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Extraction Behavior and Purification of Germanium using an Undiluted Quaternary Ammonium Ionic Liquid in Combination with a Complexing Agent

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Abstract

The recovery of germanium from low-grade ores and secondary resources requires the development of new separation and purification techniques. In this work, the solvent extraction behavior of Ge(IV) and common contaminants, i.e. Zn(II), Fe(III), Cu(II) and As(III), was studied using the undiluted ionic liquid Aliquat 336 ([A336][Cl]). A comparison was made between HCl and H₂SO₄ extraction media. It was found that upon extraction from H₂SO₄ media, organic chloride ions were exchanged for aqueous hydrogensulfate ions. This transfer of chlorides to the aqueous phase facilitated metal extraction and resulted in a similar extraction performance for the HCl and H₂SO₄ systems. Elimination of chlorides from the system by conversion of the ionic liquid to [A336][HSO₄] prior to the solvent extractions, allowed nearly full suppression of the extraction of Zn(II), Fe(III) and Cu(II). To form an extractable anionic Ge(IV) complex, the addition of tartaric acid, citric acid and catechol to the aqueous phase was studied. Tartaric acid proved superior as only five equivalents were required for quantitative extraction of Ge(IV). A separation process for the recovery of Ge(IV) from a synthetic zinc refinery residue leachate was developed, comprising the exclusion of chloride ions through the use of [A336][HSO₄], and the addition of tartaric acid to the aqueous phase. The optimized process involves the addition of five equivalents of tartaric acid and extraction with [A336][HSO₄] at an organic-over-aqueous volumetric phase ratio (O/A) of 1/2, resulting in the highly selective extraction of Ge(IV). The limited amount of As(III) that is coextracted can be scrubbed with water at O/A = 1/3. Ge(IV) is stripped with 2.0 mol L⁻¹ NaOH at O/A = 1/1. [A336][HSO₄] can thereafter be regenerated with H₂SO₄ and reused in the next extraction cycle.

<u>Keywords</u>: Aliquat 336; critical raw materials; hydrometallurgy; ionic liquids; solvent extraction; zinc metallurgy.

Introduction

Germanium is an important element for many 21^{st} century technologies with applications including fiber-optic cables, 5G connectivity, satellite solar cells, infrared optics, gamma ray detectors and electronics. The germanium demand is expected to increase continuously.^{1,2} Only a few germanium minerals, *e.g.* germanite (Cu₁₃Fe₂Ge₂S₁₆), are known, and none of these are available in sufficient amounts to allow extraction of germanium in an economically viable manner. Therefore, germanium is typically recovered as a secondary product from other industries. As germanium is found as an impurity metal in many zinc ores, it can be obtained as a by-product of zinc production. Some ashes and flue dusts generated in the combustion of certain coals also contain extractable amounts of germanium. It is estimated that 60% of the worldwide production of germanium is sourced from zinc ores, mainly sphalerite, and 40% from coal. The by-product nature and the strong market position of China, which accounts for 80% of the global production of refined germanium, have resulted in the EU classifying germanium as a critical raw material.^{3–5}

Germanium production and purification generally involves several steps. Depending on the source material, a germanium concentrate (5–30%) is obtained through either pyro- or hydrometallurgical steps. Hydrometallurgical methods are typically preferred as thermal or pyrometallurgical methods have a larger environmental footprint and can encounter issues due to the volatility of GeO and GeS.⁶ The hydrometallurgical methods are generally based on the precipitation of germanium by tannic acid or as a hydroxide or sulfide. The obtained germanium concentrate is subsequently chlorinated, followed by distillation of germanium tetrachloride. The purified germanium tetrachloride is then hydrolyzed into germanium(IV) oxide, which can be reduced with hydrogen gas to germanium metal. The final step in the purification of germanium is typically done by zone-refining as for many of the applications, high-purity germanium (up to 13N) is required.^{2,7}

In the framework of the hydrometallurgical processing of germanium containing materials and the purification of germanium, the use of solvent extraction (SX) has seen increasing interest as an alternative to the precipitation methods. Solvent extraction is a separation technique based on differences in the distribution of metals between two immiscible liquid phases. The separation of germanium from contaminants including arsenic, antimony, zinc, cadmium, nickel, cobalt, copper and iron by solvent extraction has been studied extensively in the past.⁴ Earlier research mainly involves acidic extractants such as Kelex 100, LIX 63, D2EHPA and different synergic systems.⁸⁻¹⁵ Some work with neutral extractants has been conducted as well.¹⁶ More recent work mainly involves the use of basic extractants. These processes are based on the tendency of germanium to form extractable, anionic complexes with some organic molecules such as tartaric acid, oxalic acid, catechol or citric acid, whereas the impurity elements do not under the same conditions.¹⁷ Increased selectivity and/or higher recovery yields can be obtained in this manner. Furthermore, these systems do not require the high acidity that is generally required for acidic extractants to obtain a high germanium recovery.¹⁵ Tertiary amines such as trioctylamine (TOA), N235 or Alamine 336 are basic extractants that are extensively studied for germanium purification. TOA in combination with tartaric acid, for example, has been used to recover germanium from synthetic coal fly ash leachates¹⁸, synthetic zinc residue leachates¹⁹⁻²² and optical fiber waste.²³ In combination with other organic complexants such as catechol and oxalic acid, TOA has also proven to be highly efficient in the separation of germanium from coal fly ash leachates and zinc refinery residues.^{24–26} Another basic extractant that has been the subject of some research efforts is Aliquat 336, a mixture of quaternary ammonium chlorides with trioctylmethylammonium chloride as the main component. Aliquat 336 has been used in combination with citric acid to determine the germanium content of coal fly ashes and to recover germanium from synthetic coal fly ash leachates.18,27

