Study of reaction kinetics in continuous processes for actinide separations

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Methods & Equipment

Solvent extraction

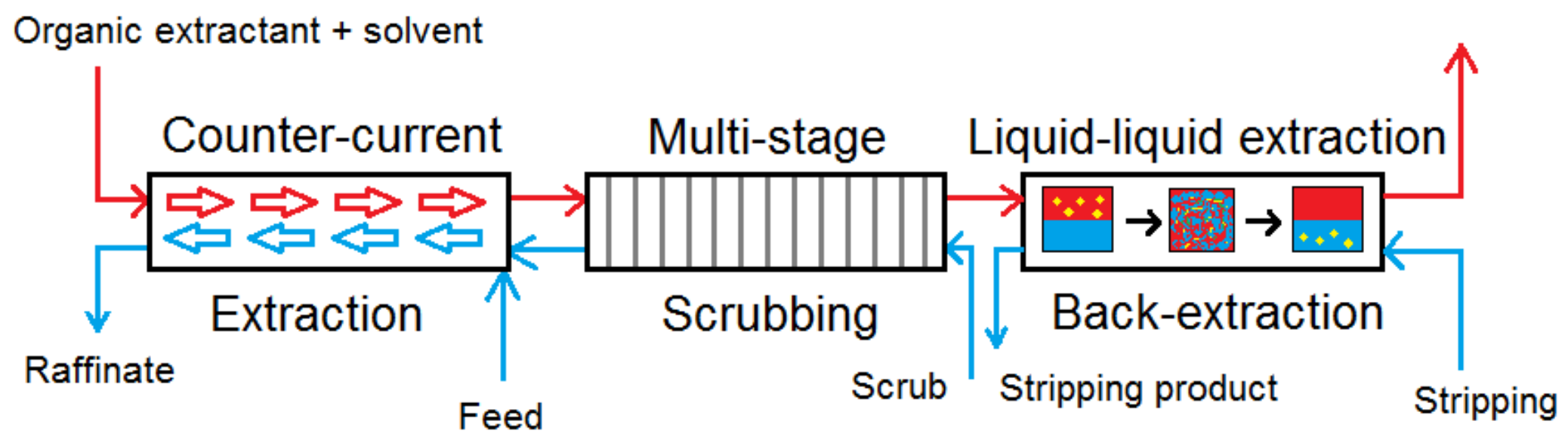

Figure 1: Counter-current multi-stage liquid-liquid extraction

Counter-current multi-stage liquid-liquid extraction (LLE) (Figure 1) is a chemical process where elements are separated from each other by selective extraction to the organic phase, followed by a scrubbing step to remove co-extracted impurities & a back-extraction step to bring the product back to the aqueous phase

