

Separation and Purification of Zirconium with Amines from Sulphuric Acid System: A Review

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Summary

Zirconium is being used as a high-technology material for industrial applications due to its excellent thermal, electrical, chemical and optical properties. Solvent extraction process is used for separation and purification of zirconium in sulphate media from different value metals including hafnium, uranium, niobium, rare earths and titanium. Efficient recovery of zirconium using solvent extraction is extremely complicated due to the fact that zirconium forms poly-nuclear complexes in sulphate solution. This polymerization is more favorable in low concentration of free acid and at high concentration of zirconium. Understanding the aqueous chemistry of zirconium species, separation technology and complex-formation reactions are most important for selecting appropriate organic media and optimization of separation conditions. In this paper, solvent extraction technique for zirconium separation and purification with amines from sulphate solution is reviewed. The solution chemistry of zirconium species and separation mechanisms are discussed to illustrate the better understanding of the process steps.

Introduction

Zirconium (Zr) is mainly produced from zircon ($ZrSiO_4$), which is found in the beach sands along with rutile, ilmenite, and monazite. Zirconium also occurs in several minerals including baddeleyite, kosnarite and Eudialyte. Zirconium dioxide is mainly used in piezoelectric crystals and as pigment in the ceramic industry. High purity metallic Zr is used in nuclear reactor due to its low neutron cross section, outstanding mechanical and chemical resistance and excellent thermal conductivity. The concentration of Hf in nuclear grade Zr should be no more than 30 mg/L [1]. Amongst various techniques, solvent extraction is quite popular for separation of Zr from other metals including Hf, Ti, Fe, rare earths and Nb. Currently, TBP(tri-butyl phosphate)/HNO₃, MIBK(methyl isobutyl ketone)/NaSCN/HNO₃ and TBP/HCl solvent extraction processes are used for separation of Zr, but the downstream contain high concentration of ammonium, cyanide and by-products of organic [2, 3].

A literature survey reveals that amine-based extractants are often chosen for the separation and purification of Zr(IV) [4-6]. The primary amine (Primene-JMT) was used by El-Yamani et al. [7] in the separation of Zr(IV) from Hf(IV) in H₂SO₄ medium. Shimizu [8] found the suitable extraction conditions of different metals including Zr(IV) from ammonium sulphate solution with the secondary amine (Amberlite LA-2) in xylene. Generally, the tertiary amines are better extractant than the primary or secondary amines [9, 10]. Sato and Watanabe[11] investigated the extraction of Zr(IV) from sulphate solutions using di-n-octylamine, tridodecylamine, trioctylamine, and tris (2-ethylhexyl) amine. The comparison of Zr extraction from sulphate solution with tri-n-laurylamine, tri-n-octylamine, di-n-nonylamine, primene-JMT and p-dodecylaniline has been performed [12]. MacDonald [13] developed a computer simulation process for separation of Zr from Hf in sulphuric acid medium using Alamine 336. In this paper, separation and purification of Zr with amine extractants in sulphuric acid solution are evaluated, and the solution chemistry and mechanism of extraction, stripping and organic regeneration are discussed.

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Solution Chemistry of Zirconium

Understanding the solution chemistry of Zr species has played an important role for the development of solvent extraction process steps. In solution, Zr exists exclusively in a +4 oxidation state and is believed to attain coordination numbers of 7 and 8 [14]. Paramonova and Voevodskii [15] concluded that, at least two processes occur simultaneously in sulphate solutions, the formation of sulphate complexes and hydrolysis. They suggested that the complex formation is related to the presence of hydrolysed Zr species with a positive (ZrSO_4^{2+}) or a zero charge ($\text{Zr}(\text{SO}_4)_2$) and the absence of negatively charged species at concentrations of H_2SO_4 lower than 0.5 M. The predominant form of Zr(IV) is the $\text{Zr}(\text{SO}_4)_3^{2-}$ at around 1 M of H_2SO_4 .

