Kinetics of scandium recovery by TVEX-TBP from the solution formed after the salt chlorinator cake leaching

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Abstract. Kinetics of scandium recovery by TVEX containing tributyl phosphate was studied from the clarified leaching solution of salt chlorinator cake. To assess the contribution of each diffusion phase, experimental data were analyzed using a graphic method. To define the contribution of chemical interaction into the scandium extraction process, recovery kinetics was quantitatively described using pseudo-first order, pseudo-second order kinetic models and Elovich equation in linearized form. It was established that recovery kinetics was most accurately described with the pseudo-second-order model.

1 Introduction

Impregnated resins and Levextrel-type materials known as "Solid Extractants" (TVEX) in countries of the Commonwealth of Independent States, which combine properties of ion-exchange resins and solvent extractants, are increasingly used for scandium recovery in addition to solvent extraction and sorption [1]. Authors of [2, 3] measured equilibrium and kinetic parameters of scandium extraction by impregnated resins based on hypercross-linked polystyrene and contained di-(2-ethylhexyl) phosphoric acid (D2EHPA) and different-radical phosphine oxide (FOR) from acidic sulphate-chloride and nitric solutions. Scandium extraction was studied [4] from a 6 mol/dm^3 sulphuric solution by TVEX contained tributyl phosphate (TBP), D2EHPA, dibenzo-18-crown-6 (DB18C6), 18-crown-6 (18C6) as well as TBP/DB18C6 and D2EHPA/DB18C6.

A set of fundamental and applied researches we performed earlier showed [5-12] that TVEX containing organophosphorus extractants are the most expedient and promising materials for scandium selective recovery from ores and industrial waste. In cooperation with Titanium Institute and Ust-Kamenogorsk Titanium Magnesium Plant (TMK), we have worked out and implemented the technology of scandium selective recovery using TVEX contained tributyl phosphate (TVEX-TBP) from hydrochloric pulps formed after leaching

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salt chlorinator cake. This technology was named TVEX-Sc-Process [9, 10] and tested later at Zaporizhzhia Titanium and Magnesium Combine.

The work described in the paper was aimed to measure kinetic parameters of scandium extraction by TVEX-TBP from the clarified solution after leaching salt chlorinator cake produced at Zaporizhzhia Titanium and Magnesium Combine State Enterprise (ZTMC SE). The need to perform the study is associated with the change of the initial raw materials, reagents and process parameters of titanium chloride production that required to specify scandium recovery parameters.

2 Methods

2.1 Materials and reagents

The research was carried out using TVEX-50 % TBP manufactured at Smoly State Enterprise (Specification TU U 20.1-30168850-051:2012) by suspension co-polymerization of styrene and divinylbenzene in extractant presence. TVEX-TBP are spheric beads of macroporous copolymer contained 50 % of tributyl phosphate and 25 % of divinylbenzene. The material features the following properties: phosphorus weight fraction – at least 5.3 %; grain size range in air-dry condition is (0.63 to 2.5) mm, weight ratio of effective size fraction is 96 %, mechanical strength is 96 %, bulk density is 0.58 g/cm^3, operating temperature range is (20 to 80) °C.

To measure kinetic parameters of TVEX-TBP, effective size fraction d = (1.0 to 1.25) mm was screened using MLW Thyr 2 vibrating sieve.

Fresh ZTMC cake of a salt chlorinator was used during experiments.

All reagents used in experiments were at least reagent grade.

2.2 Experimental technique

To study scandium extraction, salt chlorinator cake was crushed to coarseness ≤ 10 mm and leached with hydrochloric acid solution with concentration 20 g/dm^3 at phase ratio Solid:Liquid = 1:1.2 and room temperature to its complete dissolution and further filtration in a Buchner funnel under vacuum through White Ribbon filter. The prepared clarified solution had density 1.305 g/dm^3.

Extraction kinetics was studied by the limited solution volume method at phase ratio Solid:Liquid = 1:50 (TVEX-TBP weighed sample was 2 g) during 24 hours at a temperature of 20 ± 2 °C from the clarified solution with scandium concentration 53 mg/dm^3. The study was carried out in a temperature-controlled cell with agitation by a MLW ER 10 propeller-type agitator provided rotation speed more than 200 rpm. Temperature was controlled using MLW UH8 ultra thermostat.

2.3 Analytical techniques

The density of clarified solution produced from the salt chlorinator cake was measured using a picnometer.

Scandium concentration in clarified solution was measured using Labtam 8440 atomic emission spectrometer.