An interesting trend in solvent extraction research is the use of ionic liquids (ILs). ILs are solvents consisting solely of ions and characterized by a.^{28,29} Such properties make them more sustainable and safer alternatives for the volatile organic compounds often used in the industry, as the risk of both air pollution and electrostatic charge build-up are significantly reduced.^{30–32} Several works have indicated that ILs can show excellent selectivity and efficiency in the separation and purification of various metals ranging from base metals to rare earths and precious metals.^{33–35} However, the use of ILs for germanium extraction and purification has been largely neglected so far. To the best of our knowledge, only one study has been published on the solvent extraction of Ge(IV) by an undiluted IL, and this was in the context of analytical chemistry.³⁶

In the present study, undiluted Aliquat 336 was used for the purification of germanium. The use of undiluted Aliquat 336 in combination with a complexing agent is an unexplored field in the purification of Ge(IV). Zn(II), Fe(III), Cu(II) and As(III) were considered as impurity elements as they are commonly found in zinc residues and their leachates. The influence of the extraction medium, *i.e.* either a chloride or sulfate system, and the choice of complexing agent, *i.e.* tartaric acid, citric acid or catechol, were extensively studied. Using the findings, a separation process for the recovery of germanium from a synthetic zinc residue leachate was developed and optimized.

Experimental

Materials

Catechol (98%), citric acid (99.5%), CuCl₂ (>95%), DL-tartaric acid (99.5%), FeCl₃ (98%), ZnSO₄ (99%), and Aliquat 336 were purchased from Acros Organics (Geel, Belgium). ZnCl₂ (98%), CuSO₄ (>99%), H₂SO₄ (95 wt%), HNO₃ (65 wt%), and the germanium, zinc, iron, copper, arsenic, scandium, sodium and sulfur standard solutions (1000 mg L⁻¹) were bought from Chem-Lab (Zedelgem, Belgium). Fe₂(SO₄)₃ (98%), NaAsO₂ (99%), and NaOH pellets (>95%) were acquired from Fisher Scientific (Merelbeke, Belgium). Hexagonal GeO₂ (> 99.99%) was obtained from Sigma–Aldrich (Diegem, Belgium). HCl (37 wt%) and toluene (> 99.5%) were purchased from VWR (Leuven, Belgium). CsCl (>99.9%) and NaHSO₄ (>93%) were acquired from Carl Roth (Karlruhe, Germany). Water was of ultrapure quality, deionized with a Merck Millipore Milli-Q Reference A+ system. All chemicals were used as received, without any further purification.

Ionic Liquid Synthesis

The hydrogensulfate analogue of [A336][Cl], [A336][HSO4], was prepared by contacting 250 mL of [A336][Cl] ten times with an equal volume of a 3 mol L⁻¹ NaHSO₄ solution. The product was subsequently washed two times with ultrapure water to remove the last traces of chloride and dissolved salts. The absence of chlorides was confirmed by wavelength dispersive X-ray fluorescence spectrometry (WDXRF) (*vide infra*). The density, viscosity and water content of the synthesized water-saturated [A336][HSO₄] are given in Table S1 of the Supporting Information and compared with the values of water-saturated [A336][Cl].

Metal Extraction, Scrubbing and Stripping

All extraction, scrubbing and stripping experiments were performed in 4 mL glass vials on a total liquid volume of 2 mL. For scrubbing and stripping experiments, the loaded organic phases were prepared by performing extractions on a 40 mL scale using 50 mL centrifuge tubes. To facilitate mass transfer, samples were shaken at 300 rpm using a Kuhner Lab-Shaker ES-X orbital shaker. A contact time of 1 h proved sufficient to reach equilibrium, Figure S1 in the Supporting Information. After equilibration, primary break of the emulsion proceeded relatively quickly under gravity (Figure S2, Supporting Information). However, to achieve complete phase disengagement the samples were centrifuged for 5 min at 5000 rpm using an Eppendorf 5804 centrifuge.

Aqueous feed solutions were prepared through combination of certain volumes of aqueous metal stock solutions and aqueous stock solutions of the complexing agents followed by dilution with Milli-Q water and acid (HCl 37 wt% or H₂SO₄ 95 wt%, depending on the system). Prior to extraction, the organic phases were always presaturated with water or acid, depending on the matrix of the feed solution, to exclude volume changes and incorrect evaluations of the experimental data.

Instrumentation, Analysis and Quantification Methods

Aqueous metal concentrations were measured using a PerkinElmer Avio 500 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) equipped with an axial/radial dual plasma view, a GemCone High Solids nebulizer, a baffled cyclonic spray chamber and a demountable quartz torch with a 2.0 mm internal diameter alumina injector, an echelle-based polychromator, and a segmented CCD array solid state detector. Samples, calibration standards and quality control samples were always diluted with 2 vol% HNO₃. Calibration lines were constructed using solutions containing 0.1, 1, 5, 10 and 15 mg L⁻¹ of the corresponding metals. The ICP-OES spectra were always recorded in triplicate and a quality control was performed regularly using a 1 mg L⁻¹ metal solution. Sc(III) (5 mg L⁻¹) was added as internal standard to all samples but was applied only in case the quality control failed due to non-spectral matrix effects. For the measurement of Na, 0.005 mol L⁻¹ CsCl was added to the ICP-OES samples and calibration curve as an ionization buffer. The experimental error calculated on the basis of the triplicate measurement was less than 5% and error bars on graphs were omitted for the sake of legibility.