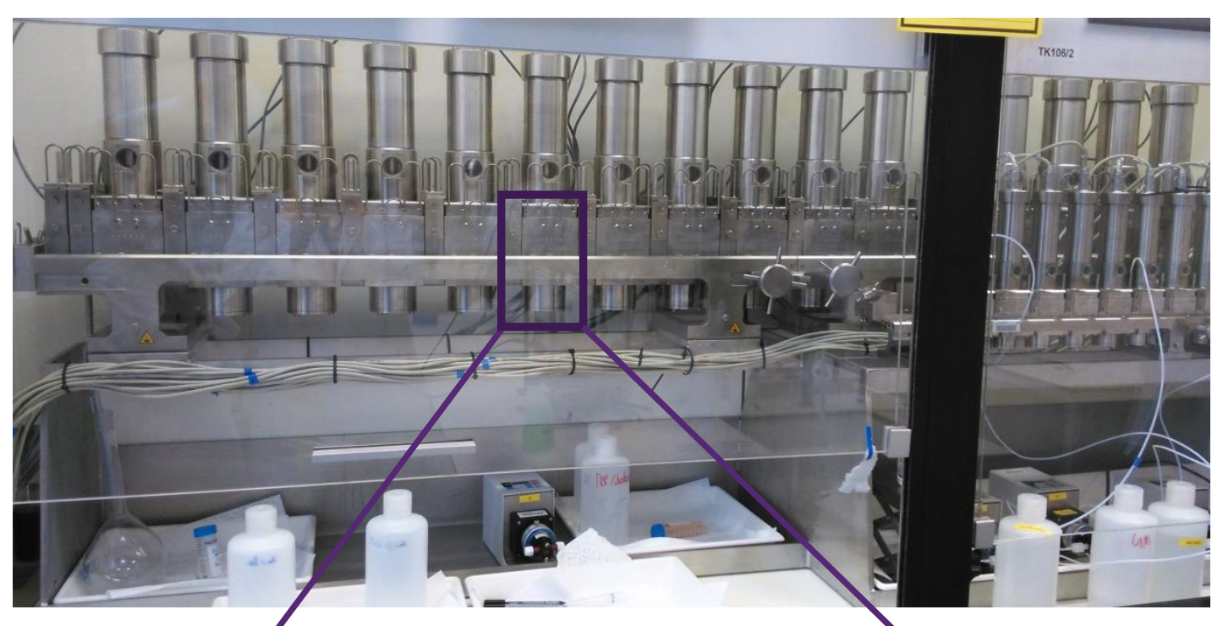

Figure 2: 16 stage annular centrifugal contactor setup

Annular centrifugal contactors (ACCs)

- Short average residence times
- Small liquid-hold up
- High throughput & flexibility
- Small footprint
- Each motor powers one rotor
- Rotor mixes heavy aqueous phase (blue) & light organic phase (red) in annular mixing zone (Figure 3)
- Spinning rotor pumps dispersion through orifice → separates both phases rapidly by centrifugal force
- Each phase is flung in a collector ring & drained in counter-current way

