Mass Transfer Intensification Implementing the Use of Static Mixers in Co/Ni Solvent Extraction

Derik J. van der Westhuizen
derik.vanderwesthuizen@nwu.ac.za

[1]Johan W. Bezuidenhout, [1]Reynhard van der Berg [1]Burgert B. Hattingh, [2]Derik J. van der Westhuizen

[1]School of Chemical and Mineral Engineering, North-West University, South Africa
[2]RFA: Chemical Resource Beneficiation, Hydrometallurgy group, North-West University, South Africa

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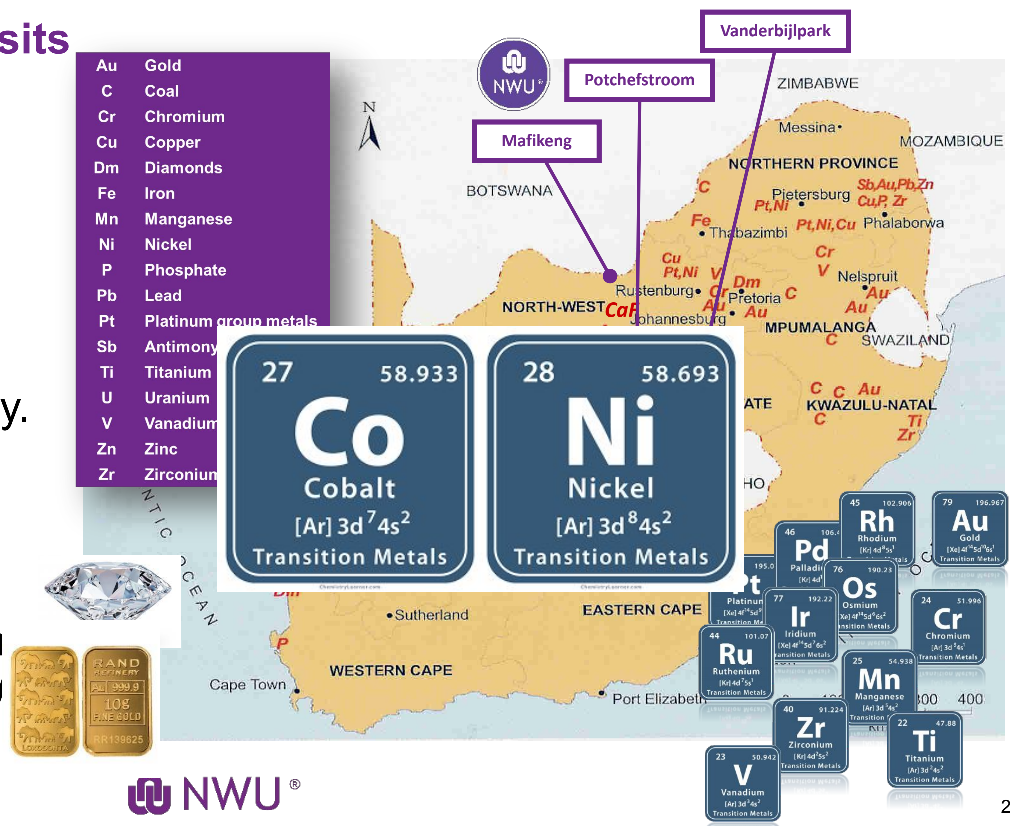
Introduction

South African mineral deposits

- RSA have the **world's 5th-largest mining sector** (gross domestic product value)
- **Mining companies** are key players in the **global** industry.
- SA holds the world's largest reported reserves of **Au** (30%), **PGMs** (88%), **Cr** (72%) and **Mn** (80%), and th 2nd-largest reserves of **Zr, V** and **Ti.**

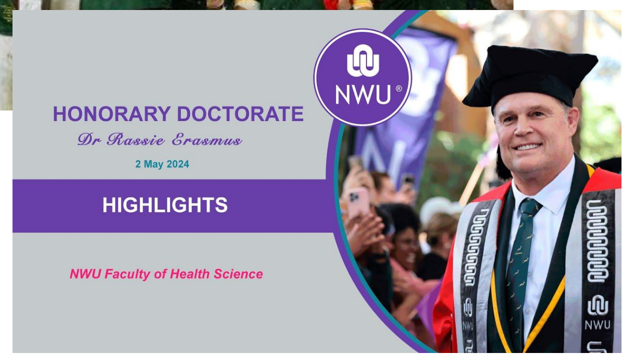


Introduction

South African mineral deposits

Country	Number of wins (years)
South Africa	**4** (1995, 2007, 2019, 2023)
New Zealand	3 (1987, 2011, 2015)
Australia	2 (1991, 1999)
England	1 (2003)

SPRINGBOKS



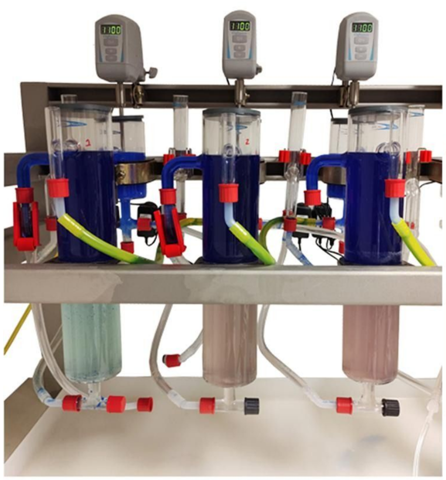
Introduction

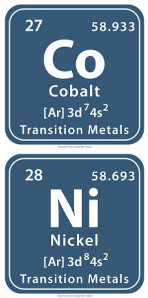
Critical Minerals: Co/Ni

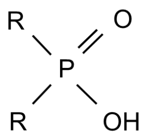
- Global Co/Ni demand is increasing
- Driven by:
  - stainless steel
  - electric vehicle
  - **energy storage solutions**

Introduction

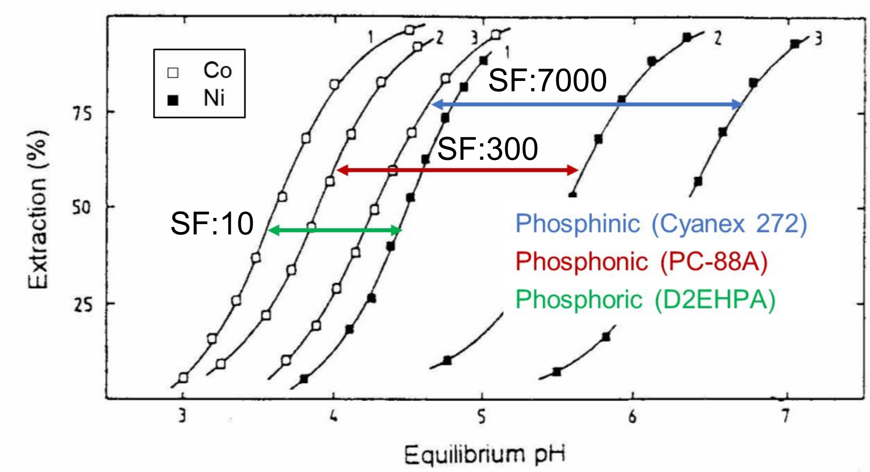
Co/Ni separation: SX







CYANEX® 272
(dialkyl phosphinic acid)

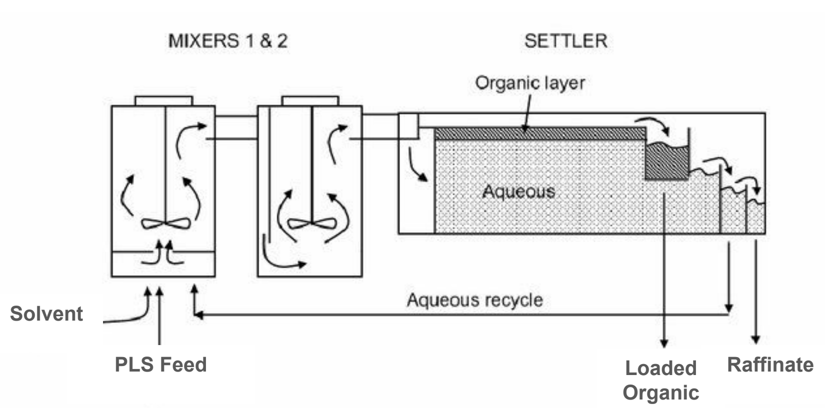


Cyanex 272:

- more stable to oxidative degradation by Co(III)
- more selective for Co over Ca
- minimises crud formation

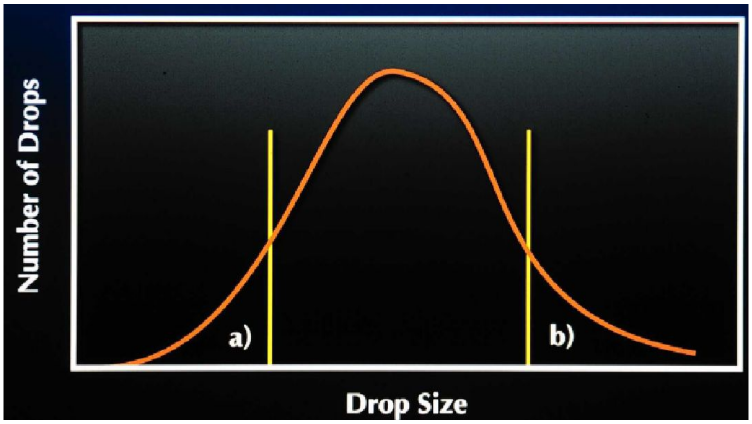
Introduction

SX contactors: Mixer-settlers



Introduction

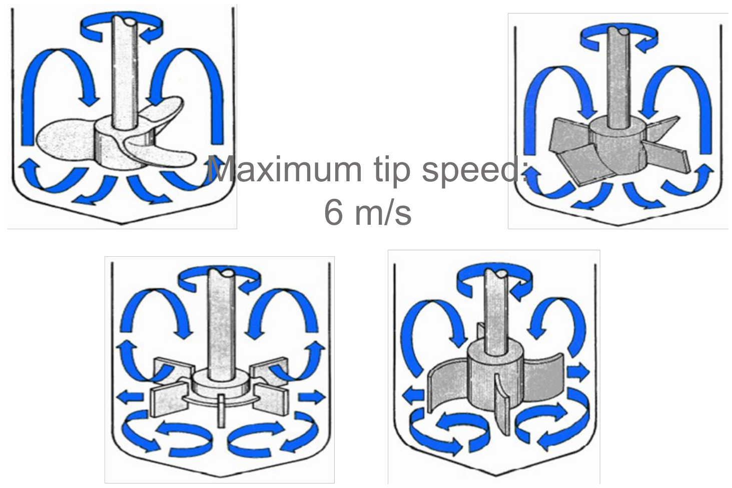
SX contactors: Mixer-settlers



a) Drops too small: tend to entrain

b) Drops too large – slow transfer kinetics

Rule-of-thumb: 100-150 µm



Maximum tip speed: 6 m/s

Introduction

SX contactors: Mixer-settlers

Foaming

Introduction

SX contactors: Mixer-settlers

Crudding

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https://www.metso.com/portfolio/vsf-x-solvent-extraction-plant/