The organic metal concentration was calculated via the mass balance using the aqueous metal concentrations before and after extraction (Eq. (1)). Using the organic metal concentration, the distribution ratio D (Eq. (2)) and extraction efficiency %E (Eq. (3)) can be calculated. The scrubbing and stripping efficiencies %S were calculated similarly (Eq. (4)).

$$C_{M,org,f} = \frac{\left(C_{M,aq,i} - C_{M,aq,f}\right)}{O/A}$$
(1)

$$D = \frac{C_{M,org,f}}{C_{M,aq,f}}$$
(2)

$$\%E = \frac{O/A C_{M,org,f}}{C_{M,ag,i}} *100$$
(3)

$$\% S = \frac{C_{M,aq,s}}{O/A C_{M,org,i}} *100$$
(4)

with $C_{M,org,f}$ the final concentration of metal M in the organic phase after extraction, $C_{M,aq,i}$ and $C_{M,aq,f}$ the initial and final concentrations of metal M in the aqueous phase, respectively, and O/A the applied volumetric organic–over–aqueous phase ratio. $C_{M,aq,s}$ represents the final concentration of metal M in the aqueous phase after scrubbing or stripping, and $C_{M,org,i}$ the concentration of metal M in the organic phase before scrubbing or stripping.

The conversion of [A336][Cl] to [A336][HSO₄] was quantified by WDXRF using a recently developed analytical method.³⁷ The calibration curve is provided in Figure S3 in the Supporting Information. The conversion was defined in Eq. (5) as the volume fraction of [A336][HSO₄] present in a mixture of [A336][Cl] and [A336][HSO₄] that can be prepared to obtain an IL of a certain residual chloride content.

Conversion =
$$\frac{V([A336][HSO_4])}{V([A336][C1]) + V([A336][HSO_4])}$$
 (5)

Measurements were performed on the Cl K α line (2.622 keV) using the Bruker S8 Tiger 4 kW WDXRF system equipped with a Rh anode, 50 μ m Be filter, PET (pentaerythritol) diffraction crystal and a gas-flow proportional counter detector. Samples were measured after a washing step with Milli-Q water to remove any dissolved salts or acids.

Raman spectroscopy was used to differentiate SO_4^{2-} from HSO_4^{-} . Measurements were performed on a Horiba Jobin Yvon LabRam HR Evolution Raman microscope equipped with a 1800 grooves/mm grating, a Peltier-cooled electron-multiplying CCD (SIN-EM FIVIS) for detection, and an Olympus BX41 microscope. A 785 nm laser was used for excitation. All spectra were measured at 22 °C in 2 mL quartz cuvettes using a ×5 microscope objective to focus the laser beam at the center of the cuvette. The obtained spectra were smoothed and subjected to a baseline correction using the Origin 2018b software (OriginLab).

Results and Discussion

Study of Extraction Medium

In a first series of experiments, the influence of the aqueous extraction medium on the extraction behavior of Ge(IV), Zn(II), Fe(III), Cu(II) and As(III) was studied with undiluted [A336][Cl]. HCl and H₂SO₄ media were compared. H₂SO₄ is commonly used as leaching agent, *e.g.* for germanium containing zinc leaching residues, and is therefore most frequently considered as the extraction medium in the literature on germanium refining.^{4,22,38} HCl is not typically used for the leaching of germanium-containing materials, but it is applied in the later stages of germanium purification flowsheets (vide supra). Moreover, it is known that Ge(IV) can form extractable anionic complexes such as GeCl_6^{2-} at high HCl concentrations.³⁹ Figure 1 shows the extraction efficiency of 200 mg L⁻¹ Ge(IV), Zn(II), Fe(III), Cu(II) and As(III) using undiluted [A336][C1] as a function of the HCl and H₂SO₄ concentration. In the HCl system, the extraction efficiency of Ge(IV) progressively increases with increasing HCl concentrations, indicating the gradual formation of the extractable $[GeCl_6]^{2-}$ complex. Cu(II) and As(III) show similar trends for their extraction behavior. Since Zn(II) and Fe(III) easily form anionic chloro complexes, their extraction efficiency is high (~100%), even at lower chloride concentrations e.g. 1 mol L⁻ ^{1.40} Surprisingly, the H₂SO₄ system shows a behavior that is remarkably similar to that of the HCl system, notwithstanding that extractable anionic complexes are not easily formed in sulfate solutions. The data seem to indicate that a non-negligible amount of chloride ions is transferred from the organic to the aqueous phase allowing the formation of extractable chloro complexes in the aqueous phase.

This exchange of the organic chloride for hydrogensulfate upon contacting with a H_2SO_4 solution was already noticed for the quaternary phosphonium ionic liquid Cyphos IL 101.⁴¹ The degree of conversion of Cyphos IL 101 to its hydrogensulfate analogue was significant, even at