Etinson and Petrov [16] concluded that Zr compounds in aqueous solution are characterized by their high degree of hydrolysis as well as their tendency to form various complex ions and polymer compounds. Consideration of hydrolysis and polymerisation of Zr is necessary because these phenomena directly affect the extraction of Zr. Yagodin et al. [17] reported that Zr sulfate may hydrolyse at less than 2 M of H_2SO_4 . Richens [14] reported that due to the high charge/radius ratio, Zr(IV) ion strongly hydrolyses in water, leading to the formation of poly-nuclear species with oxygen containing bridges. Recent publications [18] reported that the Zr is hydrolysed to form dimer ($\text{Zr}_2(\text{OH})_6^{2+}$ and $\text{Zr}_2(\text{OH})_7^+$), trimer ($\text{Zr}_3(\text{OH})_4^{8+}$ or $\text{Zr}_3(\text{OH})_5^{7+}$) and tetramer ($[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$) in aqueous solution. Under certain conditions, Zr forms extremely stable polynuclear compounds that are not in equilibrium with monomer form [8]. The extent of polymerisation depends on different parameters including aging, temperature, acidity, and concentration of Zr [14]. The polymerisation reaction of Zr(IV) is increased with decreasing acidity of solution. Yagodin et al. [17] reported that poly-nuclear compound $\text{Zr}_2(\text{SO}_4)_7$ is formed in a solution containing 1-1.5 M of Zr(IV). Moreover, Baglin and Breger [19] reported that in strong sulphuric acid solution, the sulphate ion can displace hydroxyl group to form other products.

Table 1 Commonly used different type of amines for solvent extraction study.

Extractant/Diluent	Molecular formula	Reference
Primary amines		
Primene JMT	$\text{RNH}_2(\text{R}=(\text{CH}_3)_3\text{C}(\text{CH}_2\text{C}(\text{CH}_3)_2)_4)$	[7, 20]
Secondary amines		
Di-cyclohexylamine	$\text{C}_6\text{H}_{11}\text{-NH-C}_6\text{H}_{11}$	[21]
Di-n-octylamine	$[\text{CH}_3(\text{CH}_2)_7]_2\text{NH}$	[11]
Di-n-nonylamine	$[\text{CH}_3(\text{CH}_2)_8]_2\text{NH}$	[7, 20]
Tertiary amines		
Tri-n-octylamine (Alamine 336)	$[\text{CH}_3(\text{CH}_2)_7]_3\text{N}$	[11]
Tri-n-dodecylamine	$[\text{CH}_3(\text{CH}_2)_{11}]_3\text{N}$	[11]
Tris-(2-ethylhexyl)amine	$[\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2]_3\text{N}$	[11]
Quaternary ammonium salts		
Tri-caprylmethylammonium chloride (Aliquat 336/Adogen 464)	$[\text{CH}_3(\text{CH}_2)_7]_3\text{N}^+(\text{CH}_3)\text{Cl}^-$	[7, 22]

Extraction of Zirconium (IV) with Amine Extractants

The most commonly used amine extractants in solvent extraction process steps include primary amines, secondary amines, tertiary amines and quaternary

ammonium salts. The amine extractants used for Zr(IV) solvent extraction study are listed in Table 1.

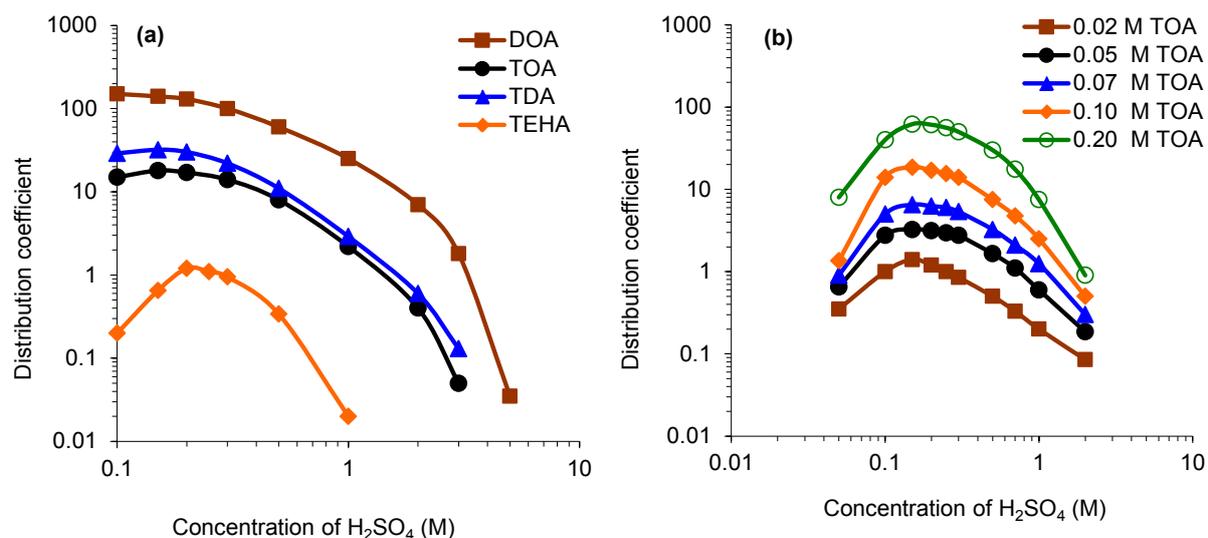


Fig. 1 Extraction of zirconium (IV) from sulphuric acid solutions with (a): 0.1 M solutions of different amines in chloroform and (b): different concentrations of TOA in chloroform [11].

