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# Kinetics of hydrochloric acid leaching of niobium from TiO2 residues

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## Abstract

Production of $TiO_2$ generates waste containing significant quantities of valuable metals which if recovered, could have a positive impact on the economics of TiO2 production and waste management. In this investigation, the kinetics of HCl leaching of niobium from $TiO_2$ residues are studied. The complex mineralisation of niobium in its primary ores makes economic recovery very difficult, often demanding the use of chlorination, carbochlorination or fusion with alkali fluxes for breakdown of its mineral concentrates and upgrading before leaching in acid, usually hydrofluoric acid. The effects of parameters leaching temperature (25 - 90 $^{o}$C), HCl concentration (0.5 - 4 M), stirring speed (100 - 500 rpm) and solid - liquid ratio were determined in the experiments. A maximum niobium extraction rate of more than 90 % was achieved within 60 minutes of leaching the residues in 4 M HCl at 70 $^{o}$C. The kinetics analysis showed that the dissolution of niobium in HCl is governed by pore diffusion of the random pore model, with an activation energy of 16.8 ± 1.2 kJ mol$^{-1}$ Nb.

*Keywords*: Dissolution kinetics; Niobium; Extraction; Leaching; Rutile; TiO2 residues

## Introduction

As much as 85 % of global niobium demand is used for making ferroniobium, which is subsequently used in the steel industry for manufacturing high strength low alloy and carbon steels. Addition of only 200 ppm niobium can significantly increase the yield and tensile strength of steel (Kirk et al. 1996), providing qualities that are required for usage of the steels in construction, oil and gas pipelines and in the automotive industry.

Commercial production of pigment grade $TiO_2$ using the chloride process generates significant quantities of byproducts, composed of unreacted coke, unreacted ore, and a mixture of metal chlorides and oxychlorides. Depending on the type of feedstock used, 0.6 - 1 tonne of wet, neutralised waste is generated per tonne of pure $TiO_2$ produced and this waste contains up to 1.5 wt.% hydrated niobium oxide. Globally, about 3.5 million tonnes of waste from the chloride process are landfilled

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annually, containing about 50 000 tonnes niobium as $Nb_2O_5$. Ironically, niobium is among the 20 critical raw materials identified by the European Commission due to:

1. Its economic importance in Europe
2. The risk associated with supply security.

Mine production of niobium in 2014 was estimated to be 59 000 tonnes (U.S Geological Survey 2015), meaning that reclamation of niobium from chloride wastes could supply a significant amount of niobium into the value chain and reduce the risky dependence on Brazil and usage of environmentally unfriendly reagents such as HF.

Compared to a lot of metals, light rare earths (RE) included, niobium has a relatively low abundance (24 ppm) in the average continental crust (Gupta & Suri 1993). Niobium mineral deposits are most commonly associated with igneous rocks, the most important mineral being pyrochlore, $(Ca,Na)_{2-m}Nb_2O_6(O,OH,F)_{1-n}xH_2O$ where the lattice positions of Ca and Na can also be occupied by elements such as Ba, Sr, RE, Th and U (Habashi 1997). In primary deposits, pyrochlore is always inter-stratified in carbonates containing between 0.5 and 0.7 % niobium pentoxide. Depending on the type of igneous rock they are associated with, niobium deposits can be divided into three main types (Küster 2009).

1. Carbonatites and associated rocks
2. Alkaline to peralkaline granites and syenites
3. Granites and pegmatites of the lithium (Li), caesium (Cs) and tantalum (Ta) (LCT family)

Although moderately high contents of niobium have been observed in some granites and pegmatites that are not part of the three categories mentioned above, there are no known economic examples (British Geological Survey 2011). Commercially important niobium deposits are in Brazil, Canada, Nigeria and Zaire, with the Brazilian ores containing the highest percentage of niobium (2.5 – 3 %) from secondary deposits where the niobium has been enriched by weathering (Habashi 1997; British Geological Survey 2011). Columbite, $(Fe,Mn)(Nb,Ta)_2O_6$ is the second most important niobium ore deposit. Niobium can also be present in RE such as stibiocolumbites ($Sb(Nb,Ta)O_4$), fergusonites ($RENbO_4$) and euxenites ($(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$). According to the U.S Geological survey (U.S Geological Survey 2015), Brazil led the niobium production industry with 90 % of global production, followed by Canada with 9 % in 2014.

Leaching of niobium containing materials in an $HF – H_2SO_4$ system is arguably the most established method (Kirk et al. 1996; Chidambaram & Banerjee 2003; Gupta & Suri 1993) for processing ores and concentrates with more than 10 % $Nb_2O_5$. An alternative method involves fusing the niobium containing ores with acidic or alkaline fluxes such as $KHSO_4$ and NaOH before leaching in water or HCl (Gupta & Suri 1993; NIIR Board of Consultants & Engineers 2005; Koerner & Smutz 1956).

A process for recovering niobium from chloride wastes has been reported by (Gireesh et al. 2014), however, no kinetics data is reported in the literature.

Understanding kinetics data is a key requirement of any process design and optimization work. Observing how changing a certain parameter affects the rate of reaction allows a scientist to infer what is going on at the molecular level and hence allow them to know how long to hold the reaction at one stage before moving on, ensuring that the reactions are finished before moving on to the next ones. The scope of the study was predominantly focused on dissolution rates of niobium from the $TiO_2$ residues and the information obtained is applicable to niobium recovery from landfill sites.

## Experimental

### Materials

The neutralised $TiO_2$ waste residues as wet cake were obtained from a titanium dioxide plant employing a typical range of ore feedstocks. Analytical grade HCl was used for dissolutions and dilutions were done using deionised water. All glassware was cleaned with dilute nitric acid and rinsed with distilled water several times before use.

### Characterisation

Niobium content of the sampled solutions was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The elemental composition of the cake (2.4 wt.% as $Nb_2O_5$, the rest being mainly $TiO_2$ and $Fe_2O_3$) was determined by X-ray fluorescence spectrometry (XRF).

### Leaching procedure

A 5 kg batch of neutralised $TiO_2$ residues was oven dried to constant weight (approximately 2.5 kg) at 80 $^oC$, ground and sieved through a 100 micron sieve. The acid leaching experiments were conducted batch-wise in a closed 1500 mL Pyrex reaction flask. Agitation was provided by a magnetic stirrer that enabled adequate dispersion of the particles without evaporation loss of the solution, and heating by a thermostatically controlled hot plate.

