Solvent Extraction in Different Lithium Recovery Processes

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As Li exists often as Li^+ cation, Li-rich solutions can be purified from divalent metals with conventional cation exchange reagents. This approach is utilized in purification of Li-rich solutions originating from natural brines, and producing pure Li raffinate from Li-ion battery waste leachates. In this paper both of these processes are demonstrated in continuous bench scale experiments. Another industrially used solvent extraction purification process for Li-rich brine is removal of B, which is done by alcohol reagents, and the process is well known from 1960's. Li can be also directly extracted from natural brines and even seawater with solvating reagents. Adding ionic liquids improves often important Li/Mg selectivity. However, these direct solvent extraction processes have not been utilized industrially. The B removal process and the direct solvent extraction processes are discussed based on literature references.

1. Introduction

Currently Li is one of the most interesting metals in markets. This is due to its use in state-of-the-art battery technology, Li-ion batteries, and since societies are moving towards electric vehicles the demand of Li among Li-ion batteries is probably increasing dramatically within next decades [1]. The most important natural sources of Li are natural brines [2], chloride solutions, which contain 5–11 wt.-% Na and 10–1600 mg/kg Li. From purification point of view most significant impurities are Mg (30–31000 mg/kg, Ca (20–3900 mg/kg) and B (30–710 mg/kg) [3]. Currently, recovering Li from these brines is done by concentrating with solar energy, and purifying the obtained concentrate by different hydrometallurgical methods [4]. Solvent extraction may be used in this process for removal of B by alcohol reagent [5], and in final purification step for removal of Mg and Ca [6]. In this article solvent extraction removal of Mg and Ca in final purification step is demonstrated in bench scale continuous counter-current operation with synthetic Li-rich brine. The solvent extraction of B from Li containing brines is discussed based on literature survey.

Use of solvent extraction has not been popular in hydrometallurgical processes for recovering Li from ores. For example, recent review article by Choubey *et al.* [7] mention solvent extraction only with one reference [8], in which Li was extracted from zinnwaldite waste leachate with mixture of LIX-54 and TOPO. However, in many Li extraction processes from ores, there are problems with Li yield or purity of the Li product [7], for which problems solvent extraction could offer help.

As the solar evaporation based process is time consuming due to long residence times in the evaporation pools, Li producers are interested in direct recovery of Li from these brines, and there solvent extraction, either by conventional reagents or by ionic liquids, is one of the most promising methods. These direct methods will be discussed in this article based on literature.

Since the amount of needed metal for Li-ion batteries is increasing, the amount of used batteries will be increasing at the same time as the lifespan of typical Li-ion battery is under 10 years [9]. This means that huge amounts of batteries become available as secondary source of Li (and other metals), but for example in 2011 the recycling rate of Li from all the end-of-life products was only 3% [10]. In hydrometallurgical processing of the used batteries, after acid leaching, solvent extraction is needed in removal of impurity metals (*e.g.* Cu, Al, Fe) [11] and in fractionation of Li+Co+Ni mixture [12]. Typical composition of battery waste is: Li 2–15%, Co 15–30%, Ni ≤10% Ni, Cu 7–17%, Al 3–10%, Fe ≤20% [13], and composition of typical sulfate leachate is: Co 21 g/L, Ni 0.5 g/L, Li 2.5 g/L, Fe 3.6 g/L, Cu 1.8 g/L, pH 3.5 [14]. In this paper producing over 99.6% pure Ni, Co and Li from synthetic battery waste leachate is demonstrated in bench-scale counter-current solvent extraction experiments.

2. Experimental

2.1 Chemicals and solutions

Chemicals used in the experiments, with their suppliers and purities (if available) were: $CoSO_4 \cdot 7H_2O$ (Outokumpu OY, Technical grade with 22% Co content), $NiSO_4 \cdot 6H_2O$ (Sigma-Aldrich Co., 99%), $Li_2SO_4 \cdot H_2O$ (Alfa-Aesar, 99%), LiCl (VWR International, 98%), $MgCl_2 \cdot 4.5H_2O$ (VWR International, 97%), $CaCl_2$ (VWR International, 98%), NaCl (VWR International, 98%), H_2SO_4 95-97% (Merck KGaA, Pro analysi), HCl 37% (Merck KGaA, Pro analysi), HNO_3 65% (Merck KGaA, Pro analysi), NH_3 25% (Merck KGaA, Pro analysi), NaOH (VWR International, 98%), Exssol D80 (ExxonMobil Chemical), Shellsol D70 (Shell Chemicals), Cyanex 272 (Cytec Solvay Group, 88%), Trioctylamine (Sigma-Aldrich Co., 98%), Tributylphosphate (Sigma-Aldrich Co., 97%), di-(2-ethylhexyl)phosphoric acid (D2EHPA), neodecanoic acid (Versatic 10).