Effect of H₂SO₄ Concentration on Zirconium Extraction

Several studies have been carried out for Zr(IV) extraction from different concentrations of H₂SO₄ solutions with amine extractants. Different extraction behaviours in H₂SO₄ solutions were observed for tertiary amines (Tri-n-octylamine (TOA), Tri-n-dodecylamine (TDA) and Tris-(2-ethylhexyl)amine (TEHA)). The distribution coefficients of Zr(IV) curve as a function of acidity are shown in Fig. 1(a, b) with tertiary amines [11]. Sato and Watanabe [11] reported that the increase in distribution coefficient at low acidities is ascribed to salting-out of sulphuric acid, while the decrease at higher acidities results either acid for association with these amines or from the formation of less extractable complexes. In contrast, distribution coefficient is decreased with increasing the concentration of H₂SO₄ in both Primene-JMT and Adogen 464, which is shown in Fig. 2(a, b) [7, 22]. These studies suggest that the decreasing of distribution coefficient with increase in sulphate ion concentration is due to the formation of inextractable anionic species presumably Zr(SO₄)₃²⁻ and/or Zr(SO₄)₄⁴⁻.

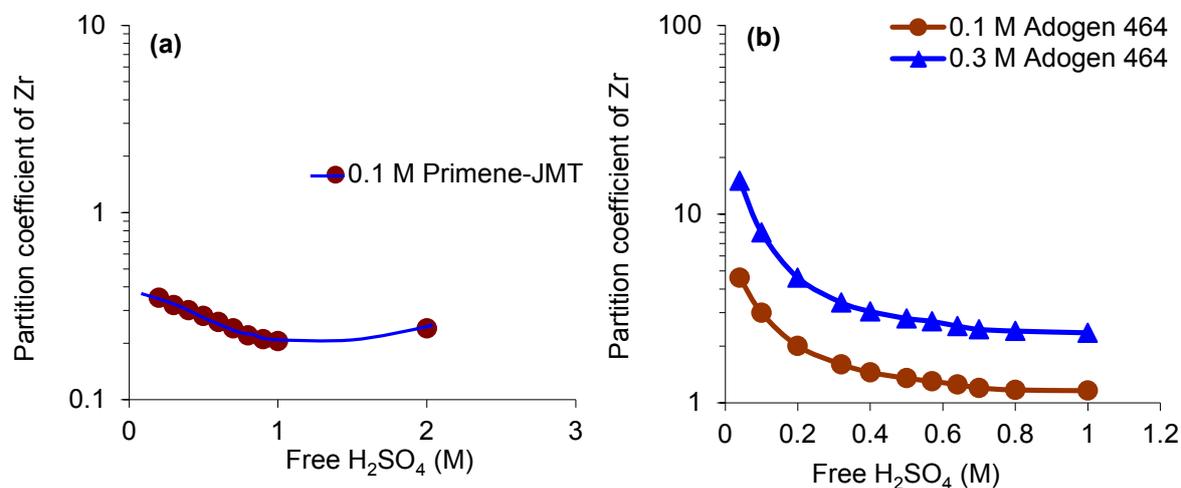
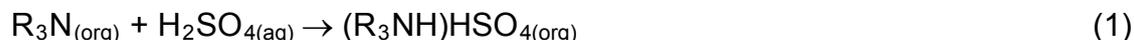
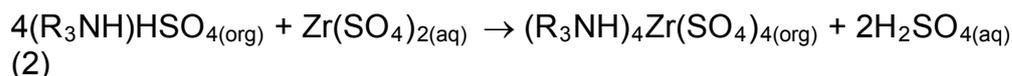


Fig. 2 Extraction of zirconium (IV) from sulphuric acid solutions with (a): 0.1 M solution of Primene-JMT in kerosene and (b): 0.1 M and 0.3 M of Adogen 464 in kerosene [7, 22].