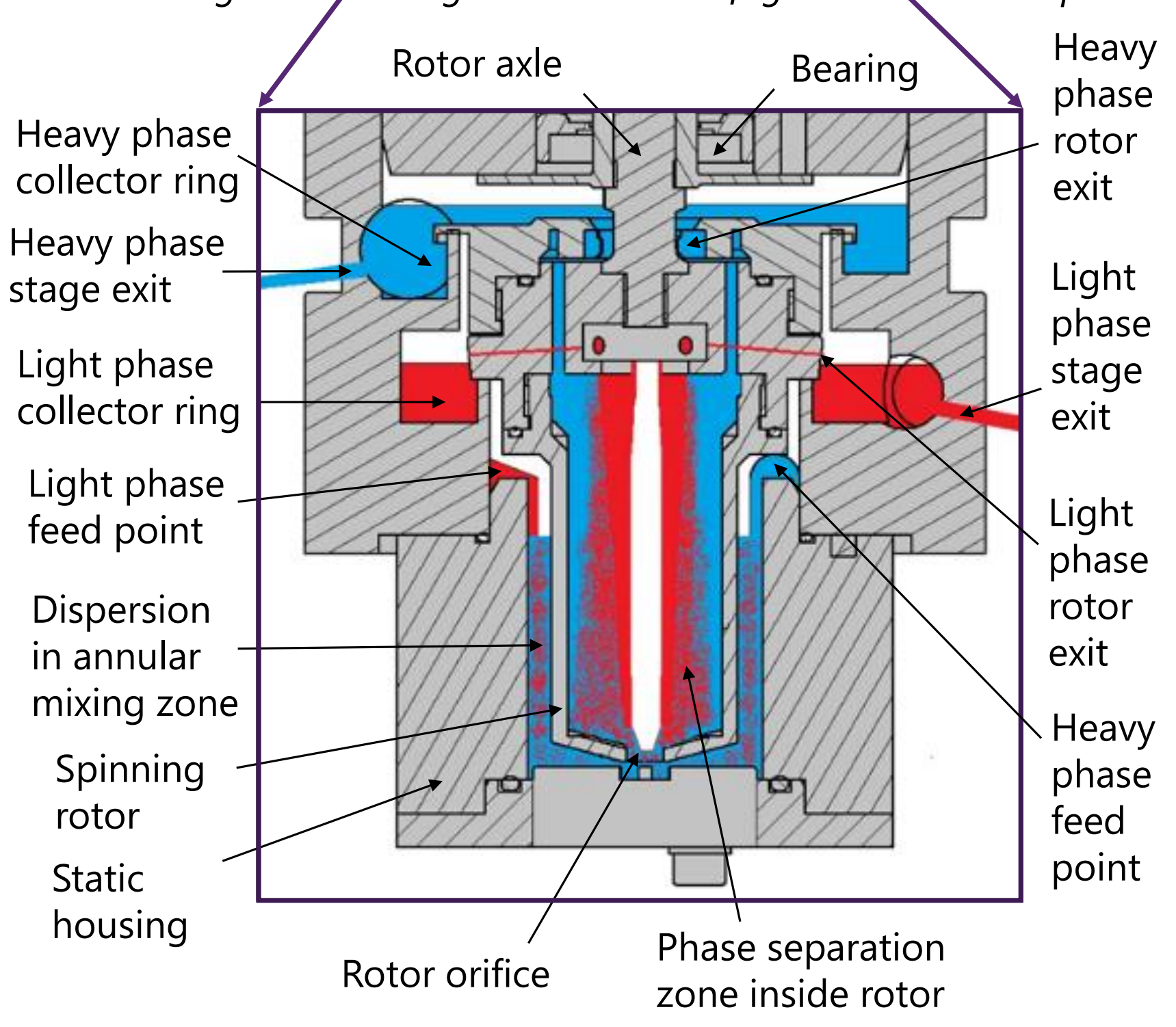

Figure 3: Cross section of ACC rotor & casing

Introduction

PhD launched 2020 → study reaction kinetics & mass transfer efficiency in continuous processes for different types of actinide separations

PUREX process (plutonium & uranium redox extraction)

- Industry standard for reprocessing spent nuclear fuel
- U & Pu separated from fission products (FPs) & minor actinides (MAs)
- Tri-n-butyl phosphate (TBP) → solvating extractant for U(VI) & Pu(IV)
- N,N-dialkylamides (D2EHiBA, D2EHBA, D2EHDMPA) extractants as future alternatives for TBP → highly selective for actinides, radiation resistant & incinerable (only CHON)

Highly active raffinate (HAR) of PUREX process → Am, Cm, FPs

- Am responsible for long-term heat loading of final repository
- Partitioning processes needed → separate management of Am

Objectives

- Develop ACC where residence time can be easily modified
- Obtain batch data to model multi-stage processes
- Gain insights in rate controlling reactions in the different systems
- Develop new processes based on gained insights

