Removal of natural uranium from groundwater by means of weakly basic anion exchangers

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Outline

lotivation - Uranium

Occurrence

Seldom up to 10 µg/L

In few cases up to / higher than 100 µg/L

Standards for uranium

Drinking water

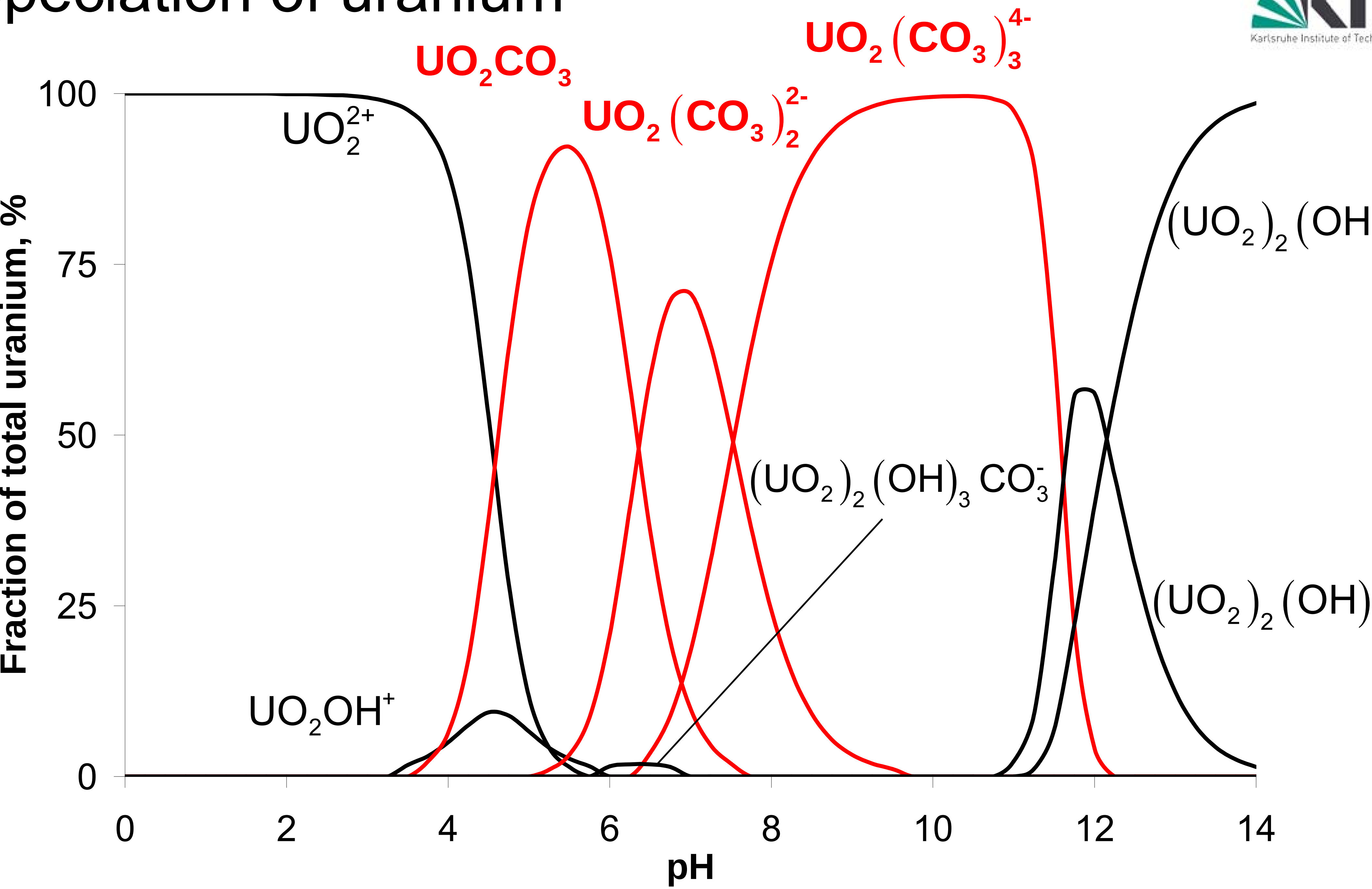
No standards appointed
Recommendation: 10 – 30 µg/L

Mineral water

Standard of 2 µg/L (GER)
"suitable for the preparation of infant food"

Chemical toxicity → Removal

Speciation of uranium



odelling with MINEQL©, c(U) = 100 µg/L, $c(HCO_3^-)$ = 240 mg/L

Mechanism of sorption

Application of weakly basic anion exchanger

$$\overline{R_3 \equiv NH^+OH^-} + UO_2(CO_3)_2^{2-} \rightleftharpoons \overline{(R_3 \equiv NH^+)_2 UO_2(CO_3)_2^{2-}} + 2\,OH^-$$

$$\overline{R_3 \equiv NH^+OH^-} + SO_4^{2-} \rightleftharpoons \overline{(R_3 \equiv NH^+)_2 SO_4^{2-}} + 2\,OH^-$$

pH ↑ → Protonation ↓

$$\overline{R_3 \equiv N|} + UO_2(CO_3)_2^{2-} \rightleftharpoons \overline{R_3 \equiv N|} + UO_2(CO_3)_2^{2-}$$

actors influencing the sorption

Karlsruhe Institute of Tech

(De-) Protonation of the functional groups

pH

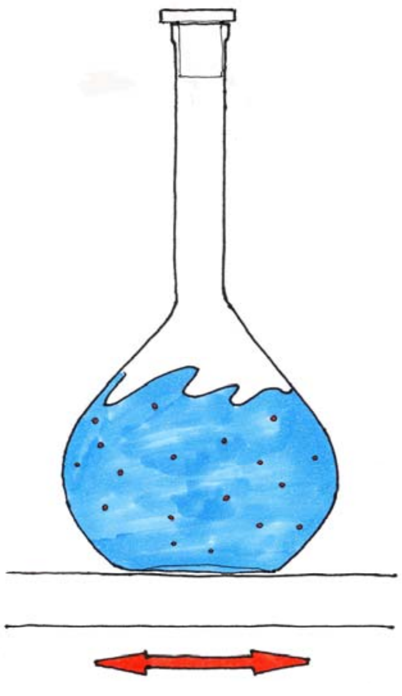
Competitive sorption

SO_4^{2-}, HCO_3^-, Cl^-, NO_3^-, NOM

Change of speciation

HCO_3^-, Ca^{2+}, Mg^{2+}, pH

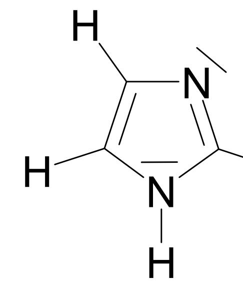
Equilibrium – Experimental setup



Sorption isotherms

Solutions:

- Pure water + HCO_3^- + imidazole buffer
- Tap water + imidazole buffer



$c(U)_0$ = 1000 µg/L

V_L = 4000 mL

m_{IEX} = 0,001 – 1 g

t > 60 h

Evaluation with

Langmuir

$$q = q_{max} \frac{K_L\ c}{1+K_L c}$$

Freundlich

$$q = K_F c^n$$

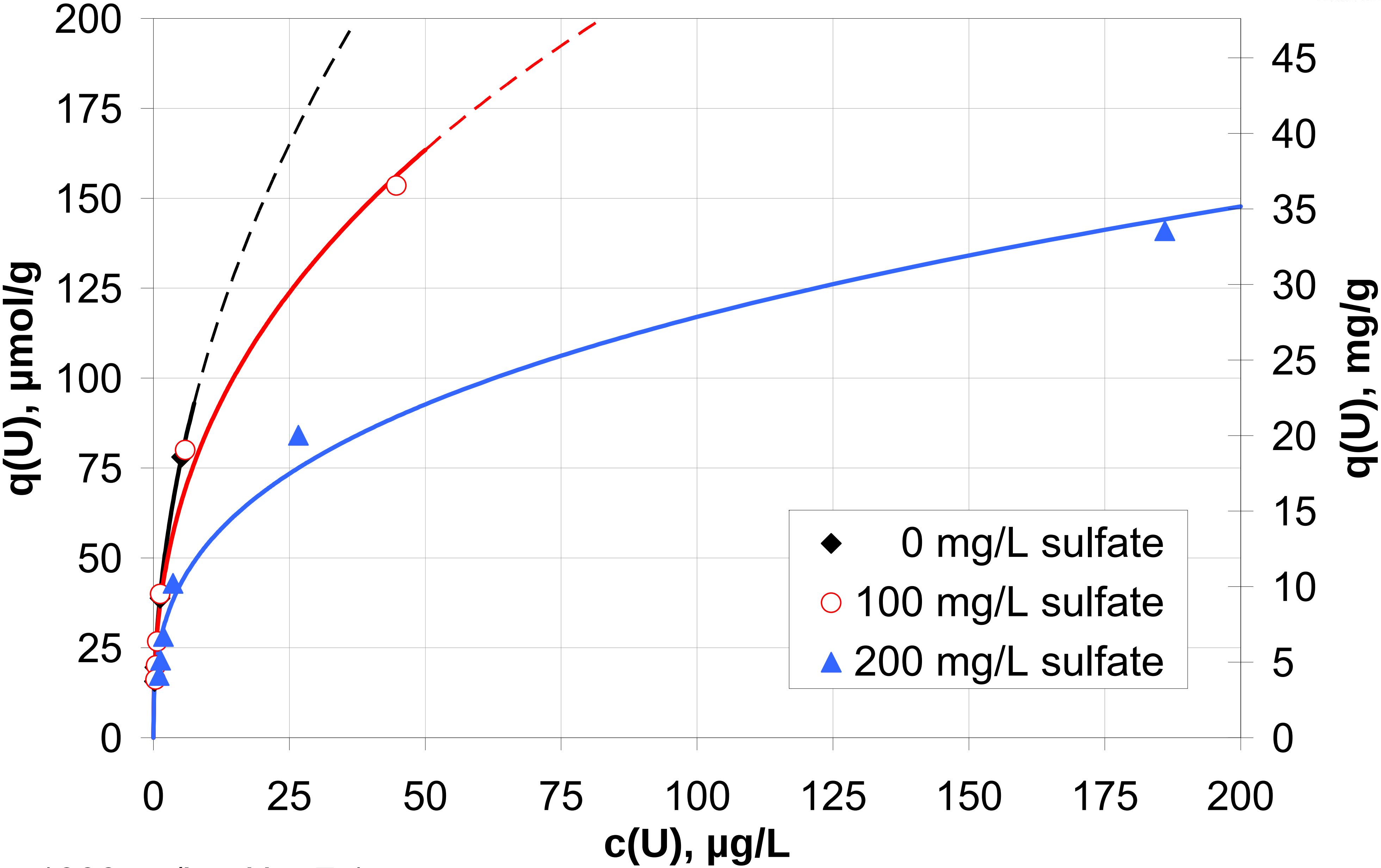
Lewatit MP 62

Matrix: Styrene - DVB - copolymer
Exclusively tertiary amine groups

Amberlite IRA 67 / PWA 8

Matrix: Acrylic - DVB - copolymer
Secondary and tertiary amine groups

