Experiments and modeling of ion exchange resins for nuclear power plants

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Abstract**—**Resins are used in nuclear power plants for water ultrapurification. Two approaches are considered in this work: column experiments and simulations. A software called OPTIPUR was developed, tested and used. The approach simulates the one-dimensional reactive transport in porous medium with convective-dispersive transport between particles and diffusive transport within the boundary layer around the particles. The transfer limitation in the boundary layer is characterized by the mass transfer coefficient (MTC). The influences on MTC were measured experimentally. The variation of the inlet concentration does not influence the MTC; on the contrary of the Darcy velocity which influences. This is consistent with results obtained using the correlation of Dwivedi&Upadhyay. With the MTC, knowing the number of exchange site and the relative affinity, OPTIPUR can simulate the column outlet concentration versus time. Then, the duration of use of resins can be predicted in conditions of a binary exchange.

Keywords**—**ion exchange resin, mass transfer coefficient, modeling, OPTIPUR

I. Introduction

ION exchange resins (resins) are used in manufacturing ultrapure water for nuclear power plants. Resins allow the removal of ionic impurities to subparts-per-million. Thereby in nuclear power plants, resins contribute to guarantee personnel safety, to control feed system fouling, and to keep materials performance. In order to improve removal efficiency of the resins process and to limit the amount of waste, mechanism of resins has to be better understood and predicted.

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Ion exchange resins are insoluble solid materials, which can exchange their own ions with the ions from the solution for a stoichiometrically equivalent [1]. The behavior of ion exchange resins can be characterized by several parameters like capacity, selectivity coefficient and mass transfer coefficient. Capacity is defined as the number of functional groups within the resin, *i.e.* the number of counter-ions in a specified amount of the materials. Selectivity coefficient gives an assessment of resins relative affinity; it is a way to quantify ion exchange preference to an ion from another at the equilibrium. Selectivity coefficient has been the subject of many studies [2]. Kinetic in column, due to the transport limiting step through the boundary layer of the resin beads, is characterized by a Mass Transfer Coefficient (MTC): it estimates the initial leakage, as low as it is. This parameter will be discussed in this work.

The MTC was measured in various conditions [3]. It can be calculated using an empirical correlation. The better expression for ultrapure water application was specified by Chowdiah, Foutch, and Lee [4].

In order to simulate the behavior of ion exchange resins used in the same conditions like in the ultrapurification of water from nuclear power plants, Mines ParisTech develops a dedicated code in collaboration with EDF[5]. Based on a reactive-transport approach, derived from HYTEC [6] already used to study the speciation in nuclear power plants circuits, which allows having a common thermodynamic database, the OPTIPUR software contains specific elements for modeling resins in columns. More particularly, a common MTC is used here in order to define transport across a Nernst film (stagnant layer around particle layer) [7]. This approach is simplified in comparison of the using the Nernst-Planck equations which describe the fluxes across Nernst film in a fluidized bed of resins [8], [9], but the model can still adequately represent an entire breakthrough data curve of one species from the initial leakage of this species.

II. Numerical Solution Methods

A. Transport in OPTIPUR

The resolution of advective/dispersive transport (1), in a column with resins, is realized by OPTIPUR's tool. It is a software for simulation, built from HYTEC in which diffusion/dispersion coefficients are considered independent of the species [6], [10]: this assumption is valid for strongly advective cases, relevant for water purification circuits in nuclear power plants.

$$\frac{\partial \varepsilon c}{\partial t} = \mathrm{div}\left(D_{dd}\,\overrightarrow{\mathrm{grad}}c - c\vec{U}\right) \quad (1)$$

Equation (1) is solved for the column with a 1D finite volume approach. This equation is discreetized spatially by a first-order upstream spatial scheme for advection and by a second order centered spatial scheme for dispersion. The time discreetization is a one-step centered scheme [10].