The synthetic Li-rich brine solutions were prepared by dissolving the chloride salts of Li, Ca, and Mg to purified water. Chloride concentration was topped up to 200 g/L with NaCl. According to the analyses, their compositions were as follows: Li 26.0–34.0 g/L, Ca 1.17–1.55 g/L, Mg 0.022–0.075 g/L, pH 7.5. The synthetic battery waste leachates were prepared by dissolving sulfate salts of Li, Co and Ni to purified water, and the composition was: Co 14 g/L, Ni 0.5 g/L, Li 2.8 g/L.

2.2 Continuous counter-current experiments

The continuous counter-current solvent extraction experiments were performed in bench scale pilot equipment (SX Kinetics Inc.) having 270 mL settlers and 1050 mL mixers. The phase ratio in the mixer was monitored during the runs, and adjusted if needed by internal circulations. The flowsheet of the equipment is given in references [6] and [12].

Temperatures and pH's were monitored online, and adjusted if needed. The pH control was done by pre-neutralization of the organic phases using aqueous ammonia (25%) or 5 M NaOH, or in the battery waste leachate case by dropwise addition of concentrated H_2SO_4 (95-97%).

In the Li-rich brine case D2EHPA and Versatic 10 were used as extractants. Residence time in the mixer was 2.0–6.1 min, A/O phase ratio in loading stage 1.5–0.6, and temperature was 23 or 31 °C. With D2EHPA the pH varied between 3.7 and 4.1, and with Versatic 10 between 6.2 and 7.4. At least 50 mixer volumes of the brine was treated in every run, and this amount was observed to be enough for achieving steady-state in the dynamic process.

The organic phase in battery waste leachate case was 1 M Cyanex 272 in Exssol D80 containing 5% v/v of a phase modifier (TOA or TBP). Residence time in the mixer was 10 min, which is, based on literature, enough to achieve equilibrium. Temperature was 23 °C. Loading (three runs), scrubbing (one run) and stripping (four runs) steps were studied in separate runs. Steady-state was again achieved in every run with fed amounts of 65 mixer volumes in loading and stripping runs, and 20.3 mixer volumes in the scrubbing run. The exact run parameters are given with the results in Tables 1 and 2.

2.3 Analytics

Metal analyses were carried out from 14% or 1 M HNO_3-media using inductively coupled plasma atomic emission spectroscopy (ICP-AES, device: IRIS Intrepid Duo, Thermo Electron Corporation), or by Thermo-Scientific iCE™ 3300 AAS Atomic Absorption Spectrometer. The organic phase metal concentrations were analyzed after stripping them with 14% HNO_3 (A/O = 10:1).

3. Results and Discussion

3.1 Solvent extraction removal of Ca and Mg from Li-rich brines

In conventional natural brine utilizing Li recovery process impurities are removed by precipitation methods, but their drawbacks are in inefficient purification and/or high Li losses, *i.e.* in selectivity [6]. On the other hand, solvent extraction seems to be feasible option for the final purification step, as in general the cation exchange reagents prefer divalent metals over monovalent, and the main impurities in the concentrated brines are Ca and Mg. In 1992 Bukowsky *et al.* [15] published a research in which Ca was removed from concentrated brine by D2EHPA. Therefore, it was decided to develop a flowsheet for solvent extraction removal of Ca and Mg by solvent extraction. Discussion below is based on authors' own experimental work.

Based on laboratory scale equilibrium experiments D2EHPA and Versatic 10 were identified as viable candidates for the purification task [6]. Nine continuous counter-current (2 stages) bench scale runs were done to study optimal run parameters (pH, phase ratio, residence time). Goal was to reduce Ca and Mg levels from 1.3 g/L and 50 mg/L, respectively, to under 20 mg/L, or preferably to ppm level.