For determining the influence of leaching temperature, 50 g of the dried cake was mixed with a pre-calculated amount of deionised water and placed in the reactor. The slurry was then heated to predetermined temperature (25, 50, 60, 70, 80 or 90 $^oC$) under continuous agitation at 300 rpm and once temperature was stabilised, a pre-calculated amount of concentrated hydrochloric acid was injected into the reactor to make 1000 mL of 1.5 M HCl solution as required. For determining the effect of HCl concentration, 50 g of the filter cake was mixed with a pre-calculated amount of deionised water and placed in the reactor. The slurry was then heated to 70 $^oC$ and predetermined amounts of concentrated HCl were injected into the reactor to make 1000 mL of 0.5, 1.5, 2.5, 3 or 4 M HCl solution. The influence of solid - liquid ratio was investigated by mixing 50 g of the filter cake with a pre-calculated amount of deionised water and placing in the reactor. The slurry was then heated to 70 $^{o}$C and predetermined amounts of concentrated HCl were injected into the reactor to make a 4 M HCl solution corresponding to required solid - liquid ratios. To investigate the influence of stirring speed, 50 g of filter cake was dissolved in 1000 mL of 1.5 M HCl and leached at stirring speeds of 0, 100, 200, 300, 400 and 500 rpm at 70 $^{o}$C for 60 minutes.

In all leaching experiments, 10 mL samples of the slurry were drawn from the reaction flask at selected time intervals using a syringe and quickly filtered to prevent further reaction between the filter cake and acid in the slurry sample. Filtration was done using a Buchner funnel connected to a vacuum pump and Whatman 541 filter paper was used to produce clear solutions. To determine the errors associated with sampling techniques, four cake batches were leached at 70 $^{o}$C for 60 minutes and filtered immediately while hot. Five samples from each of the leached batches were then drawn and analysed by ICP OES.

## Results and Discussion

### The effects of leaching temperature and time

The influence of leaching temperature and time on the extraction rate of niobium was investigated by leaching the as-received filter cake at 25, 50, 60, 70, 80 and 90 $^{o}$C. An initial HCl concentration of 1.5 M, stirring speed of 300 rpm and solid-liquid ratio of 50 $gL^{-1}$ were employed during the investigations. The extraction rate curves obtained are shown in Fig. 1.

**Fig. 1**: The effects of leaching temperature and time on the extraction rate of niobium

Fig. 1 shows that increasing the leaching temperature from 25 $^{o}$C to 80 $^{o}$C raises niobium extraction rate from nearly 30 % to just under 50 % within 60 minutes of leaching. Raising the temperature further to 90 $^{o}$C lowers the extraction rate to about 35 %. The decrease in niobium extraction rate was not expected and may be due to precipitation of hydrous oxides of niobium (Rodrigues & da Silva 2010). A method for separation and pre-concentration of niobium, where an acidic solution is heated to hydrolyse and coagulate niobium, forming niobium oxides has been demonstrated (Marczenko & Kloczko 2000). A similar phenomenon has been observed on other transition metals such as zirconium (Silva et al. 2002), nickel (Szymczycha-Madeja 2011), which precipitates as an oxalate at temperatures above 50 $^{o}$C and titanium, which precipitates as hydrous titanium dioxide at temperatures above 70 $^{o}$C (Pfaff 2008). For all temperatures investigated, the extraction rate curves show that increasing the residence time above 60 minutes will increase the fraction of niobium extracted in 1.5 M HCl.

A leaching temperature of 70 $^{o}$C was employed for all remaining investigations on metal extraction rates as both the filtration and leaching rates were similar to those observed at 80 $^{o}$C and leaching at 90 $^{o}$C lowers niobium extraction rate. Repeat experiments showed that the niobium extraction values for different cake samples are within 3 % of the median while repeat analyses of filtrates from each cake samples were within 2 %.

### Effect of HCl concentration and time

To study the effects of HCl concentration and residence time on the extraction rate of niobium, HCl concentration was varied between 0.5 M and 4 M, keeping leaching temperature, solid-liquid ratio and stirring speed constant at 70 °C, 50 $gL^{-1}$ and 300 rpm respectively. The extraction rate curves obtained are shown in Fig. 2.

**Fig. 2**: The effects of HCl concentration and time on the extraction rate of niobium

Increasing HCl concentration significantly increases extraction rate of niobium because increasing the concentration of reactants increases the concentration gradient, hence the flow rate across the interfacial boundary layer (Marsden & House 2006). Raising the HCl concentration from 0.5 M to 4 M increases the fraction of niobium extracted from under 5 % to more than 90 % after 60 minutes. Although there is no significant difference in extraction rate of niobium when either 3 M or 4 M HCl is used, all remaining investigations were carried out using 4 M HCl for cake dissolution because filtration of residues from leaching of as-received cake using 4 M HCl is significantly faster than when leached in 3 M HCl.

### The effects of solid - liquid ratio and time

Increasing solid - liquid ratio decreases the association between reactants, and often the extraction rate during leaching reactions. The effects of solid - liquid ratio and time on the extraction rate of niobium from filter cake was investigated by varying the ratio between 40 $gL^{-1}$ and 200 $gL^{-1}$ for an initial acid concentration of 4 M, a leaching time of 60 minutes and maintaining the leaching temperature at 70 °C. The results obtained are presented in Fig. 3.

**Fig. 3**: The effects of solid-liquid ratio and leaching time on the extraction of niobium

In the range of solid - liquid ratios investigated, there is no significant difference in extraction rate of niobium, meaning that the decrease in association between the HCl and filter cake is not significant.

### Effect of stirring speed

The film thickness around filter cake particles suspended in a reaction vessel varies with the stirring speed. Increasing the stirring speed minimises the diffusion layer thickness, hence increases the mass transfer rates through the diffusion layer. The sensitivity of metal extraction rates to stirring speed can be used for distinguishing between film diffusion and particle diffusion controlled reaction kinetics. For intra-particle diffusion controlled reactions, the ion exchange rates are independent of the stirring speed. The influence of stirring speed and leaching time on extraction rates of niobium from the filter cake was investigated by varying the stirring speed between 100 - 500 rpm over 60 minutes and the results are presented in Fig. 4.

Fig. 4: The effects of stirring speed and leaching time on the extraction of niobium

Fig. **4** shows that the influence of stirring speed is minimal for the extraction of niobium from filter cake. Increasing the stirring speed from 100 rpm to 500 rpm only has a 10 % increase in niobium extraction rate.

