



Received: 17 November 2015  
Accepted: 07 December 2015  
First Published: 19 January 2016

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## INORGANIC CHEMISTRY | RESEARCH ARTICLE

# Progress towards a process for the recycling of nickel metal hydride electric cells using a deep eutectic solvent

Mark R.St.J. Foreman<sup>1\*</sup>

**Abstract:** Solvent extraction experiments relating to the recycling of the transition metals and lanthanides in nickel metal hydride cells are presented. The metal extraction is occurring from a deep eutectic solvent which is formed from chemicals suitable for use in food and related products. While it has been shown that the water content of the DES has a large effect on the extraction of transition metals by a mixture of chloride ionic liquid (Aliquat 336) and an aromatic solvent, the water content has a smaller effect on the solvent extraction of lanthanides with a solution of di(2-ethylhexyl) hydrogen phosphate (DEHPA) in a saturated aliphatic hydrocarbon. This study suggests that an industrial scale solvent extraction process for the recycling of metals from nickel hydride electrical cells will be feasible.

**Subjects:** Inorganic chemistry; Solvent Extraction; Waste & Recycling

**Keywords:** nickel, cobalt; iron; lanthanides; deep eutectic solvents; ionic liquids; solvent extraction; Aliquat 336; Di(2-ethylhexyl) hydrogen phosphate (DEHPA)

### 1. Introduction

In the past, a large fraction of municipal solid waste was placed in landfills and thus buried, this waste would have contained the vast majority of the items discarded by the general public. In order



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### PUBLIC INTEREST STATEMENT

When a product or an object is no longer useful it becomes waste. Landfilling of waste is often undesirable as it places many valuable materials out of reach of society, it also can result in contamination of the environment. Additionally, the landfilling and incineration of waste industrial and automotive batteries are illegal in some states (The Waste Batteries & Accumulators Regulations 2009, 2009, Section 56). Recycling is part of the movement away from landfilling waste, the goal of a recycling process should be to obtain as much valuable material as possible from waste using the least amount of energy, producing as little secondary waste as possible and in such a way that leaves the least amount of unrecycled residual waste as possible. In this paper some early steps toward an improved industrial process based on an ionic liquid mimic for the recycling of disused nickel metal hydride electrical cells are presented. This process is designed to produce pure streams of metals from the waste while using as little energy as possible.

to prevent further proliferation of landfill sites, to reduce society's dependence on primary resources and to minimize the overall cost of waste disposal, both industry and the general public are encouraged to sort their waste into different classes to facilitate recycling and reuse. The public are encouraged to submit used electrical cells and batteries for recycling separately from their other wastes as these electrochemical devices often contain valuable and harmful materials. For example, lithium ion batteries often contain cobalt (Xu et al., 2008) which is an attractive target for recycling. Cobalt is an attractive target for recycling as it is an important material whose supply is limited. Cobalt, the lanthanides, and some other elements were identified as being critical elements by the European Commission (European Commission, 2010). The toxic metals such as mercury and cadmium in disused electrical cells need to be managed correctly to prevent the environmental contamination and human disease, one of the purposes of the recycling sector is to concentrate these toxic metals into a form suitable for reuse or a small volume of waste which is suitable for long-term storage.

While it is possible to recover nickel and cobalt from nickel metal hydride cells by heating in a furnace (pyrometallurgy) (Müller & Friedrich, 2006), the valuable lanthanides will be lost into the slag. While it might be possible to recover the lanthanides from the slag such a process will require a large input of energy and the slag would require leaching in a mineral acid to liberate the lanthanides (Kim et al., 2014). An alternative to recycling using pyrometallurgy is to use hydrometallurgy in which metals are liberated from ores or wastes using aqueous reagents, the wanted metals are then harvested from the aqueous solution using methods which include liquid-liquid extraction (Rydberg, Musikas, & Choppin, 1992), ion exchange on solid materials (Alexandratos, 2009), electrodeposition (Moskalyk & Alfantazi, 2002) and precipitation (Kyle, Breuer, Bunney, & Pleysier, 2012; Chmielewski, Urbanski, & Migdal, 1997). Already it has been shown that it is possible to recover cobalt and other metals from nickel metal hydride cells by dissolution in hydrochloric acid (8 M) followed by liquid-liquid extraction with a concentrated (70% v/v) solution of trialkyl phosphine oxides (Cyanex 923) together with tributyl phosphate (10% v/v) was able to separate cobalt and the lanthanides from the nickel containing mixture (Larsson, Ekberg, & Ødegaard-Jensen, 2012). While the Cyanex 923 process might be able to separate cobalt, lanthanides, and nickel, it does suffer from several disadvantages, firstly Cyanex 923 is able to extract hydrochloric acid from aqueous solutions into the organic phase (Sarangi, Padhan, Sarma, Park, & Das, 2006). This loss of hydrochloric acid will result in the contamination of stripping (back extraction) solutions with hydrochloric acid and will compel the operator of a plant to continually add more hydrochloric acid to the leaching process. A second disadvantage is the fact that the air above 8 M solution of hydrochloric acid (26% w/w) will contain a large amount of hydrogen chloride. This can lead to a range of corrosion issues inside a recycling plant.