TVEX-TBP capacity was calculated by the difference of scandium concentration in the aqueous phase by the following equation:

$$q_\tau = \frac{([Sc]_0 - [Sc]_\tau) \cdot V}{m}, \quad (1)$$

where $[Sc]_0$ and $[Sc]_\tau$ are initial scandium concentration and its concentration in time point τ, min, in the aqueous phase, respectively, mg/dm^3, V is the solution volume, dm^3, and m is the mass of the air dry resin, g.

3 Results and discussion

Figure 1 shows an integral kinetic curve of scandium extraction by TVEX-TBP from scandium clarified solution with initial concentration 53 mg/dm^3.

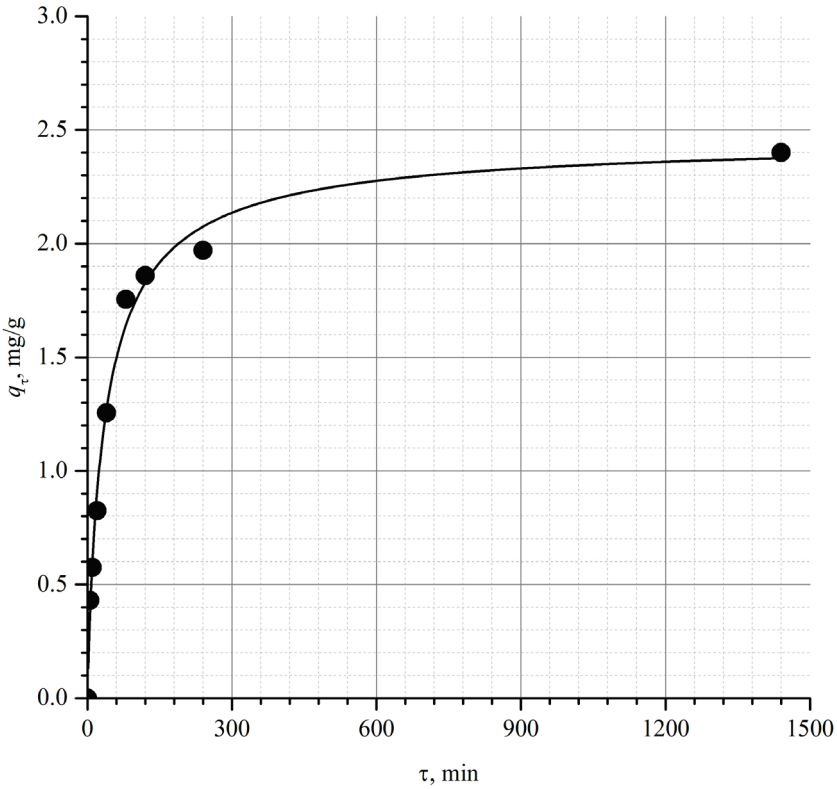

Fig. 1. Integral kinetic plot of scandium extraction by TVEX-TBP: (•) experimental data, (–) pseudo-second order fit.

As it is seen from the data obtained, TVEX-TBP featured high kinetic characteristics; thus, about 80 % of scandium were recovered during 1.5 hours. These results agreed with the data previously obtained for scandium extraction from 8 mol/dm^3 model hydrochloric solution [5]. TVEX-TBP high kinetic parameters were due to its meso- and macroporous structure, which had the following parameters [10] according to the mercury porosimetry data: total pore volume 1.39 cm^3/g, specific surface area 163.42 m^2/g, and average effective pore radius 16.95 nm. We showed previously [9, 11] that this type of materials had a globular structure, where each individual bead consisted of a large number of microglobules formed during the extractant separation into a separate phase. Microglobule dimensions and the space between them depended upon the extractant type and amount as

well as cross-linking degree. Almost the entire surface and pore volume in TVEX-TBP had multi-fractal properties.

Since impregnated resins and TVEX-TBP combine the properties of sorbents and selective solvent extractants, extraction kinetics for these materials [1] was characterized with the approaches used for ion-exchange resins [13]. Extraction process consists of several phases: metal ion diffusion through a liquid film adjacent to the TVEX-TBP bead surface (film diffusion), diffusion inside the bead in aqueous solution (intra-particle diffusion), the chemical reaction of the extracted component with the extractant and diffusion of reaction products inside the bead in extractant. The reaction with recovered component describes chemical kinetics while the rest phases are of diffusion nature and described by Fick's laws. In most cases, the recovery process is limited by the film or intra-particle diffusion phases.