low H₂SO₄ concentrations. To verify whether the conversion also occurred for [A336][Cl], a sample of water-saturated [A336][Cl] was contacted with various concentrations of H₂SO₄ using an O/A ratio of 1/1. The residual organic chloride content was monitored using WDXRF. In Figure 2, the conversion of [A336][Cl] to [A336][HSO4] is shown as a function of the H₂SO4 concentration. The data confirm that the conversion also occurs for [A336][Cl] and that this conversion is significant even at low H_2SO_4 concentrations, *i.e.* 1 mol L⁻¹ H_2SO_4 already resulted in a conversion of 44%. However, because of the similar positions of Cl⁻ and HSO₄⁻ in the Hofmeister series, a complete removal of chlorides from the organic phase is difficult and the conversion reached a maximum value of 80% around 8 mol L⁻¹ H₂SO₄.⁴¹ Figure 2 shows that a significant amount of chloride ions is indeed transferred to the aqueous phase and that this is most likely the reason for the similar behavior of the HCl and H₂SO₄ extraction systems (Figure 1). Based on the observation that the [A336][C1]/[A336][HSO4] conversion reaches a maximum of 80% and that the organic quaternary compound concentration is approximately 1.44 mol L⁻¹ (considering a quaternary compound content of approximately 80% and water saturation), it can be concluded that the aqueous chloride concentration approaches a maximum of 1.2 mol L⁻¹ when working with O/A = 1/1.^{42–44} For similar acid concentrations, the aqueous chloride concentrations are thus much lower in the H₂SO₄ system than in the HCl system. The lower chloride concentrations result in less extractable metal complexes being present and explain why overall (mainly for Fe(III) and Cu(II)) lower extraction efficiencies are observed in the H₂SO₄ system. Another difference between the H₂SO₄ and HCl system is the extraction behavior of Ge(IV) at acid concentrations lower than $<2 \text{ mol } L^{-1}$. In the H₂SO₄ system, the extraction efficiency follows a decreasing trend up to 2 mol L⁻¹ H₂SO₄, whereas this is not the case for the HCl system. At low H₂SO₄ concentrations, Ge(IV) is likely extracted as an anionic, deprotonated form of germanic acid, e.g. H₃GeO₄^{-,45} Extraction via this mechanism is possibly suppressed at higher H₂SO₄ concentrations due to an increasingly more difficult deprotonation of germanic acid and the increasing complexation of Ge(IV) with chloride ions which are increasingly transferred to the aqueous phase. In the HCl system, the extraction in the form of H₃GeO₄⁻ is not anticipated due to the immediate presence of relatively high concentrations of chloride ions and the formation of Ge(IV) chloro complexes.

Figure 1 shows that the exchange of the chloride anion for a hydrogensulfate anion is an important consideration when working with quaternary ammonium or phosphonium chlorides in combination with sulfuric acid solutions because it can have a significant influence on the speciation in the aqueous phase. The influence of this conversion may, however, be less significant when working with diluted extractants or quaternary compounds immobilized in membranes or on solid supports than for undiluted systems as the amount of availably chlorides is reduced. This is probably partly the reason for the selective Ge(IV) extraction observed in the [A336][C1] work of Haghighi *et al.*.¹⁸



Figure 1: Extraction efficiency of 200 mg L⁻¹ Ge(IV), Zn(II), Fe(III), Cu(II) and As(III) using undiluted [A336][Cl] as a function of: (a) HCl concentration; and, (b) H_2SO_4 concentration. Conditions: 300 rpm, 60 min, 22 °C, O/A = 1/1.



Figure 2: Conversion of [A336][Cl] to [A336][HSO₄] as a function of the sulfuric acid concentration. Conditions: 300 rpm, 60 min, 22 °C, 0/A = 1/1.

Figure 1 shows that Ge(IV) is extracted by [A336][Cl] at elevated HCl or H₂SO₄ concentrations. At those conditions, Ge(IV) is likely extracted as the anionic $[GeCl_6]^{2-}$ complex. However, most impurity elements are also quantitatively extracted and the process is not selective. The solvent extraction of Ge(IV) by basic extractants is therefore preferably performed through the addition of complexing agents resulting in the formation of extractable anionic complexes (vide infra). The advantage of this strategy is that chlorides are not required to facilitate Ge(IV) extraction and that they can be excluded from the system, both in the aqueous feed solution and in the solvent phase. Consequently, the coextraction of impurity elements through the formation of anionic chloro complexes can be prevented. When working with Aliquat 336, the exclusion of chlorides from the extraction system be attained by performing the can [A336][C1]/[A336][HSO4] conversion prior to the metal extractions, for instance by equilibrating [A336][Cl] with a NaHSO₄ solution (cfr. Experimental Section), in combination with an aqueous H₂SO₄ extraction medium.

The effect of the exclusion of chlorides from the extraction system is illustrated in Figure 3. The extraction efficiency of 200 mg L⁻¹ Ge(IV), Zn(II), Fe(III), Cu(II) and As(III) in 1 mol L⁻¹ H₂SO₄ is shown as a function of the chloride content of the organic phase, which was varied by making mixtures of undiluted [A336][C1] and [A336][HSO₄]. As the chloride content of the organic phase decreased, the transfer of chloride ions to the aqueous phase and the formation of extractable chloro complexes was concurrently reduced, which manifested itself in decreasing extraction efficiencies. In fact, Zn(II), Fe(III) and Cu(II) can be entirely excluded from extraction by working with pure [A336][HSO₄]. The extraction efficiencies of Ge(IV) and As(III) are not markedly affected by the varying chloride content of the organic phase, which is indicative of an alternative, "chloride-free" extraction mechanism under these conditions. As(III) is possibly extracted as an arsenite anion, *e.g.* AsO₂⁻ or AsO₃³⁻, whereas Ge(IV) extraction is likely manifested through an anionic, deprotonated form of germanic acid, *e.g.* H₃GeO₄⁻.



Figure 3: Extraction efficiency of 200 mg L⁻¹ Ge(IV), Zn(II), Fe(III), Cu(II) and As(III) using various mixtures of undiluted [A336][Cl] and [A336][HSO₄]. Conditions: 1 mol L⁻¹ H₂SO₄, 300 rpm, 60 min, 22 °C, O/A = 1/1.