In recent times, ionic liquids and the related deep eutectic solvents (Abbott, Boothby, Capper, Davies, & Rasheed, 2004) have been the subject of considerable interest (Abbott, Frisch, & Ryder, 2011). One of the perceived advantages of these solvents is that often their vapor pressures are very low, if our consideration is limited for a moment to corrosive inorganic compounds then it is clear that because of the noninfinite dissociation constants of hydrochloric acid that it is possible for an aqueous solution to contain undissociated hydrogen chloride which is available to leave the solution at the surface and thus enter the air. In the case of an ionic liquid formed from an organic cation and chloride anions (such as Aliquat 336), it is not possible for a volatile chloride to be formed at room temperature. Additionally, in the case of a deep eutectic formed from choline chloride even if the chloride anion was to combine with the choline cation, the resulting chlorospecies would be unlikely to be volatile because the alcohol group anchors it into the liquid through hydrogen bonding. While it would be foolish to blindly equate involatility with a chemical being harmless, a great reduction in the ability of a reagent to form a corrosive atmosphere is desirable in a solvent extraction plant. As it is known that deep eutectics formed from choline chloride are able to dissolve a range of metal oxides (Abbott, Capper, Davies, McKenzie, & Obi, 2006), it was decided that solvent extraction from such a deep eutectic with conventional solvent extraction reagents would be investigated for its potential to create a new industrial process.

## 2. Results and discussion

It was found that metal salts such as cobalt(II) chloride were soluble in the deep eutectic solvent formed by the combination of choline chloride and glycolic acid. The solution of cobalt(II) in this medium was

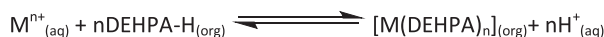
deep blue in color indicating that the cobalt is likely to have a tetrahedral coordination environment similar to that of cobalt in an aqueous medium containing a high concentration of chloride anions. It was found that when such a solution was shaken with a solution of di(2-ethylhexyl) phosphoric acid (DEHPA) in an aliphatic kerosene (Solvent 70) that the organic layer remained colorless suggesting that no cobalt extraction occurred. The reagent DEHPA was selected as it is well known to be able to extract a range of metals by means of an ion-exchange mechanism as shown in Scheme 1.

The extraction of metals by DEHPA can be reversed by shaking the metal-loaded solution of DEHPA with an aqueous solution of an acid. As an organic phase based upon DEHPA failed to extract cobalt.

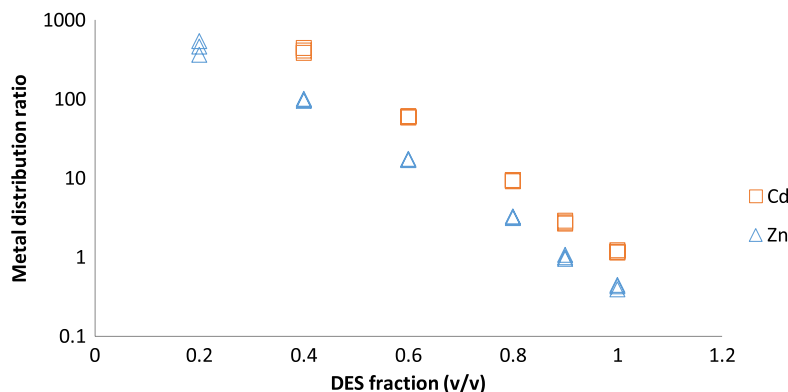
However, when the solution of cobalt was shaken with a solution of Aliquat 336 (30% v/v) in toluene, the organic phase became blue in color suggesting that cobalt extraction was occurring. It was soon understood that the rate of extraction from the DES layer into the organic layer was very slow compared with the rate at which an analogous system with an aqueous phase reached equilibrium. While papers in which metal extraction using pure ionic liquids have been reported (Wellens, Thijs, Moller, & Binnemans, 2013). It was decided that the high viscosities of pure ionic liquids such as Aliquat 336 would render them unsuitable as organic phases for solvent extraction. Additionally, the use of a pure ionic liquid in experiments would stymie any attempt to use slope analysis to determine how many formula units of ionic liquid are required per metal atom. As many laboratory and industrial solvent extraction machines, such as mixer settlers, are designed to operate using organic liquids similar to kerosene it was decided that the properties of the ionic liquid should be altered to make them compatible with the solvent extraction equipment. This was done so by the addition of carefully selected organic molecular solvents to create free flowing ionic liquid-based organic phases. As such mixtures of ionic liquids and organic solvents have been used for the extraction of metals for at least four decades (Stronski & Nahlik, 1972), rather than pursuing an ideal of a process based upon pure ionic liquids it was decided that adapting the nature of the liquid phases to suit existing solvent extraction equipment was a better goal.