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Introduction

SX contactors: Mixer-settlers

Organic Recovery Systems (Coalescers)

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Courtesy of Peter Cole

NWU®

Introduction

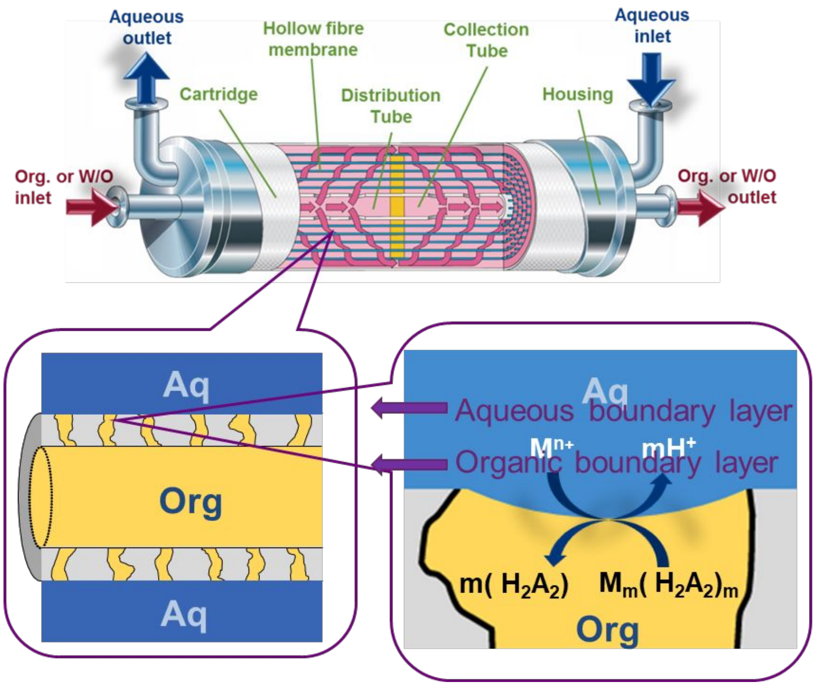
SX contactors: Pertraction (PX)

The "microfiltration" membrane:

- Does not filter
- Bubble point larger than 100 kPa
- Low diffusion resistance: thin (30 mm) and porous (40-50%)
- Compatible with solvent and feed: PP-HF & PE-potting

The contactor module:

- High area: 40-400 m^2
- Hydraulic diameter: 0.3-1 mm
- Low pressure drop: < 10 kPa/m @ V_{sup} = 2 cm/s
- Low cost: ± 50 USD/m^2

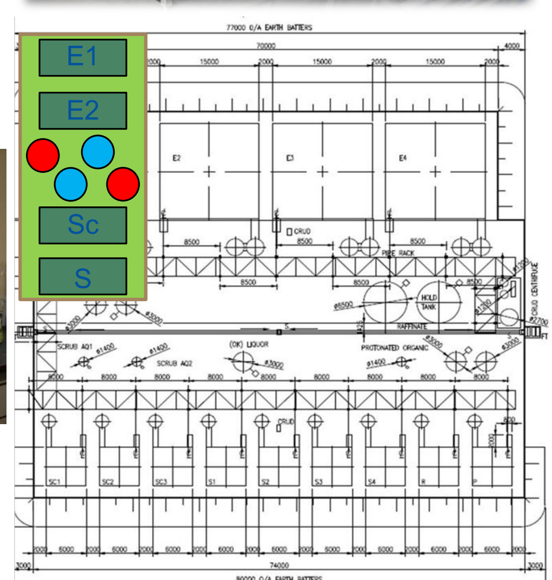


Introduction

SX contactors: Pertraction (PX)

Advantages

- High, well defined mass transfer area
- No flooding/crud: process control
- Less rotating equipment: maintenance
- Less solvent holdup & closed operation: safety
- Smaller footprint: CAPEX



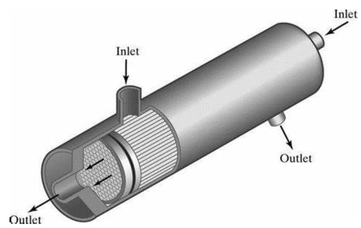
Challenges

- Membrane replacement cost
- No proven technology
- **Extra mass-transfer resistance**

Scope of study

SX contactors: Hybrid Pertraction (HPX)

“Rapid mixing and phase separation”

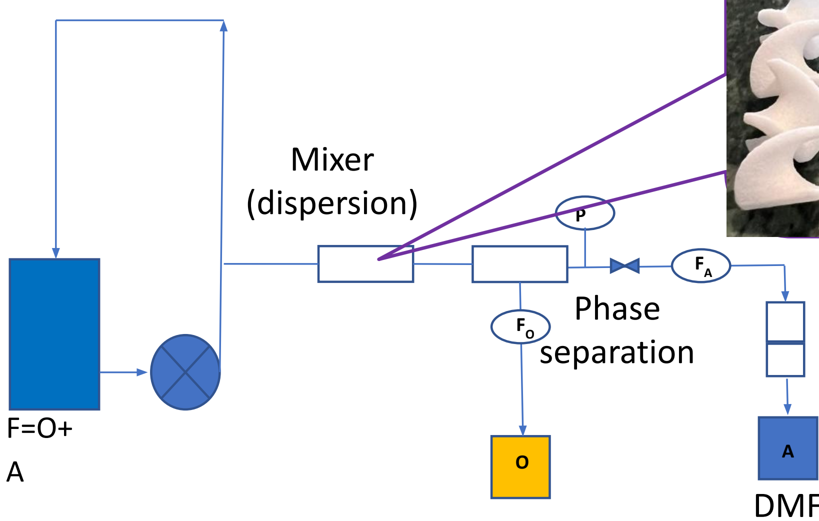


Hollow fibre membrane contactors

- Feed/Solvent Dispersion is fed into HFM
- Solvent droplets coalesce on fibre inner wall
- Solvent selectively permeates over membrane to module shell-side
- Aqueous Feed retained on lumen-side

Introduction

SX contactors: Hybrid Pertraction (HPX)



To maintain a transient flow regime:

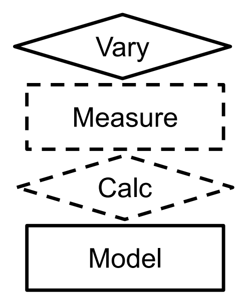
- Kenics
- Sulzer SMX

Aim & Objectives

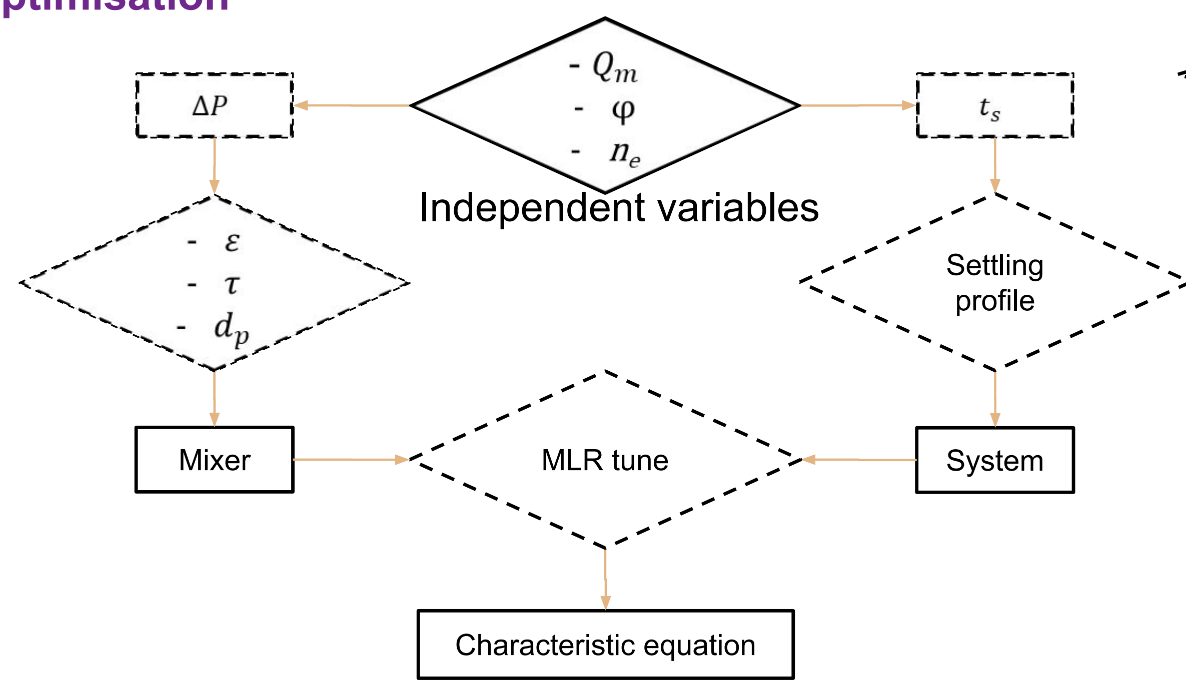
The aim of this study is to assess the suitability of static mixers to enhance the mass-transfer rate by reducing the Sauter mean diameter of the dispersion for a Co/Ni solvent extraction system.

