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<b>Thermodynamic study of W(VI) extraction using amine-based extractant and phosphonium ionic liquids</b>
Authors and affiliation
Tatsuki Igosawa <sup>1</sup> , Yusuke Tsuchida <sup>1</sup> , Masahiko Matsumiya <sup>*1</sup> , and Yuji Sasaki <sup>2</sup> <sup>1</sup> Graduate School of Environment and Information Sciences, Yokohama National University, 79-2 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan <sup>2</sup> Nuclear Science and Engineering Directorate, Japan Atomic Energy Agency, Tokai-mura, Naka-gun, Ibaraki, 319-1195, Japan *E-mail: matsumiya-masahiko-dh@ynu.ac.jp
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Abstract (less than 300 words)
<p>Recently, the development of a process to separate W(VI) component from spent tungstophosphate catalyst has become important. We had demonstrated that a novel hydrometallurgical process involving the following steps; leaching, precipitation, solvent extraction using ionic liquids (ILs) and crystallization-stripping. First, the spent catalyst was completely leached in a distilled water at 343 K for 24 h. The leaching reaction; <math>\text{H}_3[\text{PW}_{12}\text{O}_{40}] + 27[\text{OH}^-] \rightarrow 12[\text{WO}_4^{2-}] + [\text{PO}_4^{3-}] + 15\text{H}_2\text{O}</math> smoothly proceeded in leachate. After leaching, the <math>[\text{PO}_4^{3-}]</math> component was separated by the precipitation reaction using the precipitation agent; <math>\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}</math>. The separation percentage of <math>[\text{PO}_4^{3-}]</math> was 90.78% at pH=8.11 according to IC analysis.</p> <p>Solvent extraction was performed using triethyl-<i>n</i>-pentyl phosphonium bis(trifluoromethylsulfonyl)amide as the IL, and Alamine 336 was employed as the extractant for the selective separation of W(VI). The extraction percentage (<i>E</i>) of W(VI) was 94.6% at pH=1.03 and the separation factor of W/P was 100.8. The extraction mechanism of W(VI) was based on the ion association reaction; <math>[\text{H}_x\text{W}_y\text{O}_z^{n-}]_{\text{aq}} + n[\text{R}_3\text{NH}^+\text{Cl}^-]_{\text{IL}} \rightleftharpoons [(\text{R}_3\text{NH})_n\text{H}_x\text{W}_y\text{O}_z]_{\text{IL}} + [\text{Cl}^-]_{\text{aq}}</math>, where <i>x</i>, <i>y</i>, <i>z</i>, and <i>n</i> are the stoichiometric coefficients related to the complexation state and are dependent on the pH. The Van't Hoff plot of the different operating temperatures (298-358 K) yielded the linear relation. Thermodynamic result indicated the positive enthalpy (<math>\Delta H=18.32 \text{ kJ mol}^{-1}</math>) for W(VI) and favored the endothermic nature of the extraction reaction. This tendency was consistent with the reference [1].</p> <p>The stripping percentage of W(VI) reached to be 100 % on the condition of <math>8 &lt; \text{pH}</math> by the stripping reaction; <math>[(\text{R}_3\text{NH})_n(\text{H}_x\text{W}_y\text{O}_z)]_{\text{IL}} + n[\text{NH}_4\text{OH}]_{\text{aq}} \rightleftharpoons [(\text{NH}_4)_n(\text{H}_x\text{W}_y\text{O}_z)]_{\text{aq}} + n[\text{R}_3\text{NH}^+\text{OH}^-]_{\text{IL}}</math>. Finally, the crystallization reaction occurred at <math>\text{pH} \sim 5</math> and the obtained precipitates were identified as the ammonium paratungstate by XRD. A series of novel hydrometallurgical process using ILs enabled us to conclude that W(VI) component was efficiently recovered from spent tungstophosphate catalyst.</p> <p>References  [1] A. B. C. Sola et al., <i>RSC Adv.</i>, <b>10</b> (2020) 19736-19746.</p>
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