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APOR流程1B槽中镎的走向行为研究

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摘要　从Np(Ⅴ,Ⅵ)与二甲基羟胺(DMHAN)、单甲基肼(MMH)反应动力学及有机相中Np(Ⅵ)的反萃动力学两方面实验考察了APOR流程1B槽中镎的走向行为。结果表明：DMHAN还原Np(Ⅵ)的速率很快，动力学方程为$-dc(Np(Ⅵ))/dt = kc(Np(Ⅵ))c(DMHAN)/c^{0.6}(H^+)$，25 ℃时，反应速率常数 $k = 289.8\ (mol•L^{-1})^{-0.4}•min^{-1}$;进一步还原Np(Ⅴ)的速率则很慢，其中，DMHAN还原Np(Ⅴ)的动力学方程为$-dc(Np(Ⅴ))/dt = kc(Np(Ⅴ))\ c(DMHAN)\ c(H^+)$，25 ℃时，$k = 0.023\ 6\ (mol•L^{-1})^{-2}•min^{-1}$；MMH还原Np(Ⅴ)的动力学方程为$-dc(Np(Ⅴ))/dt = kc(Np(Ⅴ))\ c^{0.36}(MMH)\ c(H^+)$，25 ℃时,$k = 0.002\ 2\ (mol•L^{-1})^{-1.36}•min^{-1}$。所以，1B槽中Np主要以Np(Ⅴ)形式存在。在扩散控制模式下，DMHAN和MMH对Np(Ⅵ)的反萃动力学方程分别为：$dc_a(Np(Ⅵ))/dt = k(V/S)c^{0.5}_{o,0}(Np(Ⅵ))•c_o^{-0.14}(TBP)\ c_a^{-0.32}(NO_3^-)$，25 ℃时，$k = 2.29×10^{-4}(mol•L^{-1})^{0.96}•cm^{-1}•min^{-1}$；$dc_a(Np(Ⅵ))/dt = k(V/S)c_{o,0}^{0.63}(Np(Ⅵ))\ c_o^{-0.27}(TBP)c_a^{-0.34}(NO_3^-)$，25 ℃时，$k = 6.24×10^{-4}(mol•L^{-1})^{0.98}•cm^{-1}•min^{-1}$。可见，DMHAN-MMH存在下，Np可被快速反萃入水相。基于以上的动力学参数以及工艺过程参数，可计算出1B槽中95％的Np进入水相。

关键词　镎　二甲基羟胺　单甲基肼　动力学　还原反萃

分类号

Distribution Behavior of Neptunium in 1B Contactor in APOR Process

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Abstract In order to explain the distribution of neptunium in 1B contactor, the kinetics of reaction between Np(Ⅵ) and dimethylhyoxylamine (DMHAN) as well as Np(Ⅴ) and DMHAN, Np(Ⅴ) and methylhydrazine (MMH) was studied. The reaction rate is much faster between Np(Ⅵ) and DMHAN/MMH than that between Np(Ⅴ) and DMHAN/MMH. The rate equation of the reaction between Np(Ⅵ) and DMHAN is obtained as $-dc(Np(Ⅵ))/dt = kc(Np(Ⅵ))c(DMHAN)/c^{0.6}(H^+)$, and the apparent k is $289.8\ (mol•L^{-1})^{-0.4}•min^{-1}$ at 25 ℃. The rate equation of the reaction between Np(Ⅴ) and DMHAN is $-dc(Np(Ⅴ))/dt = kc(Np(Ⅴ))\ c(DMHAN)\ c(H^+)$, and k is $0.023\ 6\ (mol•L^{-1})^{-2}•min^{-1}$ at 25 ℃. The rate equation of the reaction between Np(Ⅴ) and MMH is $-dc(Np(Ⅴ))/dt = kc(Np(Ⅴ))\ c^{0.36}(MMH)\ c(H^+)$, and k is $0.002\ 2\ (mol•L^{-1})^{-1.36}•min^{-1}$ at 25 ℃. When the process is controlled by diffusion, the stripping rate equation for Np from 30%TBP/OK by DMHAN is obtained as $-dc_a(Np(Ⅵ))/dt = k(V/S)c^{0.5}_{o,0}(Np(Ⅵ))•c_o^{-0.14}(TBP)\ c_a^{-0.32}(NO_3^-)$, k is $2.29×10^{-4}(mol•L^{-1})^{0.96}•cm^{-1}•min^{-1}$ at 25 ℃, and $dc_a(Np(Ⅵ))/dt = k(V/S)c_{o,0}^{0.63}(Np(Ⅵ))\ c_o^{-0.27}(TBP)c_a^{-0.34}(NO_3^-)$, k is $6.24×10^{-4}(mol•L^{-1})^{0.98}•cm^{-1}•min^{-1}$ at 25 ℃. Based on these kinetic parameters, the stripping efficiency of Np in 1B contactor is calculated as 95%.

Key words neptunium _ dimethylhyoxylamine _ methylhydrazine _ kinetics _ reduction

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