- **Objectives:**
  - Prediction of the diffusion coefficients for a Co/Ni system
  - Comparison of the residence time and the Sauter mean diameter
  - Static mixer model determination and validation in a non-reactive system
  - Evaluation of the static mixer model in a reactive Co/Ni system
  - Assessment of phase separation in a hollow-fibre membrane

Methodology

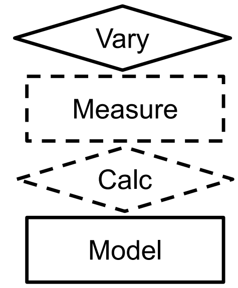


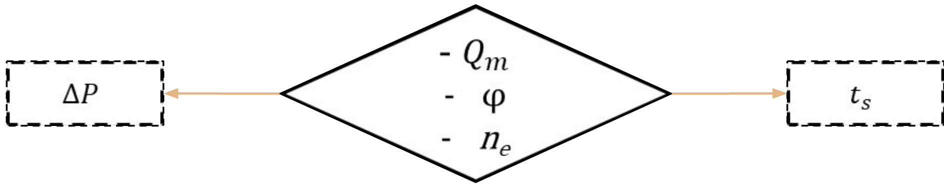
Mixing optimisation

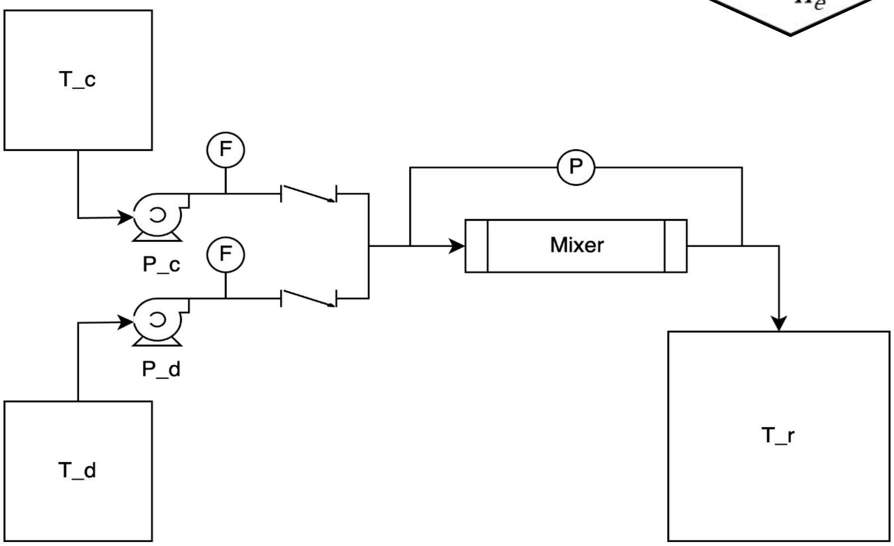


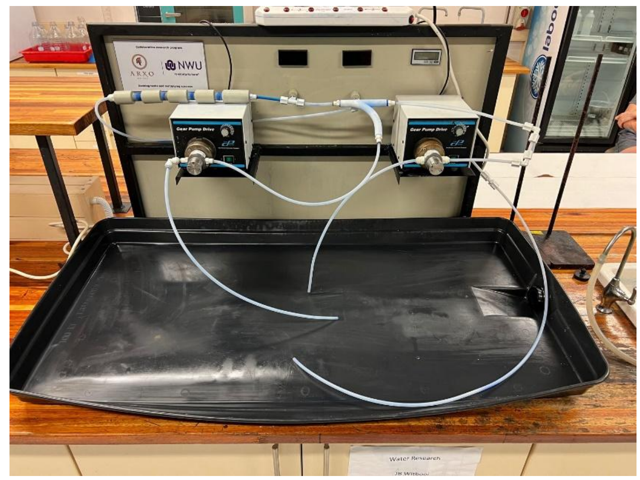
Methodology

Mixing optimisation



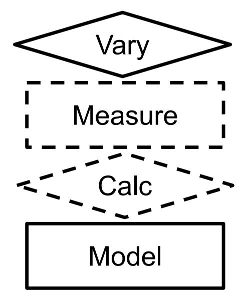


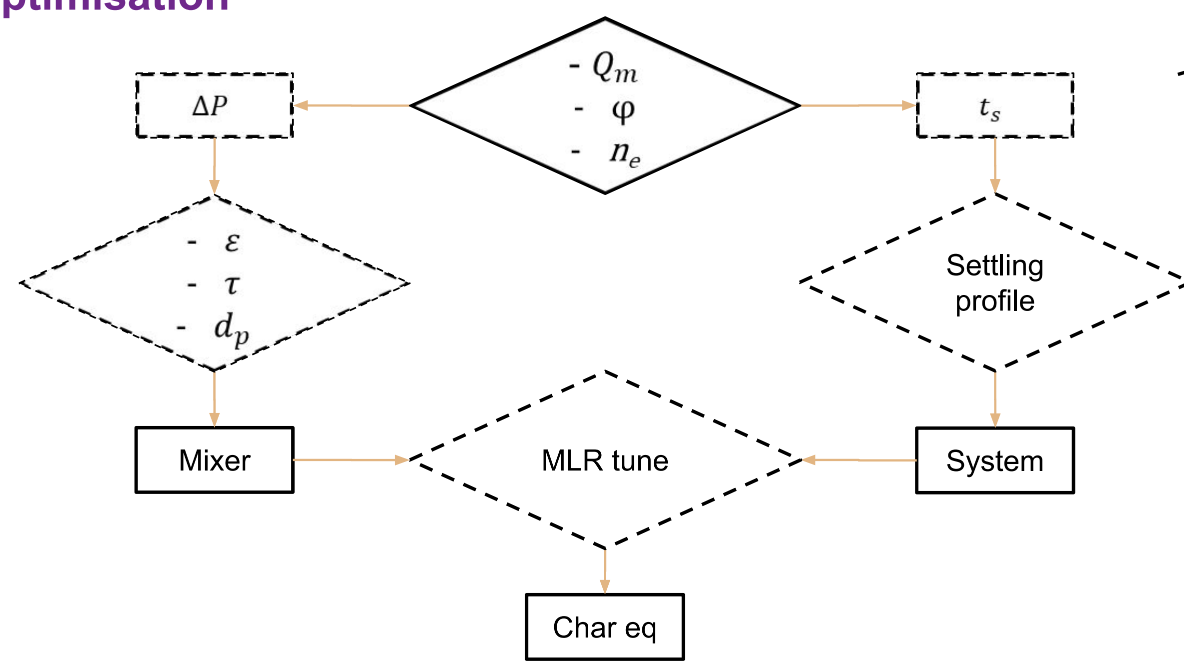




Methodology

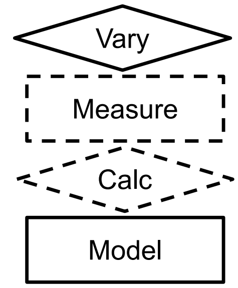
Mixing optimisation

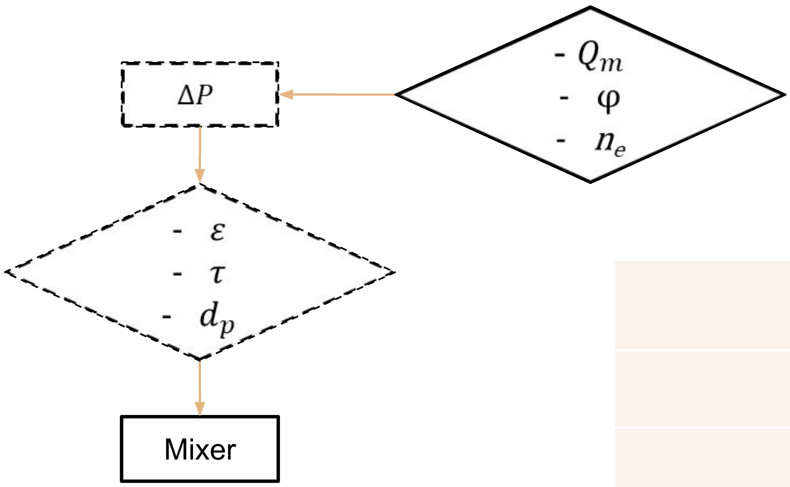




Methodology

Mixing optimisation





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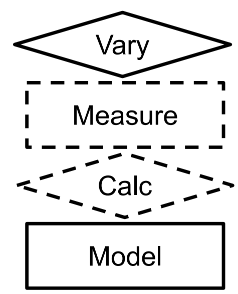
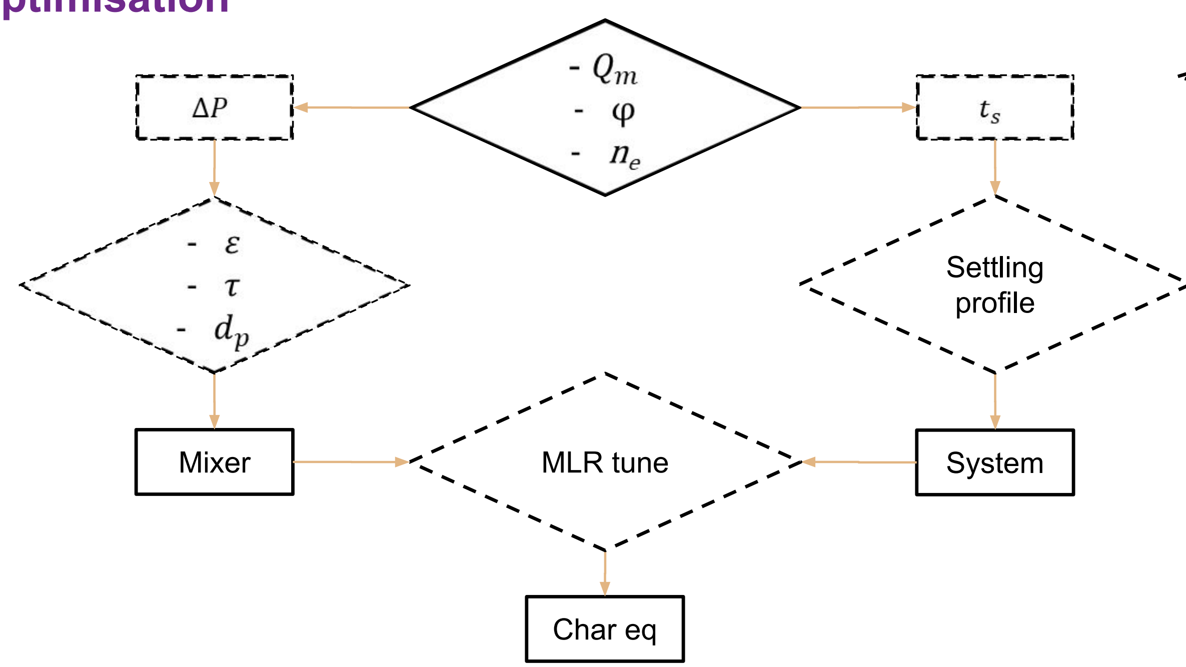
Morancais, P., et. al., 1999. Chemical Engineering Communications, 171(1), 77-93.