Addition of Complexing Agents

The exclusion of chlorides from the extraction system through the conversion of [A336][Cl] to [A336][HSO₄] is an interesting and effective method to mitigate the coextraction of impurity elements such as Zn(II), Fe(III) and Cu(II). However, with the exclusion of chlorides, the extraction of Ge(IV) remains inefficient as the formation of the extractable [GeCl₆]²⁻ is prevented. Hence, the addition of a complexing agent is required in order to create an extractable anionic complex. Literature reports on Ge(IV) extraction with basic extractants mainly involve three complexing agents: tartaric acid, citric acid and catechol.^{18,23,24,27} A comparison was made between these for the extraction of Ge(IV) with undiluted [A336][HSO₄]. Figure 4 displays the extraction efficiency of 200 mg L⁻¹ Ge(IV), Zn(II), Fe(III), Cu(II) and As(III) in 1 mol L⁻¹ H₂SO₄ using undiluted [A336][HSO₄] as a function of the molar ratio of the complexant to Ge(IV). The results show that both tartaric and citric acid can increase the extraction efficiency of Ge(IV) to the point where it can be quantitatively recovered. For tartaric acid, five equivalents of complexing agent are required for the quantitative extraction of Ge(IV) whereas for citric acid a significantly higher excess of >30 is required. For catechol, no increase in Ge(IV) extraction efficiency was observed. This is possibly caused by the relatively high acidity of the solutions resulting in a difficult deprotonation of catechol ($pK_{a1} =$ 9.45, compared to 2.89 and 3.13 for tartaric and citric acid, respectively). For tartaric acid and citric acid, the equilibrium pH of the solution had a limited influence on the Ge(IV) recovery (Figure S4 in Supporting Information). For catechol, however, it was found that quantitative extraction of Ge(IV) may only be obtained at pH values >4. The data in Figure 4 also show that the extraction efficiencies of the other elements, *i.e.* Zn(II), Fe(III), Cu(II) and As(III), are not affected by addition of either of the complexing agents. The association of Ge(IV) with the complexing agents and the formation of anionic, extractable complexes is thus highly selective.¹⁷ The preference for tartaric acid is in agreement with the findings of Haghighi *et al.* and Zhang *et al.*^{18,21,46} In the latter study, the requirement of five equivalents of tartaric acid was also observed.⁴⁶



Figure 4: Extraction efficiency of 200 mg L⁻¹ Ge(IV), Zn(II), Fe(III), Cu(II) and As(III) using undiluted [A336][HSO₄] as a function of the complexing agent/Ge(IV) molar ratio: (a) tartaric acid; (b) citric acid; (C) catechol. Conditions: 1 mol L⁻¹ H₂SO₄, pH \approx 0, 300 rpm, 60 min, 22 °C, 0/A = 1/1.

Extraction mechanism

To further emphasize the significance of the exclusion of chlorides and the addition of a complexing agent for the selectivity of the extraction system, slope analyses of the extraction mechanism of Ge(IV) were compared with those of Zn(II), the major constituent of zinc refinery residues and consequently the main contaminant in Ge(IV) solutions. It must be noted that slope analysis cannot always give a conclusive result concerning the extraction mechanism due to, among other factors, changing activity coefficients and the assumption that only one metallic species is formed in the organic phase. Despite this, a good indication of the occurring extraction mechanism can usually be obtained.⁴⁷ First, the role of chloride in the extraction mechanism was studied. Ge(IV) and Zn(II) (1000 mg L⁻¹ each) were extracted from 0.5 mol L⁻ ¹ H₂SO₄ in the presence of five equivalents of tartaric acid using various mixtures of undiluted [A336][Cl] and [A336][HSO4] at an O/A ratio 1/1. By using mixtures of both ionic liquids, the total concentration of quaternary compound remains relatively constant throughout the series. A plot of the logarithm of the distribution ratio D versus the logarithm of the organic molar chloride concentration is shown in Figure 5a. The slopes of the plots give information about the stoichiometry of the extracted complex and the number of [A336][Cl] molecules involved. The mathematical background of this approach can be found in the Supporting Information. Ge(IV) is characterized by a near-zero slope indicating that, in the presence of tartaric acid, chloride plays no role in its extraction mechanism and that the anionic germanium tartrate complex can be either extracted with [A336][Cl] or [A336][HSO4]. Zn(II) displays a slope of approximately 4 suggesting a mechanism which involves the extraction of the tetrachlorozincate(II) anion, $[ZnCl_4]^{2-}$. Based on the work of Lommelen *et al.*, which suggests that Zn(II) is extracted as $ZnCl_2$ followed by the formation of $[ZnCl_4]^{2-}$ in the organic phase, Eq. 6 to 8 are presented as the extraction mechanism of Zn(II) from H₂SO₄ media using [A336][Cl].⁴⁸ Overbars denote species in the organic phase. This extraction mechanism clearly shows that chloride ions are required for the extraction of Zn(II), and that in their absence extraction of Zn(II) cannot proceed.

$$2 \overline{[A336][Cl]} + 2 HSO_4^- \rightleftharpoons 2 \overline{[A336][HSO_4]} + 2Cl^-$$
(6)

$$\operatorname{Zn}^{2+} + 2\operatorname{Cl}^{-} \rightleftharpoons \operatorname{ZnCl}_{2} \tag{7}$$

$$\operatorname{ZnCl}_{2} + 2 \overline{[A336][Cl]} \rightleftarrows \overline{[A336]_{2}[\operatorname{ZnCl}_{4}]}$$

$$\tag{8}$$



Figure 5: Slope analysis for the extraction of Ge(IV) and Zn(II) using [A336][X] (X = Cl⁻ or HSO₄⁻) in the presence of tartaric acid. (a) Role of [A336][Cl] in the extraction of Ge(IV) and Zn(II) at constant [A336][X] concentration. (b) Role of tartaric acid in the extraction of Ge(IV) using [A336][HSO₄]. (c) Role of [A336][HSO₄] in the extraction of Ge(IV).