It was found that by the addition of a small amount of water to lower deep eutectic phase, the viscosity of that phase was decreased greatly and solvent extraction experiments could be rapidly brought to equilibrium. Using a series of mixtures of sodium chloride solution and the deep eutectic it was shown that the distribution ratio when extracting with 30% Aliquat 336 (v/v) in toluene at 40°C of many transition metals is a function of the water content of the deep eutectic solvent layer. While the relationship between the zinc and cadmium distribution ratios ( $D_{Zn}$  and  $D_{Cd}$ ) and the water content could be modeled with a simple exponential expression (Figure 1) the relationship between the cobalt, copper, iron, and manganese distribution ratios ( $D_{Co}$ ,  $D_{Cu}$ ,  $D_{Fe}$ , and  $D_{Mn}$ ) (Figures 2 and 3) and water content was complex.

**Scheme 1. Extraction equilibrium for a metal being extracted by DEHPA.**



**Figure 1. The relationship between the water content of the deep eutectic phase and the distribution ratios for cadmium and zinc.**



When the water content of the system was very low, the extraction of cobalt and copper metals was suppressed; when the water content was increased, the copper distribution ratios increased again but the cobalt distribution ratios decreased as the water content approached 80%; with water contents above 80% the cobalt distribution ratio increased again.

While the iron and manganese distribution ratios had a different relationship with the water content of the lower phase as can be seen in Figure 3.

As it was shown that industrially useful distribution ratios for key metals could be obtained, a search was made for safer diluents. While toluene might not be considered a “green solvent” it is important to note that it is a simple reagent which is available throughout the world at a reasonable cost. While some grades of diluents might be safer, a proprietary mixture is less likely to be available decades into the future so many of the proof of principle tests were made with toluene or other similar aromatic diluents. A range of diluents were screened using a lower layer containing DES 80% (v/v) and 20% water at 40°C using 30% (v/v) solutions of Aliquat 336 as the organic phase. In this experiment, toluene, Solvesso 150ND (S150), Solvesso 200ND (S200), solvent 70 (modified with 15% decanol [v/v]) (S70D), and a fatty acid methyl ester (FAME) mixture from sunflower cooking oil were compared. It was found that with both Solvesso 150ND (S150) and Solvesso 200ND (S200), the distribution ratios of the wanted transition metals were higher than those obtained with toluene, the modified solvent 70 and the FAME biodiesel (Table 1). When the experiment was attempted using Escaid 110 the organic phase separated into two layers when it was loaded with a moderate amount of metals (assumed to be Cd, Co, Cu, Fe, Mn, and Zn). Isopar L and Escaid 120 were not able to dissolve the Aliquat 336.

Figure 2. The relationship between the water content of the deep eutectic phase and the distribution ratios for copper and cobalt.

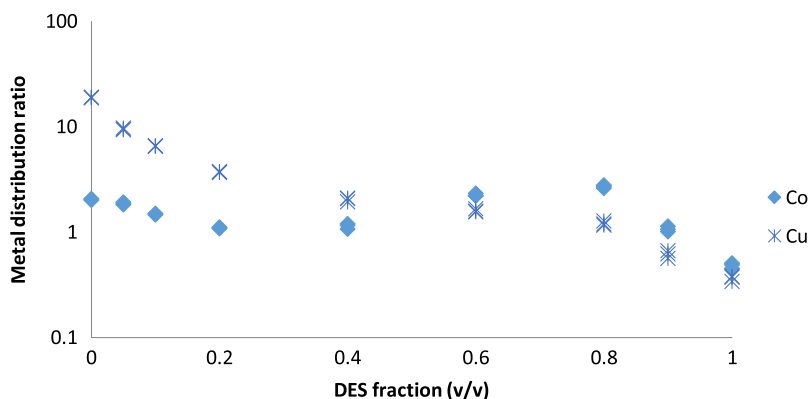
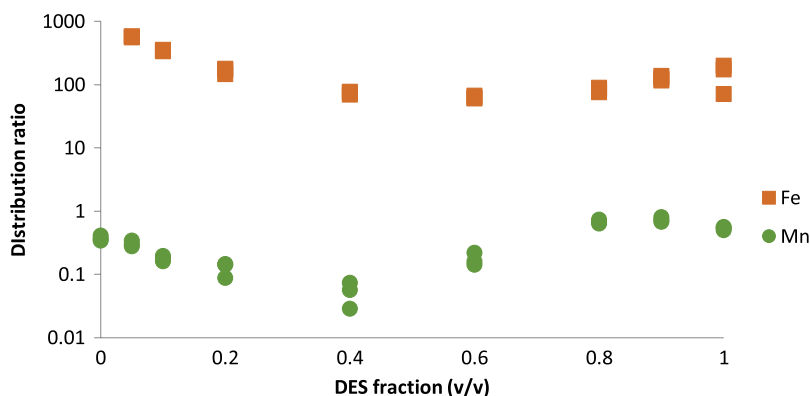


