Technology

MODELLING OF INTERFACIAL CHEMICAL KINETICS AND EQUILIBRIUM TO THE DESIGN OF LIQUID-LIQUID CONTINUOUS CONTRACTORS

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A laboratory spray column of variable height was used for the extraction of zinc from an aqueous sulphate solution by di (2-ethylhexyl) phosphoric acid (DEHPA) in n-heptane. Three sets of nozzles of different diameters were employed in order to change the Sauter mean diameter of the dispersed phase. Experiments covered a wide range of concentrations and flow rates. Experimental results were compared with predictions obtained by using the two design algorithms (one based on the interfacial chemical kinetics, the other on interfacial equilibrium). Results simulated with the kinetic model were in good agreement with experiments over the whole range of conditions investigated, the equilibrium model underestimated the column heights by factors ranging between 0.25 and 0.5.

Key words: Contractor height, Kinetic efficiency, Equilibrium model.

Introduction

Continuous countercurrent contactors are usually designed assuming interfacial equilibrium. In the case of mass transfer with interfacial chemical reaction, this assumption is only valid if the chemical reaction is very fast with respect to the mass transfer rate (Chapman *et al* 1975). The kinetics of metal extraction with chemical reaction is in general a function of the chemical kinetics and the mass transfer coefficients of the species involved. Even for relatively simple extraction processes the interplay between chemical and diffusional parameters is such that mechanistic mathematical models are required in order to establish the rate controlling steps (Perez de Ortiz *et al* 1979; Danesi and Chiarizia 1980). This explains the growing interest in the development of this type of models observed in the literature during the past few years. However, the procedure to establish unequivocally mechanistic mathematical models for liquid-liquid extraction presents experimental difficulties that are not always easy to overcome (Perez de Ortiz *et al* 1979; Danesi and Chiarizia 1980; Perez de Ortiz 1985). This raises the question of whether this effort is justified if solely undertaken to be used in the design of contacting equipment.

In this work the mathematical model for the kinetics of extraction of zinc from aqueous sulphate solutions by di(2-ethylhexyl) phosphoric acid (DEHPA) in an organic phase is used in the calculation of the height of a continuous counter-

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current spray column and compared with results obtained with the equilibrium model. Simulated results are compared with experimental results obtained in a column of 0.05 m diameter operated in the semi-batch mode.

Mathematical Model

In the extraction column the local volumetric extraction rate, r_z, is given by

$$r_z = R_z a_c \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1)$$

where R_z is the interfacial flux of zinc ions and a_c is the interfacial area per unit volume of continuous phase. Since chemical reactions are involved, the extraction flux, R_z, is a function of chemical as well as mass transfer parameters, while the specific interfacial area depends on the operating conditions of the column, i.e. dispersed phase holdup and mean drop diameter.

For extraction with interfacial chemical reactions the mass balance of zinc ions in the aqueous phase over a differential height δh for continuous operation in unsteady state is given by

$$\frac{\partial C_{za}}{\partial t}(1-\phi_D) = \frac{L_c}{S}\frac{\partial C_{za}}{\partial h} + E_{ax,c}(1-\phi_D)\frac{\partial^2 C_{za}}{\partial h^2} - R_z a_c(1-\phi_D)\dots\dots(2)$$

The first term on the right hand side of equation (2) accounts for convection, the second term for axial mixing and the third

represents the rate of interfacial transfer.

A similar differential mass balance equation can be derived for zinc in the dispersed phase

$$\frac{\partial C_{zo}}{\partial t} \phi_D = -\frac{L_d}{S} \frac{\partial C_{zo}}{\partial h} + E_{ax,d} \phi_D \frac{\partial^2 C_{za}}{\partial h^2} + R_z a_d \phi_D \dots\dots(3)$$

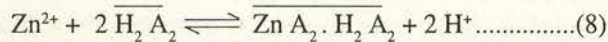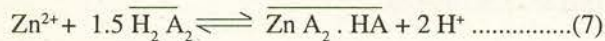At steady state, constant flow rates and neglecting backmixing, equations (2) and (3) reduce to

$$L_c \frac{dC_{za}}{dh} = R_z a_c S (1 - \phi_D) \dots\dots\dots\dots(4)$$

$$L_c \frac{dC_{zo}}{dh} = R_z a_d S \phi_D \dots\dots\dots\dots\dots(5)$$

Eq. (4) on integration gives the contractor height

$$H_c = \frac{L_c}{S} \int_1^2 \frac{dC_{za}}{R_z a_c S (1 - \phi_D)} \dots\dots\dots\dots(6)$$