TBP benchmark for U extraction

Non-equilibrium solvent extraction

Fast contact time / high throughput

From batch to multi-stage LLE

Modelling & simulation

Results

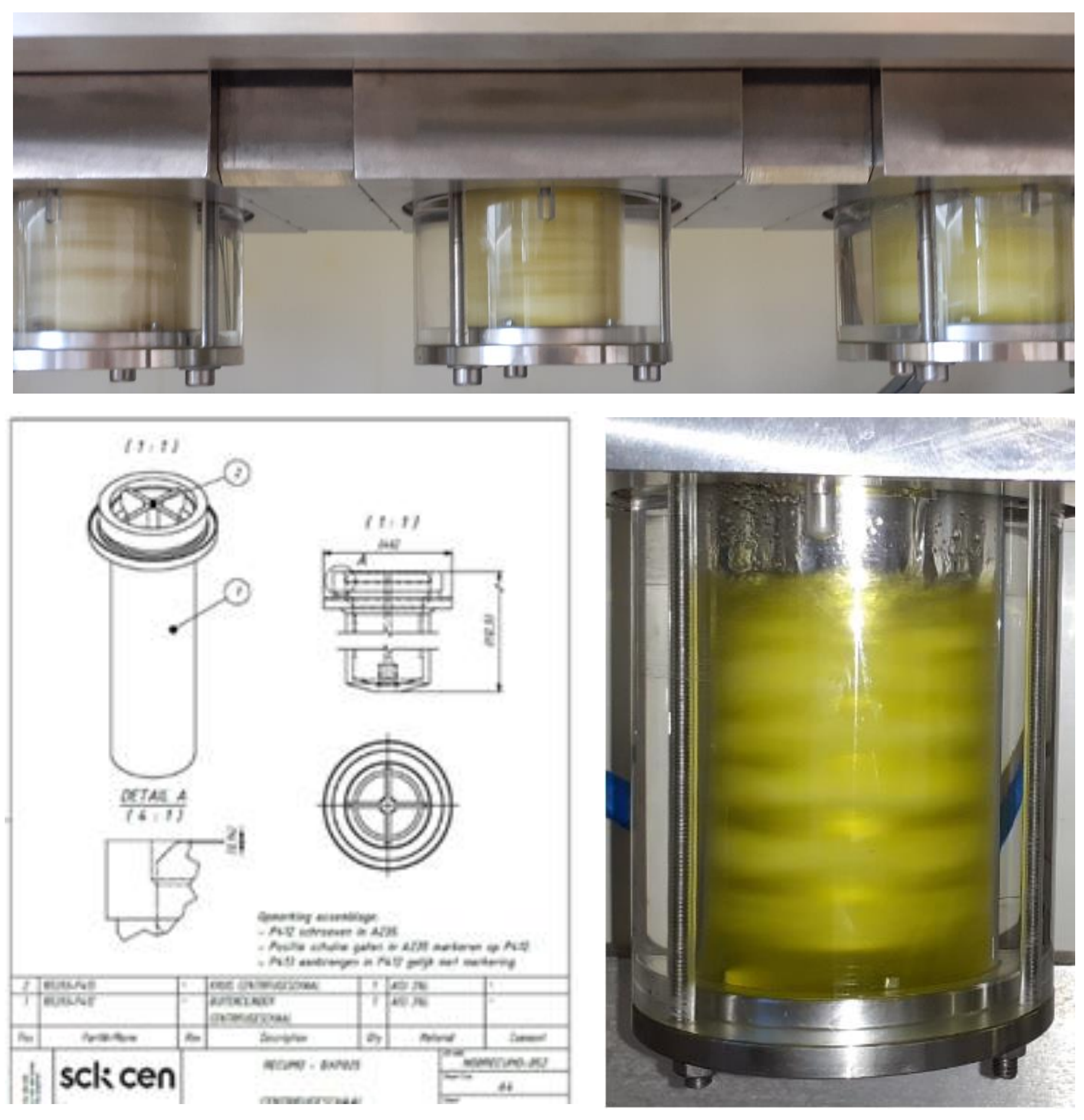

Figure 5: Plexiglass rotor surroundings & elongated stainless steel rotor

1st results focused on setting benchmark for TBP (Figure 4)

- short contact times in range of 10-15 seconds per stage
- organic phase flow rate constant throughout process
- high saturation of organic phase by U needed

→ Efficient U extraction + reproducible process conditions
→ Ru & Zr decontamination lower than expected → slow back-extraction kinetics – poor stage efficiency in scrubbing

Redesign of annular centrifugal contactors (Figure 5):

- Decrease volume in mixing zone by reducing width of annular gap → shorter contact time (for extraction)
- Increase volume in mixing zone by increasing rotor length → longer contact time (for scrubbing)
- Rotational speed (RPM) of rotor used to control level & volume in annular mixing zone
- Long residence time → improved scrubbing with TBP