Figure 3. The relationship between the water content of the deep eutectic phase and the distribution ratios for iron and manganese.



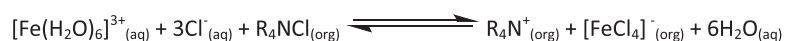
**Table 1. Distribution ratios obtained at 40°C using 30% (v/v) solutions of Aliquat 336 in different diluents**

Metal	Diluent				
	Toluene	Solvesso150 ND	Solvesso200 ND	Solvent 70 and decanol	Sunflower oil FAME biodiesel
Al	0	0	0	0	0
Cd	7,8	8,6	12,4	2,5	5.0
Ce	0,001	0,03	0,03	0,05	0.1
Co	1,55	1,66	2,14	0,62	0.88
Cu	0,69	0,90	0,82	0,37	0.27
Fe	16,5	13,8	20,1	3,7	1.1
La	0	0	0	0	0
Mn	0,28	0,37	0,50	0,18	0.17
Nd	0	0,0216	0,031	0,040	0.1
Pb	0,24	0,18	0,23	0,003	0.18
Pr	0	0	0	0	0.1
Zn	2,67	2,83	3,65	0,94	1.8

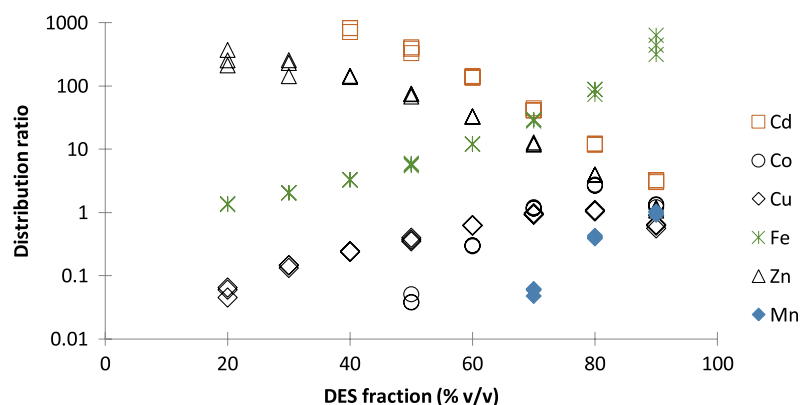
Of these solvents, Solvesso200ND was selected as the best solvent for a process as the cobalt distribution ratio was the highest and no third phase formation was observed. The water content test was repeated using Solvesso200ND as the diluent using deionized water in place of the sodium chloride solution (Figure 4) it was still found that the extraction of cadmium and zinc was favored by a high water content, while the iron extraction was favored by a high chloride content of the lower phase. The cobalt and copper distribution ratios peaked at ca. 80%.

This suggests that the dominant driving force for the extraction of iron is different to that of zinc/cadmium. For iron, the dominant factor is the chloride concentration suggesting the position of the equilibrium as shown in Scheme 2.