Zinc interfacial flux. Murthy 1987 studied the extraction equilibrium for the zinc/DEHPA system and reported that two complexes of zinc-DEHPA are formed in n-heptane according to the stoichiometry of the reactions

$$Zn^{2+} + 1.5 \overline{H_2 A_2} \rightleftharpoons \overline{Zn A_2 . HA} + 2 H^+ \dots\dots(7)$$

$$Zn^{2+} + 2 \overline{H_2 A_2} \rightleftharpoons \overline{Zn A_2 . H_2 A_2} + 2 H^+ \dots\dots(8)$$

where bars indicate the species in organic phase and H_2A_2 is DEHPA in dimer form.

He also reported that reactions (7) and (8) took place at the interface. A schematic diagram of the concentration profiles for all the species at the interface during metal extraction is shown in Fig 1. The mass transfer is assumed to proceed
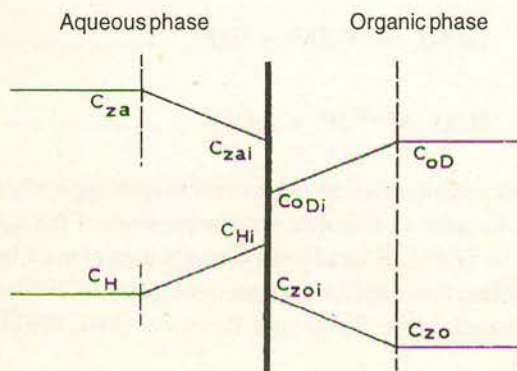

Fig 1. Concentrtion profiles at the interface during metal extraction.

according to the following steps: (1) zinc ions and DEHPA diffuse to the interface from the aqueous and the organic phase respectively. (2) Zinc ions and DEHPA react according to equations (7) and (8). (3) The zinc-DEHPA complexes and released hydrogen ions diffuse from the interface into the organic and aqueous phases respectively.

Kinetic model. The following kinetic model was proposed based on extraction and stripping studies conducted in a cell with constant interfacial area (Ajawin *et al* 1980, 1983; Murthy 1987) in the chemical control regime.

$$R_z = k_{1a} \frac{C_{za} a_o}{C_H} - k'_{1a} \frac{C_{zo} C_H}{a_o + 0.75 \sqrt{a_o}} \dots\dots(9)$$

The first term on the right hand side of this equation represents the extraction rate and the second term accounts for the stripping rate. This equation represents transfer without mass transfer control and therefore gives the maximum interfacial flux for a given set of concentrations. The activity coefficient of the DEHPA dimer and organic zinc complex (Baes Jr and Baker 1960; Baes Jr. 1962; Koncar *et al* 1988) can be calculated from equations (10) and (11) respectively:

$$\log \tau_o = -0.586 C_{oD}^{1/3} + 0.565 C_{oD} \dots\dots\dots(10)$$

$$\frac{1}{\tau_{zo}} = 1 + 0.616 \left(\frac{1.7 C_{zo}}{a_o}\right)^{1.387} \dots\dots\dots(11)$$

In the mixed control regime, the interfacial flux depends on the kinetics of both mass transfer and interfacial reaction. In this case the interfacial rate of extraction is still given by equation (9) but for interfacial instead of bulk concentrations. As the interfacial concentrations are not measureable quantities, they can be obtained from the flux equations of the species involved, which are related by the reaction stoichiometry

$$R_z = K_{za} (C_{za} - C_{zai}) = \frac{1}{1.7} K_o (a_o - a_{oi})$$

$$= -\frac{1}{2} K_H (C_H - C_{Hi}) = -K_{zo} (a_{zo} - a_{zoi}) \dots\dots(12)$$

where the subscript i indicates values at the interface.