Methodology

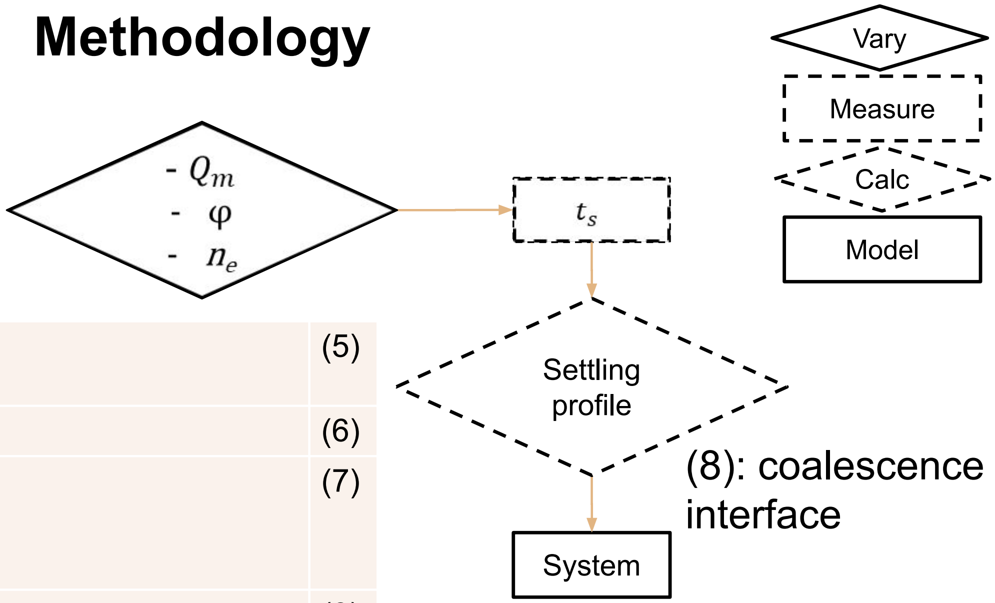
Mixing optimisation





Methodology

Mixing optimisation



	(5)
	(6)
	(7)
	(8)

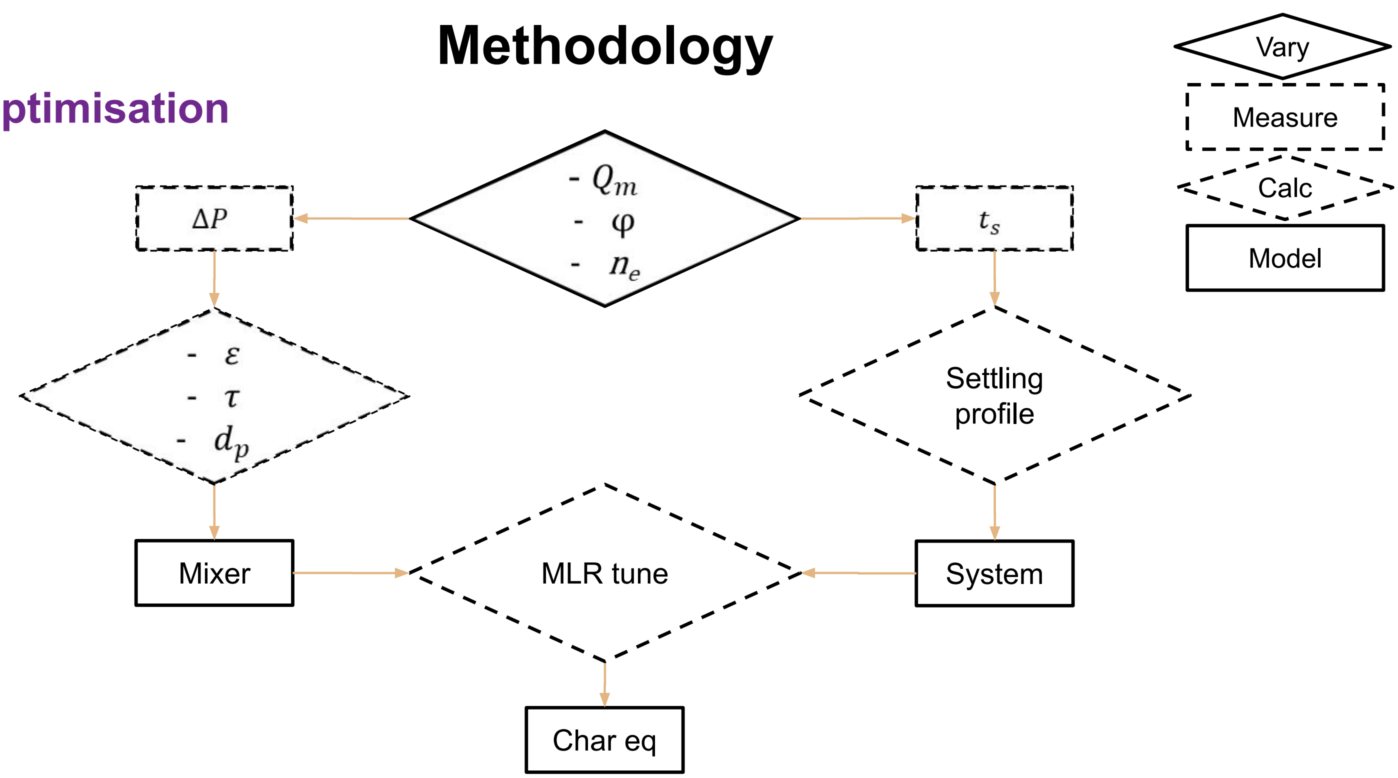
(non-linear regression)

Kumar, A. et al.., 1985. The Canadian Journal of Chemical Engineering, 63(3), 368-376.

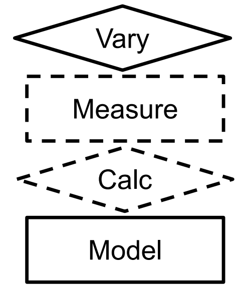
Yu, G.Z. et al.. 2004. Engineering-Biotechnology, 27(4):407-413.

Methodology

Mixing optimisation



Methodology



Mixing optimisation

(9)

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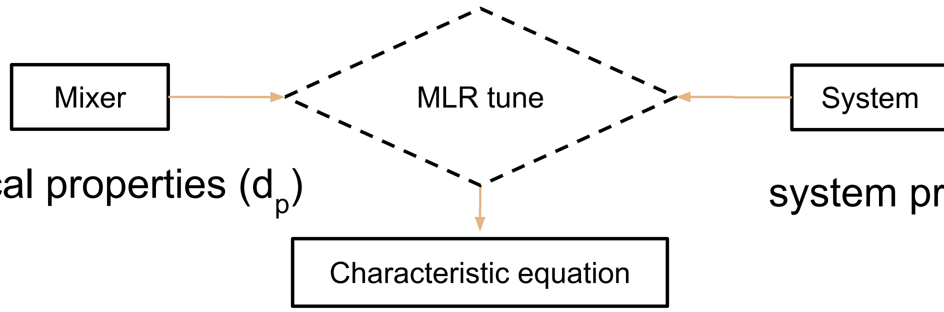


mixer physical properties (d_p)

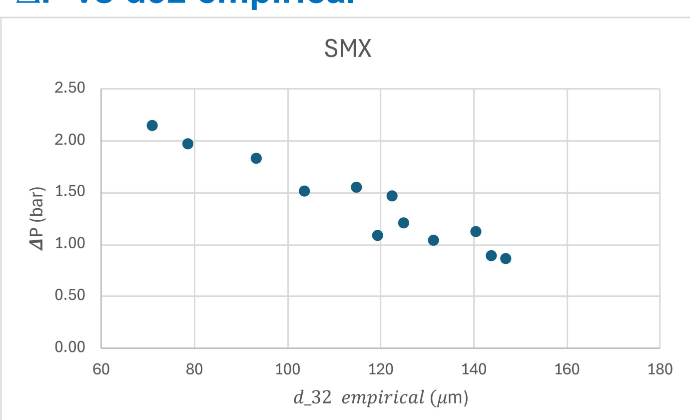
system properties (d_{32})

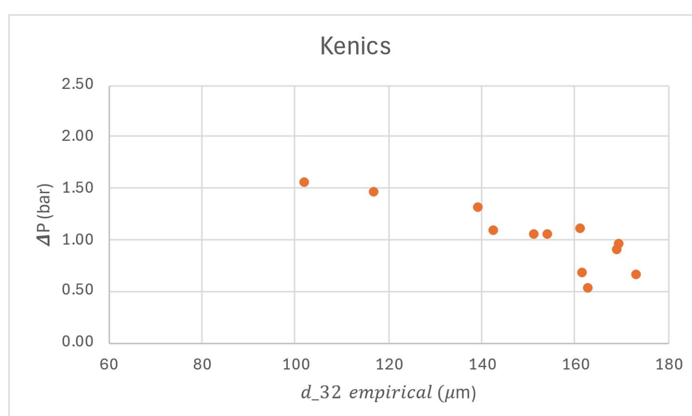
(each mixer)