..quilibrium - Influence of sulfate

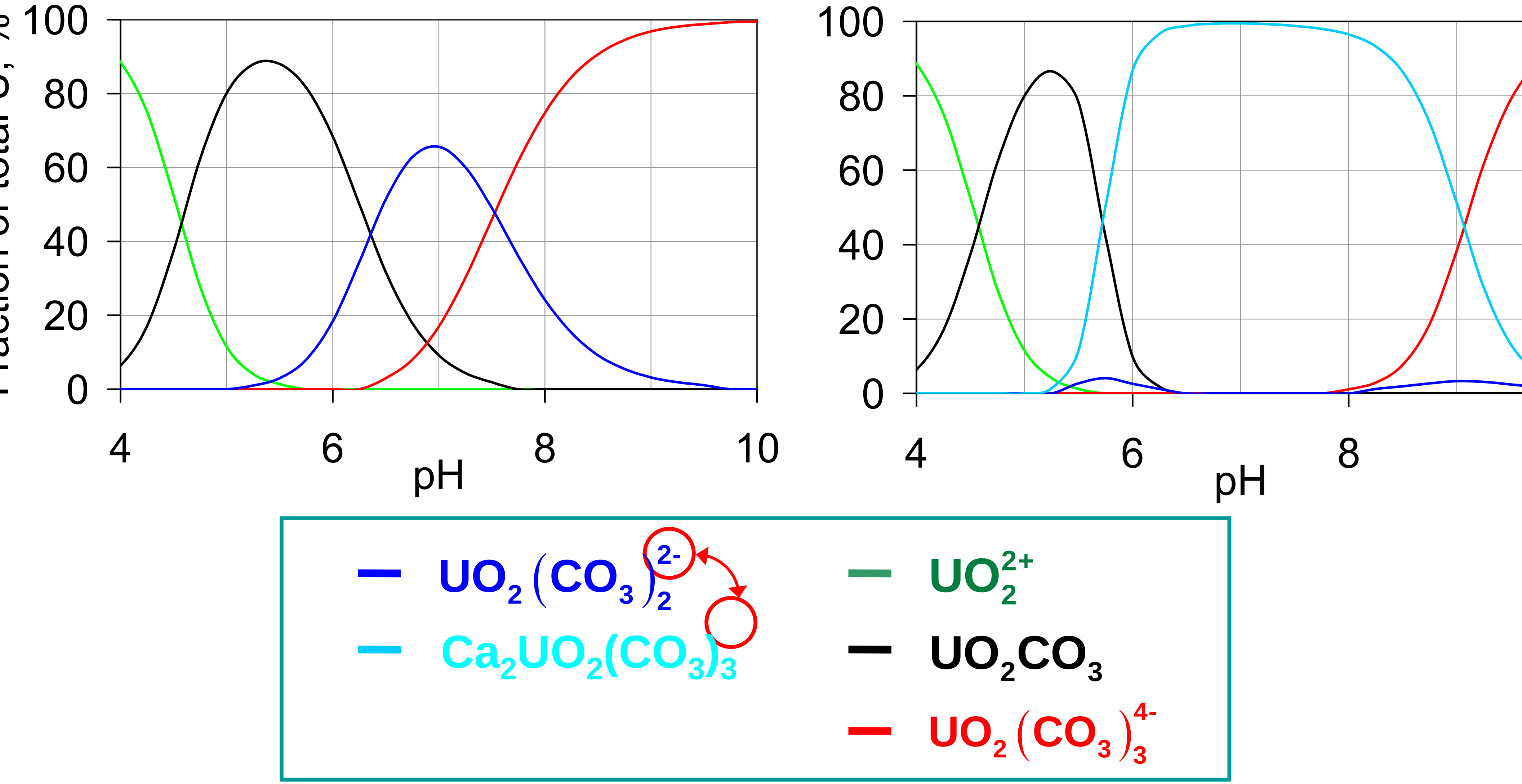


..)$_0$ = 1000 µg/L, pH = 7.1

..: Lewatit MP 62, matrix: deionised water spiked with 240 mg/L of HCO_3^-

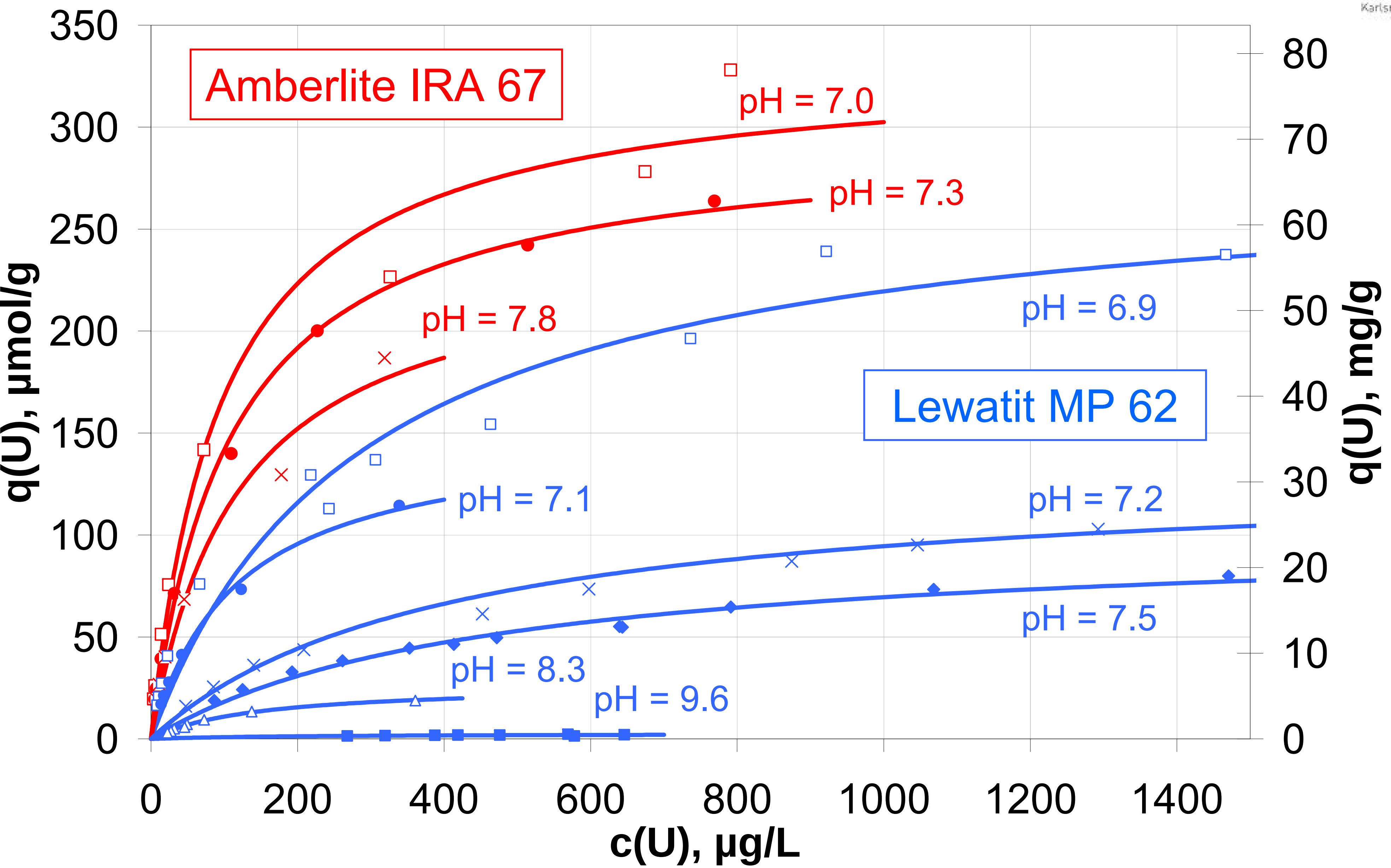
quilibrium - Influence of calcium

Without calcium | **100 mg/L calcium**



odelling with MINEQL©, c(U) = 1000 µg/L, c(HCO_3^-) = 240 mg/L

Equilibrium - Influence of pH / IEX

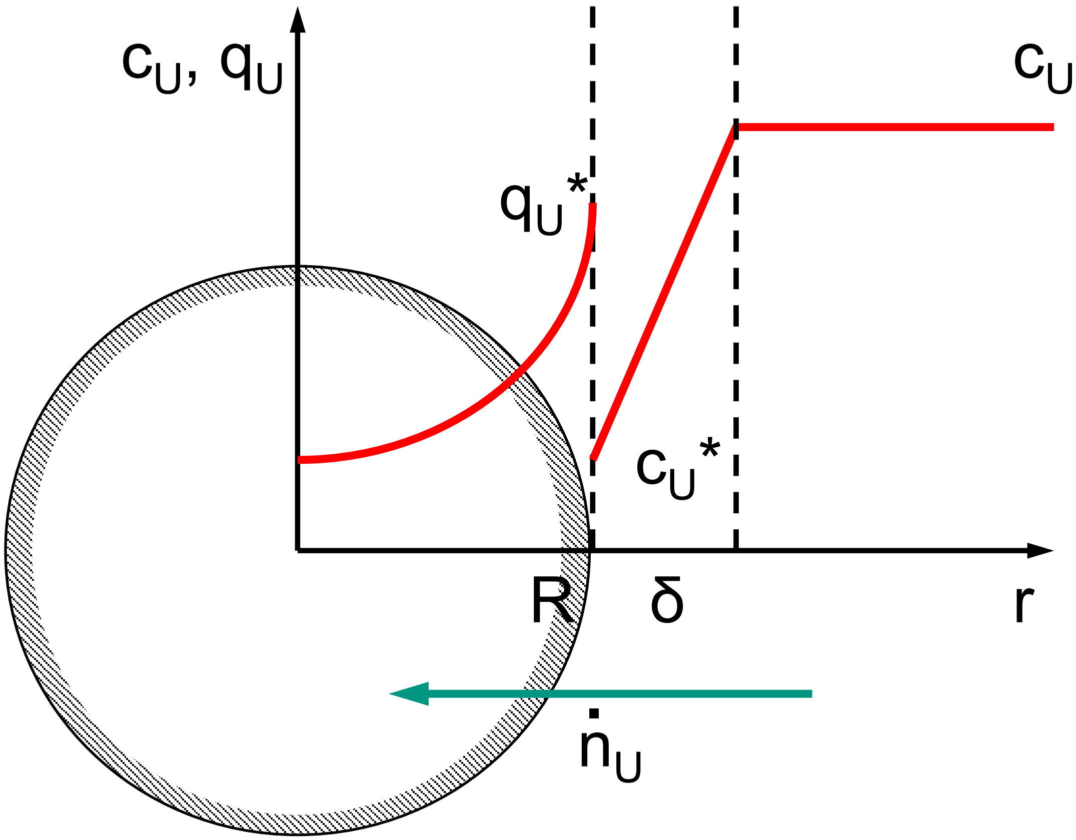