Eliminating the interfacial values from equations (9) and (12), the final kinetic expression for the interfacial flux becomes

$$R_z = k_{1a} \frac{(C_{za} - \frac{R_z}{K_{za}})(a_o - 1.7\frac{R_z}{K_o})}{(C_H + 2\frac{R_z}{K_H})}$$

$$- k'_{1a} \frac{(a_{zo} + \frac{R_z}{K_{zo}})\ (C_H + 2\frac{R_z}{K_H})}{(a_o - 1.7\frac{R_z}{K_o}) + 0.75\ (a_o - 1.7\frac{R_z}{K_H})} \qquad ....(13)$$

This gives R_z in terms of bulk concentrations of the species involved, individual mass transfer coefficients and specific reaction rate constants for the extraction and stripping reactions. It should be noticed that equation (9) gives the maximum possible interfacial flux for a given set of bulk concentrations.

Equilibrium model. The equilibrium conditions for the interfacial reactions (7) and (8) are given by

$$(\frac{a_{zoi}}{C_{zai}})_{eq} = K_{E1}(\frac{a_{oi}^{1.5}}{C_{Hi}^2})_{eq} + K_{E2}(\frac{a_{oi}^2}{C_{Hi}^2})_{eq} ....(14)$$

Assuming that interfacial reactions are at equilibrium (Chapman *et al* 1975) and combining equation (14) with the equations for the fluxes of the different species, the following expression for R_{ZE} is obtained in terms of bulk concentrations, mass transfer coefficients and equilibrium constants:

$$\frac{(a_{zo} + \frac{R_{ZE}}{K_{zo}})}{(C_{za} - \frac{R_{ZE}}{K_{za}})} = K_{E1}\frac{(a_o - 1.7\frac{R_{ZE}}{K_o})^{1.5}}{(C_H + 2\frac{R_{ZE}}{K_H})^2} + K_{E2}\frac{(a_o - 1.7\frac{R_{ZE}}{K_o})^2}{(C_H + 2\frac{R_{ZE}}{K_H})^2} ....(15)$$

Experimental

Experiments were performed in a glass spray column of 0.05 m diameter and adjustable height. Effective heights of 1.25, 1.55 and 2.4 m were used. Details of the apparatus description, procedure and photographic set-up is given elsewhere (Saeed 1989; Saeed and Jamil 1994 a). The continuous aqueous phase contains zinc sulphate, sodium sulphate and sulphuric acid whereas the dispersed phase consists of di(2-ethylhexyl) phosphoric acid in n-heptane. The zinc sulphate, sodium sulphate and sulphuric acid were of Analar grade. The di(2-ethylhexyl) phosphoric acid (DEHPA) was of technical grade obtained from BDH Ltd. and purified by the method given elsewhere (Partridge and Jensen 1969).

Results and Discussion

Dispersed phase holdup, residence time and interfacial area. Analysis of the photographic films gave drop size distribution holdup, specific interfacial area and rising velocity. It was observed both visually and from the film that the rising drops were oscillating (Saeed *et al* 1994 b).

The equivalent diameter of single drops, d'_e, and the Sauter mean diameter, d_{32}, of the dispersion were calculated by using standard equations, namely

$$d'_e = \sqrt[3]{d^2_1 d_2} ....(16)$$

$$d_{32} = \frac{\Sigma\ nd'e^3}{\Sigma\ nd'e^2} ....(17)$$

where d_1 and d_2 are the horizontal and vertical axis lengths of the drops and n is the number of drops of diameter d'_e.

The average drop size increased with height in the stripping runs due to coalescence. This was observed both visually and by comparison of dispersion photographs taken at the bottom and top of the column. However, no substantial changes of holdup with height were observed.

For the extraction experiments good agreement was obtained between experimental values and predictions from the drop size correlations proposed by Hayworth and Treybal 1950, Kumar and Hartland 1984, and Scheele and Meister 1968. The same correlations were used for stripping but experimental drop diameters were always greater than the predicted values (Saeed *et al* 1994 b).

