1 week live storage preferred by operators
  - 1 day live storage preferred by accountants
  - Surge analysis must include all direct and indirect costs
  - Life of project estimates needed for quantitative comparison
- Allow for level measurement, cleaning and leak detection

# Feed Control

- **PLS Storage Design; 25000 m$^3$, approx 11 hours live.**



# Feed Control

- **PLS Storage Design; 15,000 m$^3$, approx 24 hours live.**

# Process Stages

- Objectives of mass transfer processes include;
  - Concentration of value elements
  - Separation of impurity elements

- Desirable features of process stages.
  - Operational and design simplicity
  - Safe and hygienic facilities
  - Optimum life-of-project costs

# Extraction Stage

- **Extraction; transfer of uranium and impurities**
  - **Optimize rate; depends on extractant, temperature, tenor**
  - **Approach to equilibrium mass transfer;**
    - **mixer stages, numbers and retention**
  - **Minimize impurity transfer by maximum uranium loading**
    - **Impurities in feed includes recycle from scrubbing**
  - **Minimize entrainment; OinA & AinO**
  - **Diligent management of crud**
- **Must operate organic continuous emulsion**
  - **Limits silica transfer and polymerization**
    - **In columns; Advance phase ratio, A:O = 12:1or lower**
    - **In Mixers; Stage phase ratio, A:O = 1.0 or higher**

# Downstream Stages

- Scrubbing displaces impurities and entrainment
  - water wash for chloride, fluoride & suspended solids
  - dilute sulphate displaces silica and other anions
  - conditioning of solvent for downstream stripping
- Stripping with dilute or concentrated anionic solution
  - strong acid if source is ‘white’ and cheap
  - carbonate scrub suited to caustic precipitation
  - sulphate wash to control pH into AMSUL strip
  - ammonium sulphate requires ‘tight’ water balance

# Exchange Equipment

- **Mixer-settlers are mainstay of USX technology**
  - **Various design improvements common with CuSX**
- **Pulse columns are proven for extraction stage**
  - **Favoured for multiple stages & crud handling**
- **Comparison needed for each project**
  - **Capex & opex**
  - **Operability and fire safety**
  - **Toleration of feed variations**
  - **Integration with upstream & downstream stages**

# Exchange Equipment – Pulse Columns

# Exchange Equipment – Mixer Settlers

# Solvent Condition

- Maintain concentrations of solvent components
    - Operators must track loading capacity
    - Direct assay or max-load test
- Avoid or manage degradation products
    - Prevent, Tolerate, Remove or Regenerate?
    - Recycle of dumped solvent with Caution
    - Protect solvent during suspension of operation
- Crud accumulation will promote solvent losses
    - Regular and routine collection and treatment
    - Avoid sudden or large changes of flow
    - Crud ‘runs’ will propagate stable emulsions

# Phase Disengagement

- **Standard design & operating parameter**
  - **E.g. specific settling rate and phase break time**
- **Depends in solvent character and condition**
  - **Generally worsens over time**
  - **Caused by high Eh or excess oxidant in PLS**
  - **And accelerated with crud accumulation**
- **Regular observation and measurements**
  - **Track and chart solvent conditions**
  - ***Eternal vigilance is the price of freedom***

# Crud Formation and Handling

- **Dirty PLS is the major cause of crud in extraction**
  - **Target < 20 mg/L suspended solids**
  - **Control post-leach silica gypsum and jarosite precipitation**
  - **Every site had different crud which must be characterized**
- **Polymerization of silica**
  - **Slurry retention in ore leach at less intense conditions**
  - **Long retention of PLS can promote silica precipitation**
  - **Polish filtration of PLS after storage**
  - **Essential to operate mixers with organic phase continuity**
- **Crud also occurs in downstream stages**
  - **Transfer & Hydrolysis of metals; Zr, Ti, Bi, Mo, Fe**