)$_0$ = 1000 / 2000 µg/L, matrix: tap water

Amberlite IRA 67: ACRYLIC copolyme
Lewatit MP 62: STYRENE copolymer

inetics

lodel: **Film / Surface Diffusion**



Profiles of concentration and loading

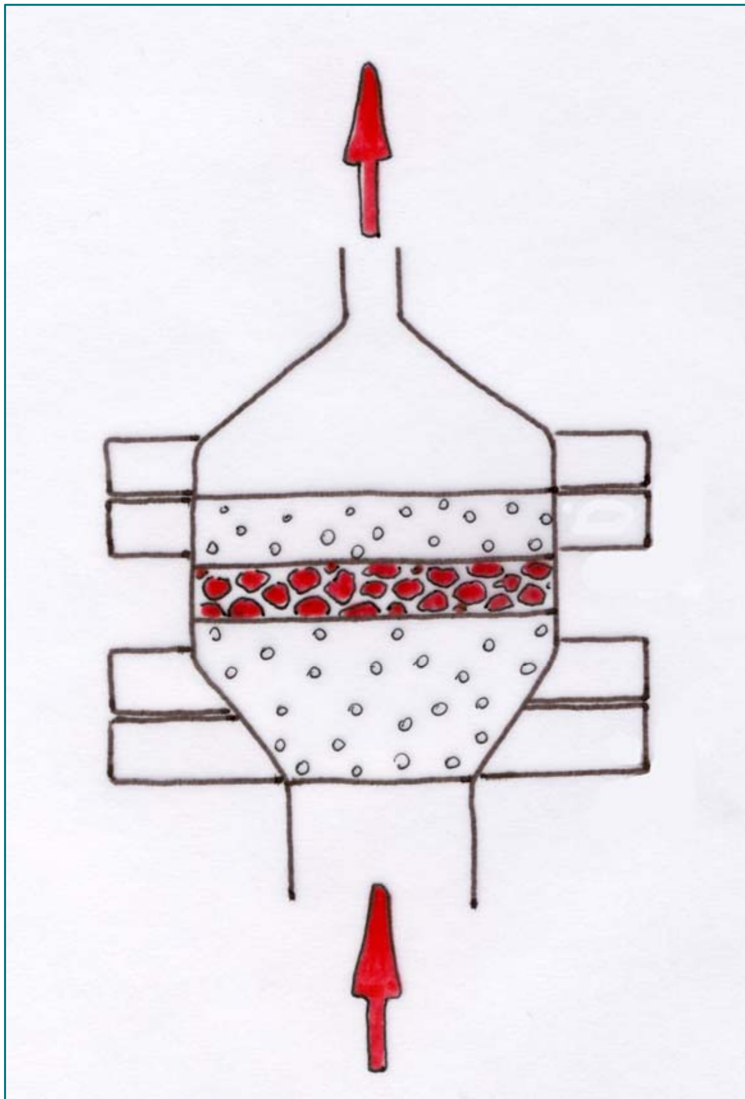
Transport in the film:

$$\dot{n}_U = \beta_L (c_U - c_U{}^*)$$

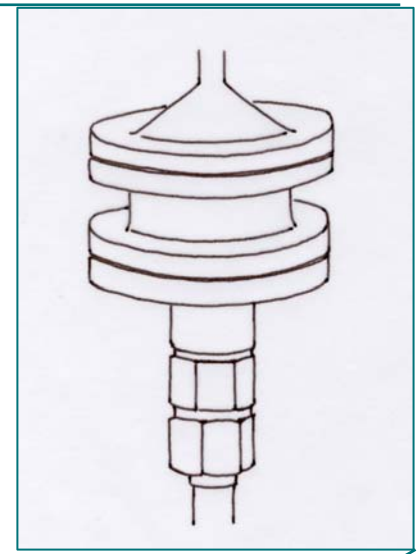
Transport in the particle:

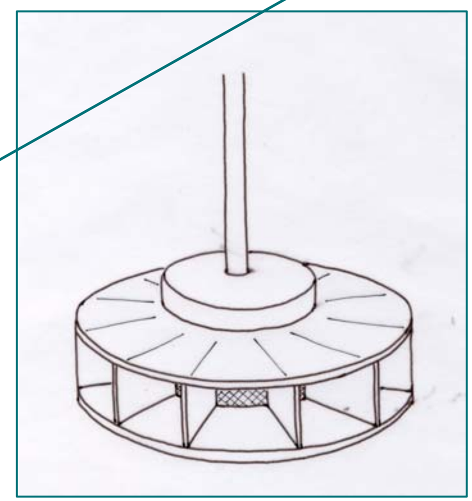
$$\dot{n}_U = \rho_P D_s \frac{\partial q_U}{\partial r}$$