With D2EHPA the pH adjustment (pre-neutralization) needs to be done so that the pH in both extraction stages is 3.6–3.8 (Table 1). If the pH is higher, Li losses are too high (Run D-1), and if it is lower, Mg yield decreases. For Versatic 10 the behavior is similar (and reasonable); increasing the pH increases Li losses (Run V-1), but these are in general lower than with D2EHPA.

In operation with two counter-current stages optimal phase ratio with both reagents is near unity. However, the yield for Mg can be increased by increasing the organic phase low, and at the same time the Li losses are increased a little bit. Decreasing the residence time from 5.1 to 2.0 min had positive effect to Mg extraction yield, but at the same time Li losses were also increased (Runs V-5 and V-6). With D2EHPA no significant effects with residence time were observed.

Table 1. Bench scale experiments for studying solvent extraction removal of Ca and Mg from Li-rich brine [6]. In Run-id. D stands for D2EHPA and V for Versatic 10.

Run id.	pH 1st	pH 2nd	A/O	τ, min	E_{Ca}, %	E_{Mg}, %	E_{Li}, %
D-1	3.9	4.1	0.85	6.0	99	94	9.1
D-2	3.7	3.6	1.25	6.1	99	90	4.0
D-3	3.7	3.8	1.20	2.0	98	86	5.3
V-1	6.7	7.1	1.00	4.5	100	95	4.6
V-2	6.2	6.8	1.25	6.1	97	34	1.4
V-3	6.9	7.4	1.35	6.0	99	50	2.1
V-4	6.4	6.9	1.25	2.0	99	40	2.1
V-5	6.6	6.9	0.60	5.1	100	90	3.3
V-6	6.4	6.9	0.60	2.0	100	98	5.5

In general, the performance of solvent extraction purification was satisfactory. Li purity increase from 95.1–96.6% to 99.9% was achieved with both of the reagents, and the Ca and Mg concentrations in raffinates were in ppm level (excluding Runs V-2, V-3 and V4 in Table 1). The Li losses in the effective purification runs were typically 5% or less, which is also much better than the 10% or more losses in the conventional precipitation purifications. With Versatic 10 a bit more pure raffinates were obtained as 100% Ca extractions and over 95% Mg extractions were recorded. The needed residence time is low (*e.g.* 2.0 min) meaning that high brine volumes could be treated with reasonable sized reactors.

3.2 Solvent extraction removal of B from Li-rich brines

B content in Li-rich brines is typically 30–710 mg/kg [3], which needs to be reduced to ppm level in order to obtain battery grade Li_2CO_3. In that purification step solvent extraction has been extensively used. Discussion below is based exclusively on literature references.

First industrial B recovery process from brines was operated already in 1960's [16–17]. The chemistry of the process has not been changed since then, and alcohols, especially polyols, have been almost exclusive used as extractants [18]:

$$H_3BO_3\,(aq) + 2R(OH)_2\,(org) \rightleftarrows R_2BO_4^{-}M^{+}\,(org) + 3H_2O + H^{+} \qquad (1)$$

Diluent has some effect to the separation efficiency, but with kerosene the efficiency is not significantly worse than with some other suggested diluents [18–19]. Therefore it would be probably preferred in industrial operation, like it was used in the first B extraction plants [16–17].

Kumar *et al.* [18] suggested recently, based on laboratory experiments, a solvent extraction process for B removal from Uyuni salar brine (B 450 mg/L, Li 1100 mg/L). 2,2,4-trimethyl-1,3-pentanediol in chloroform is used as an extractant, and the extraction is most efficient (~100%) in pH range 3–5. Scrubbing was done successfully with 0.1 M H_2SO_4 with minor B losses, and stripping with 99% efficiency with 25% aqueous ammonia. Final purity of the B product is not given, but it can be assumed to be very high due to mentioned efficient scrubbing.

Patent literature contains few methods for the B removal from Li-rich brines. All of them use simple fatty alcohols in kerosene as extractants [20–22]. In a patent by Perez *et al.* [22] TBP (5–20%) is used as modifier. The B removal is efficient with abovementioned organic phases, and for example over 99% overall yield from 7.85 g/L B containing Salar de Atacama Li-rich brine is reported in a journal article of Orrego *et al.* [23]. In these processes stripping of B is done by NaOH.