To assess the contribution of each diffusion phase, experimental data were analyzed using a graphic method in coordinate systems F–$\tau^{1/2}$, and $B\tau$–τ (Fig. 2, 3), where: τ is time, F is the fractional equilibrium attaining function, $B\tau$ is dimensionless time proposed by Boyd and tabulated as the $B\tau=f(F)$ dependence [13]. Linearity of plots in corresponding coordinate systems allowed to determine the recovery limiting phase. Determination factor R^2 served a linearity criterion.

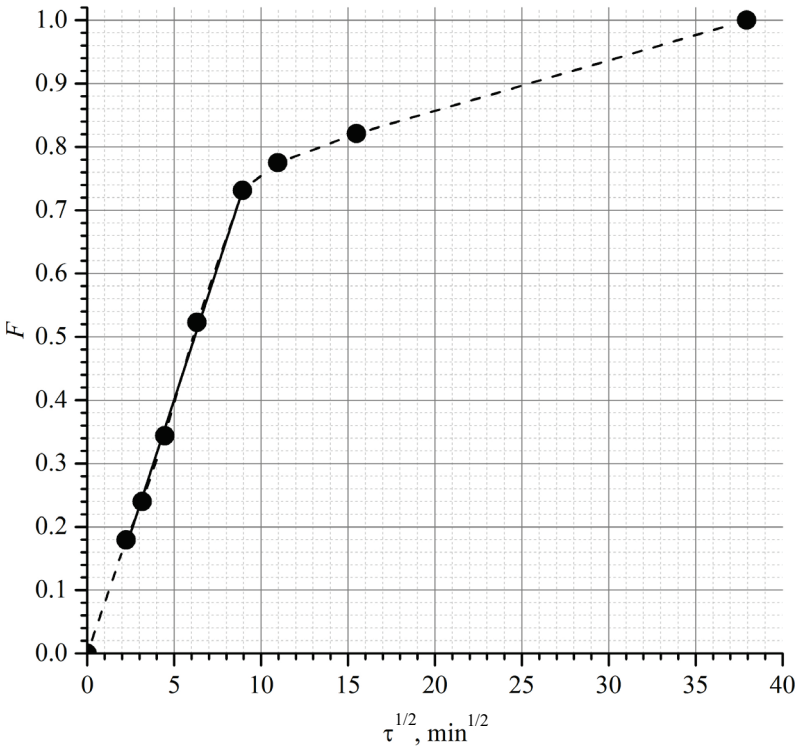

Fig. 2. Kinetic modelling of scandium recovery in coordinates $F=f(\tau^{1/2})$.

Kinetic plot of scandium recovery in coordinates $F=f(\tau^{1/2})$ (Fig. 2) was a straight line extended almost from the coordinate origin up to the equilibrium attaining degree 0.74 (R^2=0.9981) that indicated intra-particle diffusion as a limiting phase. Then, deviation from the linear dependence was observed indicating significant contribution of film diffusion.

Linear dependence $B\tau=f(\tau)$ (R^2= 0.9770) was also typical for intra-particle diffusion (Fig. 3), where relative rate [13] of scandium recovery was also directly proportional to

diffusion factor and inversely proportional to the square of the TVEX-TBP bead radius; and effective diffusion factor could be calculated as:

$$D = \frac{B\tau \cdot r^2}{\pi^2 \cdot \tau}, \quad (2)$$

where D is effective internal diffusion factor, m^2/s; r is average bead radius, m, calculated by the formula [5]:

$$r = 0.435 \cdot (r_{min} + r_{max}), \quad (3)$$

where r_{min} and r_{max} are minimum and maximum bead radius, correspondingly, m.

Effective diffusion factor was $D = 3.64 \cdot 10^{-12}$ m^2/s that agreed with the previously calculated diffusion factor $D = 3.6 \cdot 10^{-12}$ m^2/s for scandium extraction by TVEX-TBP from the model 8 mol/dm^3 hydrochloric solution [5].

Half-recovery time, s, calculated by the formula:

$$\tau_{1/2} = 0.03 \cdot r^2 / D \quad (4)$$

is about 32.9 minutes and close to experimental data ($\tau_{1/2}$ about 40 minutes).