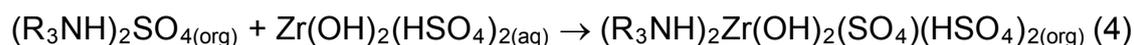
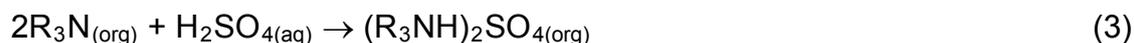
The following extraction mechanism is proposed for nonhydrolysed Zr sulphate extraction with tri-n-octylamine: neutralised tri-n-octylamine in organic solution reacts in the presence of excess H₂SO₄ solution according to the reaction:



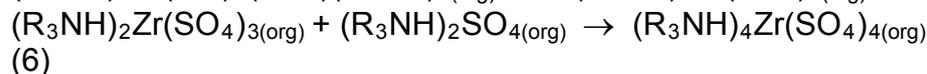
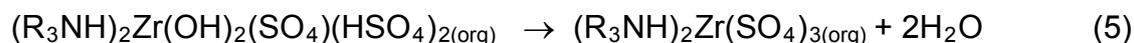
in which R₃N represents the tertiary amine. The extraction equilibrium corresponds to the reaction:



Extraction of polymeric hydrolysed zirconium sulphate with tertiary amine is possible through the destruction of this polymer into the monomeric hydrolysed zirconium sulphate (for an example, Zr(OH)₂(HSO₄)₂). At the moment of formation of monomer, the coordination sphere of such a complex is not saturated; therefore, their extraction at the first stage follows the additional mechanism [23]:



Then a slow decrease in the rate of Zr hydrolysis in the organic phase occurs, which is shown in reactions (5) and (6).



Extraction of stable hydrolysed polymers is also possible following the exhaustion of hydrolyzed monomers and destruction of unstable multinuclear complexes in conformity with the extractability series of Zr sulphate by TOA: nonhydrolysed complexes > hydrolysed monomers > stable hydrolysed polymers [17, 23].

Table 2 Stripping of Zr(IV) from loaded amines by different solution at the A/O ratio of 1.

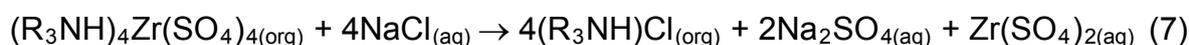
Extractant Name	Conc. (M/%)	Diluent	Stripping solution	Stripping (%)	Reference
Primene-JMT	0.25 M	BDR-Z [*]	0.75 M HNO ₃	71	
			1.0 M HNO ₃	98	[20]
			2.0 M HNO ₃	Complete	
N-n-Octylaniline	0.25 M	Benzene	4.0 M NaCl + 0.5 M HCl	--	[12]
	3%	Xylene	0.5 M HNO ₃	Complete	[24]
Di-n-nonylamine	0.25 M	Benzene	4.0 M NaCl + 0.5 M HCl	--	[12]
Tri-n-octylamine	10%	Kerosene	1.0 M Na ₂ CO ₃	Complete	[25]
	0.25 M%	Benzene	4.0 M NaCl + 0.5 M HCl		[12]
Alamine 336	10%	Kerosene	1.5 M NaCl + HCl	Complete	[26]
	10%	Kerosene	4.0 M NaCl + 0.5 M HCl	Complete	[27]
	10%	Kerosene	10% HCl	--	[28]

Tri-n-laurylamine	0.25 M%	Benzene	4.0 M NaCl + 0.5 M HCl	--	[12]
Adogen 464	0.2 M	Kerosene	0.5 - 1.0 M HNO ₃	Complete	[22]
Aliquat 336	0.2 M	Kerosene	0.5 - 1.0 M HNO ₄	Complete	[29]

BDR-Z: Mixture of aliphatic hydrocarbons.

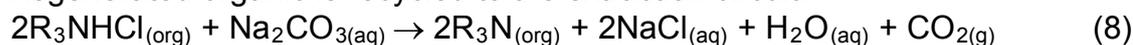
Impurities Scrubbing and Zirconium (IV) Stripping

MacDonald et al. [26] reported that the Hf content of the Zr-bearing organic phase can be decreased to any desired level by multistage counter-current extraction followed by scrubbing with dilute sulphuric acid solution. Takahashi et al. [30] reported that the separation of Zr from most of the elements including Al, Ca, Co, Fe, Mn, Ti, V and rare earths is possible in extraction stages with tri-n-octylamine in paraffin. Zr(IV) can be completely stripped from Alamine 336 in kerosene by three stage counter-current stripping with NaCl-HCl solution [26]. Stripping can be shown by the following reaction [30]. Stripping of Zr(IV) from loaded amines by different aqueous solutions is summarised in Table 2.