Results and Discussion

Mixing optimisation

ΔP vs d32 empirical



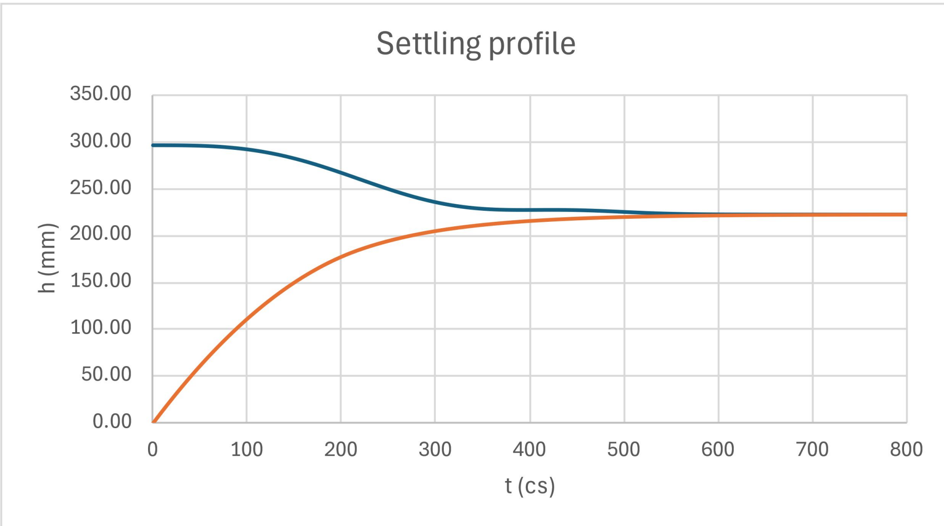


- Kenics: lower pressure drop
- However: increased droplet sizes

Results and Discussion

Mixing optimisation

Settling graph

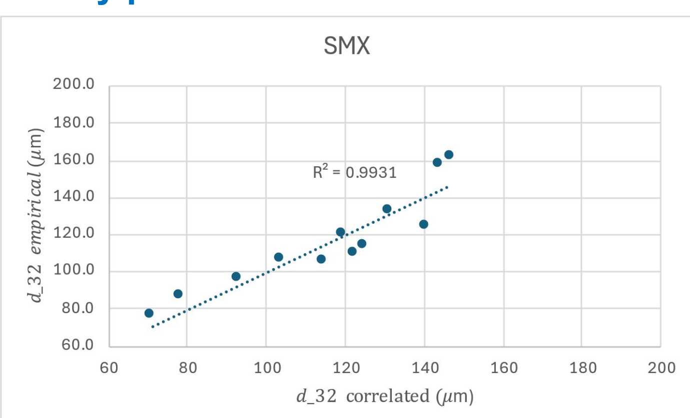


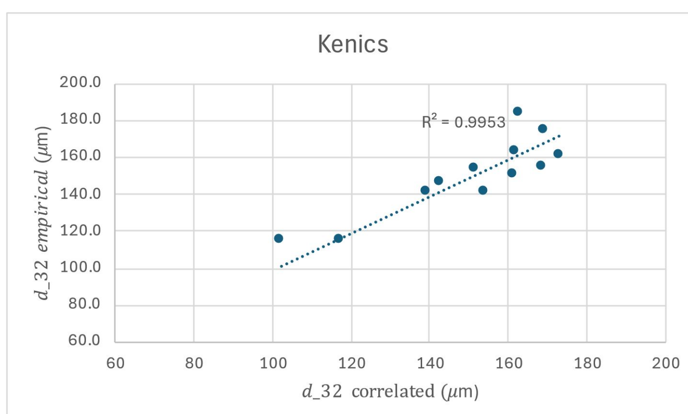
- The data could be fairly well fitted
- The suitable data were used to better approximate j and k
- Used to correlate the empirical Sauter diameter more efficiently

Results and Discussion

Mixing optimisation

Parity plots





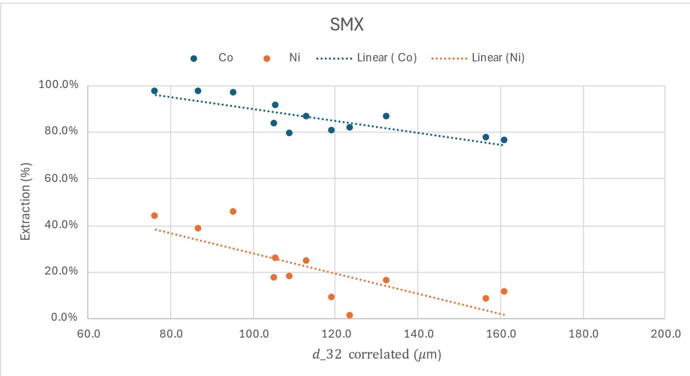
	SMX	Kenics
α	36.42	45.55
β	-4.04	-6.12
γ	1.37	2.83
δ	-0.21	-0.05

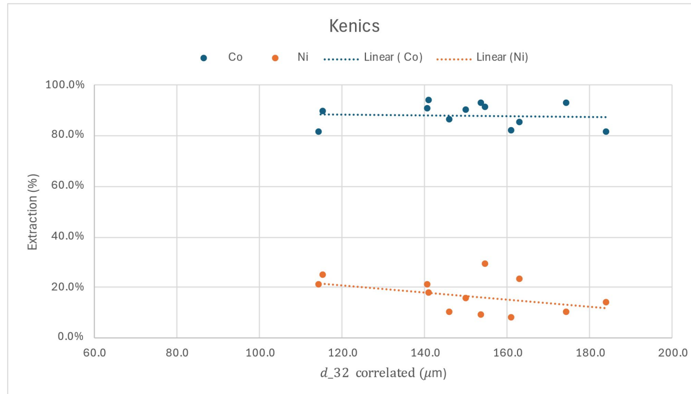
- Kenics: Smaller distribution, but better fit

Results and Discussion

Mixing optimisation

%E vs correlated d32





- The smaller droplets in the SMX: higher Co extraction
- Larger droplet size: decreased the extraction rapidly

- Kenics: better contact obtained
- However, a relative higher Ni transfer was also obtained – reduce selectivity

Scope of study

SX contactors: Hybrid Pertraction (HPX)

"Rapid mixing and phase separation"

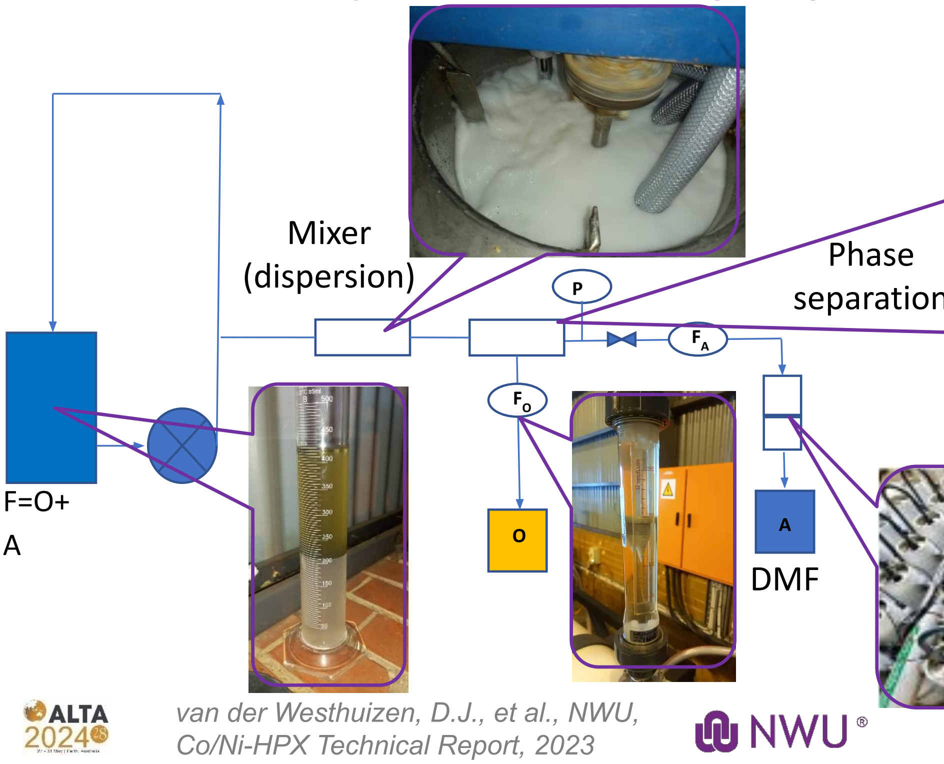
Hollow fibre membrane contactors

- Feed/Solvent Dispersion is fed into HFM
- Solvent droplets coalesce on fibre inner wall
- Solvent selectively permeates over membrane to module shell-side
- Aqueous Feed retained on lumen-side

van der Westhuizen, D.J., et al., NWU, Co/Ni-HPX Technical Report, 2023

Introduction

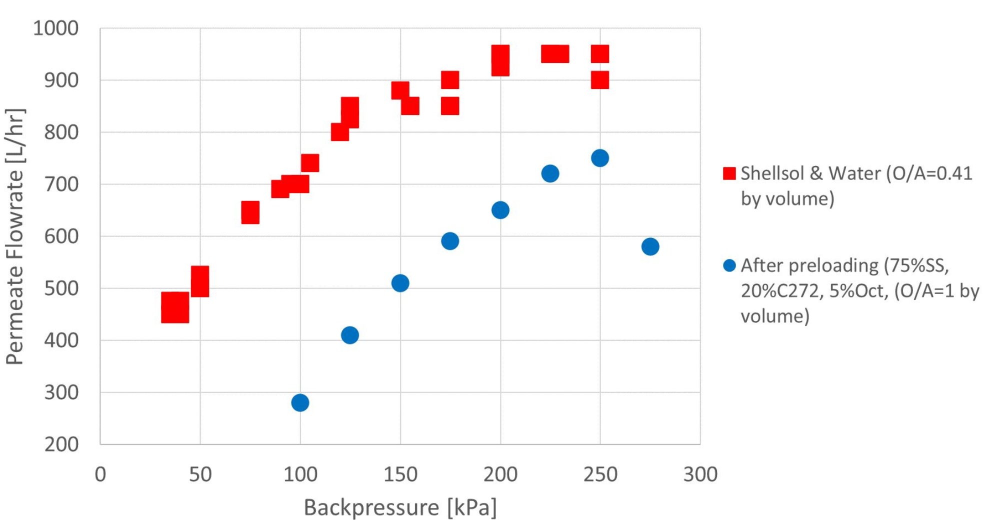
SX contactors: Hybrid Pertraction (HPX)