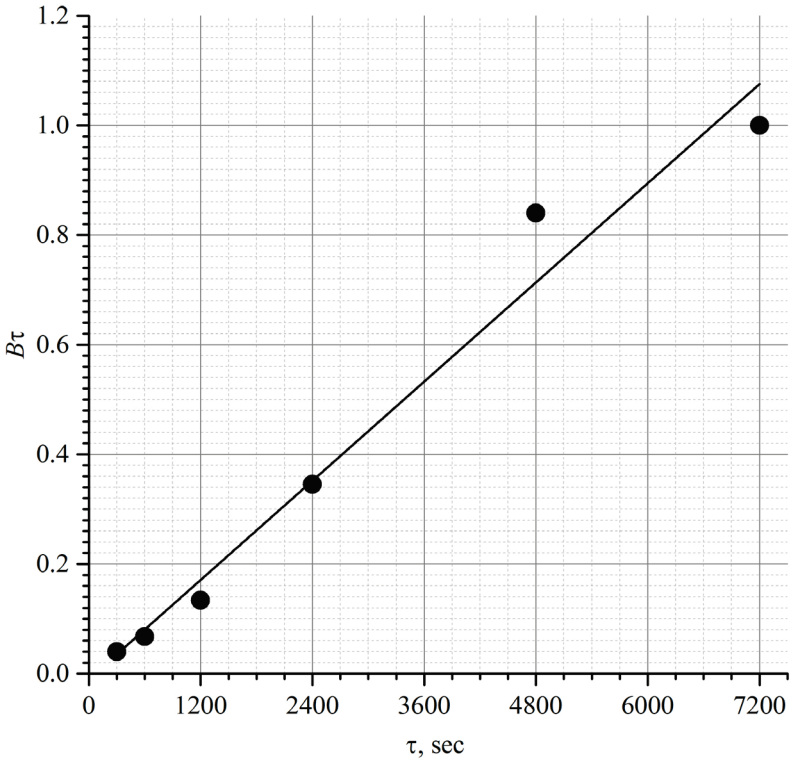

Fig. 3. Kinetic modelling of scandium recovery in coordinates $B\tau = f(\tau)$.

To define the contribution of chemical interaction into the scandium extraction process, recovery kinetics was quantitatively described using pseudo-first order, pseudo-second order kinetic models and Elovich equation in linearized form; their parameters are given in Table 1. Initial recovery rate h for the pseudo-second model, mg/(g·min), was calculated by the equation:

$$h = k_2 \cdot q_e^2 . \quad (5)$$

The pseudo-second-order model fitted most precisely ($R^2 = 0.9996$) experimental data. Rate constant k_2 for the pseudo-second order model was $1.095 \cdot 10^{-2}$ g/(mg·min).

Calculated equilibrium capacity q_e and experimental capacity q_{exp} had similar values 2.456 mg/g and 2.40 mg/g, correspondingly.

Table 1. Kinetic data processing results.

Model equation	Parameters	Value
Pseudo-first-order $q_\tau = q_e(1 - \exp(-k_1 \cdot \tau))$	Calculated equilibrium capacity q_e, mg/g	1.630
	Rate constant k_1, min^{-1}	$6.702 \cdot 10^{-3}$
	Determination factor R^2	0.8204
Pseudo-second-order $q_\tau = \frac{\tau \cdot k_2 \cdot q_e^3}{q_e + \tau \cdot k_2 \cdot q_e^2}$	Calculated equilibrium capacity q_e, mg/g	2.456
	Rate constant k_2, g/(mg·min)	$1.095 \cdot 10^{-2}$
	Determination factor R^2	0.9996
	Initial sorption rate h, mg/(g·min)	3.976
Elovich $q_\tau = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(\tau)$	Initial sorption rate α, mg/(g·min)	0.242
	Desorption constant β, g/mg	2.603
	Determination factor R^2	0.9478
Experimental equilibrium capacity q_{exp}, mg/g		2.40

The pseudo-second-order model adequately fitted kinetics of scandium recovery by FOR-impregnated resin from nitric solutions [3] and by Lewatit TP 272 contained Cyanex 272 from sulphuric ones [1].

4 Conclusions

As a result of the study, it was established that TVEX-TBP had high kinetic properties during scandium recovery from the clarified solution produced by leaching the salt chlorinator cake.

Sorption kinetics was most accurately described with the pseudo-second-order model. Experimental data were evaluated in coordinate systems F–$\tau^{1/2}$ and $B\tau$–τ. Scandium effective diffusion factor in TVEX-TBP was calculated. It was shown that its value correlated to the diffusion factor value when extracting scandium by TVEX-TBP from the model hydrochloric solution.

The results obtained may be used when creating the complex processing and disposal technology of salt chlorinator cake formed as a waste at Zaporizhzhia Titanium and Magnesium Combine State Enterprise.

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