**Scheme 2. Extraction equilibrium for iron(III) being extracted by a quaternary ammonium salt such as Aliquat 336.**



**Figure 4. The relationship between the water content of the deep eutectic phase and the distribution ratios for cadmium, cobalt, copper, iron, manganese and zinc when no attempt is made to maintain a constant chloride concentration.**



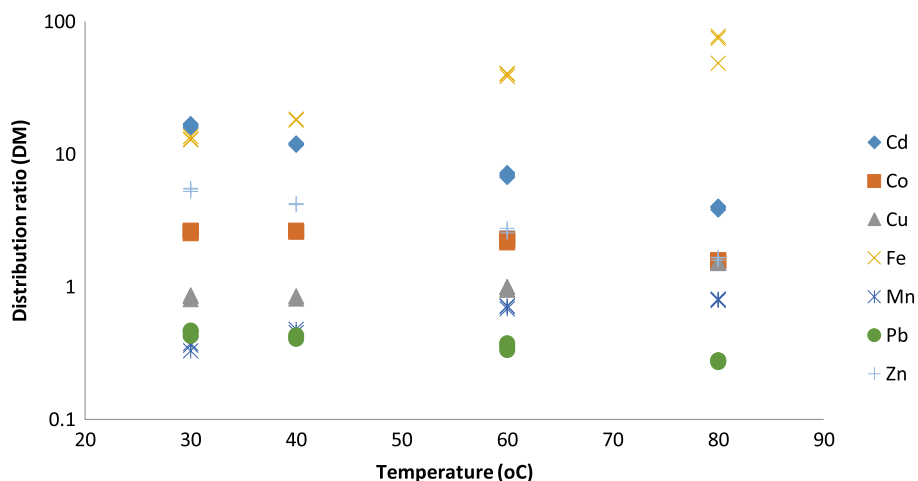
Is driven to the right by a high chloride concentration. While in the case of the zinc and cadmium some other effect dominates. One possibility was that the increase in entropy when the number of free molecules and ions which occurs in the following extraction reaction was the important factor. With the data which has been obtained so far, it is not possible to state with certainty the reason for the difference in the behavior of the iron and zinc/cadmium. It is possible that when the water activity (and concentration) is low that highly charged anion cadmium and zinc chloro complexes such as  $[\text{CdCl}_5]^{3-}$  and  $[\text{ZnCl}_6]^{4-}$  could be present in the lower phase. In the solid state,  $[\text{CdCl}_5]^{3-}$  and  $[\text{CdCl}_6]^{4-}$  have been observed (Bouchene, Bouacida, Berrah, & Roisnel, 2014) suggesting that such complexes could form in a concentrated chloride medium where the water content is low. While the formation of an extractant/metal complex is normally associated with metal extraction, it is important to note that an excessive concentration of a charged ligand can result in a suppression of extraction because of the formation of charged complexes. For example, the extraction of promethium(III) by acetylacetonate into benzene is suppressed by the formation of  $[\text{Pm}(\text{acac})_4]^-$  complexes when the concentration of acetylacetonate anions is high (Rydberg & Albinsson, 1989).

To test the hypothesis, the iron and cadmium/zinc extractions are mainly determined by different factors, a variable temperature experiment was performed. In this experiment, mixtures of the two liquids were shaken at different temperatures before phase separation and sampling. It was found that extraction of manganese and iron was favored by an increase in temperature while the zinc, lead, and cadmium extractions were favored by a reduction in temperature (Figure 5). The copper and cobalt extractions were less sensitive to changes in temperature which is advantageous for process development.

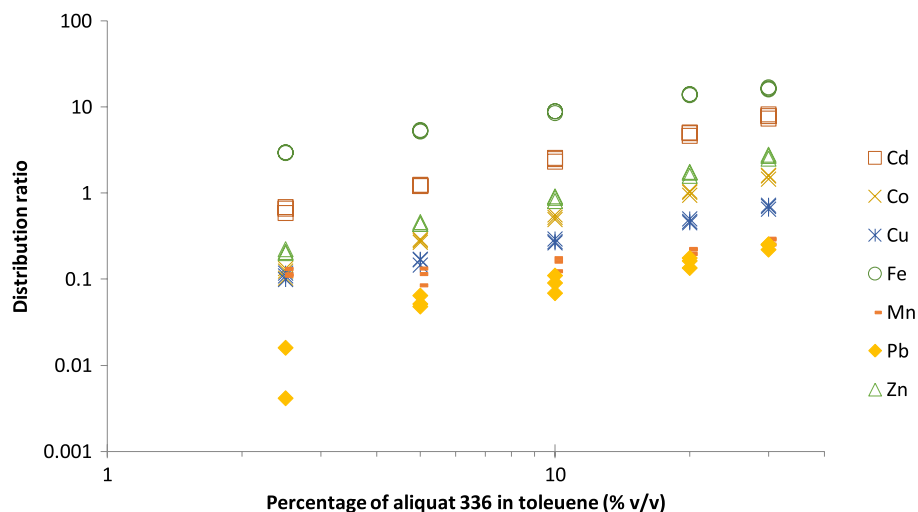
It is important to stress that the distribution ratio of a metal depends on a series of equilibria which in turn depend on the enthalpy and entropy of these reactions. With the results obtained so far, it would be premature to state the reason why the different elements have different relationships between their distribution ratios and the temperature and water content of the DES phase. It might be possible using microcalorimetry and variable temperature EXAFS to obtain an insight into the extraction chemistry.