inetics – Determination of the transport coefficients

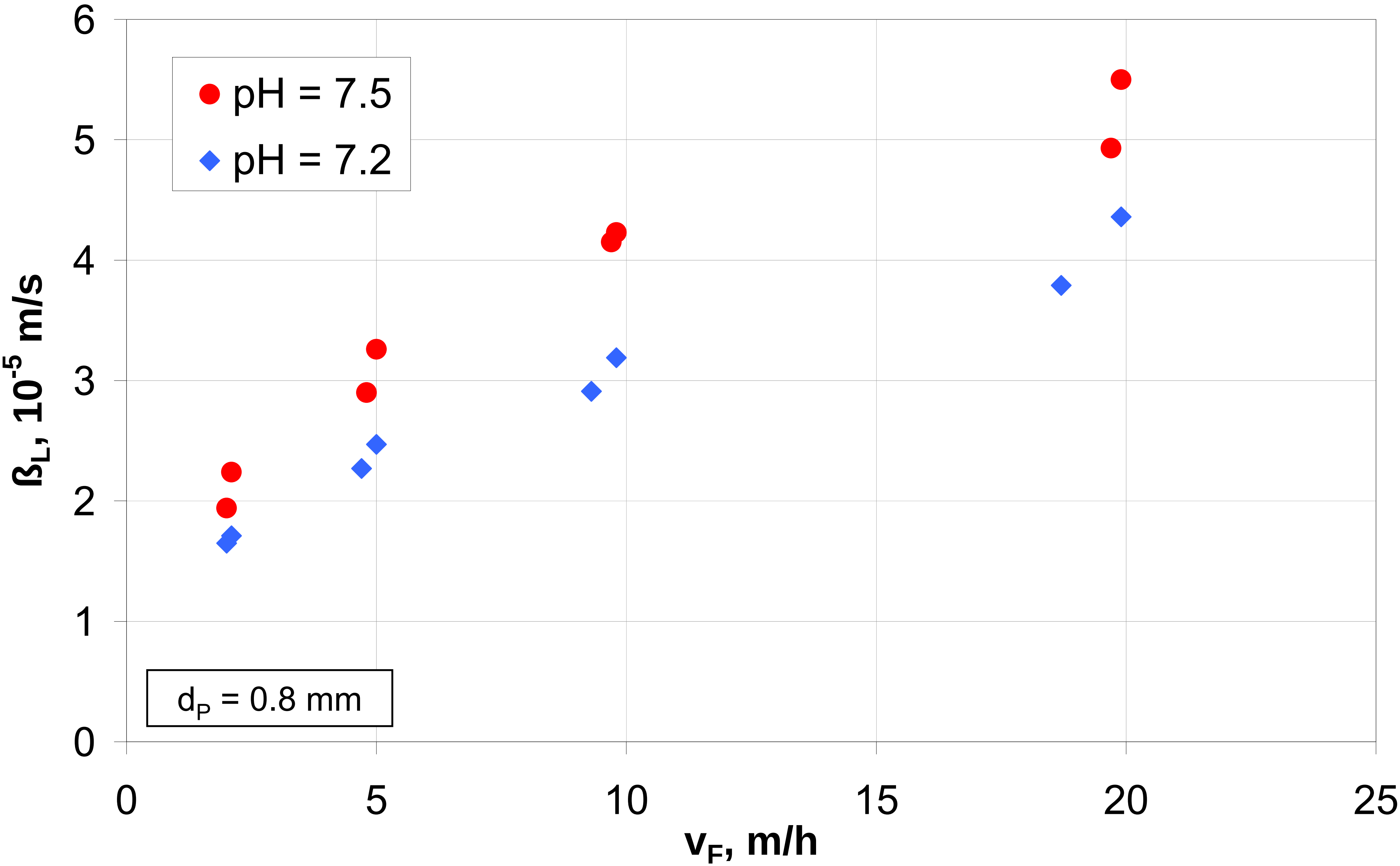


Short fixed bed reactor



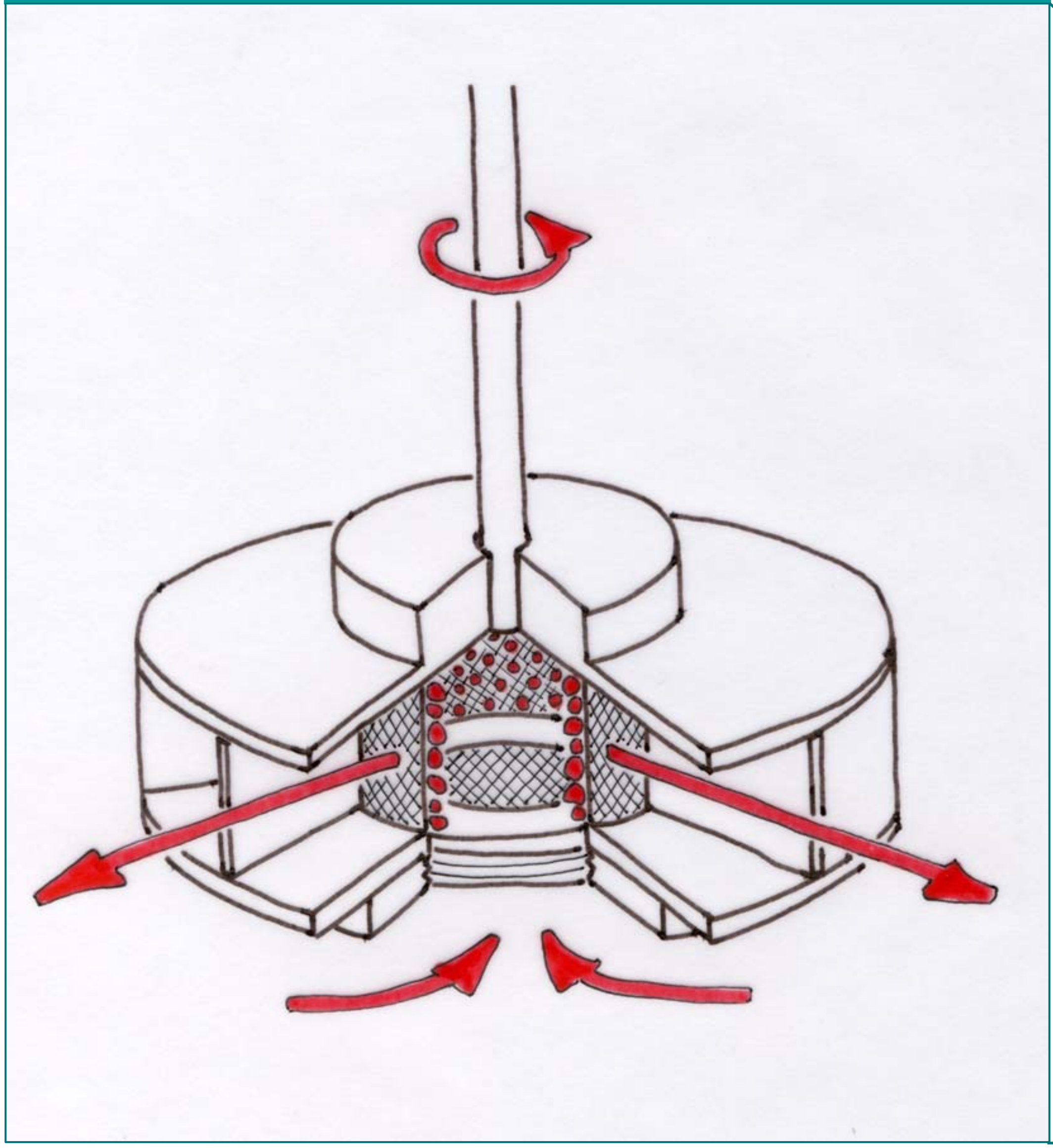


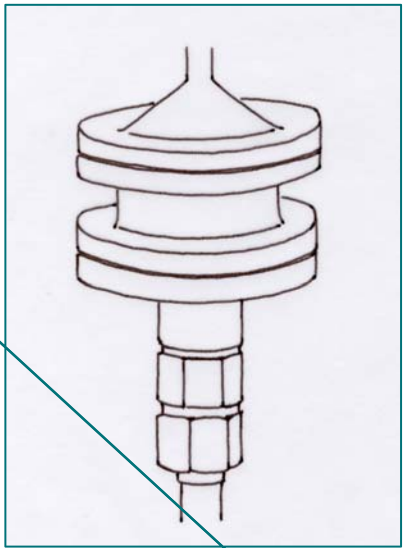
Kinetics – Mass transfer coefficient $ß_L$