B. Chemistry in OPTIPUR

The chemistry in OPTIPUR is based on chemical library from CHESS [11]. The aqueous reaction and the ion exchange reaction are considered at equilibrium. No chemical kinetic is taken into account, considering that the limiting phenomenon is the diffusion within the Nernst film. The resolution is based on the basis component formalism: chemically independent basis species are chosen, in such way that all the derivative species, aqueous complexes or sorption sites, can be expressed with these basis species. The chemical system is obtained from the mass balance equations associated to each basis species (mass balance equation of total concentration) and from the mass action law equations associated to each derivative species.

C. Coupling of chemistry and transport

- Base of the coupling between chemistry and transport [5]

The coupling is based on a sequential iterative algorithm. At the first iteration of a new time step, initial condition is given specifying the concentration of free and sorbed species. The transport modifies the total aqueous concentration for each basis species locally at each discreetization node. A chemical resolution then calculates the new speciation, particularly the new concentration of sorbed total concentration of each basis species: the evolution of the sorbed total is then used as a chemical source term within the transport equation for a new iteration. The successive iterations take place until the system converges. The convergence criterion is calculated based on the difference of total sorbed concentration of each basis species and for each node between two iterations.

- With a diffusive term [5]

Nernst's model postulates that near the resin-water interface, there is a stagnant layer called Nernst film, where the transport is only diffusive. The transport is then convective-dispersive between the particles of resin and diffusive in the Nernst film (fig. 1).

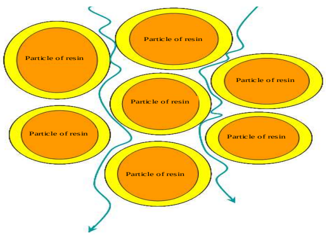

Fig. 1 Schematic diagram of the fluidized bed of resin

This representation is implemented in OPTIPUR, with a separation of the water in the Nernst film, the water between the particle of resin into which ions exchange is forbidden, and the water at the interface with resin, which have their owns concentrations (fig. 2). Chemical equilibrium is assumed in the different areas, which have their own porosity.

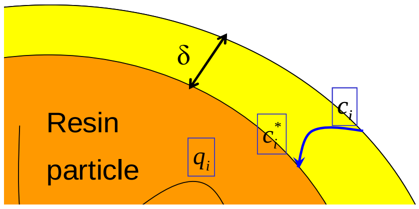

Fig. 2 Schematic diagram of the particle of resin and the Nernst Film with the correspondent concentration

The flux of basis species between « interstitial water » area and interface area, for a same height in the column is proportional to the difference of mobile species concentration between these two zones.

$$J_i = k.a_S.(1-\varepsilon_b).(c_i - c_i^*) \quad (2)$$

For the transport, it is then necessary to solve the following system of equations:

$$\begin{cases} \dfrac{\partial(\varepsilon_b c_i)}{\partial t} = \mathrm{div}\left(D_{dd}\,\overrightarrow{\mathrm{grad}}c_i - c_i\vec{U}\right) - k.a_s.(1-\varepsilon_b).(c_i - c_i^*) \\ \dfrac{\partial\left(\varepsilon_n c_i^* + (1-\varepsilon_b)\,q_i\right)}{\partial t} = k.a_s.(1-\varepsilon_b).(c_i - c_i^*) \end{cases} \quad (3)$$

In this model, MTC is the ratio of the diffusion coefficient to the boundary layer thickness; it has a velocity dimension and allows to characterize the limitation by mass transfer across Nernst film (2). The MTC is the same for all the species.

III. Experimental Methods

A series of experiments were conducted in order to characterize the behavior of the resins. We focus on a cationic resin (table 1), used to eliminate corrosion products like Fe, Co, and Ni. Ni has been chosen because this element is a relevant radioactive contaminant. The influences on the initial leakage of the inlet concentration of nickel on the one hand, and of the velocity on the other hand have been investigated. Indeed, these parameters can vary in nuclear power plants operations. Representative mixtures of nuclear power plant shutdown were prepared. First of all, a nickel powder with a high purity (99.9 %) was dissolved in a boric acid solution with bore concentration 2000 ppm. In order to make improve the dissolution, the flasks were put in a thermal chamber at 323 K. After two weeks, the solution was filtered.