The hypothesis that Aliquat 336 is required for the metal extraction was tested by shaking a series of different concentrations of the extractant in toluene with a mixture of metals in the wet (20% water v/v) deep eutectic solvent. It was found that as the Aliquat 336 concentration in the organic phase was increased, the metal distribution ratios increased (Figure 6). During the experiments, no extraction of lanthanides or nickel by Aliquat 336 in chloride media was observed. This can be rationalized by the facts that lanthanides have a low affinity for chloride anions and that the crystal field stabilization energy of nickel(II) octahedral and square planar complexes inhibits the formation of tetrahedral  $[\text{NiCl}_4]^{2-}$  complexes in aqueous media.

Figure 5. The relationship between the temperature and the distribution ratios for cadmium, cobalt, copper, iron, manganese, lead and zinc for an extraction from the deep eutectic solvent into a solution of Aliquat 336.



**Figure 6. The relationship between the concentration of Aliquat 336 in toluene and the distribution ratios for cadmium, cobalt, copper, iron, manganese, lead, and zinc for an extraction from the deep eutectic solvent.**



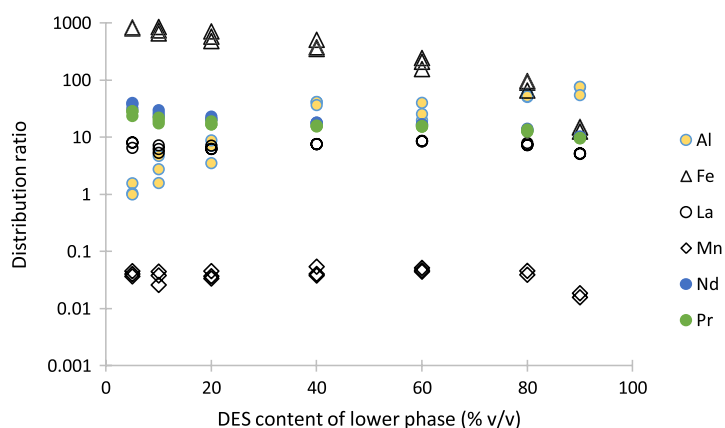
It is well known that transition metals such as cobalt, copper, and iron can be stripped from an organic phase formed from Aliquat 336 by contacting the organic phase with dilute aqueous chloride solutions. As this is so well established and occurs in a part of the process separate from the deep eutectic solvent, the stripping will not be discussed in detail here.

While the extraction of cobalt and other transition metals from the deep eutectic solvent is not fully understood with the information in this paper, it is possible to create the core of a process for cobalt recovery from a cobalt rich leach liquor obtained by the digestion of nickel metal hydride electrical cells. As the disused electrical cells contain large amounts of lanthanides, the extraction of lanthanides from the deep eutectic solvent was considered.

A series of mixtures of lanthanides and other metals in a range of mixtures of the deep eutectic solvent and aqueous sodium chloride solution were shaken with DEHPA (30% v/v) in solvent 70. It was found that the lanthanide and manganese distribution ratios changed only slightly as the composition of the lower phase was changed (Figure 7). While the aluminum extraction was favored by a low water content of the lower phase, the extraction of the iron was favored when the water content of the lower phase was high.

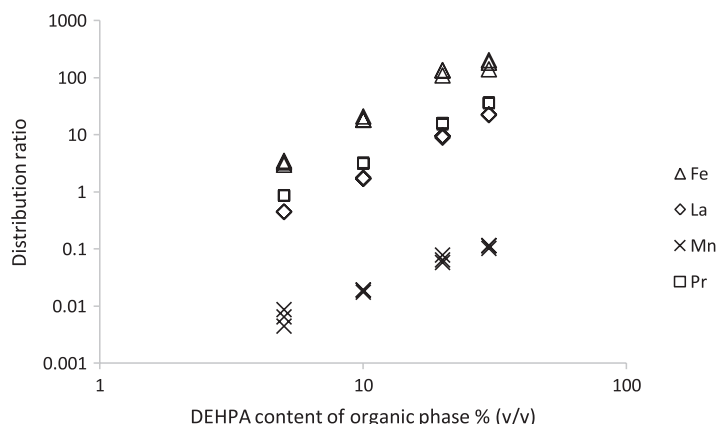
By using a series of different concentrations of DEHPA in solvent 70, the effect of changing the extractant concentration on the distribution ratios of iron, manganese, and the lanthanides was tested. It was found that while the slopes were smaller than three, the results were broadly in

**Figure 7. The relationship between the water content of the lower deep eutectic solvent phase and the distribution ratios for aluminum, iron, manganese, and the lanthanides when the organic phase was a solution of DEHPA in solvent 70.**





**Figure 8. The relationship between the DEHPA concentration in the upper phase and the distribution ratios for iron, lanthanum, manganese and praseodymium when the organic phase was a solution of DEHPA in solvent 70.**



agreement with those obtained by others (Peppard, Mason, Maier, & Driscoll, 1957). In general, an increase in the DEHPA concentration causes an increase in the metal distribution ratios (Figure 8).