3.3 Direct solvent extraction of Li from naturally occurring brines and seawater

Discussion below is based exclusively on literature references. TBP is most conventionally used as a direct Li extractant. It needs some salt (typically $FeCl_3$ is used) to form an extractable ion pair (Equation 2). Typical problem with the TBP is selectivity, and Na, K and Mg salts hinder the extraction [24]. Kerosene is usually used as a diluent, but for example using MIBK can increase the distribution coefficient of Li [25].

$$Li^+ (aq) + FeCl_4^- (aq) + nTBP (org) \rightleftarrows LiFeCl_4 \cdot nTBP (org) \qquad (2)$$

Gabra and Torma [26], and Bukowsky and Uhlemann [27] suggest using alcohols as Li extractant from brines. Gabra and Torma have gotten 99.6% purity Li from synthetic brine containing Na, K and Ca as impurities. If high selectivity over Mg is needed, diols can be added [27]. β-diketone mixed with TOPO has been suggested in patent of Baldwin and Seeley [28], which was inspired by journal article of Lee *et al.* [29], in which the extraction mechanism has been proposed to be adduct formation between Li, dibenzoylmethane and TOPO. With this synergistic system selectivities over alkali metals (*e.g.* K, Na) are high, but selectivities over Ca and Mg have not been studied.

Ionic liquids have been extensively studied for direct Li extractants from brines. Gao *et al.* used 1-butyl-3-methyl-imidazolium hexafluorophosphate ($[C_4mim][PF_6]$), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ($[C_4mim][NTf_2]$) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ($[C_2mim][NTf_2]$) in TIBP (triisobutyl phosphate) and kerosene to extract Li from 2.3 g/L Li and 77 g/L Mg containing brine. High selectivity over Mg was obtained and reusability of the organic phase was successfully tested in ten consequent extraction-stripping cycles. The extraction mechanism was studied with spectroscopic methods and claimed to be solvation of LiCl by TIBP [30]. Shi *et al.* [31–33] have used 1-octyl-3-methyl-imidazolium hexafluorophosphate ($[C_8mim][PF_6]$), $[C_4mim][NTf_2]$ and $[C_4mim][PF_6]$ with TBP and also gotten decent selectivity over Mg. In these articles the mechanism is claimed to be cation exchange reaction, in which the cation of ionic liquid is transferred to the aqueous phase. With all of these ionic liquid extractions, the Mg/Li ratio after stripping is low enough so that pure Li can be obtained by precipitation.

In article by Harvianto *et al.* [34] using ionic liquids for direct Li extractants from seawater has been suggested. With mixture of thenoyltrifluoroacetone (TTA) and TOPO in kerosene over 65% yield was obtained, but Mg needs to be precipitated first, and problems appear also with durability of the extractant. Extraction of Li from seawater by different membrane processes has been studied extensively in Japan. One of the processes utilizes ionic liquids as carrier between the membranes. The ionic liquid (N,N,N-trimethyl-N-propylammonium-bis(trifluorometaani-sulfonyl) imide, TMPA-TFSI) rejects Li transfer, but carries the other metals (Na, K, Ca, Mg) through the membrane [35].

3.4 Solvent extraction fractionation of battery waste leachate

In fractionation step for producing pure metals from battery waste leachates, Ni is often present in the feed, and thus solvent extraction with bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272, Mextral 272P, P507) is seen as the best choice. Although, this kind of process has been proposed previously [36–37], it was decided to seek for simpler flowsheet, higher purities, and to demonstrate the process in bench scale. Discussion below is based on authors' own experimental work.

Based on laboratory equilibrium experiments, Cyanex 272, with 5% TOA (or TBP in Run L-3, Table 2) as phase modifier, was chosen as extractant. Suggested flowsheet had mutual loading for Co and Ni, Li scrubbing and selective Ni stripping steps. The fractionation was demonstrated in bench scale with three loading, one scrubbing and four stripping runs.