Results and Discussion

Phase separation

Permeate flowrate as a function of retentate back-pressure



Evident that:

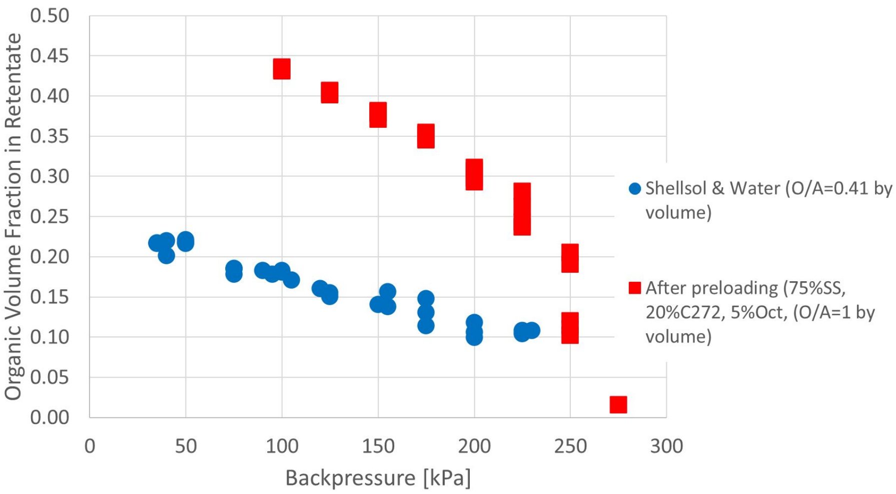
- System can be controlled
- Obtain a clean permeate
- Dispersion Viscosity effects the flow rates directly

- Next step: Co/Ni-system

Results and Discussion

Phase separation

Clarification of retentate (aqueous raffinate)



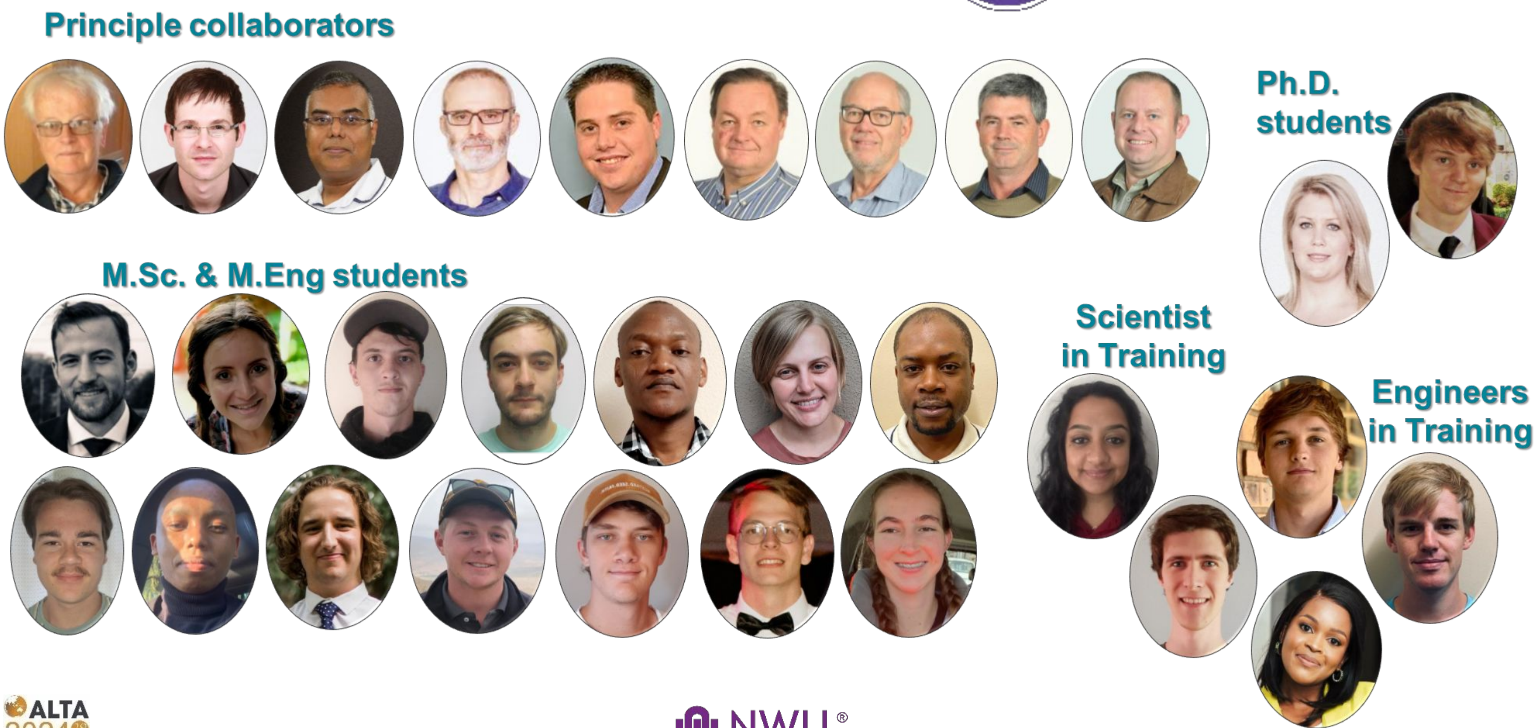
- At 270kPa < 1% Org in retentate
- Needs to be reduced further to < 10ppm
- At max back-pressure: the org fraction SS-H_2O equals the C272-H_2O

van der Westhuizen, D.J., et al., NWU, Co/Ni-HPX Technical Report, 2023

Conclusion and Future work

- Static-mixer connected with an overhead stirrer and homogeniser produces milky dispersion and generates feed pressure to HPX module.
- 8x80 Liqui cell separates aqueous from the organic with a clear organic permeate but does not produce clear aqueous retentate (yet).
- DMF removes fine organic droplets from oil in water dispersion, but it is not effective enough.
- Use PPG hydrophilic membranes as clarifier (<10ppm).
- Procure on-line turbidimeter.
- Repeat and optimise for real feed solution, incl. Ni-scrubbing and Co-stripping

Thank you!



Questions?

Contact details:

Group leader: Derik van der Westhuizen
E: derik.vanderwesthuizen@nwu.ac.za
T: +27182992346
W: https://natural-sciences.nwu.ac.za/hydrometallurgy

Droplet Size and mass transfer modelling

- GENERAL INFO
- WHY?
- AIM

Mass transfer modelling

- Mass transfer occurs between the dispersed and continuous phase and is described by diffusion and reaction parameters.
- Mass transfer is halted when the dispersed and continuous phase are in equilibrium – This occurs at the equilibrium time t_{eq}.
- The equilibrium time, t_{eq}, is dependent on the radius of the droplets in the dispersed phase.

Mass Transfer Modelling

- Model Assumptions
  - All dispersed droplets are spherical
  - The concentration of the extractant species is equal at all points within the droplet at $t = 0$.
  - The surface of the droplet is always in equilibrium with the dispersed and continuous phase
  - …

Mass Transfer Modelling

- The rate of extraction can be written as the combined effect of radial diffusion and the reaction rate.

$$\partial_t c_i = D_{ij} \left\{ \partial_r^2 c_i + \frac{2}{r} \partial_r c \right\} + R_i$$

- The solution of the reaction-diffusion rate equation can be deduced from the non-reactive diffusion equation considering the following boundary conditions and taking $u = rc_1$.

$$u = 0, \qquad r = 0 \; \forall \; t > 0$$

$$u = rc_0, \qquad t = 0 \; \forall \; r \in (0, r_s)$$

$$u = r_s c_{eq}, \qquad t > 0, \qquad r = r_s$$

- For the purpose of model simplification, we assume that the reaction rate, R_i, is first order and given by

$$R_i = k_1 c_i$$

In this case k_1 becomes a fitting parameter

Mass Transfer Modelling

- Using Danckwert's method (reference) the solution to the reaction-diffusion model is given by:

$$c = k_1 \int_0^t c_1 e^{-k_1 t'} dt' + c_1 e^{-k_1 t}$$

which equates to

$$c = \left(2e^{-k_1 t} - 1\right)\left\{\{c_{eq} - c_0\}\left\{1 + \frac{2r_s}{\pi r}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sin\frac{n\pi r}{r_s}\exp(-Dn^2\pi^2 t/r_s^2)\right\} + c_0\right\}$$

- Rewriting the solution in the form $(c - c_0)/(c_{eq} - c_0)$ allows for dimensionless analysis of the equilibrium time needed for the extraction, scrubbing or stripping to occur. This also allows the user to investigate the concentration distribution of a component at any radial position within the droplet as a function of time

Mass Transfer Modelling

- MODEL PROS and CONS (TABLE FORMAT)
- The model can be used to estimate equilibrium times based on droplet sizes produced using chosen mixer types or to estimate droplet sizes based on target equilibrium times for a specific system
- The model can be applied to almost any dispersive extraction system – both non-reactive and reactive extraction.
- *The model associates a fitting parameter – Value must be determined experimentally (SOFAR…)*
- *The model does not consider physical interactions in the mixing process*
  - *coalescence, shearing, etc…*

Model Validation – Cobalt Solvent extraction with Cyanex 272

Literature, constants, initial conditions, etc.