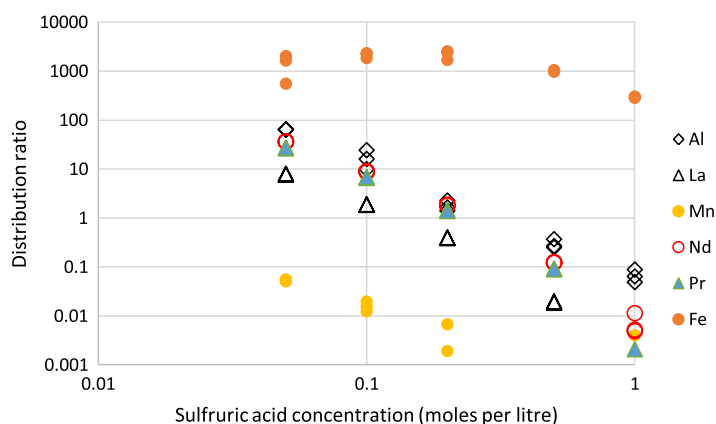
One of the long-term goals is to create a process which uses hydrotreated vegetable oil as a diluent for the DEHPA extraction, as part of the effort to enable a smooth transition to such a diluent a series of alternative grades of kerosene were tested using a 8:2 mixture of the deep eutectic solvent and water. It was found that with four different grades of aliphatic kerosene (Solvent 70, Escaid 110, Isopar L and Escaid 120) similar results were obtained (Table 2). However, when the aliphatic diluent was replaced with an alkylarene (*tert*-butylbenzene TBB), the distribution ratios of all the metals were reduced.

It is likely that a mixture of *n*-alkanes formed by the hydrogenation and hydrodeoxygenation of vegetable oil (Huber, O'Connor, & Corma, 2007) will be suitable for use as a diluent for the lanthanide extraction. While the stripping of lanthanides from organic phases containing DEHPA is well established, it was shown by shaking a series of solutions of metals in dilute sulfuric acid that such a

**Table 2. Distribution ratios obtained by shaking DEHPA (30% v/v) in different diluents with a solution of metal salts in the deep eutectic solvent**

Metal	Diluent				
	TBB	Solvent 70	Escaid 110	Escaid 120	Isopar L
Iron	39	206	204	248	232
Lanthanum	4.7	22.9	23.5	27.5	27.5
Neodymium	7.4	37.5	37.4	45.1	43.9
Praseodymium	7.5	36.3	37.2	43.2	42.6
Manganese	0.034	0.13	0.14	0.15	0.15

**Figure 9. A graph of the distribution ratios of aluminum, iron, manganese, and the lanthanides against the initial sulfuric acid concentration in the aqueous phase.**





stripping is thermodynamically possible using the organic phase used in the extraction experiments. However, the iron(III) has such a high affinity for the DEHPA that it is not possible to prevent its extraction into the organic phase with sulfuric acid (1 M) (Figure 9).

### 3. Conclusions

It was shown that cobalt and some other transition metals can be extracted from the deep eutectic solvent by an organic phase containing Aliquat 336, an organic phase which is nonflammable could be formulated. In a series of experiments, it was shown that an industrial process for the extraction of cobalt and the lanthanides from the deep eutectic of lactic acid and choline chloride is plausible. The selectivity of the extraction reagents observed in the experiments was similar to that which can be expected from experiments using more conventional aqueous media. Further experiments will be required to create and demonstrate the process.

