# REDROP – AN EFFICIENT MONTE-CARLO METHOD FOR SIMULATING EXTRACTION COLUMNS

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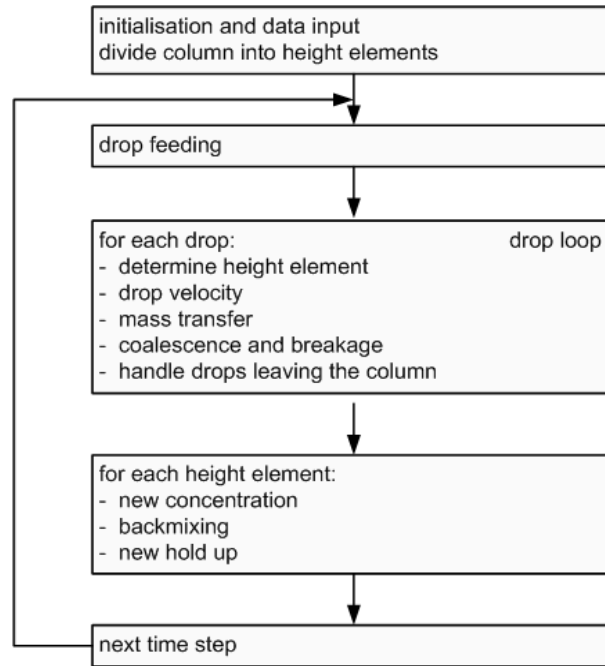*Andreas Pfennig, AVT - Thermal Process Engineering, RWTH Aachen University, Aachen, Germany*

## Introduction

Due to increase in the price of fossil fuels and the decrease in their reserves, renewable raw materials are industrially used more and more frequently. Therefore extraction, as an energy-saving unit operation has gained additional importance. Precise design methods for technical columns are required for the future. So far, pilot-plant experiments are carried out as a basis for equipment design. These cost-intensive experiments can be minimized or even avoided by simulating the behavior of extraction columns. The simulations have to account for drop movement, axial dispersion, mass transfer, coalescence and drop breakage. The key to a successful simulation is solving the drop-population balances. A large number of researchers have tried to numerically solve the system of equations. A great disadvantage of this procedure is the increase in numerical efforts if additional properties of the drop population have to be regarded. An alternative approach solving the population balances is using the Monte-Carlo method. ReDrop (Representative Drops) is a simulation program which can successfully predict the behavior of pilot-plant columns.[1,2] Because different internal types (random packing, regular packing, sieve tray) can be modeled with ReDrop, simulations can reveal which kind of internal is the best for the interested material system. Also the dimension of the internals as well as the operating conditions can be optimized If the design of the technical column is based on pilot-plant experiments, a type of internal has to be chosen in a early design of the design procedure. A later change of the internals is cost-intensive. In this paper, ReDrop is explained in detail and results are compared to experimental values in literature. Finally, an outlook is given on the extensions of ReDrop which are currently treated.
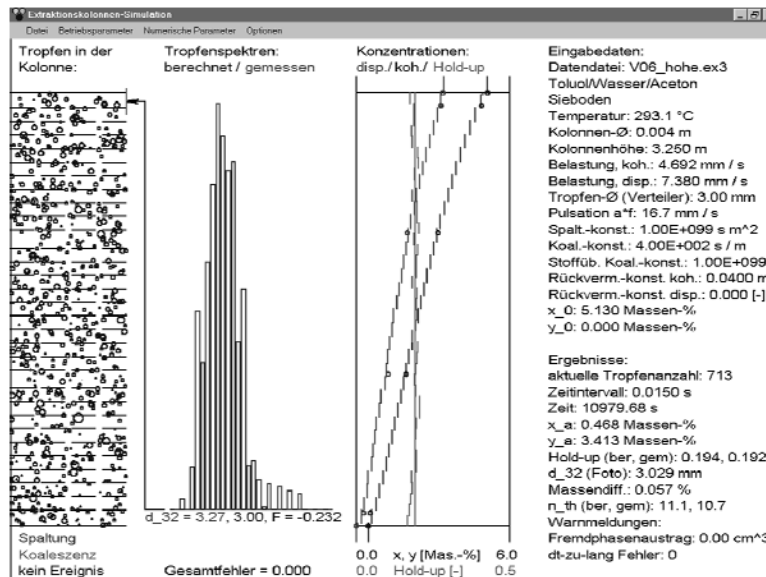
## ReDrop