A certain quantity (6 g) of humid resins was put in a 15 mm-diameter column. After that, the resin in column was regenerated with chlorydric acid (1 mol. L^{-1}) and rinsed with ultrapure water (18.2 MΩ). Finally, the resin in the column was compacted using a high flow rate injection. The height of the fluidized bed was equal to 46 mm.

Finally, the initial solution with a known concentration (table 2) was injected through a column with a Darcy velocity similar to nuclear power plant velocity (table 3).

Two samples were collected at the column outlet after two minutes. Each sample was analyzed four times with an Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) ICAP 6500 from Thermo Fisher. The experiment was reproduced on many columns in the same conditions. The experimental system used is schematized fig 3.

With the initial leakage measured at the beginning of the experiment, it is possible to calculate the mass transfer coefficient. In this intent, and to simplify the transport equations, the concentration at the particle-film, the accumulation in aqueous phase (both acceptable assumptions at the early stage of injection) and the term of diffusion-dispersion are considered negligible.

TABLE I
PHYSICAL PROPERTIES OF THE AMBERLITE IRN 97H

Parameter	Cationic resin
Name	AMBERLITE™ IRN97H
Capacity (meq.g^{-1} of humid resin)	2.74 (H^+ form)
Medium diameter of particle (mm)	0.52 [a]
Density (g.L^{-1})	800 [a]
Water retention (%)	45 – 49 [a]
% DVB	10 [a]

[a] given by manufacturer [b] obtained experimentally

TABLE II
CONCENTRATIONS TESTED IN THESE EXPERIMENTS

Inlet concentrations (ppm) (Re = 15)
Nickel
3.8 ± 2 %
5.5 ± 2 %
8.9 ± 2 %
13.5 ± 2 %

TABLE III
VELOCITY TESTED IN THESE EXPERIMENTS

Darcy velocities ([Ni] = 20 ppm)		
Volumetric (mL.min^{-1})	Linear (m.s^{-1})	Reynolds number
40 ± 5 %	0.003	6
70 ± 5 %	0.007	10
120 ± 5 %	0.011	17
177 ± 5 %	0.017	25

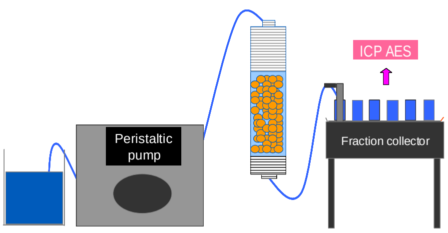

Fig. 3 Schematic diagram of the experimental system

The transport equations can this be simplified to obtain, which can be solved analytically:

$$0 = \frac{\partial}{\partial z}(-c_i U) - (1-\varepsilon_b).k.a_s.c_i \tag{4}$$

After integration, the expression of mass transfer coefficient obtained is:

$$k = -\left(\frac{1}{6(1-\varepsilon_b)}\right) \times \frac{U}{Z} \times d_p \times \ln\left(\frac{c_i^{outlet}}{c_i^{inlet}}\right) \tag{5}$$

The model used in OPTIPUR leads to an expression of mass transfer coefficient during an initial leakage similar to the one used by Chowdiah and al. [4]. These authors have demonstrated [12] that the most appropriatedempirical correlation to estimate the mass transfer coefficient in domain of ultrapure water production is the following relationship:

$$k = \frac{D}{d_p} \times Sc^{1/3} \times \mathrm{Re} \times \left[\frac{0{,}765}{(\varepsilon_b\,\mathrm{Re})^{0{,}820}} + \frac{0{,}365}{(\varepsilon_b\,\mathrm{Re})^{0{,}386}}\right] \tag{6}$$

This formula is particularly adapted for our experimental conditions, as its limit of validity depends mainly on a Reynolds number with values between 0.03 and 42000 [12]. Application of the equation (6) in a binary exchange of ions with different mobility supposes to have a representative diffusion coefficient. In this study, without means to do an *a priori* estimation, the diffusion coefficient is considered as an adjutable parameter.