To further elucidate the extraction mechanism of Ge(IV), the role of tartaric acid and [A336][HSO4] was studied. The mathematical background of the slope analyses are again provided in the Supporting Information. In Figure 5b, the logarithm of the distribution ratio D versus the logarithm of the molar tartaric acid concentration is shown. The tartaric acid concentration was varied between 2 and 20 times the molar concentration of Ge(IV). Extractions were performed using undiluted [A336][HSO₄] and solutions containing 200 mg L⁻ ¹ Ge(IV) and 1 mol L⁻¹ H₂SO₄ solutions. A slope of 0.86 is found, indicating that one tartaric acid molecule is involved in the extraction of Ge(IV). In Figure 5c, the logarithm of the distribution ratio D versus the logarithm of the molar [A336][HSO₄] concentration is shown. The [A336][HSO₄] concentration was varied between 10 and 60 vol% by dilution with toluene. Extractions were performed from 0.5 mol L⁻¹ H₂SO₄ solutions containing 1000 mg L⁻¹ of Ge(IV) and five equivalents of tartaric acid. The slope of the plot is 0.75, which gives a good indication that one [A336][HSO4] molecule is involved in Ge(IV) extraction. Based on both observations, Eq. 9 and 10 are proposed to present the extraction mechanism of Ge(IV) from tartaric acid-containing solutions. Ge(IV) forms a negatively charged complex with a single tartaric acid molecule. As the formed complex is extracted by a single quaternary ammonium molecule, it should be monovalent. In accordance with other literature reports, the $[Ge(OH)_2(HT)]^-$ complex is proposed, with H₄T representing a tartartic acid molecule.^{17,49} As it was found that the counter anion of the quaternary ammonium compound can be either Cl⁻ or HSO_4^- for the extraction of Ge(IV) (vide supra), X⁻ is used in Eq. 10.

$$Ge(OH)_4 + H_3T \rightleftharpoons [Ge(OH)_2(HT)] + 2H_2O$$
(9)

$$[Ge(OH)_2(HT)]^- + \overline{[A336][X]} \rightleftharpoons \overline{[A336][Ge(OH)_2(HT)]} + [X]^-$$
(10)

This extraction mechanism differs from the one presented by Haghighi *et al.* for the [A336][Cl] – tartaric acid system, where these authors proposed that the Ge(IV) tartrate complex is divalent

and extracted by two quaternary ammonium molecules. One reason for this discrepancy could be the significantly lower acidity of the solutions in that study, leading to an easier second deprotonation of the tartrate complex. However, the formation of such a divalent complex in moderately acidic solutions containing low tartaric acid concentrations, *i.e.* 2 to 10 equivalents compared with Ge(IV), does not agree with other literature reports.^{49,50}

Development of a Separation Process

Because of the radically different extraction mechanism of Ge(IV) and impurity elements such as Zn(II) (*vide supra*), a highly selective extraction system can be developed by combination of (1) the addition of a complexing agent, *e.g.* tartaric acid, and, (2) the exclusion of chlorides from the system. This strategy was used to develop a separation process for the recovery of Ge(IV) from a synthetic zinc refinery residue leachate. The selected metal concentrations were based on values of industrial solutions reported in literature (Table 1).^{8–10,12,15,46,51} The solutions also contained 1 mol L⁻¹ H₂SO₄ and five equivalents of tartaric acid with respect to Ge(IV). Undiluted [A336][HSO₄] was always used as the solvent for extraction.

	Concentration (mg L ⁻¹)
Ge(IV)	500
As(III)	1500
Zn(II)	30000
Fe(III)	3000
Cu(II)	1000

Table 1: Metal concentrations (mg L⁻¹) of the used synthetic zinc refinery residue leachate.

In a first experiment, extractions were performed on the synthetic leachate using varying amounts of undiluted [A336][HSO4]. The extraction efficiency as a function of the O/A

volumetric phase ratio is shown in Figure 6. As expected, based on the results of Figure 3, the extraction efficiencies of Zn(II), Fe(III) and Cu(II) are low, in general less than 5%. There seems to be little to no effect of the O/A ratio on their extraction efficiency. The extraction efficiency of Ge(IV) is overall high, typically >90%, and shows a slightly decreasing trend with a decreasing O/A phase ratio. However, the extraction efficiency of As(III) is affected most strongly by a change in the O/A ratio and the coextraction of As(III) can be markedly reduced by working at small O/A ratios. For example, the As(III) extraction decreased from 22 to 15% when the O/A ratio of less than unity results in higher concentrations of Ge(IV) in the organic phase. An O/A phase ratio of 1/2 was selected as the optimum. Under these conditions, Ge(IV) recovery remained >95% while a significant reduction in As(III) coextraction could be achieved.



Figure 6: Extraction efficiency of 500 mg L⁻¹ Ge(IV), 30 g L⁻¹ Zn(II), 3 g L⁻¹ Fe(III), 1 g L⁻¹ Cu(II) and 1.5 g L⁻¹ As(III) using undiluted [A336][HSO4] as a function of the O/A volumetric phase ratio. Conditions: 1 mol L⁻¹ H₂SO₄, 5 equivalents of tartaric acid with respect to Ge(IV), 300 rpm, 60 min, 22 °C.