## Kinetics

Leaching processes usually involve several simultaneous elementary reactions, with each subject to mass action kinetics. This means simplifying assumptions are used to develop closed-form rate equations and such assumptions include:

- **Pseudo-steady-state**: assuming that concentration of unstable intermediates does not change during reaction.
- **Equilibrium**: for certain fast reversible reactions and completion of very fast irreversible steps.
- **Rate determining step**: assumes that the reaction rate is determined by the slowest steps in the reaction network composing the overall reaction.

Assuming that the rate-determining step is the slowest step in the leaching process and it controls the overall leaching kinetics, several steps in the leaching process can be eliminated in deriving the kinetic equations. The rate-limiting step can either be:

1. Diffusion in the liquid film surrounding the solid particles (film diffusion).
2. Diffusion within the particles, in pores or through the solid phase itself (particle diffusion).
3. Chemical reaction at the surface of the particle (surface reaction).

Leaching experiments were carried out at various stirring speeds, ensuring that particles were always fully suspended, thereby excluding film diffusion from being the rate-controlling step. As shown in Fig. **4**, stirring speed has a negligible influence on dissolution of niobium, confirming that film diffusion does not control the metal dissolution process.

Several models for fluid - solid reactions, including the shrinking core model, uniform pore model; random pore model, grain model and homogeneous model were assessed for describing the niobium dissolution kinetics. The shrinking core and random pore models assume that an inert product layer forms as the reaction progresses and analysis of leach residues shows no such material, meaning that the models cannot be used for describing the kinetics.

The random pore model assumes that the filter cake has void elements of similar geometry, such as cylindrical pores or spherical voids with random intersections

(Georgiou & Papangelakis 1998). The grain model visualises cake particles as pellets consisting of individual dense grains compacted together and each grain reacts individually following an unreacted shrinking core pattern where the HCl diffuses through the interstices of the solid grains while undergoing reaction, progressively reducing the amount of unreacted filter cake. According to (Bhatia & Perlmutter 1981), the random pore and grain models are similar in their descriptions and solutions, however only graphical solutions exist for the random pore model when pore diffusion controls. The grain model however offers the analytical solution, which gives a good fit to the data and should adequately represent the random pore model. Based on its description, the random pore model was chosen for describing the kinetics of dissolution of niobium in hydrochloric acid. For chemically controlled reactions, the analytical expression derived by (Bhatia & Perlmutter 1981) is:

$$\alpha = 1 - e^{[-kt - \psi(\frac{kt}{2})^2]} \qquad (1)$$

where

$$k = rs_o \qquad (2)$$

$$\psi = \frac{4\pi L_o(1-\varepsilon_o)}{S_o^2} \qquad (3)$$

$s_o$ is the initial molar surface area (m$^2$ mol$^{-1}$), $L_o$ is the initial characteristic length of a pore per unit volume (m m$^{-3}$) and $S_o$ is the initial reaction surface area per unit volume (m$^2$ m$^{-3}$).

When pore diffusion controls the leaching process, the analytical expression suggested by (Bhatia & Perlmutter 1981) is:

$$1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha) = \frac{\tau^*}{\sigma^2} \qquad (4)$$

where

$$\tau^* = (\frac{bkC_{a,f}}{\rho_m}\frac{A_g}{F_g V_g})t \qquad (5)$$

$$\sigma = \frac{R_p}{3}(\frac{3k(1-\varepsilon)}{2D_e}\frac{A_g}{F_g V_g})^{1/2} \qquad (6)$$

$F_g$ represents the grain shape factor, with a value of either 1, 2 or 3 for grain shapes of flat plate, cylinder or sphere respectively. $A_g$ and $V_g$ represent the external surface area (cm$^2$) and volume (cm$^3$) of grains respectively. $\rho_m$ is the molar density of the cake particles (mol cm$^{-3}$), $R_p$ is the radius of the cake particles (cm), ε is the porosity of cake particles, $b$ is the stoichiometric factor and $k$ is the reaction rate constant (mol m$^{-2}$ min$^{-1}$).

Modeling of the kinetics using the chemical reaction control expression (equation 1) gave a negative structural parameter ($\psi$) value, indicating that pore diffusion probably dominated the leaching kinetics.

In Fig. 5, the variation of $1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha)$ with time ($t$) is plotted for leaching temperature (5a), HCl concentration (5b), solid-liquid ratio (5c) and stirring speed (5d) according to the random pore model. As is evident from the figure, the random pore model equation correlates well with experimental data. Leaching temperature and acid concentration show the most influence on niobium dissolution.

Fig. 5: Plots of $1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha)$ with time for leaching temperature, acid concentration, solid-liquid ratio and stirring speed respectively

(5a) Variation of $1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha)$ with *t*
(5b) Variation of $1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha)$ with *t*
(5c) Variation of $1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha)$ with *t*
(5d) Variation of $1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha)$ with *t*

The activation energy can be calculated by employing the linearised form of the Arrhenius equation (equation 7).

$$\ln k = \ln A_o - \frac{E_a}{RT} \quad (7)$$

$A_o$ represents the pre-exponential frequency factor, computed from the intercept of the $\ln k$ against $1/T$ plot. $R$ is the universal gas constant (8.314 kJ mol$^{-1}$ K$^{-1}$) and $T$ is the reaction temperature (K).

Plotting $\ln k$ against $1/T$ for all temperatures gives a linear relationship and activation energy $E_a$ can be determined from the slope.

Fig. 6: Arrhenius plot for niobium dissolution in HCl

Fig. 1 highlighted that at 90 $^{o}$C, niobium may be undergoing a hydrolysis precipitation reaction, leading to a lower than expected recovery. When calculating the activation energy, the $\ln k$ value for leaching at 90 $^{o}$C is therefore not used. From the Arrhenius plot, the minimum energy required for dissolution of niobium from the filter cake was calculated to be 16.8 ± 1.2 kJ mol$^{-1}$ Nb. The activation energy is well within the typical range for pore diffusion controlled reaction kinetics (Han 2002; Lasaga 2014). Some researchers have obtained comparable values of activation energy for the acid dissolution of niobium ores, reporting figures in the region of 15 - 22 kJ mol$^{-1}$ (Ayanda et al. 2012; Ayanda & Adekola 2012).