Extraction and stripping rates. A total of 41 runs were carried out in the column including extraction and stripping. In order to keep the activity of the species in the aqueous phase constant, an ionic strength of one was used in all runs with exception of four runs in which it was equal to 0.3. The required pH of the feed solution was obtained by addition of 1.5M H_2SO_4. The aqueous phase contained zinc sulphate, sodium sulphate and sulphuric acid. Zinc sulphate and bisulphate ions are not dissociated completely. These two solutes dissociate according to the following equations:

$$Zn\ SO_4 \rightleftharpoons Zn^{2+} + SO^{2-}_4 ....(18)$$

$$HSO^-_4 \rightleftharpoons H^+ + SO^{2-}_4 ....(19)$$
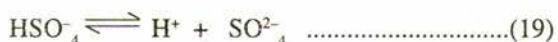
whereas sodium sulphate is assumed to be completely dissociated. In order to calculate the composition of the aqueous phase, i.e. $[Zn^{2+}]$, $[H^+]$ and ionic strength, a set of mass balance and dissociation equilibrium equations (Baes Jr. 1957; Smith and Martell 1976; Saeed and Perez de Ortiz 1991) were solved.

Considering a_c and R_z constant along the column height and that the column was operated with no flow of continuous

phase, equation (2) becomes

$$\frac{dC_{za}}{dt} = -R_z\, a_c \quad\text{..}(20)$$

Fig 2 shows the variation of zinc concentration in the aqueous phase with time for different dispersed phase flow rates. The initial slopes (t=0) were obtained by quadratic curve fitting to the concentration time data. Values of initial interfacial fluxes were calculated for each run by dividing the initial slope of the corresponding curves by the specific interfacial area.

The interfacial flux values were predicted for the extraction experiments with or without preloading of the organic phase with zinc using the kinetic and the equilibrium models (equations 13 and 15). The mass transfer coefficients (Saeed *et al* 1994 c) for the continuous and the dispersed phases were calculated from single drop correlations (Rose and Kintner 1966; Hughmark 1967; Yamaguchi *et al* 1975) for oscillating drops. Under the experimental conditions the equilibrium model overestimated the interfacial flux by more than 100% whereas the data was well fitted by the kinetic model (Saeed *et al* 1994 c).
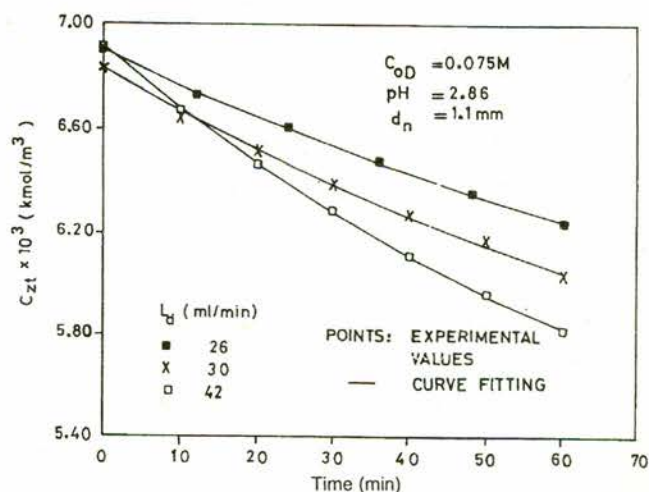

Fig 2. Variation of aqueous phase zinc concentration with time at different dispersed phase flow rates.

Height predictions from kinetic and equilibrium models. In order to test the models, samples of the outlet dispersed organic phase were taken to estimate the zinc concentration in the organic phase. A known volume of the organic phase was stripped with 2 M H_2SO_4 and the aqueous phase was analysed using an atomic absorption spectrophotometer.

Table 1
Comparison of actual and predicted heights from kinetic and equilibrium models

Expt No.	C_{zt} (10^{-3}) kmol/m^3	pH	$C_{zo,out}$ (10^{-3}) kmol/m^3	$H_{c,exp}$ m	$H^{\dagger}_{c,exp}$ m	$H^{\ddagger}_{c,exp}$ m	$H_{c,k}$ m	$H_{c,E}$ m
R5◊	9.65	2.66	2.95	1.25	1.26	1.26	1.34	0.36
R6◊	19.5	2.37	3.72				1.32	0.31
R7◊	4.79	2.98	2.11				1.31	0.46
N1◊	1.47	3.03	1.68	2.4	2.41	2.41	2.54	1.12
N2•	4.84	2.98	3.64				2.63	0.82
N3	5.9	2.97	4.59				2.6	0.86
Nold1*	9.84	2.96	2.17	1.55	1.56	1.56	1.62	0.38
Nold2*	19.7	2.66	2.74				1.61	0.37
Nold3	4.82	2.98	2.46				1.6	0.54
Nold4	6.67	2.83	1.67		1.6	1.64	1.77	0.59
Nold5	8.94	2.7	1.84				1.72	0.53
Nold6	6.64	2.83	1.53		1.62	1.69	1.73	0.57
Nold7	9.10	2.7	1.7				1.66	0.5
Nold8	6.73	2.83	1.58		1.64	1.74	1.78	0.58
Nold18	6.66	2.81	1.2		1.58	1.61	1.65	0.55

