



Uranium recovery from strong acidic solutions by solvent extraction with Cyanex 923 and a modifier



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ABSTRACT

Uranium stripping with strong acid solution is always highly desired due to its simple operation and less pollution. However, intensive acid neutralisation for uranium precipitation in the subsequent step limited its application. A new solvent extraction process has been developed to transfer uranium from strong to weak sulphuric acid solutions suitable for uranium precipitation without intensive neutralisation. An organic system consisting of 10% Cyanex 923 and 10% isodecanol as the modifier in ShellSol D70 was optimised for the process. It was found that uranium was extracted efficiently from 4 to 6 M H₂SO₄ solutions with the organic system, and it could be efficiently stripped with 0.2–0.5 M H₂SO₄ solutions. Both extraction and stripping kinetics of uranium were very fast, reaching the equilibrium within 0.5 min. Temperature between 30 and 60 °C has slight effect on uranium extraction and stripping. Four theoretical stages could effectively extract more than 98% uranium from a solution containing 17.5 g/L U and 6.0 M H₂SO₄ at an A/O ratio of 1:1.5, and it could generate a loaded organic solution containing about 12 g/L U. More than 99% U could be stripped from the loaded organic solution containing 14.6 g/L U with 0.5 M H₂SO₄ using five stages at an A/O ratio of 1:3. As a result, the loaded strip liquor containing more than 40 g/L U would be obtained which is suitable for uranium recovery by precipitation using hydrogen peroxide. A conceptual process has been proposed for uranium transfer from strong to weak sulphuric acid solutions for its recovery.

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1. Introduction

Uranium is a naturally occurred nuclide used for nuclear power generation. From uranium ore to nuclear fuel, solvent extraction technology plays an essential role for its recovery and purification (Edwards and Oliver, 2000; Lunt et al., 2007; van Tonder and Kotze, 2007; Zhu and Cheng, 2011). Tertiary amines, i.e. Alamine 336 (tri-octyl/dodecyl amine), are commonly used as the extractant (Mackenzie, 1997; Sole et al., 2011; Zhu and Cheng, 2011). Tertiary amines are very selective for uranium extraction over other impurities such as iron, aluminium, zirconium and titanium. Among the commonly associated impurities, only molybdenum is extracted stronger than uranium (Coleman et al., 1958; Ritcey, 2006; Mottay and du Preez, 2015).

Uranium stripping from tertiary amines is usually achieved with ammonia/ammonium solutions, although other alternatives could be available (Kotze et al., 2012; Mackenzie, 2014). By comparison, stripping with ammonia/ammonium solution is currently the cheapest method. However, the method still has some

disadvantages including wastewater discharge containing ammonium and difficulty in ammonia storage and transport. With more and more stringent limitations for the discharge of wastewater containing nitrogen, it will lead to a significant challenge for uranium stripping using the solution containing ammonia and ammonium. Therefore, alternative stripping methods are becoming very important. Amongst the potentially alternative methods, stripping with strong sulphuric acid is mostly preferred (Taylor, 2007; van Tonder and Edwards, 2012) and it has been used as an alternative in the Rabbit Lake uranium project in Canada (Kotze et al., 2012).

Apart from amine processes, uranium stripping with strong acid is also preferred for some newly developed processes with organic systems including mixtures of D2EHPA (di-2-ethylhexyl phosphoric acid) and Alamine 336 for the Honeymoon uranium project (Quinn et al., 2013; Ballestrin et al., 2014), mixtures of D2EHPA and Cyphos IL 101 (tri-hexyl tetradecyl phosphonium chloride) (Zhu et al., 2014) and Cyanex 272 (bis 2,4,4-trimethyl pentyl phosphonic acid) (Soldenhoff and Quinn, 2015).

Uranium stripping with H₂SO₄ is advantageous in that it is readily available on site where H₂SO₄ is used for the leach. Additionally and most importantly, if it can be recycled, the stripping method will have less, or even no waste generation. However, at present,

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high concentration of acid left in the loaded strip solution cannot be recycled economically and requires to be neutralised before uranium precipitation for its recovery (Morais et al., 2005; Kotze et al., 2012; van Tonder and Edwards, 2012). Extensive neutralisation will consume large amounts of alkaline reagent, and also result in the generation of large amounts of solid waste for disposal. Consequently, uranium stripping with strong H_2SO_4 solution is not widely accepted due to its high cost and high risk of solid waste pollution arising from intensive neutralisation.

To overcome the problem presented for uranium stripping by H_2SO_4 , a new solvent extraction method using Cyanex 923 (a mixture of trialkylphosphine oxides; alkyl is hexyl or octyl) and isodecanol as the modifier was developed to transfer uranium from strong into weak acidic solutions, which are suitable for uranium precipitation without intensive neutralisation.