### 4. Experimental

All reagents were purchased from Aldrich and were used as received unless stated otherwise. All pipetting was done using the forward pipetting method using piston driven air displacement pipettes made by Gilson. Solvent extraction experiments were performed by pipetting equal volumes of an organic phase and either an aqueous phase or a deep eutectic solvent phase into a glass vial (3.5 ml). It was normal to add the aqueous or deep eutectic solvent phase before the addition of the organic phase to the vial. With the exception of the part of the study in which different diluents are used for the extractions and the experiment in which the DEHPA concentration was altered the phase ratio was checked by measuring the mass of the empty shaking vial, then again after the addition of the first liquid and then finally after the addition of the last liquid layer. Using the densities of the liquids, the phase ratio was then calculated and used to correct the concentration of the metals within the organic layer. When deep eutectic phases, ionic liquids or other viscous liquids were pipetted; additional care was taken as these fluids require a greater time to flow out of the pipette tip. Additionally, filter tips were used to reduce the likelihood of the pipette becoming contaminated with a splash of the liquid. It was found that the moment when the push button of the pipette is released after the liquid had been ejected from the tip was the time when splashing of liquid upward was most likely to occur. After the liquids had been dispensed into the vial, it was sealed with a push on polyethylene cap before being shaken using a IKA Vibrax VXR basic machine equipped with a thermostated sample holder feed with warm water from a Grant TC120 circulating water bath. Unless otherwise stated all samples were shaken at 40°C. After shaking the samples were centrifuged (Heraeus Labofuge 200) at 4,000 rotations per minute for at least five minutes to ensure good phase disengagement. Samples (200–500  $\mu$ l) of the lower phase were taken using a Gilson pipette in the following manner. A pipette bearing a tip was set to the required volume, the push button depressed to the first stop before the tip was inserted into the lower phase. Through additional pressure on the button one or two bubbles of air were expelled from the nozzle of the tip. The pressure on the push button was slowly relaxed allowing liquid to enter the tip. The pipette and tip were then removed from the shaking vial, using tissue paper the outside of the tip was wiped to remove any trace of the upper phase before the liquid inside the tip was dispensed into a preweighed polyethylene vial (17 ml). To the polyethylene vials was added dilute (0.1 M) nitric acid containing ruthenium (1–2 ppm). In early tests, a  $\times 20$  dilution was used but this was associated with the formation of carbon on torch components in the ICP machine (axial view), to reduce this problem the dilution was increased to  $\times 50$ . If the Kistiakowsky–Wilson rules (Akhavan, 1998) or similar rules apply to the conditions in the ICP machine's plasma then a reduction in the amount of organic matter entering the torch will result in a reduction in the formation of carbon. The ruthenium was present as an internal standard in case the operation of the ICPOES machine (Thermo Scientific iCAP6500) was subject to some variation. Normally the internal standard was not needed, but was present as a contingency against a pump or nebulizer malfunction.

The metal content of the lower phase before the extraction experiments was measured under the same conditions using samples feed into the ICP machine which have similar dilution factors to ensure that the measurements of the metals were made with the same matrix. The concentration of

metals within the organic phase was calculated by measurement of the difference between the lower phase before and after the extraction.

A metal stock was prepared by dissolving the following metal salts, aluminum chloride hexahydrate (18.2 g), cadmium nitrate tetrahydrate (5.2 g), cerium chloride heptahydrate (6.4 g), cobalt chloride hexahydrate (8.1 g), iron(III) chloride (8.6 g), lanthanum chloride heptahydrate (5.8 g), neodymium chloride (1.7 g), praseodymium chloride (1.3 g), and zinc chloride (4.0 g) in water, to this mixture was added acetic acid (2.5 ml) and the mixture diluted to a total volume of 250 ml. This solution was normally diluted by a factor of 20 with water and the deep eutectic solvent obtained by combining choline chloride with two equivalents of lactic acid. The resulting mixture was used for the majority of solvent extraction experiments. When copper, nickel, or manganese was required in solvent extraction experiments then an aqueous solution containing these metals (16 grams per liter) as the sulfate, chloride, and chloride were diluted by a factor of 40 by its addition to a combination of water and the deep eutectic solvent. For those experiments in which lead(II) was required a deep eutectic solvent bearing the other metals which had been stored for many days in contact with solid lead(II) chloride was used.

Sunflower oil FAME biodiesel was formed by the reaction of sunflower oil with methanol using sodium hydroxide as the catalyst. After the reaction the glycerol rich layer was separated and the product washed with water before use.

#### Supplementary material

Supplementary material for this article can be accessed here <http://dx.doi.org/10.1080/23312009.2016.1139289>.

#### Funding

The research leading to these results has received funding from the European Community's Seventh Framework Programme ([FP7/2007–2013] under grant agreement number 603482 (Project named CoLaBats)). Mark Foreman is grateful to Exxon for their gift of Solvesso 150ND, Solvesso 200ND, Escaid 110, Isopar L and Escaid 120.

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#### Citation information

Cite this article as: Progress towards a process for the recycling of nickel metal hydride electric cells using a deep eutectic solvent, Mark R.St.J. Foreman, *Cogent Chemistry* (2016), 2: 1139289.

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