◊ Temperature = 27°C, •Temperature=22°C, *C_{oD}=0.025 kmol/m^3, †column height corresponds to $t_r + t_f$, ‡ column height corresponds to $t_r+t_f+t_c$, C_{oD}= 0.075 kmol/m^3 $C_{zo,\,in}$ = 0 kmol/m^3.

Equations (3) and (20) were solved numerically by the method of finite difference using the kinetic and equilibrium models for the interfacial fluxes. The dispersive term in equation (3) was assumed to be negligible. Column heights were estimated for the corresponding outlet concentrations of organic zinc in the dispersed phase. Mass transfer coefficients for the continuous and dispersed phases were estimated using correlations of Yamaguchi *et al* or Hughmark and Rose and Kintner respectively. Correlations of Yamaguchi *et al* and Hughmark were also used for the estimation of continuous phase mass transfer coefficients for the experiments carried out under jetting and non-jetting conditions respectively. The values of chemical reaction rate constants and equilibrium constants given elsewhere (Ajawin *et al* 1980, 1983; Murthy 1987) were modified by taking into account the incomplete dissociatio. of zinc sulphate in the aqueous phase. The modified values, $k_{Ia} = 3.95 \times 10^{-6}$ m/s, $k'_{Ia} = 2.965 \times 10^{-5}$ m/s, $K_{E1} = 0.0418$ $(kmol/m^3)^{1/2}$ and $K_{E2} = 0.0554$ at 25°C and an ionic strength of one, were used in the kinetic and equilibrium models. In the calculations, it was assumed that mass transfer rate during drop formation and coalescence was the same as the rate for rising drops. Further it was also assumed that the rising velocity of the drops is the same throughout the column. Comparison of calculated heights by using both models (kinetic and equilibrium) and actual heights are shown in Table 1. Fig 3 shows the comparison between experimentally measured and predicted dispersed phase zinc concentration from both models for different column heights. It can be seen from the Table that while the kinetic model gives good estimates of the column height, the equilibrium model underestimates it substantially. The heights
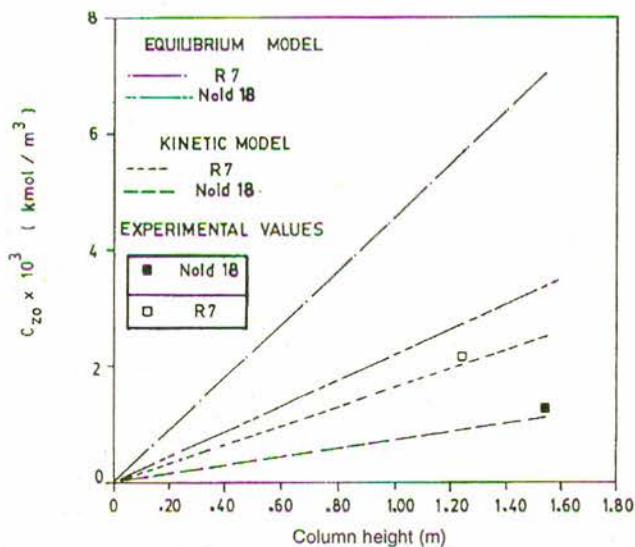
predicted with the kinetic model are in all cases higher than the actual column height. This may be due to the lower predicted interfacial flux as the experimental continuous phase mass transfer coefficients are higher than the values predicted from correlations.

Prediction of concentration-time profiles. The kinetic model was used to predict the concentration time profiles (for semi-batch operation) which were compared with experimental data. For the semi-batch operation as used in this work, the aqueous phase zinc concentration versus time curves were obtained by numerical integration of equation (20) using equation (13) to calculate the flux, R_z. The differential equation (20) was solved by using the Runge-Kutta method.