The basic idea of the ReDrop model is to follow a discrete number of drops through their total life-time in an extraction column. Every effect which influences each drop is taken into account. The structure of the code is module-based. So any new phenomena which have to be considered can be easily implemented. The ReDrop algorithm is shown in Fig. 1. Before starting the simulation, the user has to supply raw data like mass flows, initial concentrations or type of the internals. Every time step of the simulation starts with feeding of new drops into the column. In the drop loop, all effects which act on every single drop are calculated. For a given diameter, the sedimentation velocity of the drop is calculated. The new concentration of the solute in the drop is computed. Models are used to determine the probability of each drop to coalesce or to break. After all drops are worked through the program focuses on the continuous height elements. Regarding back mixing the new concentration of the transfer component is calculated for each height element. After determining the holdup for each height element the simulation continues with the next time step. The core of the ReDrop algorithm are the single-drop models which can predict the sedimentation and the mass transfer of the drop. These models include system-specific parameters which have to be obtained in simple-lab scale experiments. Thus experiments are unavoidable because even small amounts of impurities can change the drop behavior drastically. But compared to pilot-plant scale column experiments, the required amount of

substance is negligible for the lab-scale measurements. After the model parameters are successfully fitted to single- drop experiments, they are input for ReDrop. For the calculations, the influence of other drops and of the internals is included.

initialisation and data input
divide column into height elements

drop feeding

for each drop:                                    drop loop
- determine height element
- drop velocity
- mass transfer
- coalescence and breakage
- handle drops leaving the column

for each height element:
- new concentration
- backmixing
- new hold up

next time step

**Figure 1.** The ReDrop algorithm.

Usually 1000 drops per meter column are considered. Simulation time on a PC with a Pentium IV processor is typically 10 minutes to reach steady state. The output of the simulation can be followed on a Windows console (Fig. 2).  Menu bars at the top of the window allows the user to immediately change operational parameters as mass flows. Thus dynamic simulations are allowed for.

Extraktionskolonnen-Simulation
Datei  Betriebsparameter  Numerische Parameter  Optionen

Tropfen in der Kolonne:

Tropfenspektren: berechnet / gemessen

Konzentrationen: disp./ koh./ Hold-up

Eingabedaten:
Datendatei: V06_hohe.ex3
Toluol/Wasser/Aceton
Sieboden
Temperatur: 293.1 °C
Kolonnen-Ø: 0.004 m
Kolonnenhöhe: 3.250 m
Belastung, koh.: 4.692 mm / s
Belastung, disp.: 7.380 mm / s
Tropfen-Ø (Verteiler): 3.00 mm
Pulsation a*f: 16.7 mm / s
Spalt.-konst.: 1.00E+099 s m^2
Koal.-konst.: 4.00E+002 s / m
Stoffüb. Koal.-konst.: 1.00E+099 s
Rückverm.-konst. koh.: 0.0400 m
Rückverm.-konst. disp.: 0.000 [-]
x_0: 5.130 Massen-%
y_0: 0.000 Massen-%

Ergebnisse:
aktuelle Tropfenanzahl: 713
Zeitintervall: 0.0150 s
Zeit: 10979.68 s
x_a: 0.468 Massen-%
y_a: 3.413 Massen-%
Hold-up (ber, gem): 0.194, 0.192
d_32 (Foto): 3.029 mm
Massendiff.: 0.057 %
n_th (ber, gem): 11.1, 10.7
Warnmeldungen:
Fremdphasenaustrag: 0.00 cm^3
dt-zu-lang Fehler: 0

Spaltung
Koaleszenz
kein Ereignis

d_32 = 3.27, 3.00, F = -0.232

Gesamtfehler = 0.000

0.0  x, y [Mas.-%]  6.0
0.0  Hold-up [-]  0.5

**2**

**Figure 2.** The ReDrop program

### Single-Drop Experiments

For any new material system, sedimentation experiments in a lab-scale cell have to be carried out in order to run ReDrop. In Fig. 3, the sketch of such a cell is shown. The cell is divided into sections in order to determine the sedimentation velocity as a function of the residence time of the drop. In order to keep a constant temperature, the cell is temperature controlled. A drop is produced by a computer-driven syringe and a nozzle. Due to the density difference, the drop will rise through the stagnant continuous phase. The sedimentation of the drop is recorded by a video camera. By evaluating the videos, the sedimentation velocity of the drop can be determined. The experiments are performed for at least 15 drop diameters.