## Conclusions

HCl leaching of $TiO_2$ residues is effective for dissolution of niobium for subsequent selective precipitation and recovery. Leaching temperature and HCl concentration have a significant role on niobium extraction rates, with more than 90 % extraction achieved within 60 minutes of leaching the residues at 70 $^oC$ using 4 M HCl. Leaching of the filter cake in 3 M HCl is efficient but the pulp has poor filtration characteristics therefore 4 M HCl is recommended. Leaching of the residues at 90 $^oC$ results in lower niobium extraction rates, possibly due to precipitation induced by hydrolysis. Kinetics analysis shows that the acid dissolution is governed by pore diffusion kinetics of the random pore model and the calculated activation energy value of 16.8 ± 1.2 kJ $mol^{-1}$ Nb is within the typical figures reported in literature. This study shows that it may be possible to recover niobium not only from fresh neutralised waste, but also from landfill sites where the neutralised residues have been placed over the last few decades.

## Nomenclature

| | |
|---|---|
| $s_o$ | Initial molar surface area |
| $L_o$ | Initial characteristic length of a pore per unit volume} |
| $\varepsilon$ | porosity of particle, $\varepsilon_o$ initial porosity of particle} |
| $\alpha$ | conversion |
| $\psi$ | dimensionless structural parameter of random pore model ($\psi > 0$)} |
| $\rho_m$ | molar density (mol $cm^{-3}$) |
| $A_g$ | grain external surface area ($cm^2$) |
| $b$ | stoichiometric coefficient |
| $C_A$ | concentration of fluid reactant (mol $L^{-1}$) |
| $C_{a,f}$ | bulk concentration of fluid reactant (mol $L^{-1}$) |
| $D_e$ | effective diffusivity of a fluid in porous solid ($cm^2$ $s^{-1}$) |
| $F_g$ | grain shape factor |
| $r$ | rate of reaction (mol $m^{-2}$ $min^{-1}$) |
| $R_p$ | particle radius (m) |
| $t$ | time (minutes) |
| $V$ | volume of solution (ml) |
| $V_g$ | volume of grain ($cm^3$) |
| $A_o$ | pre-exponential frequency factor |
| $E_a$ | activation energy (kJ $mol^{-1}$) |
| $R$ | universal gas constant (8.314 kJ $mol^{-1}$ $K^{-1}$) |
| $T$ | reaction temperature (K or $^oC$ as specified) |

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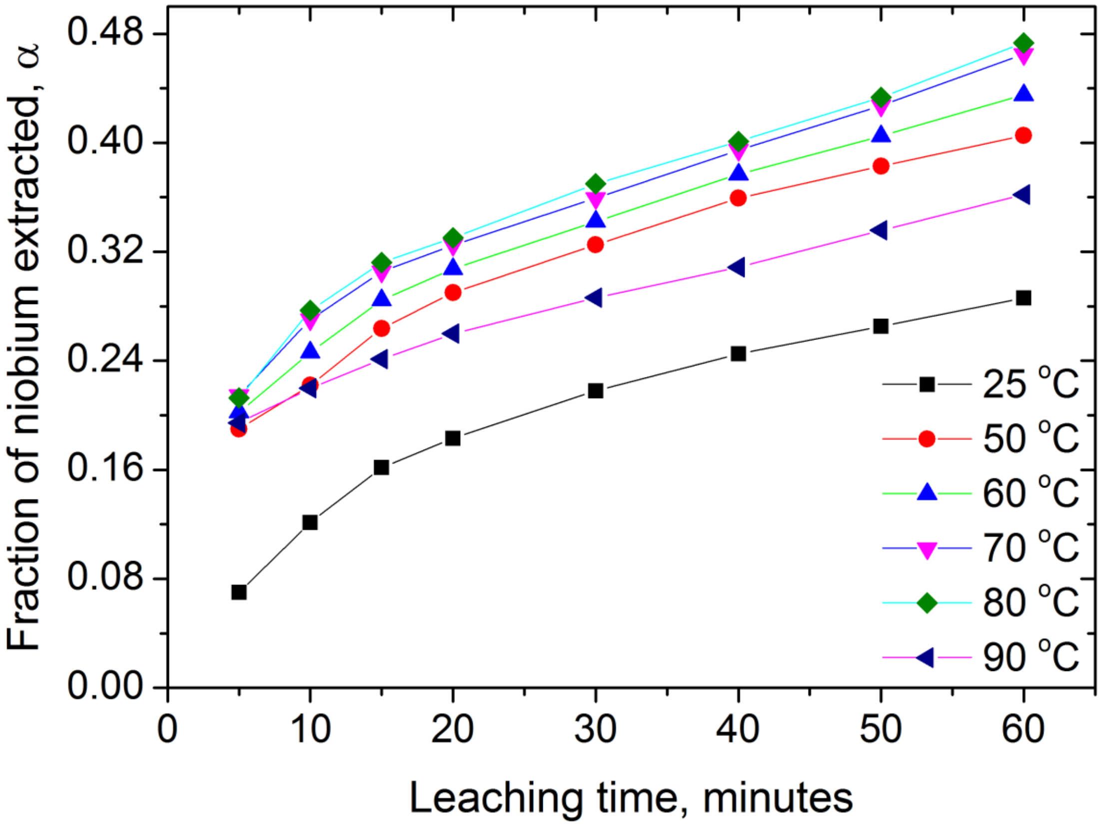
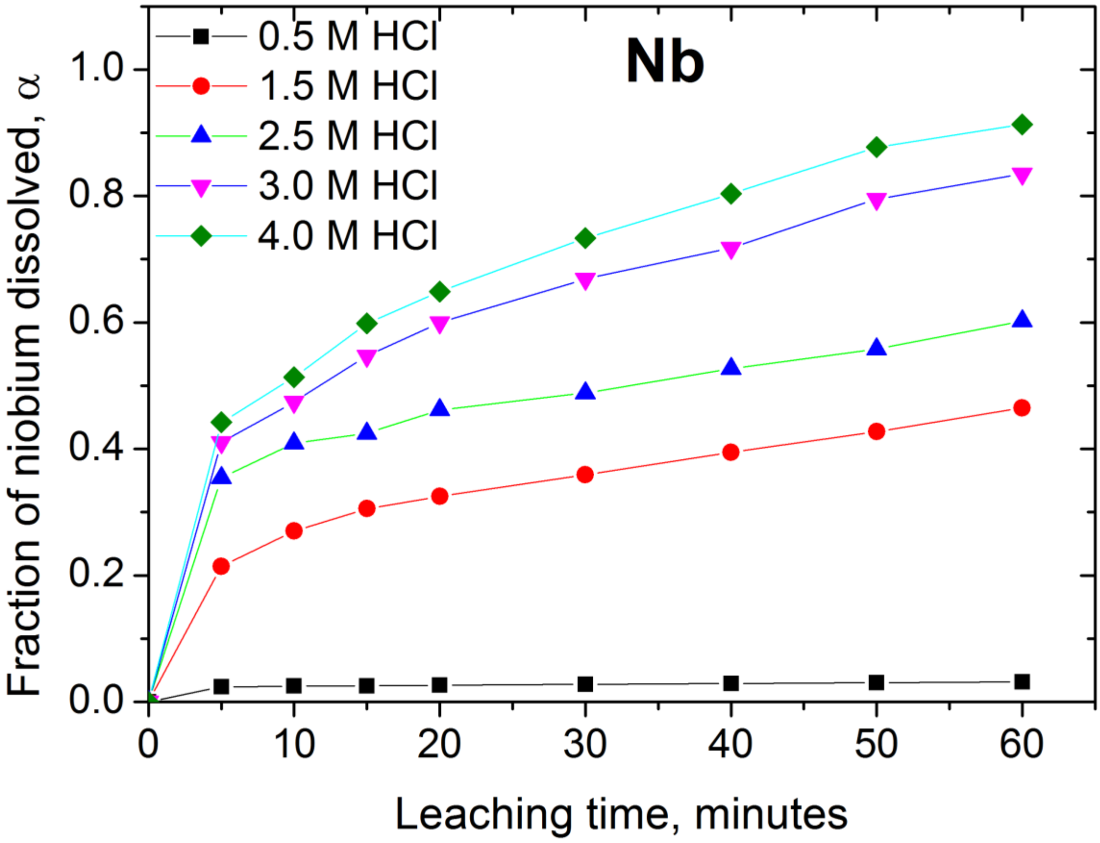