Predicted C_{zt} versus t curves were calculated for all extraction runs. Some of these results are compared with experimental data in Fig 4. Agreement between predicted and experimental data is good.

Conclusions

The extraction of zinc from an acidic aqueous sulphate solution with a solution of di(2-ethylhexyl) phosphoric acid in n-heptane has been carried out in spray column of different heights.

Comparison of experimental and predicted column heights showed that the kinetic model gave satisfactory results over the whole range of conditions investigated, while the equilibrium model underestimated the height by factors ranging between 0.25 and 0.5. Predictions become closer as the simulated system approaches the conditions under which mass
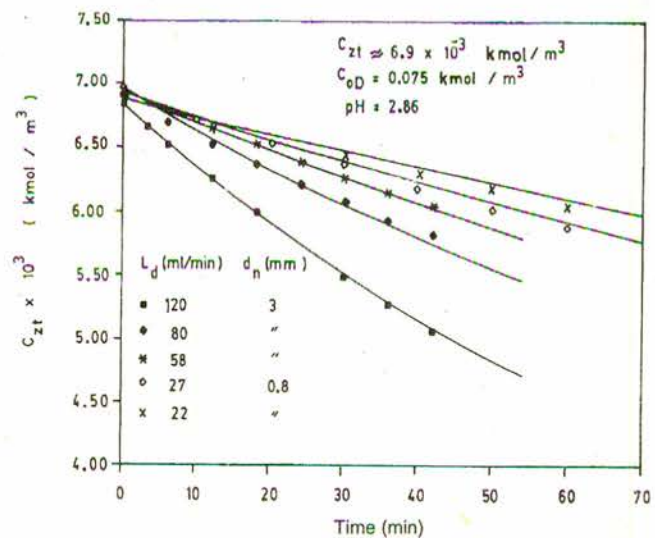

Fig 3. Comparison between experimental and predicted organic zinc concentration from kinetic and equilibrium models.

Fig 4. Experimental and predicted concentration—time curves at different operating conditions.

transfer is the only rate controlling mechanism. Also concentration-time profiles simulated with the kinetic model using hydrodynamic parameters and mass transfer coefficients calculated from correlations reported in the literature are in good agreement.

Nomenclature

a_c = Interfacial area per unit volume of continuous phase, m^{-1}.

a_d = Interfacial area per unit volume of dispersed phase, m^{-1}.

a_O = Activity of DEHPA dimer, kmol/m³.

a_{zo} = Activity of organic zinc, kmol/m³.

C = Molar concentration, kmol/m³.

d_1 = Major axis of ellipsoid, m.

d_2 = Minor axis of ellipsoid, m.

d_{32} = Sauter mean drop diameter, m.

d_e = Equivalent diameter of the dispersion, m.

d'_e = Equivalent drop diameter of single drops, m.

d_n = Inside nozzle diameter, m.

E_{ax} = Axial dispersion coefficient, m²/s.

H_c = Column height, m.

I = Ionic strength, kmol/m³.

K_{E1} = Equilibrium constant of the reaction (7), $(kmol/m^3)^{1/2}$.

K_{E2} = Equilibrium constant of the reaction (8).

K = Mass transfer coefficient, m/s.

K_{1a} = Extraction rate constant, m/s.

K'_{1a} = Stripping rate constant, m/s.

L = Volumetric flow rate, m³/s.

L' = Volumetric flow rate per nozzle, m³/s.

R_z = Interfacial flux, kmol/m² s.

r_z = Volumetric extraction rate, kmol/m³ s.

S = Cross-sectional area of column, m².

t = time, s.

t_c = Average time of coalescence, s.

t_f = Average time of drop formation, s.

t_r = Average time of drop rise, s.

Greek Letters

γ = Activity coefficient.

ϕ_D = Dispersed phase holdup for countercurrent flow.

Subscripts

1 = outlet

2 = inlet

c = continuous phase

d = dispersed phase

E = equilibrium model

eq = equilibrium values

exp. = experimental values

H = Hydrogen ion

i = interfacial values

in = inlet

k = kinetic model

o, oD = DEHPA dimer

out = outlet

za = aqueous phase zince ions.

zo = organic phase zinc

zt = total aqueous phase zinc

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