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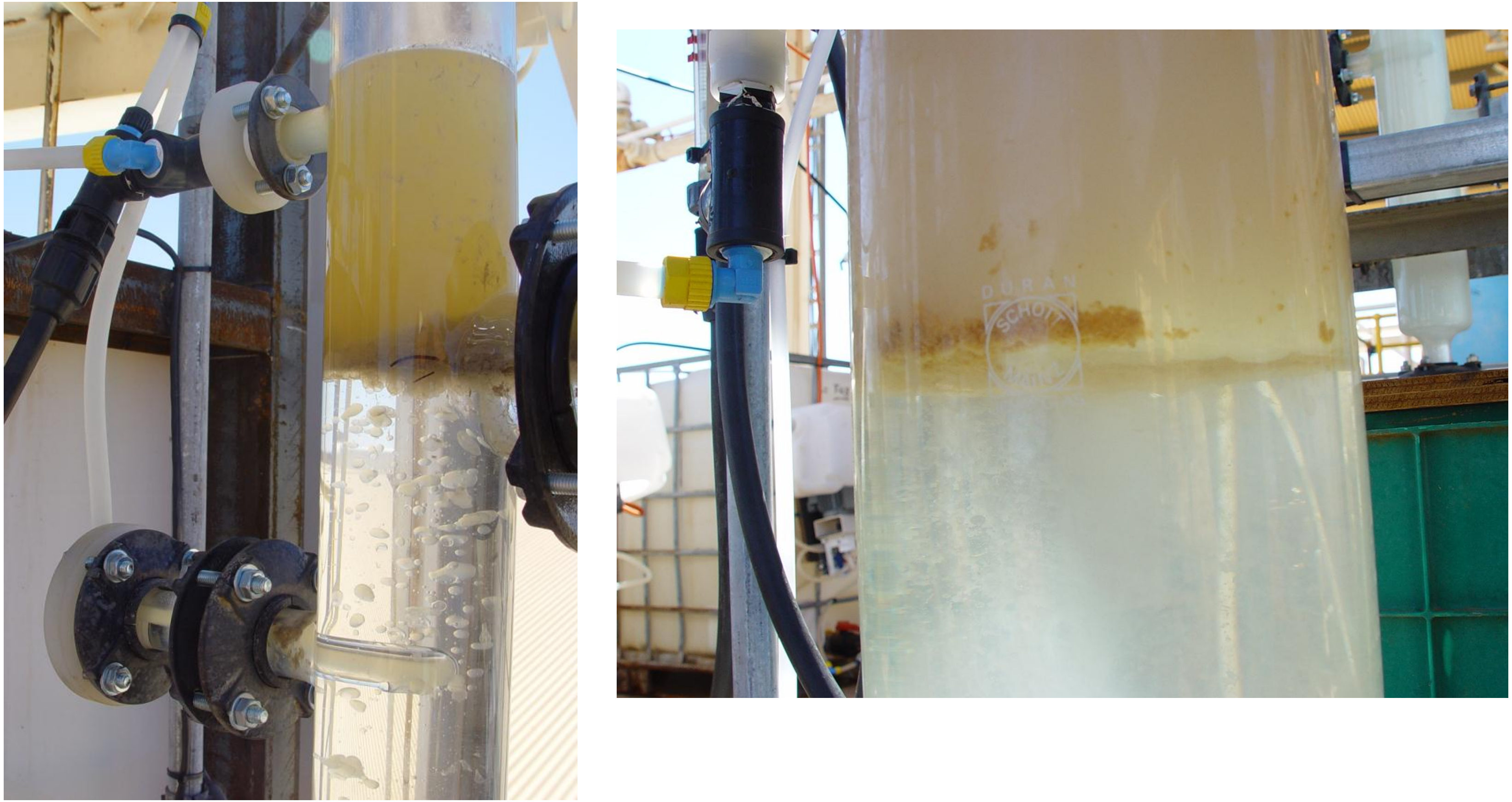

# Recent Operation at Honeymoon USX

- Commissioning at Honeymoon Mine began in July 2011 following the successful water treatment and the subsequent commencement of leaching in the wellfields.
- Dried UOC product from Honeymoon was produced by late September.
- USX column operations throughput and recovery approached design rates by April 2012

- Operational issues during process commissioning included:
  - Organic entrainment caused by crud generation in Pulsed Columns;
  - High volumes of aqueous entrainment in the barren organic leaving strip settler no.2
  - Presence of a third phase typically in strip settler no. 2
  - High phase disengagement times in strip mixers

# Recent Operation at Honeymoon USX

- Focus on reagent effects can be utilized in future USX plant designs may include:
    - Organic entrainment lowered by operator vigilance and stable phase continuity
    - The solubility of organic reagents is important in controlling entrainment in raffinate.
    - Metallurgical recovery requires stable conditions, e.g. extractant and modifier tenor
    - Frequent draining of the barren organic tanks leads to lower disengagement times
    - Additional organic acidification of PLS may be utilized
    - Solubility of third-phase must be managed by control of relative concentration of reagents
    - Off-site TBP analysis caused operational difficulties and may be expedites
    - Fresh strip solution to Strip 1improved pH control and lowered phase disengagement time
    - Operating Strip 2 with aqueous continuity could improve phase disengagement times
    - Alternatives to TBP as a third-phase modifier can be considered for future operations

# Towards the Future

- **USX has featured in uranium production for over 50 years**
    - Utilised in Australia two largest uranium mines
- **Future USX will reflect the expected trends of new projects**
    - lower grade ores
    - tighter controls on water supply or discharge
    - higher proportion via in-situ recovery
- **To remain competitive USX will need**
    - greater stage recovery
    - lower solvent losses
    - higher tolerance of salinity.

# Towards the Future

| **Operation & Location** | Ranger, Northern Territory | Olympic Dam South Australia | Beverley South Australia | *Honeymoon South Australia* | Four Mile South Australia |
|---|---|---|---|---|---|
| **Ore Category** | Unconformity | Breccia | Sandstone | *Sandstone* | Sandstone |
| **Leach Chemistry** | Acid sulphate | Acid sulphate, 3 g/L chloride | Acid sulphate, 4 g/L chloride | *Acid sulphate, 8 g/L chloride* | Acid sulphate |
| **Recovery Technique** | Amine SX | Amine SX | Strong base IX | *Mixed SX* | Strong base IX |
| **Nominal Capacity, tU** | 4660 | 3820 | 850 | *340* | 1150 |

| **Operation & Location** | *Kintyre, Western Australia* | *Wiluna, Western Australia* | *Yeelirrie, West Australia* | *Lake Maitland West Australia* | *Ranger Expansion* |
|---|---|---|---|---|---|
| **Ore Category** | *Unconformity* | *Surficial/calcrete* | *Surficial/calcrete* | *Surficial/calcrete* | *Stockpiles* |
| **Leach Chemistry** | *Acid sulphate* | *Alkali carbonate* | *Alkali carbonate* | *Alkali carbonate* | *Acid sulphate* |
| **Recovery Technique** | *DP* | *DP* | *DP* | *DP* | *Amine SX* |
| **Nominal Capacity, tU** | *2000* | *680* | *3000* | *850* | *TBC* |