Fraction of niobium extracted, α
0.00
0.08
0.16
0.24
0.32
0.40
0.48
0
10
20
30
40
50
60
Leaching time, minutes
25 °C
50 °C
60 °C
70 °C
80 °C
90 °C

Fig. 1



Nb
Fraction of niobium dissolved, α
0.0
0.2
0.4
0.6
0.8
1.0
0
10
20
30
40
50
60
Leaching time, minutes
0.5 M HCl
1.5 M HCl
2.5 M HCl
3.0 M HCl
4.0 M HCl

Fig. 2

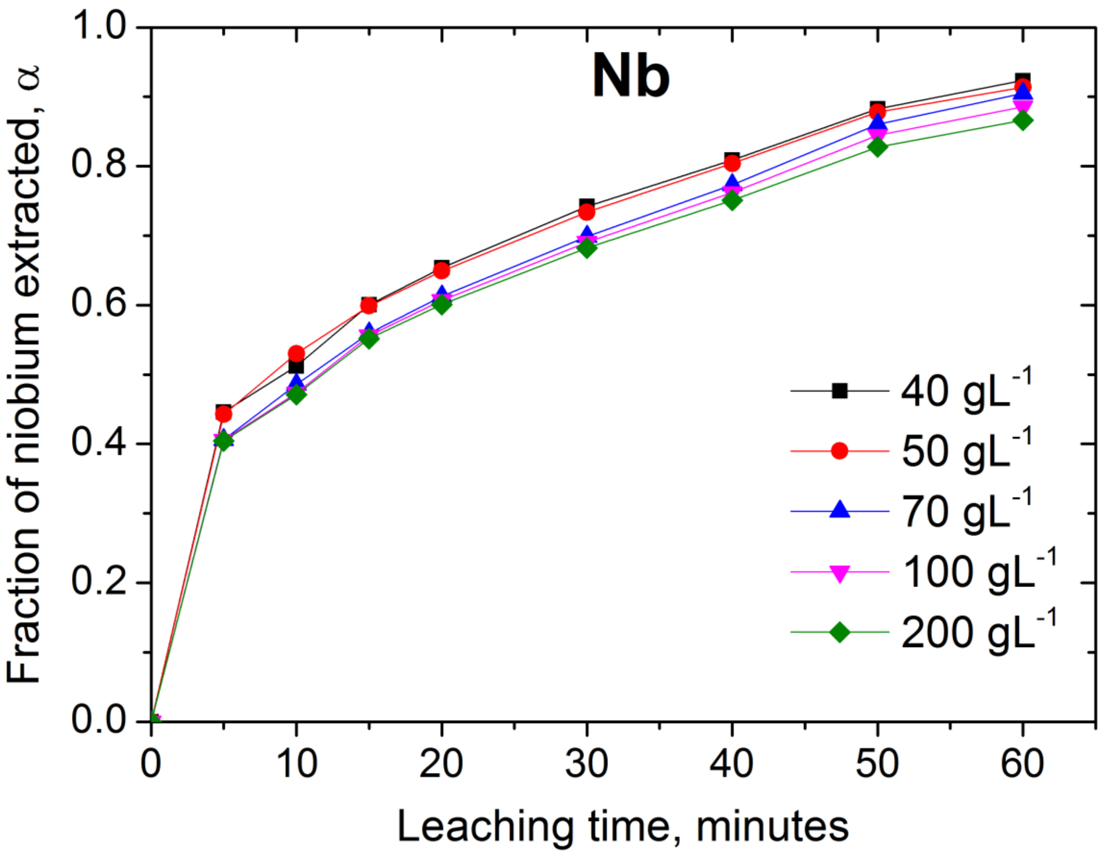

Nb
Fraction of niobium extracted, α
Leaching time, minutes
0.0
0.2
0.4
0.6
0.8
1.0
0
10
20
30
40
50
60
40 gL-1
50 gL-1
70 gL-1
100 gL-1
200 gL-1