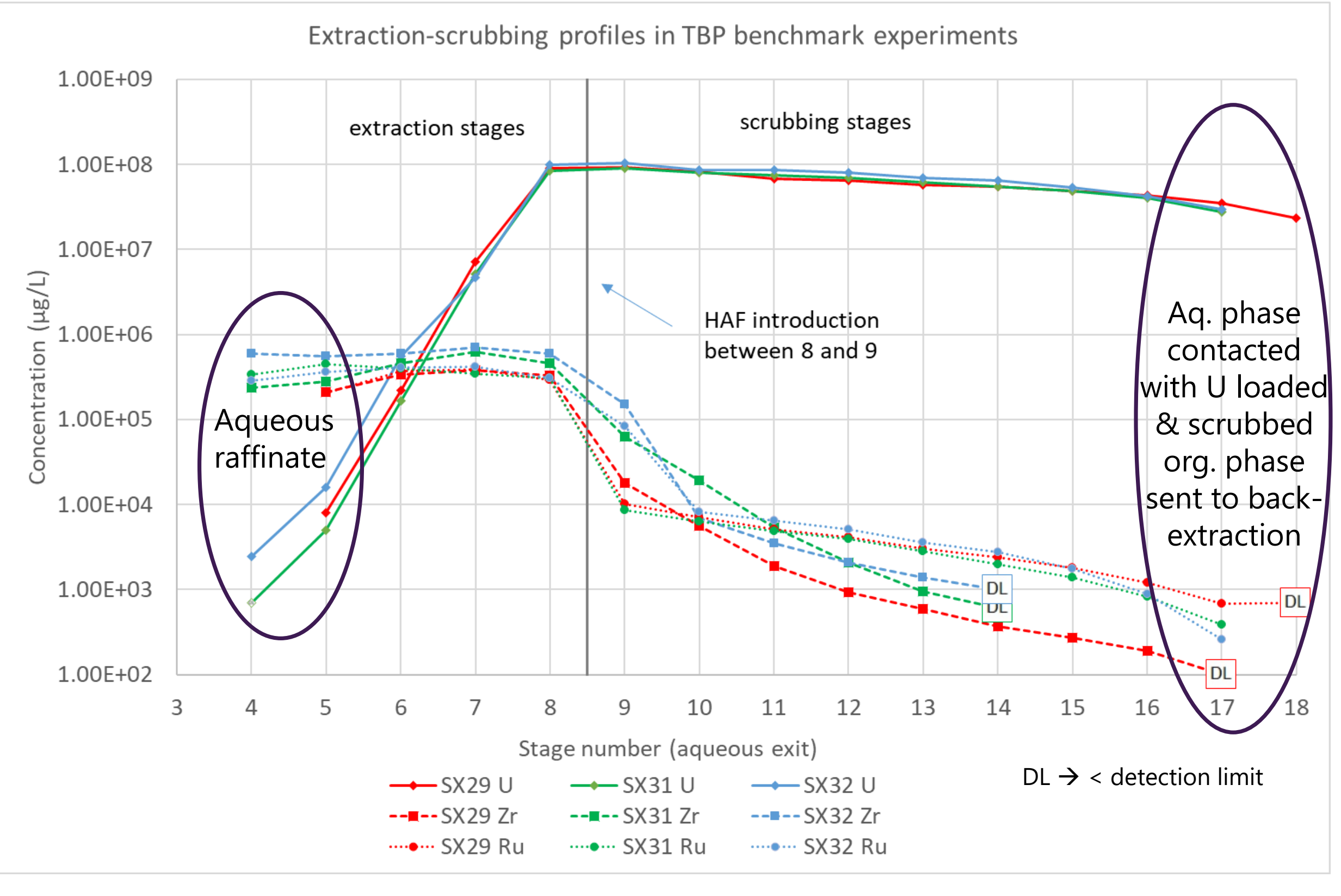

Figure 4: Multi-stage extraction-scrubbing concentration profiles in 3 TBP benchmark experiments