Organic Regeneration and Uranium Removal

MacDonald et al. [26] reported that in process leach solution when U and Zr are present, they are loaded together to organic phase. If the chloride ion activity is high enough in Zr stripping solution, Zr is selectively stripped over U from the loaded organic phase. Uranium remaining in the Zr-depleted organic phase can be removed by the following reaction with Na₂CO₃ solution in the organic regeneration stages [30]. Regenerated organic is recycled to the extraction circuit.



Conclusion

Separation of Zr by solvent extraction with amines from sulphate system is summarised by the following steps:

- (1) Due to the high charge/radius ratio, Zr(IV) ion is strongly hydrolysed to form poly-nuclear species including dimer, trimer and tetramer in aqueous solution.
- (2) The polymerisation of Zr(IV) is increased with increasing aging, temperature and concentration of Zr, and with decreasing acidity of solution.
- (3) The distribution coefficient is increased at low acidities due to salting-out of sulphuric acid, while decreases at higher acidities results either association with amine or formation of less extractable Zr(IV) complexes.
- (4) Stable hydrolysed polymers are also possible to extract with amines by the exhaustion of hydrolyzed monomers and destruction of unstable complexes.
- (5) Zirconium (IV) can be selectively extracted over most of the metals with Alamine 336 while Hf can be scrubbed from Zr-loaded organic by controlling the O/A phase ratio.
- (6) Zirconium followed by U can be selectively stripped from loaded Alamine 336 with NaCl-HCl and Na₂CO₃, respectively. An overall flowsheet for separation

and purification of Zr from sulphuric acid solution with tertiary amine (Alamine 336) in kerosene is shown in Fig. 3.

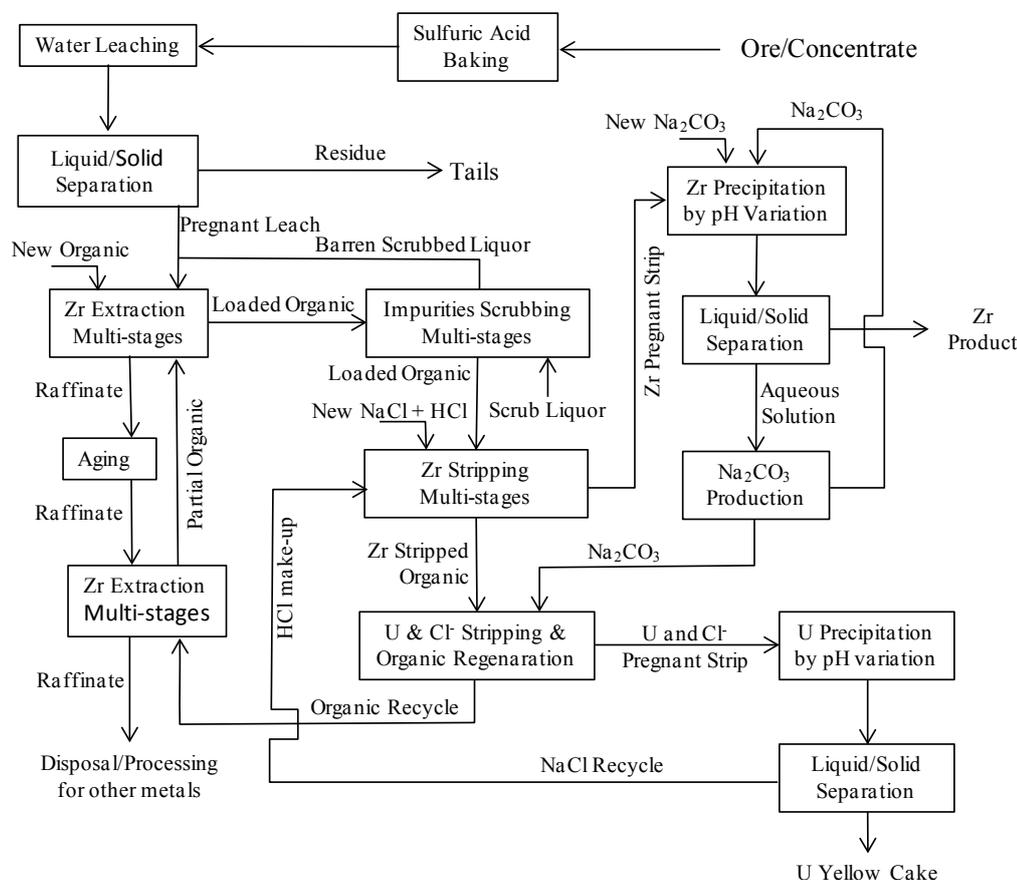


Fig. 3 Flowsheet for separation and purification of zirconium from sulphuric acid solution with tertiary amine (Alamine 336) in kerosene.

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