IV. EXPERIMENTAL RESULTS AND THEIR MODELING

A. Experiments and Modeling of Initial Leakage

Fig. 4 shows the influence of the inlet concentration on the mass transfer coefficient. The MTC is determined using (5) with an experimental uncertainty of ± 10 %. The MTC seems to be stable for the tested range of concentrations and equal to 8.05×10^{-5} m.s^{-1}; this is consistent with the underlying theory.

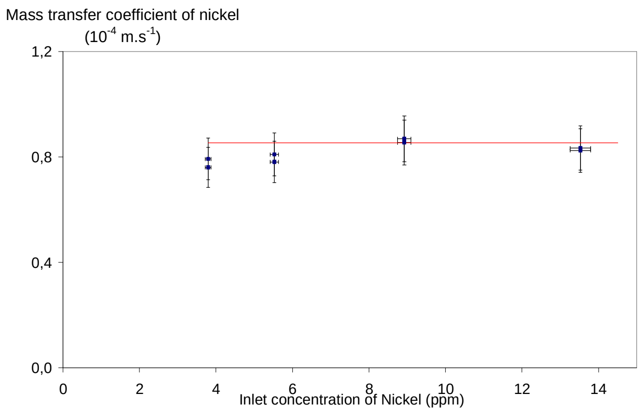

Fig. 4 Mass transfer coefficient of nickel versus inlet concentration for fixed Re=15 ■: experimentally measured and —: calculated from Dwivedi and Upadhyay[12] correlation with D=6.6 x 10^{-10} $m^2.s^{-1}$

On the contrary, the mass transfer coefficient increases linearly as a function of the Reynolds numbers (Fig. 5). In fact, the Nernst film thickness declines when the Darcy velocity grows up. The MTC is more important in this case. The MTC values experimentally obtained with their uncertainty and the MTC values from correlation presents important domains of covering. Consequently, the correlation of Dwivedi and Upadhyay could be used in order to estimate the velocity influence on the mass transfer coefficient in OPTIPUR.

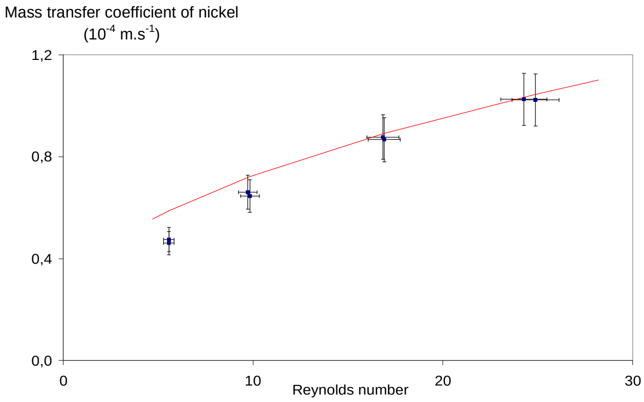

Fig. 5 Mass transfer coefficient of nickel versus Reynolds number for a inlet nickel concentration fixed at 20 mg.kg^{-1} ■: experimentally measured and —: calculated from Dwivedi and Upadhyay correlation [12] with D=6.6 x 10^{-10} $m^2.s^{-1}$

B. Experiments and Modeling of Saturation

An entire breakthrough data curve was simulated with OPTIPUR (fig. 6) using a porosity of 0.38. The curve was compared with experimental data obtained by Gressier[2].