Fig. 3

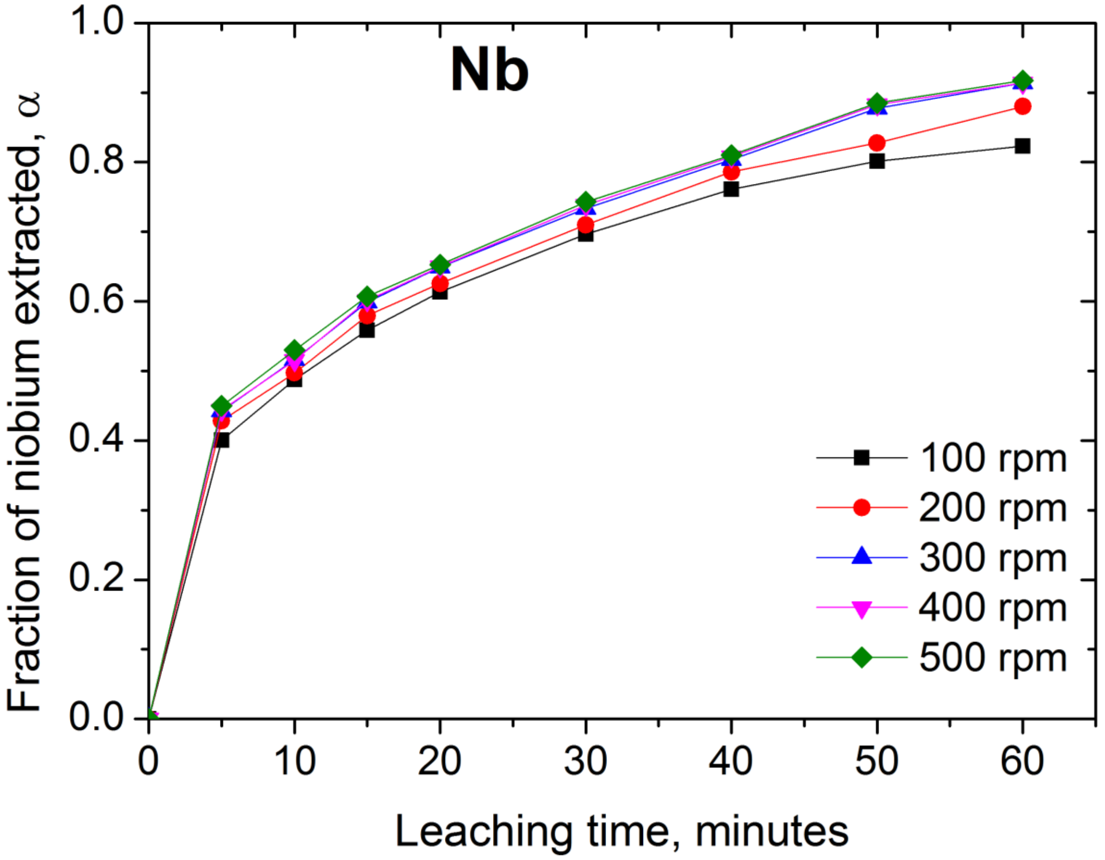

Nb
Fraction of niobium extracted, α
Leaching time, minutes
0.0
0.2
0.4
0.6
0.8
1.0
0
10
20
30
40
50
60
100 rpm
200 rpm
300 rpm
400 rpm
500 rpm

Fig. 4

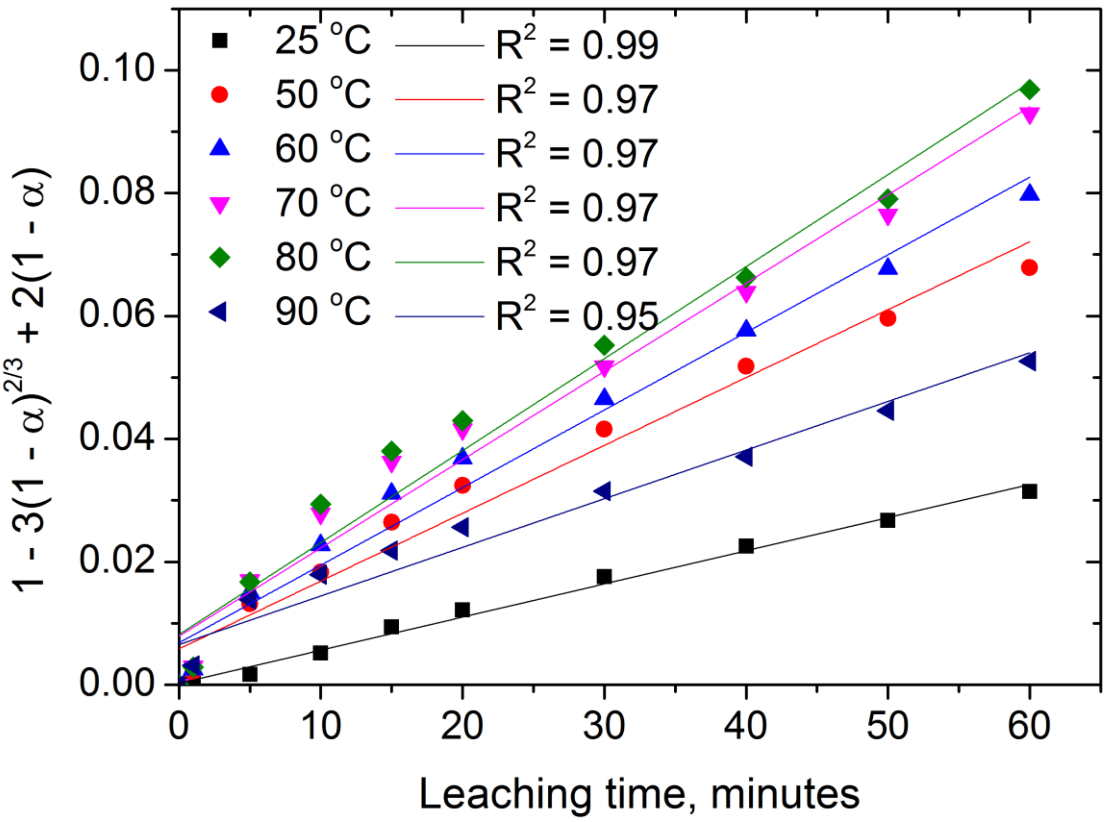

■ 25 °C R² = 0.99
● 50 °C R² = 0.97
▲ 60 °C R² = 0.97
▼ 70 °C R² = 0.97
◆ 80 °C R² = 0.97
◀ 90 °C R² = 0.95
0.00
0.02
0.04
0.06
0.08
0.10
0
10
20
30
40
50
60
1 - 3(1 - α)^2/3 + 2(1 - α)
Leaching time, minutes