Finding Diffusivity and Equilibrium

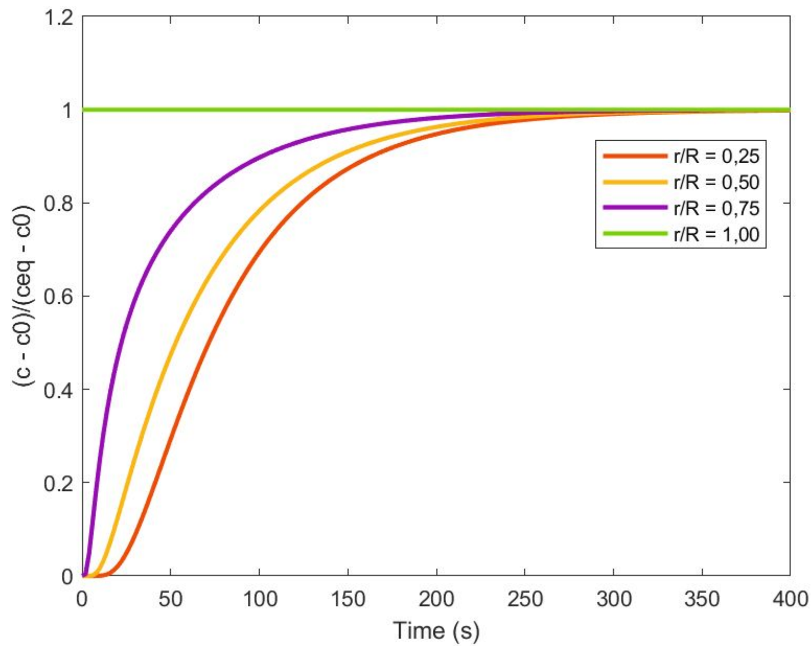
Shake Flask Tests for equilibrium composition determination

Molecular Dynamics Simulations for Diffusivity determination

- Amorphous cell – Organometallic species, Solvent environment, etc.
- Forcite geometry optimizations, cell annealing cycles and Molecular dynamics simulations
- Mean Square displacement and curve fitting
- Determination of the Diffusivities

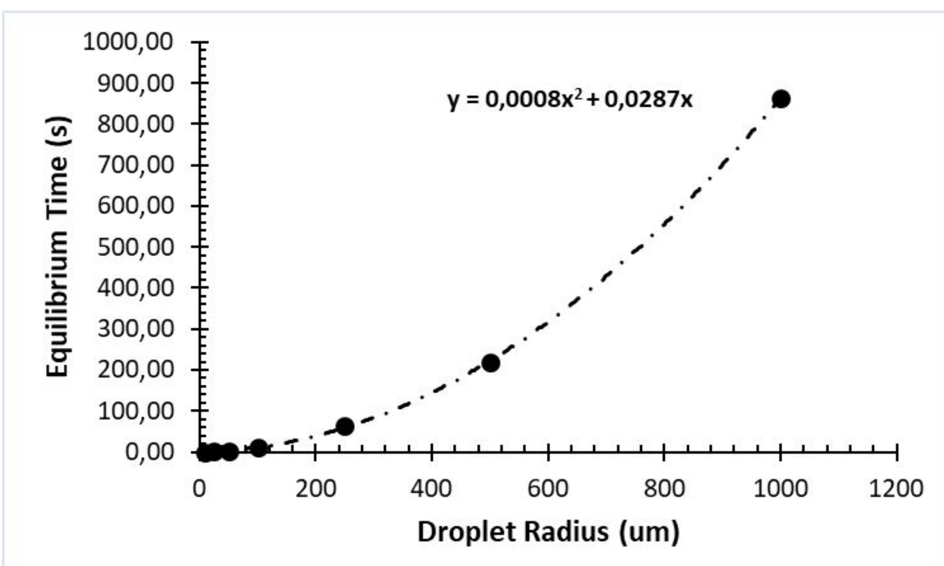
Cobalt Mass Transfer model

- Results based on values and constants from literature vs results from MDS
- Equilibrium times are chosen such that all radial positions converge at unity



Equilibrium time vs droplet size

- Extrapolated equilibrium times compared to various droplet sizes with curve fitting to suitable function



Mixing optimisation

Extraction efficiency $\propto \frac{1}{d_{32}}$

Static mixers

- Static mixers consist of moulded elements, e.g., vanes or baffles, housed in a tube
- These elements are engineered to form tortuous pores
- Turbulent flow is often realised within these narrow pores
- Flow down these pores causes vortices and eddies that promote mixing
- Contact is increased between the solution and solvent

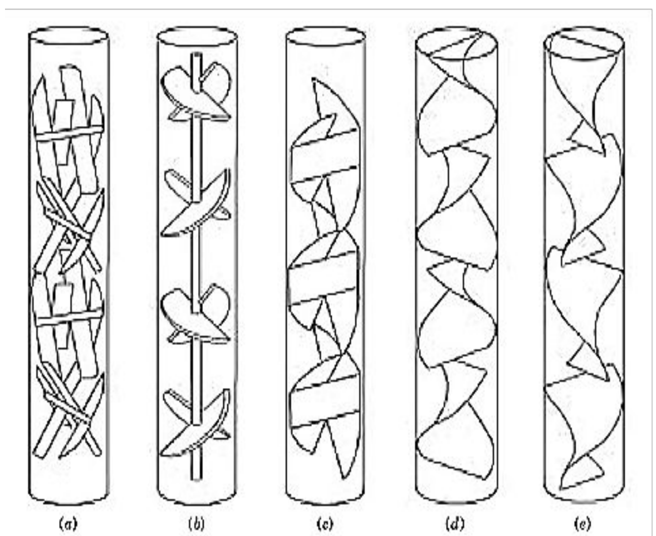
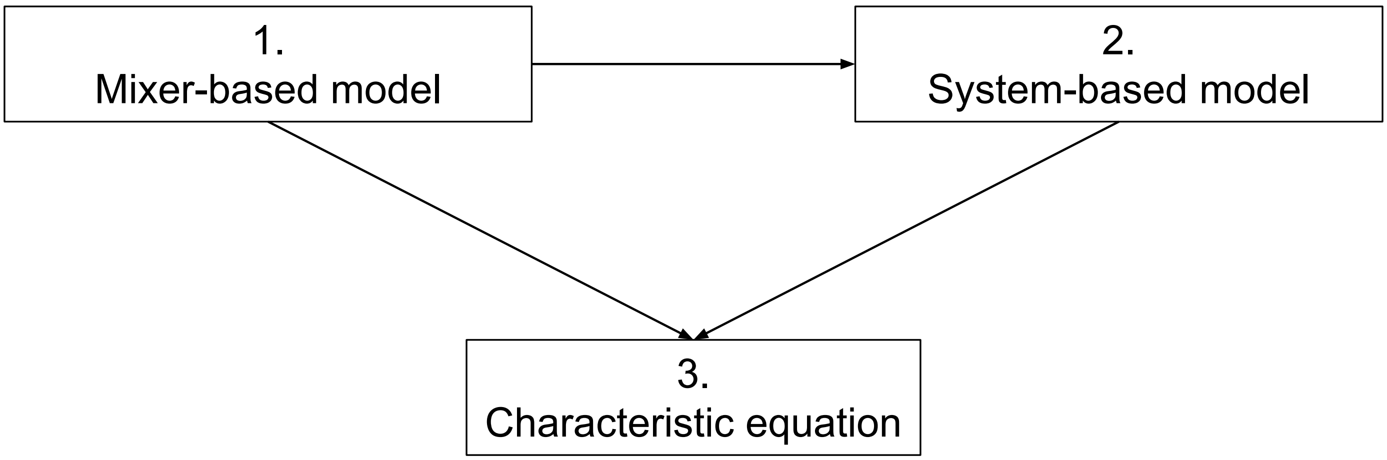


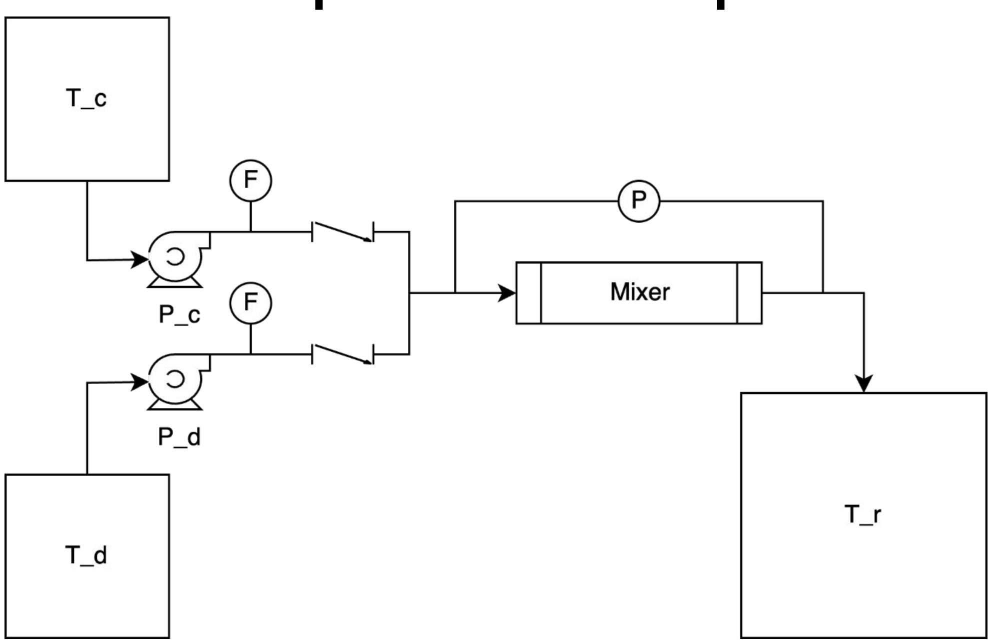
Figure 1: Examples of static mixers
(a) Sulzer SMX (b) Ross LPD (c) Komax (d) Kenics (e) FixMix

Adapted from: Gyenis, J., 2002. Motionless Mixers in Bulk Solids Treatments–A Review. KONA Powder and Particle Journal, 20, pp.9-23.

Experimental regime



Experimental setup



T_c: Continuous phase tank; T_d: Dispersed phase tank; T_r: Residence tank;
P_c: Continuous phase pump; P_d: Dispersed phase pump; F: Flowmeter; P: Pressure meter.

Experimental regime variables

- Independent variables:
  - Mixture flow rate
  - Oil fraction
  - Number of mixing elements
- Dependent variables:
  - Pressure drop over the mixer
  - Settling time of the dispersion

Experimental regime

1.
Mixer-based model

- Measure the pressure drop over the mixer
- Calculate:
  - Porosity
  - Tortuosity
  - Pore diameter

using the method from Morancais *et al. (1998)*.

Mixer-based model

- Porosity:

$$\varepsilon = \frac{v_0}{v}$$

with v_0: void volume (m^3); v: mixer volume (m^3).

- Pore diameter (m):

$$d_p = \left(\frac{32}{K}\right)^{0.75} \left(\frac{J}{0.3872}\right)^{0.5} \varepsilon^{0.25}$$

- Tortuosity:

$$\tau = \left(\frac{32}{K}\right)^{0.25} \left(\frac{J}{0.3872}\right)^{0.5} \varepsilon^{0.75}$$

J, K: slope and intercept of pressure drop equation.