The data in Figure 6 show that the coextraction of As(III) cannot be entirely suppressed by adjusting the O/A phase ratio without negatively affecting the Ge(IV) recovery. A scrubbing step was therefore performed to facilitate the further separation of As(III) from Ge(IV). Based on Figure 1, As(III) scrubbing can be expected to occur at those conditions where its extraction is inefficient *i.e.* at low acid concentrations or using water. The scrubbing efficiency of As(III) using water is displayed in Figure 7 as a function of the O/A ratio. The loaded organic phases were prepared through extraction of the synthetic leachate using O/A 1/2. The As(III) scrubbing efficiency increases progressively with decreasing O/A ratios. At O/A =1/3 a near-complete (>97%) scrubbing of As(III) can be achieved. Ge(IV) was not significantly removed from the organic phase during the scrubbing with water. It should also be noted that complete separation of As(III) from Ge(IV) is usually not required as the final As(III) removal is typically performed in the later stages of Ge(IV) processing. For this, As(III) is oxidized to As(V), allowing the subsequent selective distillation of GeCl₄ after chlorination. Apart from the removal of coextracted impurities, an additional benefit of the application of a scrubbing step is that some of the coextracted H₂SO₄ is removed from the organic phase. This is important as Ge(IV) stripping is performed by NaOH (vide infra). The removal of coextracted H₂SO₄ minimizes unnecessary base consumption by neutralization. Some amount of Zn(II), Fe(III) and Cu(II) can also be scrubbed with water, but a complete removal of these elements from the organic phase cannot be achieved in a single scrubbing step. Still, as their initial extraction efficiencies are limited (cfr. Figure 6), the remaining organic concentrations of Zn(II), Fe(III), Cu(II) after scrubbing are low: *i.e.* $<5 \text{ mg } \text{L}^{-1} \text{Cu(II)}$, $<100 \text{ mg } \text{L}^{-1} \text{Fe(III)}$ and $<700 \text{ mg } \text{L}^{-1} \text{Zn(II)}$.



Figure 7: Scrubbing efficiency of Ge(IV) and As(III) from undiluted [A336][HSO₄] using water as a function of the O/A volumetric phase ratio. [A336][HSO₄] was loaded by extraction of the synthetic leachate at O/A = 1/2. Conditions: 300 rpm, 60 min, 22 °C.

The stripping of Ge(IV) after extraction with a basic extractant is generally performed by an alkaline stripping solution, typically NaOH or NH₃.^{23,24,26} In Figure 8 the stripping efficiency of Ge(IV), as well as the stripping behavior of the remaining As(III), is shown as a function of the NaOH concentration. The loaded [A336][HSO₄] phases were prepared through an extraction of the synthetic leachate at O/A = 1/2, followed by a scrubbing with water at O/A = 1/3. The stripping experiments were always performed at O/A = 1/1. The data show that the stripping of Ge(IV) only becomes efficient at NaOH concentrations higher than 1.5 mol L⁻¹. This is not surprising as NaOH preferentially reacts with the strongest acid in the system, *i.e.* the HSO₄⁻ in the organic phase. Only when all the HSO₄⁻ has been consumed (approximately 1.44 mol L⁻¹ for water-saturated [A336][HSO₄]), the remaining NaOH can facilitate the stripping of Ge(IV). Subsequent ICP-OES analysis of the stripping solutions showed that half of the organic SO₄²⁻ was transferred to the aqueous phase to maintain the charge balance during

this acid–base reaction rather than that some amount of Na⁺ was extracted to the organic phase. The reaction of [A336][HSO₄] to [A336]₂[SO₄] during stripping with NaOH is supported by Raman analysis of the organic phases (Figure 9). The stripping of Ge(IV) is likely promoted by the further deprotonation and subsequent decomposition of the germanium tartrate complex at pH >9.⁴⁹ As SO₄²⁻ ions are abundant in the stripping solution and are positioned higher in the Hofmeister series than hydroxide and tartrate, it is likely that this anion replaces the germanium tartrate in the organic phase. The stripping of Ge(IV) from [A336][HSO₄] can thus be described by the reactions shown in Eq. 11 and 12, respectively. Based on this stripping mechanism, stripping could also be envisioned at a higher NaOH concentration and higher O/A ratios in order to concentrate the Ge(IV) in the stripping solution. However, care must be taken to prevent decomposition of the quaternary ammonium ion via the Hoffmann elimination at high NaOH concentrations.⁵² For this reason, a moderate NaOH concentration and O/A ratio, *i.e.* 2 mol L⁻¹ NaOH and O/A = 1/1, were chosen as the optimal stripping conditions.

$$2\overline{[A336][HSO_4]} + 2NaOH \rightarrow \overline{[A336]_2[SO_4]} + 2Na^+ + SO_4^2 + 2H_2O$$
(11)

$$2\overline{[A336][Ge(OH)_{2}(HT)]} + 2NaOH + SO_{4}^{2-} + 2H_{2}O$$

$$\rightarrow \overline{[A336]_{2}[SO_{4}]} + 2Na^{+} + 2H_{2}T^{2-} + 2Ge(OH)_{4}$$
(12)

The stripping efficiency of As(III) shows a similar trend to that of Ge(IV) with an increase near $1.5 \text{ mol } L^{-1}$. However, its concentration in the stripping solutions remains low (<50 mg L^{-1}) as most of the coextracted As(III) is removed during the scrubbing operation. The minor amounts of Zn(II), Fe(III) and Cu(II) that are still present, are also not stripped to an appreciable degree (<5%).