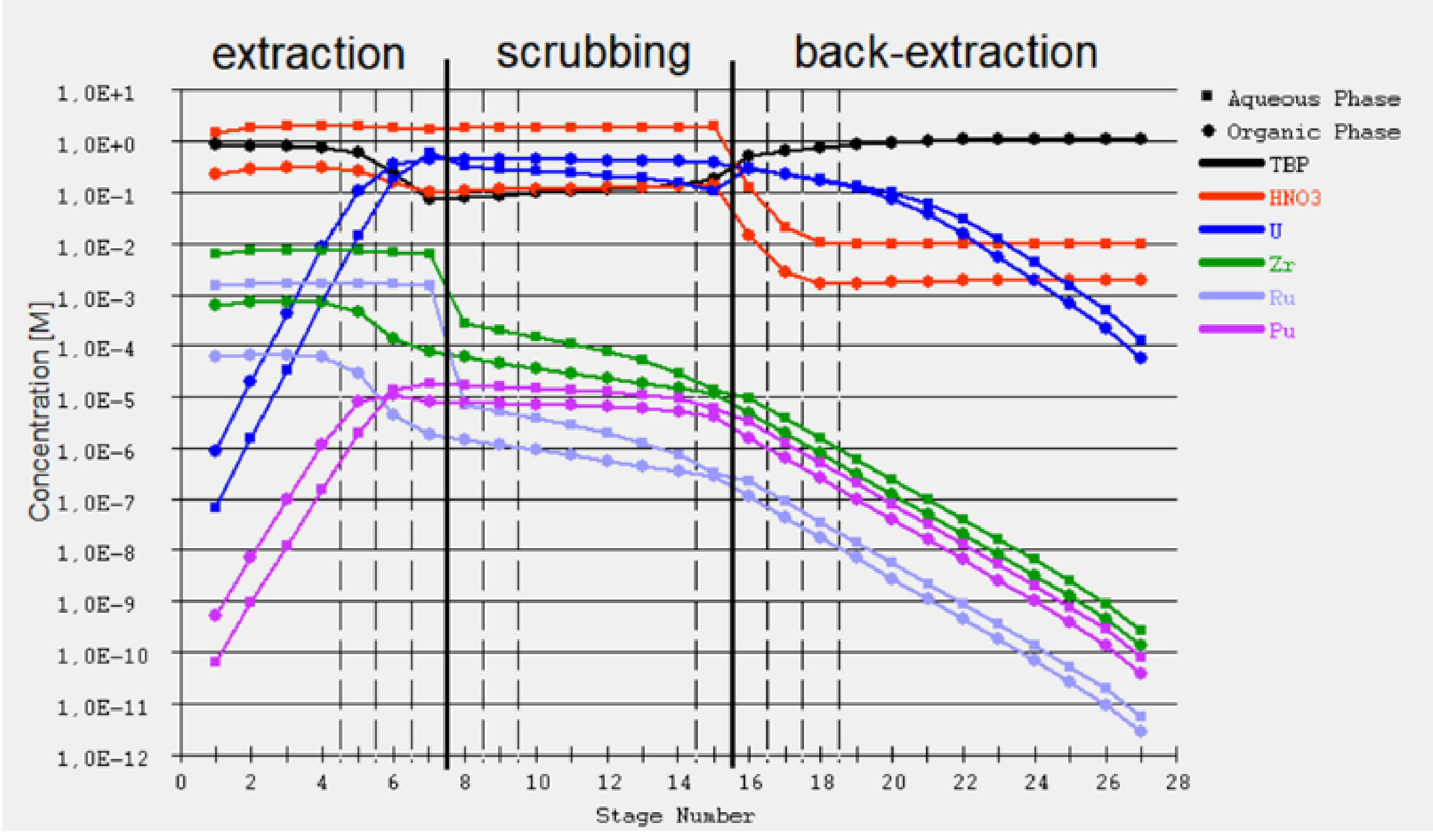

Figure 7: Flow sheet modelling of TBP process with SX Process software

1st tests with D2EHiBA for selective U extraction (Figure 6)

- Better Ru & Zr decontamination vs. TBP benchmark
- Lower throughput → to be improved

SX Process software used to model TBP based LLE process (Figure 7)

- Program requires description of all distribution ratio’s → D = $[M]_{org}/[M]_{org}$ in function of $[HNO_3]_{aq}$ and $[M]_{aq}$ → calculated from extraction isotherms in MATLAB
- Other input parameters: # stages, flow rates, stage efficiency,..