Mixer-based model

- Pressure drop equation [1]:

$$\frac{\Delta P}{L \mu_m U_s} = J \frac{\rho_m U_s}{\mu_e} + K$$

with ΔP: pressure drop over mixer (Pa); L: length of mixer (m);
μ_e: viscosity of mixture ($Pa . s$); U_s: superficial velocity ($m . s^{-1}$);
ρ_m: density of mixture ($kg . m^{-3}$).

[1]: Morancais, P., Hirech, K., Carnelle, G. and Legrand, J., 1999. Friction factor in static mixer and determination of geometric parameters of SMX Sulzer mixers. *Chemical Engineering Communications*, *171*(1), pp.77-93.

Experimental regime

2.
System-based model

- Measure the settling time in T_r
- Calculate:
  - Experimental settling velocity
  - Calculated settling velocity
  - The Sauter mean drop diameter

using the method from Kumar & Hartland (1985).

System-based model

- Theoretical settling velocity $(m\,.\,s^{-1})$ [2]:

$$v_{0,calc} = \frac{12\mu_c}{0.53\rho_c d_{\max}}\left[-1 + \sqrt{1 + \frac{0.53\rho_c \Delta\rho g d_{\max}^3 (1 - \varphi)}{108\mu_c^2 (1 + 4.56\varphi^{0.73})}}\right]$$

with μ_c: Viscosity of continuous phase $(Pa.s)$; ρ_c: Density of continuous phase $(kg.m^{-3})$; $d_{\max}$: Maximum droplet diameter (m); $\Delta\rho$: Density difference $(kg.m^{-3})$; g: Acceleration due to gravity $(m.s^{-2})$; φ: Oil fraction.

[2]: Kumar, A. and Hartland, S., 1985. Gravity settling in liquid/liquid dispersions. *The Canadian Journal of Chemical Engineering*, *63*(3), pp.368-376.

System-based model

- Experimental settling velocity ($m\,.s^{-1}$):

$$v_{0,exp} = \frac{h_t - h_\mathrm{d}}{t}$$

with h_t: Total dispersion height (m); h_d: Height of dispersed phase (m); t: Settling time (s).

- $d_{32} = 3\beta d_{\max}$

with d_{32} : Sauter mean diameter (m); β: Size distribution parameter (≈ 0.13).

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Experimental regime

3.
Characteristic equation

- Calculate the tuning parameters specific to a static mixer using multiple linear regression.
- Oil fraction:

$$\varphi = \frac{\dot{Q}_d}{\dot{Q}_d + \dot{Q}_c}$$

with $\dot{Q}_c$, $\dot{Q}_d$: Continuous, dispersed phase flow rate ($m^3\,.s^{-1}$).

- Mixture flow rate ($m^3\,.s^{-1}$):

$$\dot{Q}_m = \dot{Q}_d + \dot{Q}_c$$

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Characteristic equation

- Mixture density ($kg\,.m^{-3}$):

$$\rho_m = \varphi\rho_d + (1-\varphi)\rho_c$$

with ρ_c, ρ_d: Continuous, dispersed phase density ($kg\,.m^{-3}$).

- Mixture viscosity ($Pa\,.s$):

$$\mu_m = \mu_c\left[1 + 2.5\varphi\left(\frac{\mu_d + 0.4\mu_c}{\mu_d + \mu_c}\right)\right]$$

with μ_c, μ_d : Continuous, dispersed phase viscosity ($Pa\,.s$).

Characteristic equation

- Superficial velocity ($m\,.s^{-1}$):

$$U_s = \frac{4\dot{Q}_m}{\pi D^2}$$

with D: Pipe diameter (m).

- Pore velocity ($m\,.s^{-1}$):

$$U_p = \frac{U_s\tau}{\varepsilon}$$

Characteristic equation

- Pore Reynold's number:

$$Re_p = \frac{\rho_e U_p d_p}{\mu_e}$$

- Pore Weber number:

$$We_p = \frac{\rho_e U_p^2 d_p}{\sigma}$$

with σ: Interfacial tension ($\mathrm{N}\,.\,m^{-1}$).

Characteristic equation

- Characteristic equation:

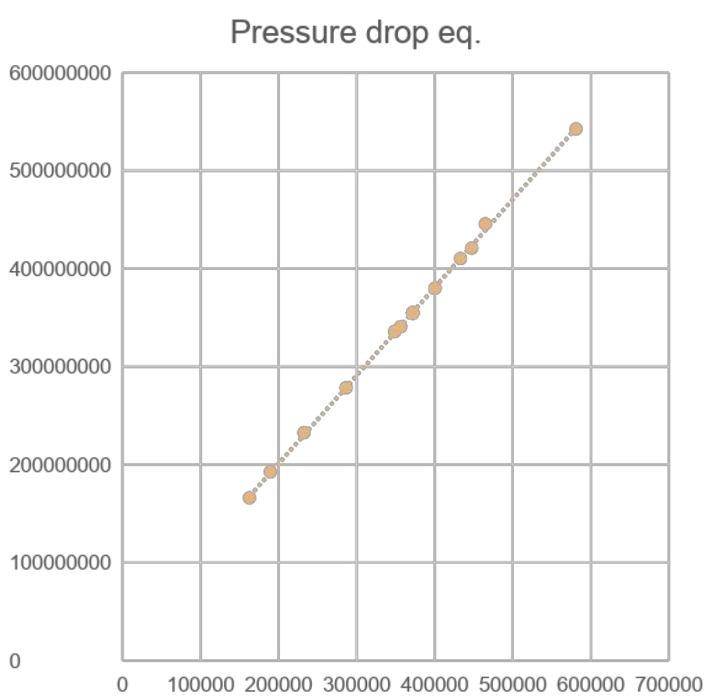
$$\frac{d_{32}}{d_p} = \alpha\, Re_p^{\beta}\, We_p^{\gamma}\, n_e^{\delta}$$

with n_e: Number of mixing elements; $\alpha, \beta, \gamma, \delta$: Tuning parameters.

Results: Static mixer 1

#	Q (ml/s)	φ	n_e
1	35	0.3	16
2	50	0.3	16
3	75	0.3	16
4	100	0.3	16
5	125	0.3	16
6	80	0.2	16
7	80	0.25	16
8	80	0.33	16
9	80	0.5	16
10	80	0.3	2
11	80	0.3	6
12	80	0.3	10
13	80	0.3	20
14	80	0.3	40
15	35	0.2	2
16	125	0.5	40

Results: Static mixer 1

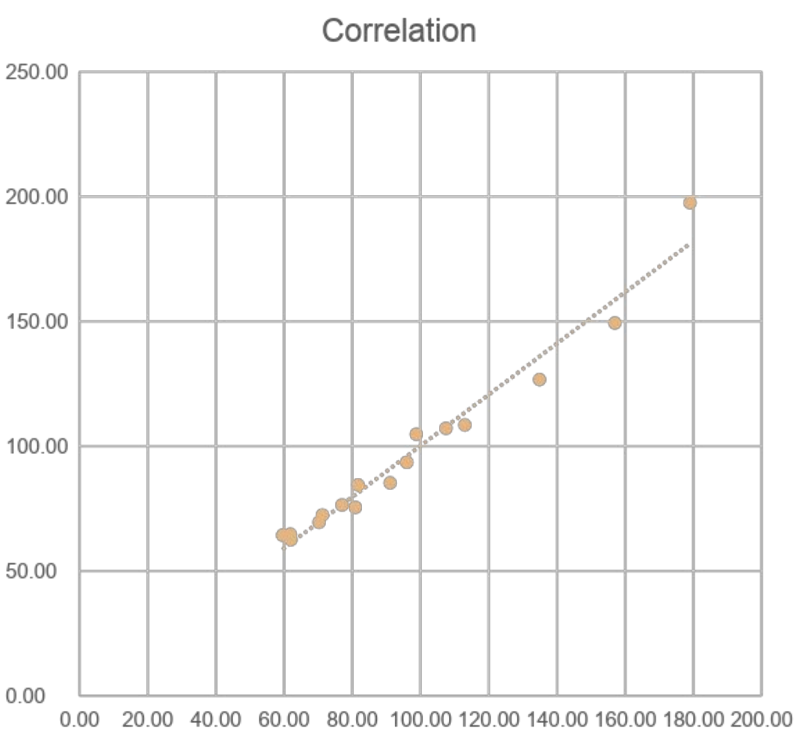


J	898.41
K	21405000
ε	0.77
d_p (mm)	1.93
τ	1.38

Results: Static mixer 1

#	Re	We	d_32 SV (micron)
1	564.44	1.28	134.90
2	806.34	2.62	98.78
3	1209.51	5.90	81.70
4	1612.68	10.49	71.23
5	2015.85	16.39	59.54
6	1502.65	6.83	70.24
7	1389.25	6.77	80.90
8	1236.47	6.68	91.09
9	993.54	6.47	107.47
10	1290.15	6.71	156.99
11	1290.15	6.71	113.00
12	1290.15	6.71	96.00
13	1290.15	6.71	77.00
14	1290.15	6.71	62.00
15	657.41	1.31	179.02
16	1552.41	15.80	61.84

Results: Static mixer 1



	130.475
	-1.082
	0.275
	-0.291

#	d_32 SV (micron)	d_32 corr (micron)	Error (%)
1	134.90	126.63	6.13
2	98.78	104.74	6.03
3	81.70	84.41	3.33
4	71.23	72.43	1.69
5	59.54	64.33	8.03
6	70.24	69.49	1.07
7	80.90	75.47	6.71
8	91.09	85.28	6.38
9	107.47	107.14	0.31
10	156.99	149.31	4.89
11	113.00	108.48	4.00
12	96.00	93.51	2.59
13	77.00	76.44	0.73
14	62.00	62.49	0.79
15	179.02	197.49	10.32
16	61.84	64.73	4.68

CFD validation

- Which model will be used
- CFD setup
- CFD results

Separation validation

Membranes to the rescue!

Phase separation

- The chemical environment – Solvent and Aqueous composition
- Factors that influence Phase Separation
- Hollow Fiber membrane contactors

Hybrid pertraction

Membranes to the rescue!