2. Experimental

2.1. Reagents and solution preparation

Cyanex 923 was kindly supplied by Cytec Industries Inc. and was used as received without further purification. The modifiers isodecanol and nonyl phenol were purchased from Huntsman Corporation, Australia, with >98% purity, while other modifiers including TBP (Tri-butyl phosphate) and 1-octanol with analytical grade were purchased from Sigma–Aldrich Corporation. The diluent ShellSol D70 (100% aliphatic) was used for the study except for the tests of diluent effect. ShellSol 2046 (mixture of about 19% aromatic and about 81% aliphatic hydrocarbons) and ShellSol A150 (100% aromatic hydrocarbons) were used for the tests of diluent effect. All these diluents were kindly supplied by Shell Chemicals, Australia, and were used as received. Organic solutions were prepared by dissolving Cyanex 923 and the modifier in a diluent to make desired concentrations in volume percentage (v/v%). Analytical grade uranium acetate ($UO_2(Ac)_2$) was used to prepare uranium stock solutions. The $UO_2(Ac)_2$ was first dissolved in de-ionised water and then precipitated with NaOH at pH 8–9. The precipitate was washed twice with de-ionised water and finally dissolved in sulphuric acid solution to make the uranium stock solution.

2.2. Shake-out test

Shake-out tests were carried out with 300 mL hexagonal glass containers immersed in a temperature-controlled water bath. Eurostar digital overhead stirrers with 30 mm diameter Teflon impellers were used for mixing. Equal volumes of the two immiscible solutions were mixed at 40 °C, except the tests for uranium distribution isotherms and temperature effects. Samples were taken for analysis using a syringe with a plastic tubing extension.

2.3. Kinetics of uranium extraction and stripping

For the kinetics study, 100 mL of each of the aqueous and organic solutions were pre-heated to 40 °C separately, and then the organic solution was rapidly transferred into the aqueous solution during stirring at 1300 RPM. Timing started immediately after the mixing commenced. Sample solutions were taken at 0.5, 1, 2, 3 and 10 min using syringes with plastic tubing extensions.

2.4. Uranium distribution isotherms

To determine the stage numbers for effective extraction and stripping of uranium with the Cyanex 923 system, distribution isotherms for uranium extraction and stripping were obtained at

various A/O ratios. On the basis of distribution isotherm curves, McCabe Thiele diagrams were constructed, and the theoretical number of stages for uranium extraction and stripping were determined.

2.5. Sampling and analysis

During the tests, the mixture of the two phases was separated using Whatman 1PS papers which only allow organic solution to pass through. After phase separation, the aqueous phase was filtered again through a 0.45 μm Supor membrane filter to completely remove the entrained organic. The aqueous solution was diluted of 50 or 100 times with de-ionised water and then the uranium concentration was assayed by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry). The concentration of sulphuric acid was measured by pH titration using standard NaOH solution under masking of U(VI) with 0.1 M Mg-EDTA solution referred to the method reported (Rolia and Dutrizac, 1984). pH 6.0 was selected to indicate the end point of titration.

3. Results and discussion

3.1. Uranium extraction with Cyanex 923 system

Uranium extraction with an organic system consisting of 10% Cyanex 923 and 10% isodecanol as the modifier from various sulphuric acid solutions containing 1.8 g/L U at an A/O ratio of 1:1 is shown in Fig. 1. For a comparison, the results obtained by Gupta et al. (2002) with 0.1 M Cyanex 923 (~4.3%, v/v) in toluene from a sulphate solution containing 10^{-4} M U(VI) (0.0238 g/L) at a phase ratio of 1:1 and room temperature (around 25 °C) is also shown in Fig. 1. Uranium extraction with the Cyanex 923/isodecanol system reached its maximum over H_2SO_4 concentration range of 4–6 M, and the lowest uranium extraction was obtained over H_2SO_4 concentration range of 0.5–1.0 M. Uranium extraction variation with the H_2SO_4 concentration was similar to that reported by Gupta et al. (2002) with Cyanex 923 alone for acid concentrations <6.0 M (Fig. 1). It is unknown why uranium extraction decreased when sulphuric concentration was higher than 6.0 M, which was opposite to the result obtained by Gupta et al. (2002). However, it has been reported that uranium extraction with TOPO (trioctylphosphine oxide), an analogue of Cyanex 923, also decreased when the H_2SO_4 concentration was higher than about 3 M as shown in Fig. 2 (Sato, 1980; Yang et al., 1998). On the basis

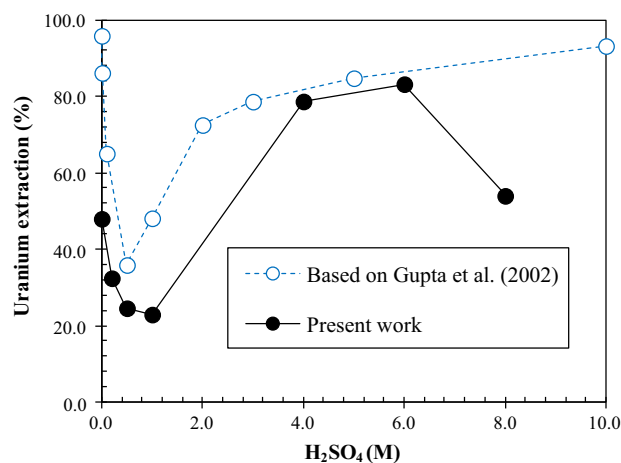


Fig. 1. Uranium extraction with organic system consisting of 10% Cyanex 923 and 10% isodecanol and comparison with the reference work based on Gupta et al. (2002).

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