Co and Ni were effectively loaded to the organic phase (Runs L-2 and L-3 in Table 2) in two extraction stages from the synthetic battery waste leachate at equilibrium pH around 7. However, the flowrate of the organic feed needs to be higher than the flowrate of the aqueous phase (compare Runs L-2 and L-1), and also the amount of co-extracted Li is high. The amount of co-extracted Li could be lowered by adding more loading stages, but here an approach of having Li scrubbing by acidic (pH 1.3) $NiSO_4$ solution was taken. The results are not shown here, but the scrubbing removed Li efficiently without significant losses of Co or Ni [12]. With TOA as a modifier, the Li losses in loading were lower than with TBP (Runs L-2 and L-3). The high Co and Ni yields mean also high Li purity in raffinate, which was 99.9% in Runs L-2 and L-3.

In two stage stripping, either the purity of the Co in organic phase, or Ni in aqueous phase remained under 99% (Runs S-1 and S-2 in Table 2). Therefore, it was decided to add one more stage. With this configuration a bit lower equilibrium pH was achieved (Run S-4) yielding less Co losses to the aqueous phase (higher Ni purity) while still having high Ni stripping percentage resulting at the same time high purity Co in organic phase.

Table 2. Bench scale experiments for studying solvent extraction fractionation of Co, Ni and Li from battery waste leachate [12]. In Run-id. L stands for loading and S for stripping. In stripping runs *P* stands for phase purity in target phase (org. for Co and aq. for Ni). In run L-3 phase modifier was 5% TBP instead of TOA.

Run id.	pH 1st	pH 2nd	pH 3rd	A/O	E_{Co}, %	E_{Ni}, %	E_{Li}, %
L-1	5.0	7.2	-	0.95	100	80.1	7.6
L-2	6.8	7.1	-	0.77	100	99.6	17.3
L-3	6.7	7.0	-	0.77	100	99.9	26.2
					P_{Co}, %	P_{Ni}, %	
S-1	6.3	5.2	-	0.65	99.6	97.6	-
S-2	6.3	5.4	-	0.67	98.7	99.6	-
S-3	6.3	6.1	5.4	0.67	98.2	99.9	-
S-4	6.0	5.8	5.0	0.65	99.6	99.7	-

4. Conclusion

Li exists in aqueous solutions mostly as Li^+ cation, and therefore it is not strongly extracted with cation exchange reagents. However, this feature can be utilized in purification of Li-rich brines from divalent cations. The process for effective removal of Ca and Mg has been demonstrated in this article with continuous bench scale runs using D2EHPA as extractant. The other solvent extraction utilizing purification stage in producing battery grade Li salts from natural brines is removal of B. Diols are used here as solvating extractants. The approach of having the pure Li product as raffinate can be used in producing 99.9% pure Li from battery waste leachates. Also this process has been demonstrated in this article with continuous bench scale runs.

Li^+ cation is not very strongly hydrated, which is probably the reason why it can be extracted fairly selectively from different solutions with solvating extractants, with or without ionic liquids in the organic phase. Though, for example with TBP $FeCl_4^-$ is needed as counter-ion, and the system does not have the desired high selectivity over Mg. With ionic liquids in organic phase direct cation exchange reaction with cation of the ionic liquid, or ionic liquid promoted solvation have been proposed as possible extraction mechanisms. With these systems, the selectivity over Mg is high, and from stripping solutions battery grade Li salts can be precipitated. However, the ionic liquids are expensive, and in the systems with the cation exchange mechanism the cation of ionic liquid needs to be recovered from the stripping solution.

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References

1) L.F. Cabeza, A. Gutierrez, C. Barreneche, S. Ushak, Á.G. Fernández, A. Inés Fernádez, M. Grágeda, *Renew. Sustain. Energy Rev.*, **42**, 1106–1112 (2015).
2) S.E. Kesler, P.W. Gruber, P.A. Medina, G.A. Keoleian, M.P. Everson, T.J. Wallington, *Ore Geol. Rev.*, **48**, 55–69 (2012).
3) J.W. An, D.J. Kang, K.T. Tran, M.J. Kim, T. Lim, T. Tran, *Hydrometallurgy,* **117–118**, 64–70 (2012).
4) D.E. Garrett, *Part 1 — Lithium, Handbook of Lithium and Natural Calcium Chloride*, Academic Press, Oxford, 1–235 (2004).
5) P.M. Brown, D.A. Boryta, *US5219550 A* (1993).
6) S. Virolainen, M. Fallah Fini, V. Miettinen, A. Laitinen, M. Haapalainen, T. Sainio, *Hydrometallurgy*, **162**, 9–15 (2016).
7) P.K. Choubey. M-S. Kim, R.R. Srivastava, J-C. Lee, J-Y. Lee, *Min. Eng.*, **89**, 119–137 (2016).
8) J. Jandová, P. Dvořák, H.N. Vu, *Hydrometallurgy*, **103**, 12–18 (2010).
9) J.B. Goodenough, K.S. Park, *J. Am. Chem. Soc.*, **135**, 1167–1176 (2013).
10) L. Talens Peiró, G. Villalba Mendez, R.U. Ayres, *JOM*, **65**, 986–996 (2013).
11) T. Suzuki, T. Nakamura, Y. Inoue, M. Niinae, J. Shibata, *Sep. Purif. Technol.*, **98**, 396–401 (2012).