Fig. 5a

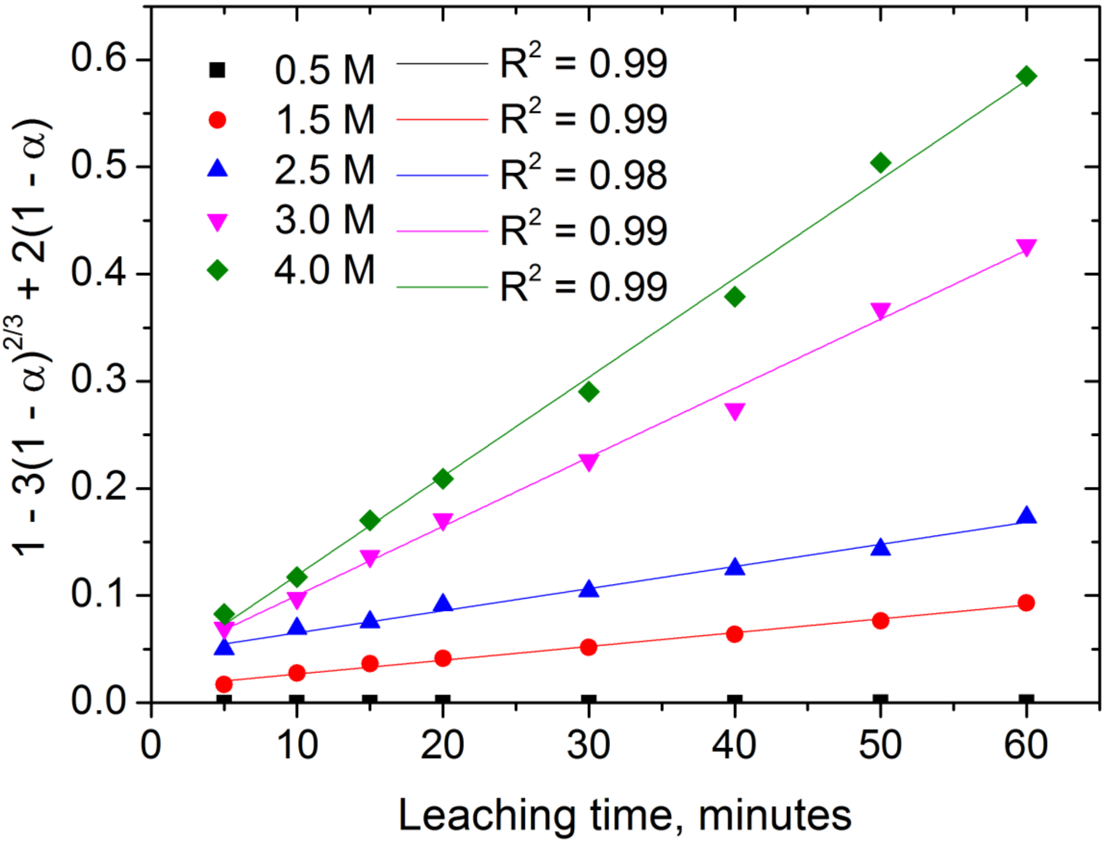
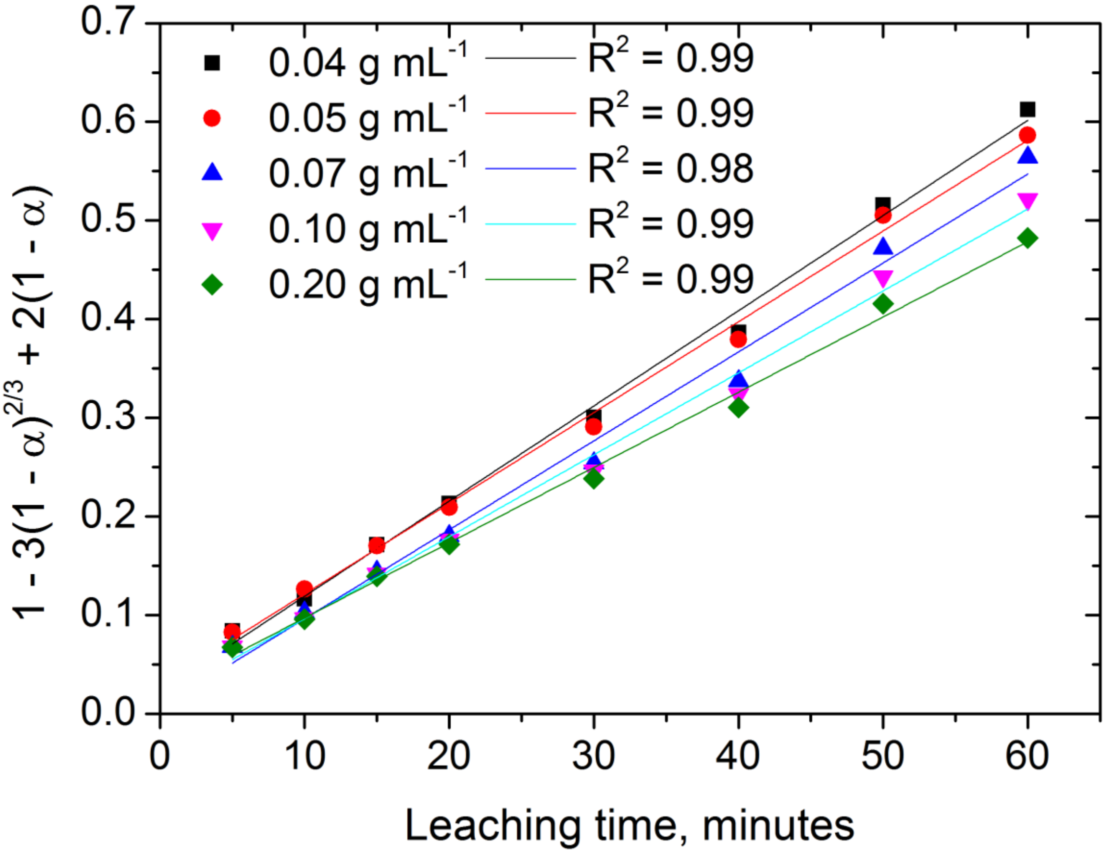
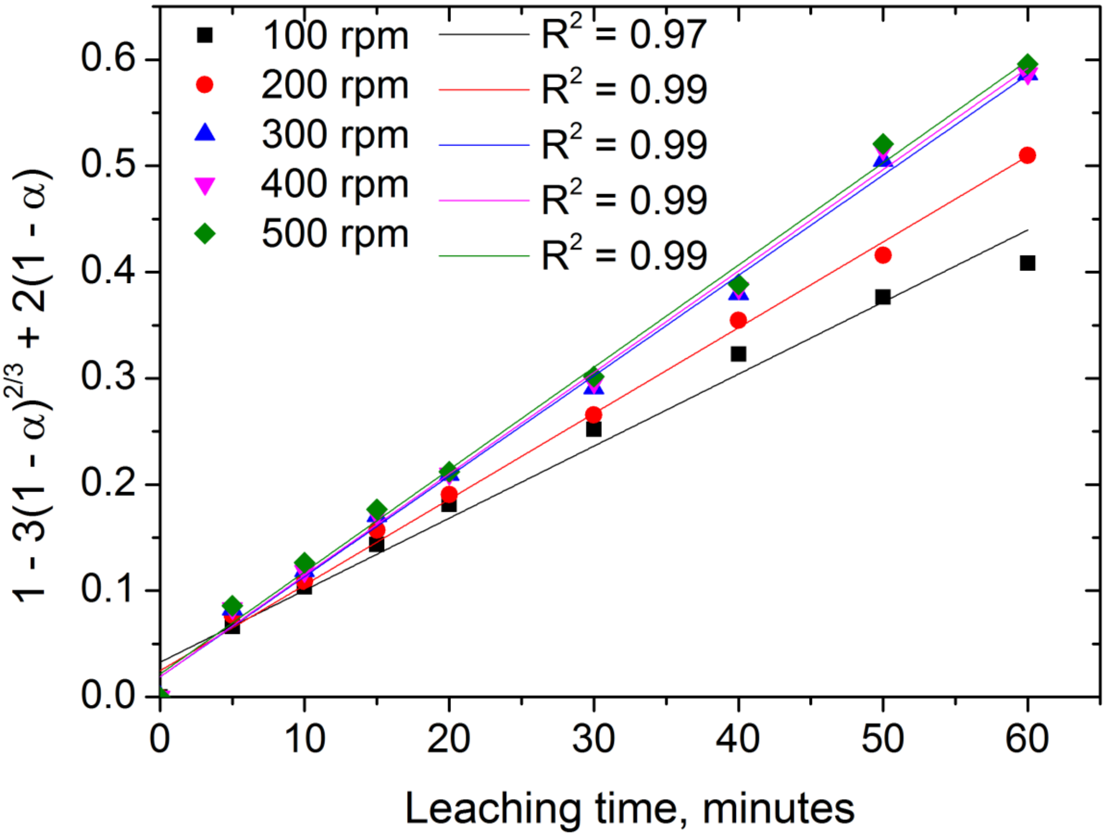