The obtained experimental values are then with the model of Henschke.[1] This model combines 4 single models for rigid drops, drops with totally mobile interface, oscillating drops and deformed drops. This combination results in one model which is valid over the complete range of drop diameter. The model has in total 5 parameters, two of which are fixed to typical characteristic values while three have to be fitted to the results of the single-drop experiments. In Fig. 4 such a fit is shown with the two limiting cases of an ideally-mobile and a rigid interface. The influence of internals and holdup is included in the ReDrop program.
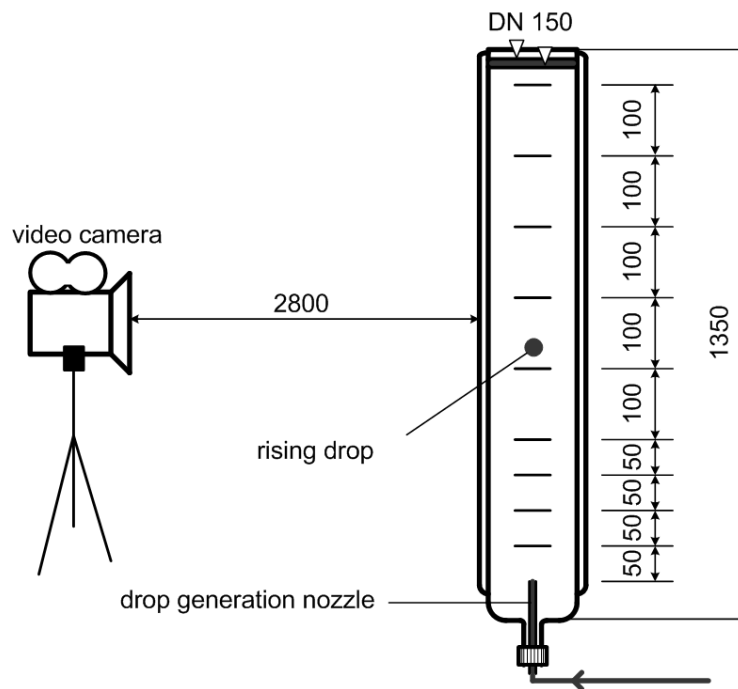


**Figure 3.** The sedimentation cell.

As for sedimentation, single-drop experiments deliver the necessary information about the dependency of mass transfer from drop diameter, contact time and concentration of the components in both phases.[1] A mass-transfer model with one additional parameter will be used to fit the experimental values. The mass-transfer model is based on the Handlos-Baron model.[3] The Handlos-Baron model assumes always the same effective diffusion coefficient for the same material system. In reality, the effective diffusion coefficient depends on the intensities of interfacial eruptions and on the presence of

contaminants. Henschke and Pfennig extended the Handlos-Baron model in such a way that eruptions and contaminants are considered by an adjustable parameter.[4] Experiments with packing or sieve-tray will reveal the influence of the geometry of the chosen internal. These experiments are necessary because it has been seen that internals can have different influence for different material systems. While for physical extraction a sieve-tray improved the mass transfer this effect has not been seen for the reactive standard test system zinc + D2EHPA.[5]
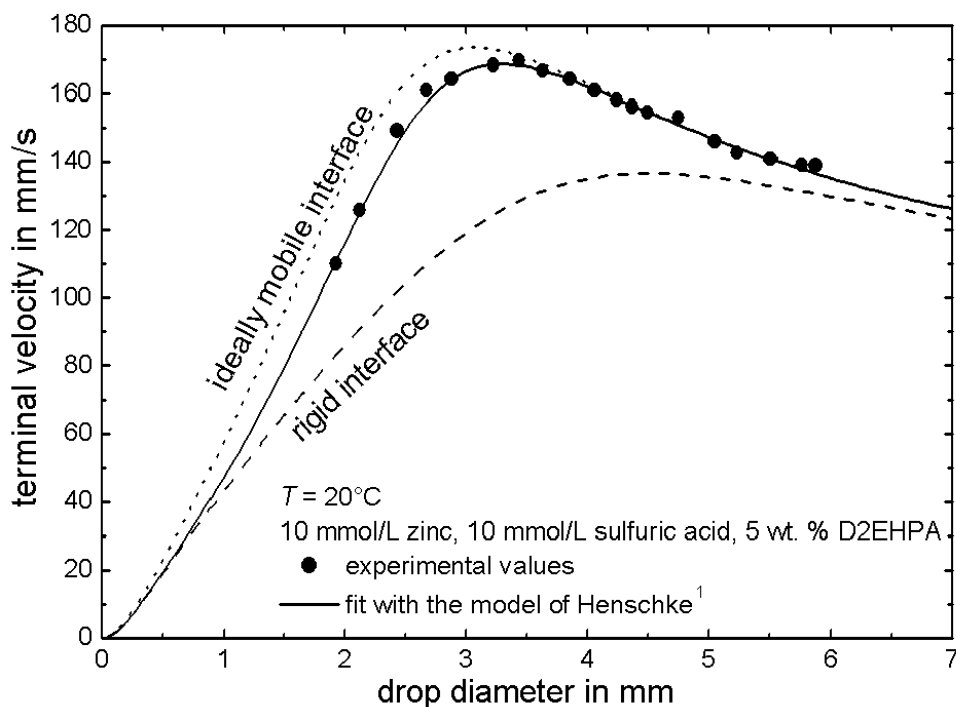