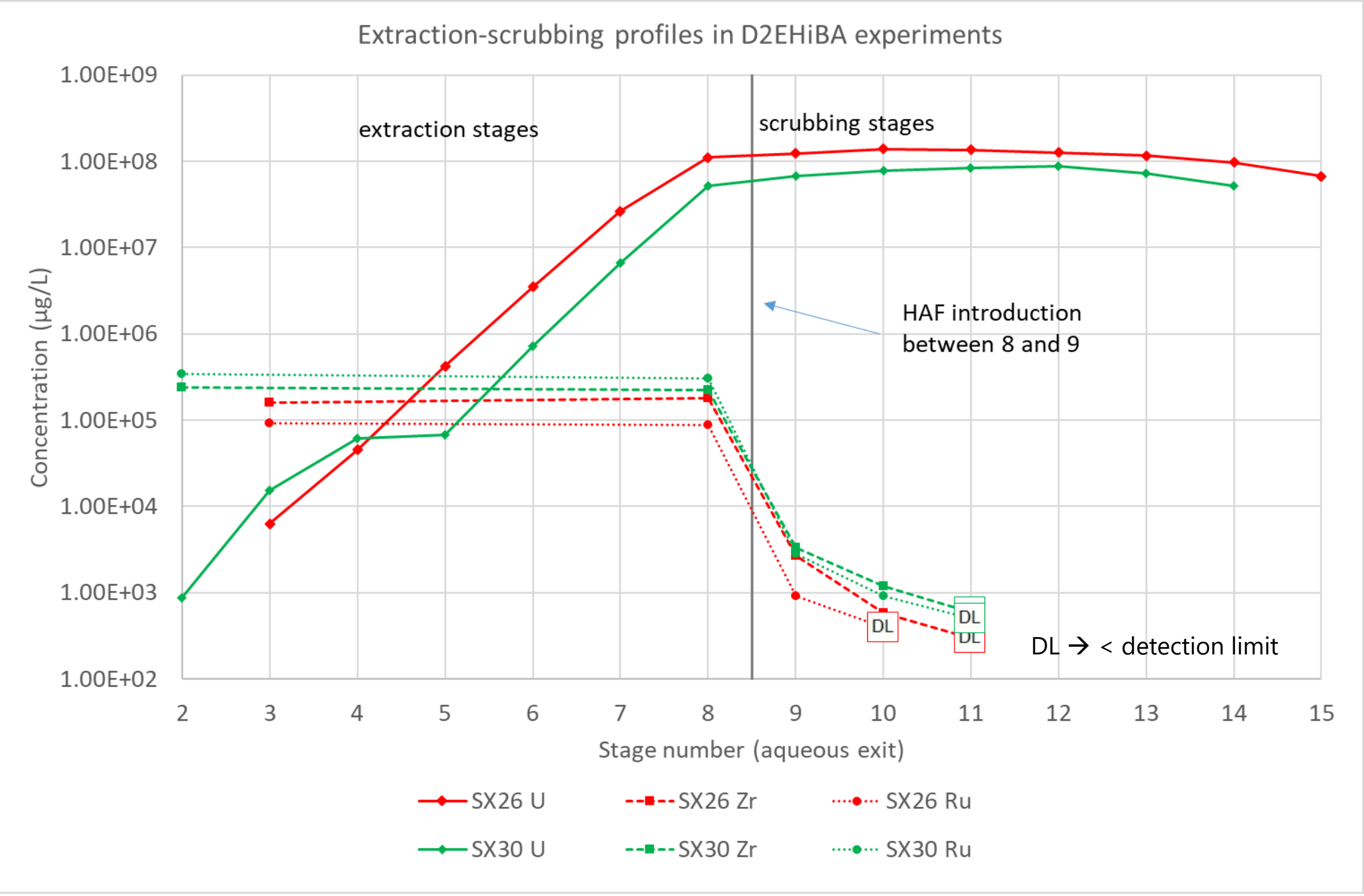

Figure 6: Multi-stage extraction-scrubbing concentration profiles in 2 D2EHiBA experiments

Discussion

- First adaptations to ACC were performed → difference in average residence time of factor of 5 obtained between scrubbing and extraction section of the LLE process
- Benchmark experiments with TBP revealed efficient U extraction but challenging Zr & Ru decontamination
- Mass transfer efficiency (reaction kinetics) to be investigated → determination of interfacial surface area in mixer required
- N,N-dialkylamide D2EHiBA already showed great potential to replace TBP for selective U extraction process
- Modelling software → excellent tool for flow sheet optimizations

Future work

- Optimization of TBP system taking reaction kinetics & stage efficiency into account → significant improvements expected from longer contact times in scrubbing & shorter in extraction
- Collection of batch data for each N,N-dialkylamide extractant to obtain necessary extraction isotherms: $[M]_{org}/[M]_{org}$ in function of $[HNO3]_{aq}$ and $[M]_{aq}$ → calculate function descriptions of distribution ratio (D) for SX Process software → simulate optimized flow sheets
- Compare N,N-dialkylamides processes to optimized TBP system
- Further investigate deviations between SX Process model predictions & batch equilibrium data → non-equilibrium solvent extraction

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