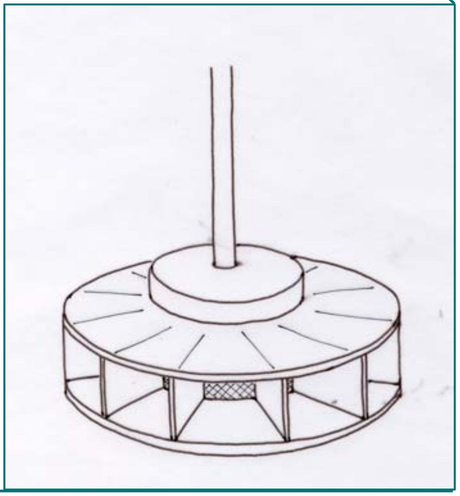


IX: Amberlite IRA 67 & Lewatit MP 62, matrix: tap water, $c(U)_0$ = 1000 µg/L

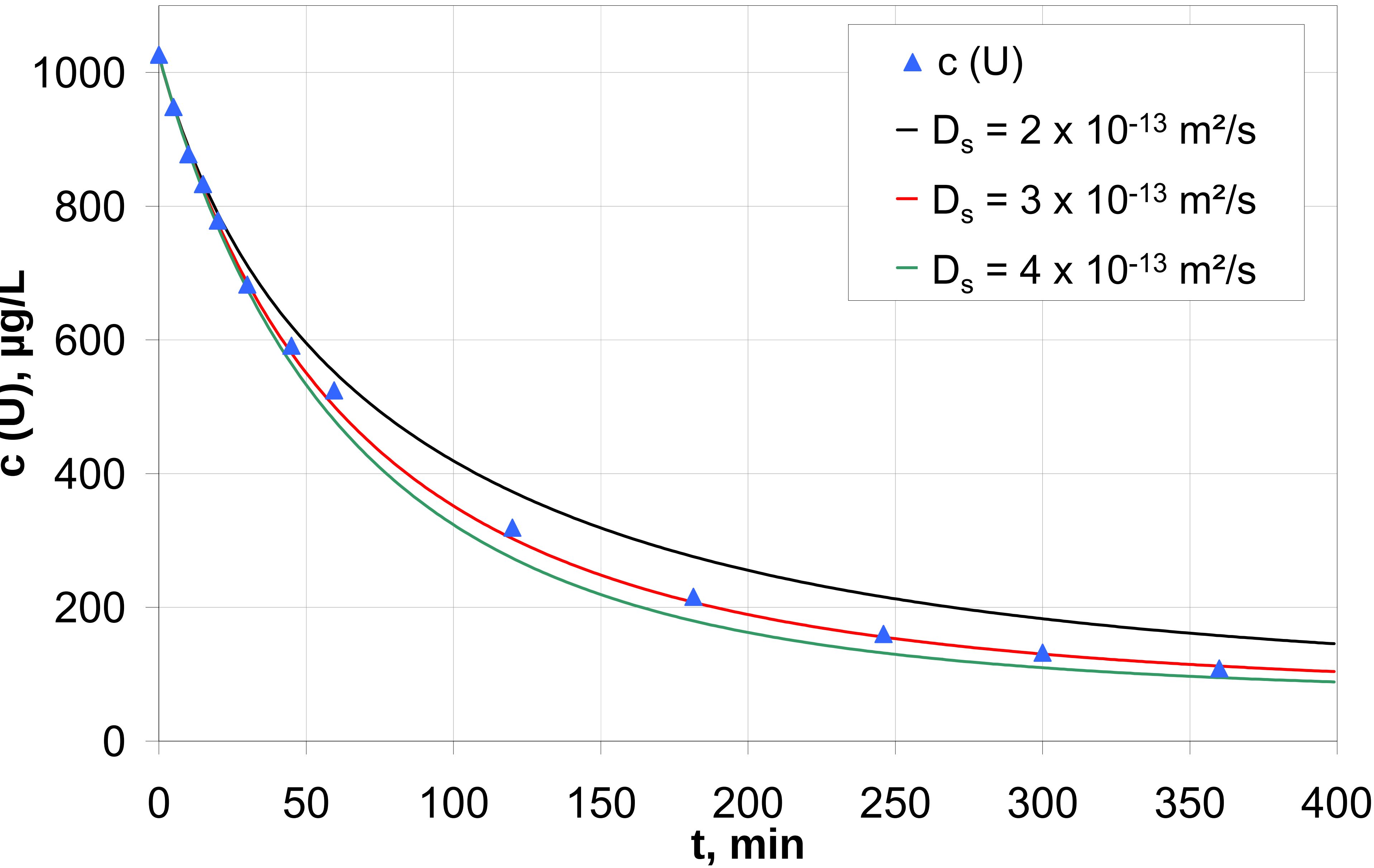
Rotated basket reactor





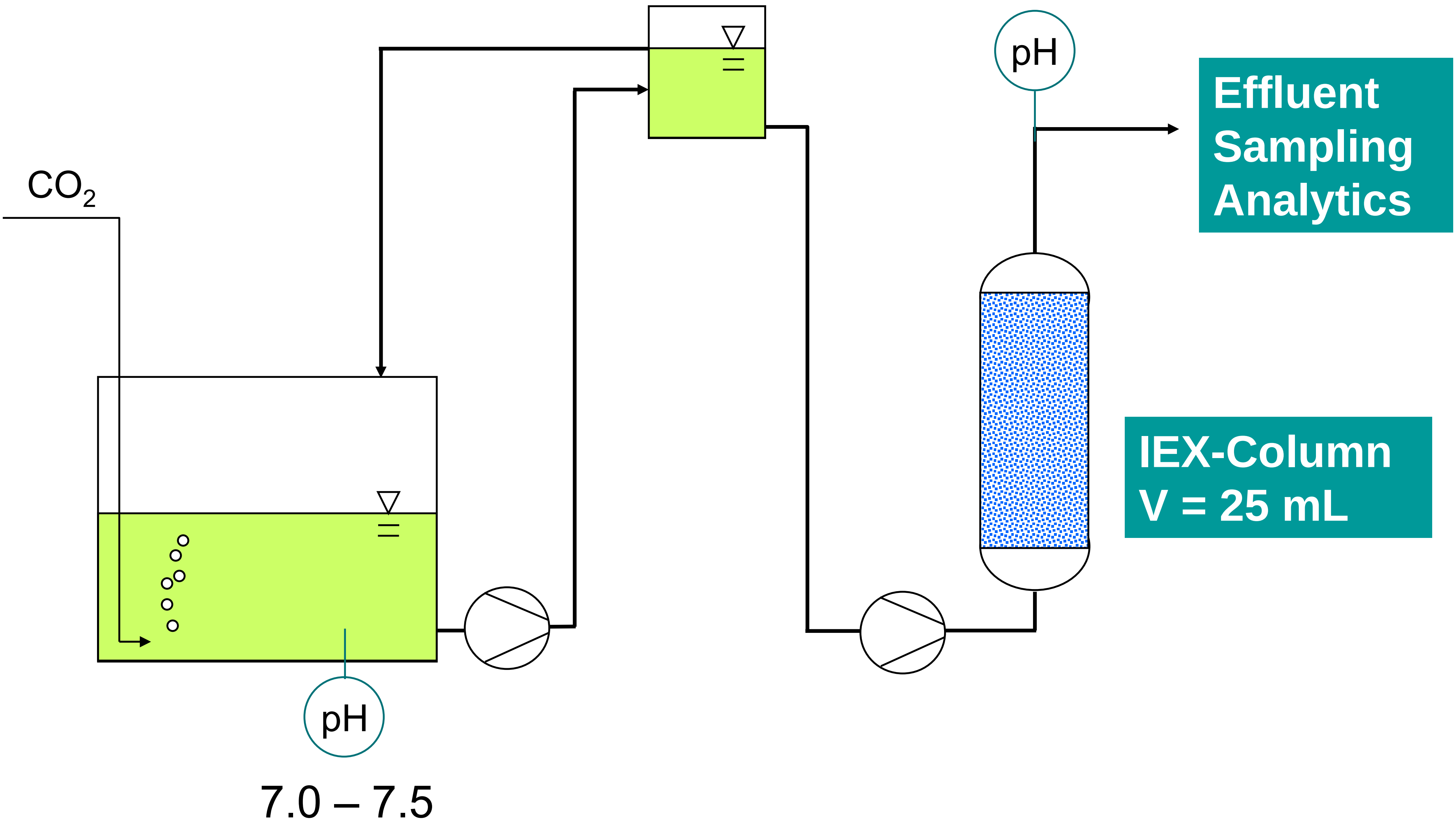


Kinetics – Diffusion coefficient D_s

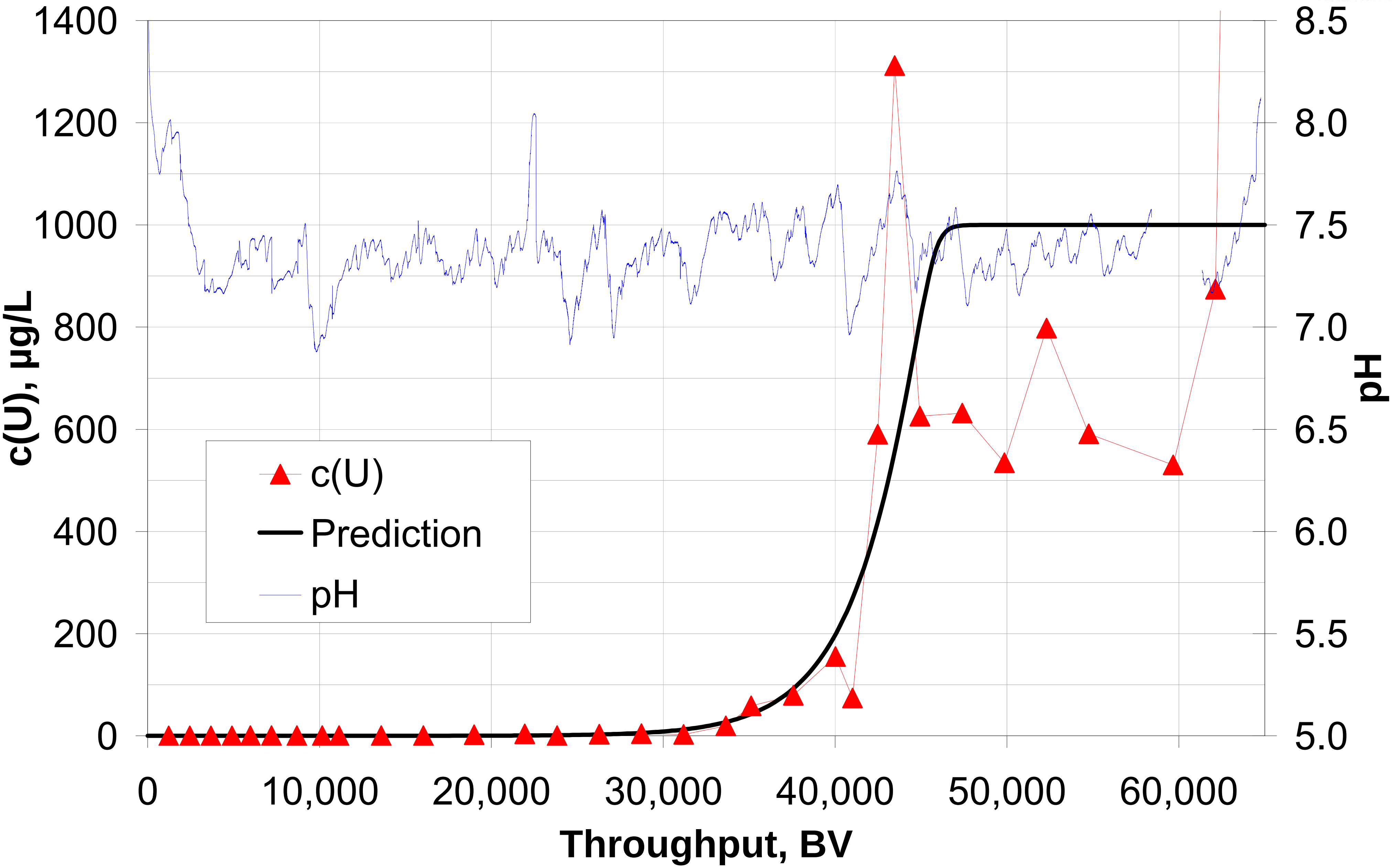