**Figure 4.** Experimental values and fit of the sedimentation model.

***Population models***

Single-drop sedimentation as well as mass transfer are calculated by a deterministic model. Drop breakage and coalescence are determined stochastically for each drop. For the drop breakage, the diameter of the drop is compared to a stable diameter.[1] The stable diameter depends on the type of internal, material properties, drop diameter and drop velocity. Drops with a diameter smaller than the stable diameter pass an internal without being broken. If the drop diameter is bigger than the stable diameter, the breakage probability will be calculated. By comparison of the probability with a random number, it is decided if the drop will truly break. For a drop which will split, the number of daughter drops and as well as their drop size distribution are generated again based on distribution functions and random numbers.

Coalescence is the second effect which is based on stochastic calculations. For each drop, a coalescence probability $p_k$ is calculated, depending on holdup, drop diameter, viscosity of the continuous phase, density difference and surface tension.[1] A random variable between 0 and 1 is generated. If this random number is smaller than the coalescence probability, the drop is marked for coalescence. If a second drop (close to the first one) is also marked, the coalescence of both drops is carried out. A detailed description of the models is given by Henschke.[1]

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# Results

ReDrop simulations have been validated for the physical test systems toluene + water + acetone and butyl acetate + water + acetone.[1] Due to the numerical approach, ReDrop is not only able to simulate the concentration profiles, but also of the predetermination of dynamic limits of the column as flooding. In a recent project with industrial partners ReDrop has proven his applicability for technical systems.[6] The predicted concentration profiles and flooding limits agree within 10 % with experimental points.

# Actual work

### *Reactive Equilibrium and Kinetics*

The next goal is to extend ReDrop to reactive extraction. Contrary to physical extraction, chemical reactions have to be considered. So modules are added which are capable of calculating an arbitrary number of reaction equilibria. For slow reactions, reaction kinetics are the rate-determining factor and, therefore, must be modeled and can be quantified in a modified Lewis cell.[7] If diffusion or convection is rate-determining, a multi-component mass transfer model for reactive systems must be developed. Today investigations and validation of ReDrop for reactive extraction are carried out with the reactive standard test system.[8] The reaction equation for this test system is:

$$Zn^{2+} + 1.5\overline{R_2H_2} \leftrightarrow \overline{ZnR_2RH} + 2H^+ \tag{1}$$

D2EHPA ($\overline{R_2H_2}$) is a cation exchanger which extracts zinc from the aqueous phase by an interfacial reaction. Bars are indicating components in the organic phase. Activity coefficients are used to include the non-ideality in both phases.[9] Currently, the Pitzer model for aqueous phases and the Hildebrand-Scott model are used for reactive equilibria. In future, an IK-CAPE interface will allow to use any $G^E$ model. In Fig. 5, calculated equilibria versus own experimental data for the reactive standard test system are shown. The equilibrium module is programmed in such way that an arbitrary number of reactive equations can be solved simultaneously.