■ 0.5 M R² = 0.99
● 1.5 M R² = 0.99
▲ 2.5 M R² = 0.98
▼ 3.0 M R² = 0.99
◆ 4.0 M R² = 0.99
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0
10
20
30
40
50
60
1 - 3(1 - α)^2/3 + 2(1 - α)
Leaching time, minutes

Fig. 5b



0.04 g mL$^{-1}$ R$^2$ = 0.99
0.05 g mL$^{-1}$ R$^2$ = 0.99
0.07 g mL$^{-1}$ R$^2$ = 0.98
0.10 g mL$^{-1}$ R$^2$ = 0.99
0.20 g mL$^{-1}$ R$^2$ = 0.99
1 - 3(1 - α)$^{2/3}$ + 2(1 - α)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
10
20
30
40
50
60
Leaching time, minutes

Fig. 5c



100 rpm R$^2$ = 0.97
200 rpm R$^2$ = 0.99
300 rpm R$^2$ = 0.99
400 rpm R$^2$ = 0.99
500 rpm R$^2$ = 0.99
1 - 3(1 - α)$^{2/3}$ + 2(1 - α)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0
10
20
30
40
50
60
Leaching time, minutes

Fig. 5d

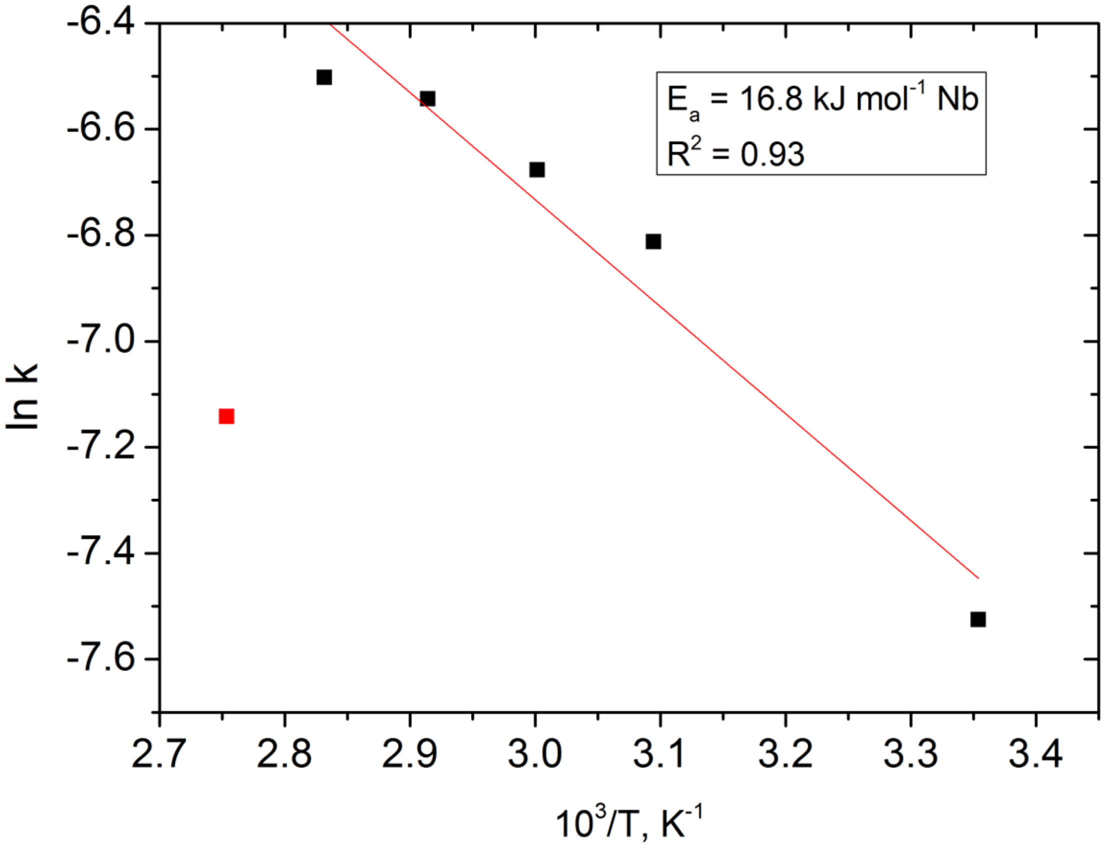

-6.4
-6.6
-6.8
-7.0
-7.2
-7.4
-7.6
ln k
$E_a$ = 16.8 kJ mol$^{-1}$ Nb
$R^2$ = 0.93
2.7
2.8
2.9
3.0
3.1
3.2
3.3
3.4
10$^3$/T, K$^{-1}$

Fig. 6