12) S. Virolainen, M. Fallah Fini, A. Laitinen, T. Sainio, *Sep. Purif. Technol.*, **179**, 274–282 (2017).
13) X. Zeng, J. Li, N. Singh, *Crit. Rev. Environ. Sci. Technol.*, **44**, 1129–1165 (2014).
14) L. Chen, X. Tang, Y. Zhang, L. Li, Z. Zeng, Y. Zhang, *Hydrometallurgy*, **108**, 80–86 (2011).
15) H. Bukowsky, E. Uhlemann, K. Gloe, P. Mühl, *Hydrometallurgy*, **28**, 323–329 (1992).
16) C.R. Havighorst, *Chem. Eng.*, **70**, 228–232 (1963).
17) R.K. Klopfenstein, D.S. Arnold, *Journal of Metals*, **18**, 1195–1197 (1966).
18) J.R. Kumar, C-J. Kim, H-S. Yoon, D-J. Kang, J-Y. Lee, *Korean J. Met. Mater.*, **53**, 578–583 (2014).
19) K. Poslu, W.L. Dudeney, *Hydrometallurgy*, **10**, 47–60 (1983).
20) P.M. Brown, S.J. Beckerman, *US4980136 A* (1990).
21) P.M. Brown, D.A. Boryta, *US5219550 A* (1993).
22) W.A. Perez, H.A.C. Barrientos Ruiz, *US20130101484 A1* (2013).
23) P. Orrego, C. Goldman, P. Reveco, E. Valdes, M.E. Flores, D. Bustos, D. Jandragholica, *Nucleotecnica*, **14**, 39–46 (1994).
24) G. Zeming, Z. Shenlin, *Chinese Journal of Chemical Engineering*, **6**, 124–129 (1998).
25) Z. Zhou, W. Qin, W. Fei, *J. Chem. Eng. Data*, **56**, 3518–3522 (2011).
26) G.G. Gabra, A.E. Torma, *Hydrometallurgy*, **3**, 23–33 (1978).
27) H. Bukowsky, E. Uhlemann, *Sep. Sci. Technol.*, **28**, 1357–1360 (1993).
28) W. Baldwin, F. Seeley, *US3793433 A* (1974).
29) D.A Lee, W.L. Taylor, W.J. McDowell, J.S. Drury, *Journal of Inorganic and Nuclear Chemistry*, **30**, 2807–2821 (1968).
30) D. Gao, X. Yu, Y. Guo, S. Wang, M. Liu, T. Deng, Y. Chen, N. Belzile, *Chem. Res. Chin. Univ.*, **31**, 621–626 (2015).
31) C. Shi, Y. Jia, Y, Jing, *CIESC J.*, **66**, 253–259 (2015).
32) C. Shi, Y. Jing, Y. Jia, *J. Mol. Liq.*, **215**, 640–646 (2016).
33) C. Shi, Y. Jia, C. Zhang, H. Liu, Y. Jing, *Fusion Engineering and Design*, **90**, 1–6 (2015).
34) G. Harvianto, S.-H. Kim, C.-S. Ju, *Rare Met.*, 1–6 (2015).
35) T. Hoshino, *Fusion Engineering and Design*, **88**, 2956–2959 (2013).
36) V.T. Nguyen, J.C. Lee, J. Jeong, B.S. Kim, B.D. Pandey, *Met. Mater. Int.*, **20**, 357–365 (2014).
37) V.T. Nguyen, J.C. Lee, J. Jeong, B.S. Kim, B.D. Pandey. *Korean Chem. Eng. Res.*, **53**, 137–144 (2015).