### *Single-Drop Experiments With A Reactive System*

Sedimentation experiments with the standard test system have been carried out. For physical test systems it was known that mass transfer slows drops down. This is due to the destruction of the internal circulation of the drop by mass-transfer induced convections. However, for the reactive system, mass transfer accelerates drops. In case of missing mass transfer, the interfacially active D2EHPA can accumulate at the interface, the drop will thus show rigid behavior. The extraction of zinc by D2EHPA will lead to partly free areas on the interface where more momentum can transferred between the phases. The different behavior of both types of extraction systems is illustrated in Fig. 6.
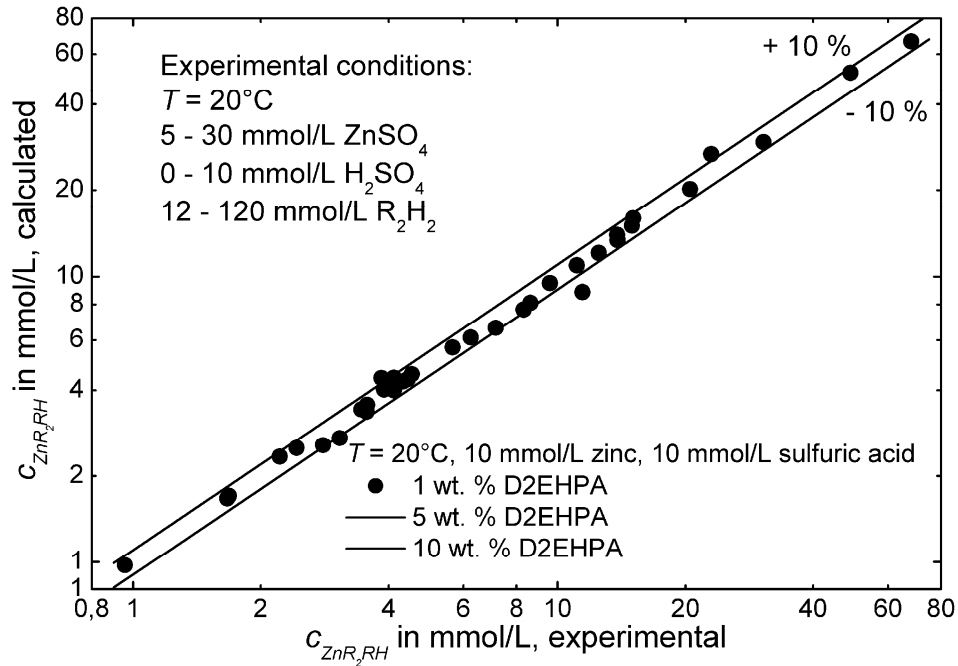
**Figure 5.** Reactive equilibria for the standard test system of reactive extraction zinc + D2EHPA.
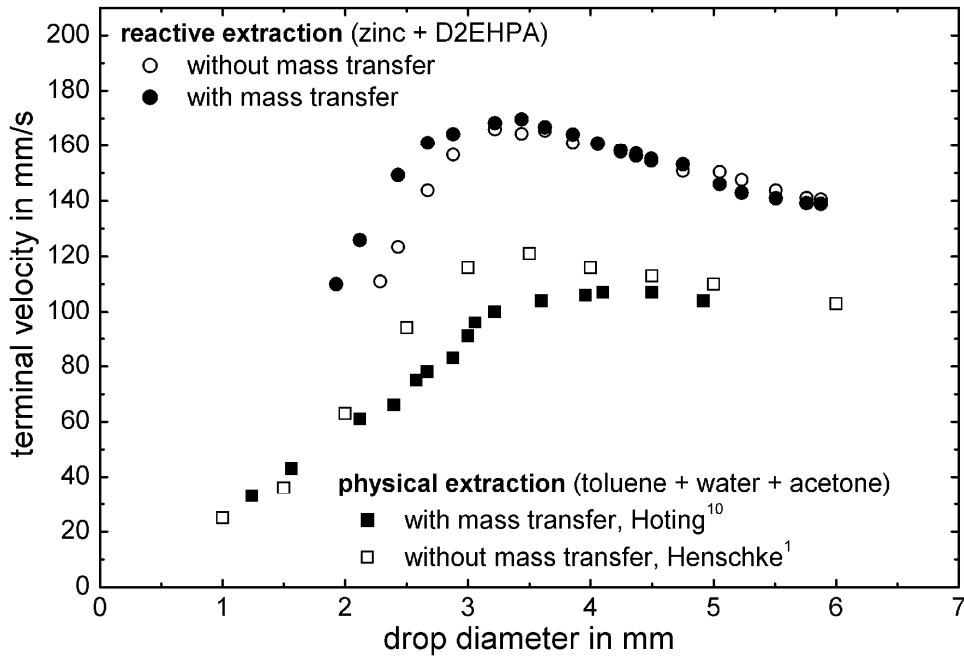


**Figure 6.** Influence of sedimentation on mass transfer.

## Summary

ReDrop is an efficient Monte-Carlo method to predict the behavior of pulsed pilot-plant extraction columns. Necessary single-drop model parameters are determined in lab-scale experiments. For physical systems (even for technical) ReDrop has proved its applicability. By designing columns

with the ReDrop program, strong savings in time and costs are possible. Actual work is on the extension of ReDrop to reactive extraction. So modules for calculating reactive equilibriums and mass transfer are being developed.

## Acknowledgements

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