IX: Lewatit MP 62, pH = 7.3, d_P = 0.6 mm, matrix: tap water

Column experiments – Laboratory scale



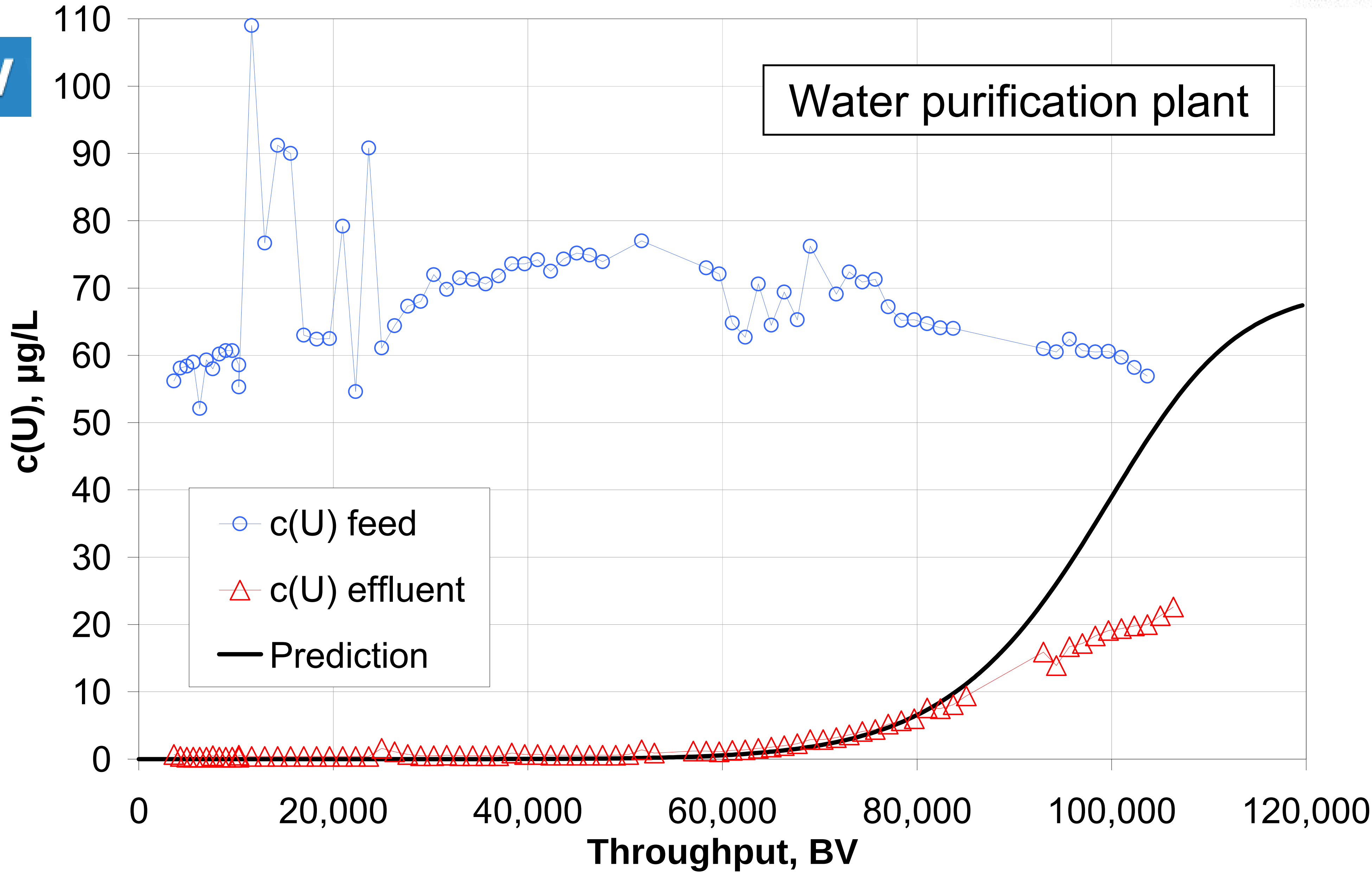
olumn breakthrough curve – Laboratory scale



K: Amberlite IRA 67, $c(U)_0$ = 1000 µg/L, $\dot{V}$ = 20 BV/h, matrix: tap water