Figure 8: Stripping efficiency of Ge(IV) and As(III) from undiluted [A336][HSO₄] as a function of the NaOH concentration. The loaded [A336][HSO₄] was obtained by extraction of the synthetic leachate at O/A = 1/2 and scrubbing using water at O/A = 1/3. Conditions: 300 rpm, 60 min, 22 °C, O/A = 1/1.



Figure 9: Raman spectra of the undiluted ionic liquid [A336][HSO₄] after extraction, stripping with NaOH and regeneration with H₂SO₄.

A conceptual flowsheet of the developed separation process is presented in Figure 10. Five equivalents of tartaric acid are added to the zinc refinery residue leachate after which an extraction is performed by [A336][HSO4] using O/A = 1/2. The extraction of Ge(IV) is highly selective and only a small amount of As(III) is coextracted. After extraction, the loaded organic phase is scrubbed with water to remove most of the coextracted As(III). Ge(IV) can subsequently be stripped with NaOH. After stripping, [A336][HSO4] can be regenerated via a contacting with fresh H₂SO4 (cfr. Figure 9) and the ionic liquid can be recycled to the extraction step and reused (*vide infra*). As the developed separation process avoids the use of volatile and flammable compounds entirely, it can be considered more environmentally friendly and safer than other, existing Ge(IV) solvent extraction systems. Furthermore, the process refrains from the frequently used precipitation methods and avoids possible issues with filtration. The process allows for the highly selective removal of Ge(IV) from Zn(II) and might as such also be of interest for the purification of the electrolyte for electrowinning of zinc, where the presence of Ge(IV) is undesirable.⁵³ Likewise, the absence of chlorides in the process is beneficial for the subsequent electrowinning of zinc.⁴⁶



Figure 10: Conceptutal flowsheet of the separation process for the recovery of Ge(IV) from zinc refinery residue leachates using the undiluted ionic liquid [A336][HSO₄].

Recyclability of the Ionic Liquid

The performance of the extraction system was investigated by recycling the ionic liquid five times through the separation process. At the end of the process, before recycling to the extraction step, [A336][HSO4] was regenerated by 1.0 mol L⁻¹ H₂SO₄ and O/A 1/2. Figure 11 shows that the extraction efficiencies did not significantly change over the course of the various cycles and that the extraction system remained highly selective for Ge(IV). Additionally, the stripping efficiency of Ge(IV) remained high throughout the different cycles (Supporting Information, Figure S6). It must be noted, however, that the scrubbing and stripping efficiencies of As(III) decreased slightly from cycle to cycle (Supporting Information, Figure S5 and S6). This is caused by a buildup of As(III), and some amount of Zn(II), Cu(II) and Fe(III), in the organic phase due to incomplete scrubbing or stripping. In practice, this issue might be mitigated via a bleed stream which is subjected to harsher scrubbing or stripping conditions.



Figure 11: Extraction efficiency of 500 mg L⁻¹ Ge(IV), 30 g L⁻¹ Zn(II), 3 g L⁻¹ Fe(III), 1 g L⁻¹ Cu(II) and 1.5 g L⁻¹ As(III) using undiluted [A336][HSO₄] throughout five consecutive cycles of the separation process.
 Conditions: 1 mol L⁻¹ H₂SO₄, 5 equivalents of tartaric acid with respect to Ge(IV), 300 rpm, 60 min, 22 °C, O/A = 1/2.

Conclusion

The extraction behavior of Ge(IV), Zn(II), Fe(III), Cu(II) and As(III) using undiluted [A336][C1] was studied and a comparison was made between HCl and H₂SO₄ media. The similar extraction behavior of the HCl and H₂SO₄ systems was found to be caused by an exchange of the organic chloride for aqueous hydrogensulfate upon the contacting of [A336][Cl] with a H₂SO₄ solution. By performing the [A336][Cl]/[A336][HSO₄] conversion prior to the metal extractions, chlorides could be excluded from the extraction system and the extraction efficiencies of Zn(II), Cu(II) and Fe(III) could be drastically reduced. The extraction of Ge(IV) could subsequently be facilitated by formation of an anionic complex with a complexing agent. Among tartaric acid, citric acid and catechol, tartaric acid was the preferred complexing agent as only five equivalents were required for a quantitative Ge(IV) extraction. A highly selective extraction system for Ge(IV) was obtained through the exclusion of chlorides and the addition of tartaric acid. The selectivity of the system finds its origin in the radically different extraction mechanisms of Ge(IV) and e.g. Zn(II), which was confirmed by slope analyses. Based on these findings, a separation process was developed for the recovery of Ge(IV) from sulfuric acid zinc refinery residue leachates. After the addition of tartaric acid, Ge(IV) is extracted using [A336][HSO₄]. Only As(III) is significantly coextracted, but this coextracted As(III) can be scrubbed to a large extent from the organic phase by water. Ge(IV) is then stripped by a NaOH solution. Finally, the organic phase can be regenerated by H₂SO₄ after which it can be recycled to the extraction step without any loss of performance or selectivity.

Supporting Information

Physical properties of water-saturated [A336][Cl] and [A336][HSO4], study of the extraction rate, pictures of the phase disengagement process, calibration of the WDXRF system, study of pH for the use of complexing agents, mathematical derivations of the slope analyses, scrubbing and stripping efficiencies of Ge(IV) and As(III) throughout the cycling experiment.

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Conflict of interest

There are no conflicts to declare.

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TOC graphic



<u>Synopsis</u>: A highly selective separation procedure for Ge(IV) recovery from Zn(II), Fe(III), Cu(II) and As(III) was developed with a hydrogensulfate ionic liquid and tartaric acid.