A solution of cobalt chloride with a concentration of 62 mg.kg^{-1}, passed through a resin (Table 1) column (height 15.3 mm, diameter 15 mm). During the first experiment, the flow rate is maintained at 450 mL.h^{-1}, corresponding to a Reynolds number of 1.06. The MTC is adjusted following the initial leakage in cobalt from (5) and is equal to 2.53x10^{-5} m.s^{-1}.In the second experiment, the flow rate is maintained to 16 mL.h^{-1}, corresponding to a Reynolds number of 0.04. In this case, the mass transfer coefficient is equal to 1.15x10^{-5} m.s^{-1}, calculated from (6) since the initial leakage is not experimentally measurable in this case.

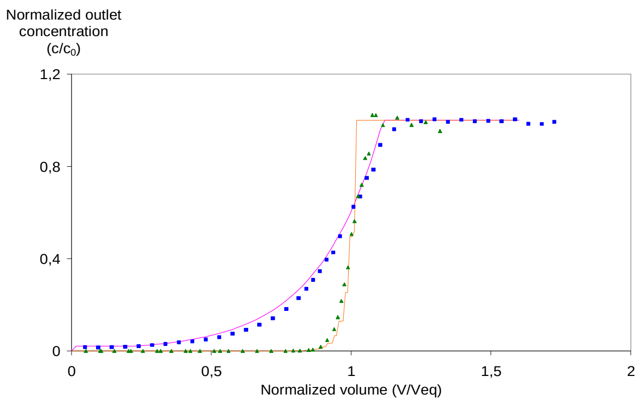

Fig. 6 Evolution of normalized outlet concentration of cobalt depending on normalized passed through volume of solution by equivalent volume obtained with a Reynolds number equal to 1.06 ■:experimentally measured [2] et —: simulated with OPTIPUR then for a Reynolds number equal to 0.04 ▲:experimentally measured [2] et —: simulated with OPTIPUR

The mass transfer coefficient model implemented in OPTIPUR correctly reproduces the evolution of the normalized outlet concentration versus time for a binary exchange from the initial leakage.

V. Conclusion

In order to understand behavior of ion exchange in columns, a numerical tool was developed. It couples the chemistry and the transport aspects including diffusion. A mass transfer coefficient has to be introduced and validated. An experimental work was performed to study the initial leakage and estimate the mass transfer coefficients. Their values were compared to those obtained by the Dwivedi&Upadhyay correlation. Apparently, the inlet concentrations have no influence, whereas the MTC values seem to increase with the Reynolds numbers. This is explained by the decrease in the Nernst film thickness with increasing velocity. When the mass transfer coefficient is known, and using the ion selectivity values for the resin, OPTIPUR can simulate the behavior of the resins during a binary exchange. The code yields the curves of the outlet concentration as a function of time; it is thus possible to anticipate the breakthrough, and consequently the life-time of the resins. This study will be completed by improvement of OPTIPUR in progress, in order to consider the multi-component exchange with a diffusion coefficient adapted for each species.

Notations

a_s specific surface area of resin ($m^2.m^{-3}$ resin) $6/d_p$
c concentration (mol.m^{-3})
c_i concentration of species i in interstitial water (mol.m^{-3})
c_i^* concentration of species i at the interface Nernst film-particle of resin (mol.m^{-3})
c_i^{inlet} inlet concentration of species i (mol.m^{-3})
c_i^{outlet} outlet concentration of species i (mol.m^{-3})
D_{dd} diffusion / dispersion coefficient ($m^2.s^{-1}$)
D diffusion coefficient ($m^2.s^{-1}$)
d_p particle diameter (m)
k mass transfer coefficient (m.s^{-1})
J flux (mol.s^{-1})
q_i concentration of species i in particle of resin (mol.m^{-3})
Sc Schmidt number (ν/D)
Re Reynolds number ($(d_pU\rho)/(\mu\varepsilon)$)
t time (s)
U velocity of Darcy (m.s^{-1})
Z column highest (m)
ε_b principal porosity (volume of water between resin's particles / total volume)
ε_n interface porosity (volume of water on the interface of resin's particles / total volume)
ρ volume mass (kg.m^{-3})
μ dynamic viscosity (kg.m^{-1}.s^{-1})

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