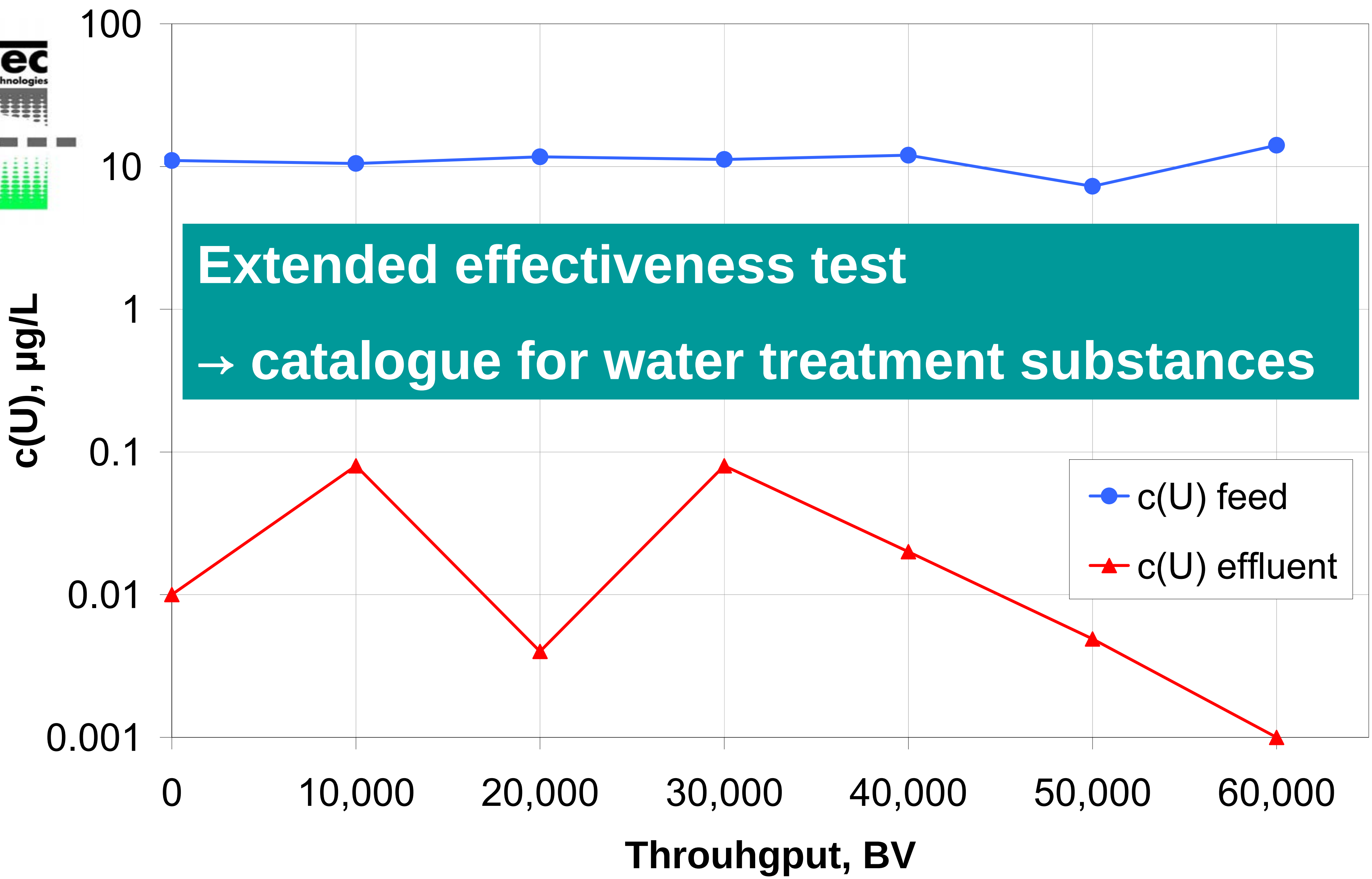
olumn breakthrough curve – Pilot plant scale

ZW



X: Amberlite IRA 67, V_{IEX} = 7.5 L, $\dot{V}$ = 28 BV/h, pH = 7.2

olumn breakthrough curve – Full plant scale



Extended effectiveness test

→ catalogue for water treatment substances

X: Amberlite IRA 67, V_{IEX} = 300 L, $\dot{V}$ = 20 BV/h, pH = 6.9

nstallation of the first technical plant in GER

IEX: Amberlite IRA 67

$c(U)_0$ = 37 µg/L

V_{IEX} = 5 m³

$\dot{V}_{av}$ = 32 m³/h = 6,5 BV/h

pH = 7,3

After half a year (30,000 BV): c(U) < 0,1 µg/L

Expected operation time: at least 1½ years (90,000 BV)

Conclusions

Equilibrium of sorption

Elimination of uranium is possible with weakly basic anion exchangers

Influencing factors: pH and water matrix

Sorption kinetics

Combined film / surface diffusion
→ input for modelling of column performance

Sorption dynamics

Very long operation time
Technical implementation already accomplished

cknowledgement

Sibylle Heidt

Volker Schlitt - TZW Karlsruhe

Günther Mann - GUTec

Klaus Hagen - Krüger Wabag GmbH

BMBF

DVGW

Thank you very much for your attention

Add on

Model to predict column performance

Assumptions

Single component

Plug flow

Film / surface diffusion

Basics

Equilibrium at exchanger surface

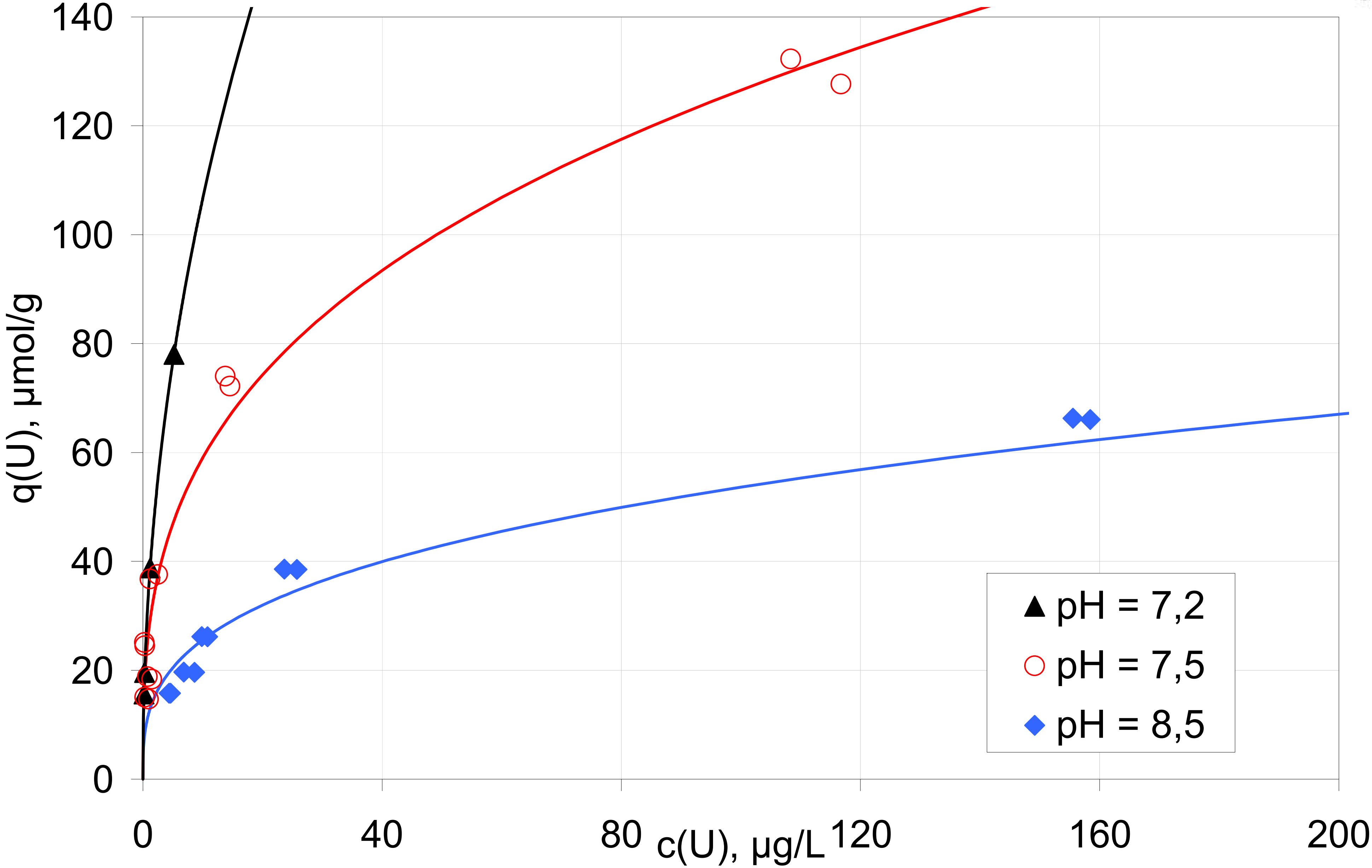
Mass balance of the liquid column phase

Kinetic approach of film / surface diffusion

Mathematics

3 coupled differential equations

quilibrium – Influence of pH



$U)_0$ = 1000 µg/L

: Lewatit MP 62, matrix: deionised water spiked with 240 mg/L of HCO_3^-