Developing Solvent Extraction for the Future of the Energy Industry

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The energy industry of the modern world is changing. Uranium and lithium consumptions are expected to increase in order to allow carbon-free energy sources to provide a higher proportion of global energy requirements. In order to meet the expected increase in demand for these commodities and to keep energy costs low, efficiency improvements during metallurgical processing will be required. Solvent extraction is a key processing step for generating high purity chemical products and already has widespread acceptance in the uranium industry. Recent improvements in solvent extraction in the uranium and lithium industries, including improvements in organic phase compositions and phase separation, are reviewed in this paper and are exemplified by recent project experiences within Hatch. Innovators and early adopters of the improved efficiencies offered by the discussed improvements should be well placed to lead the way diversifying the energy market.

1. Introduction

Coal production in China likely reached its peak in 2014 [3]; global production is expected to continue to fall as concerns over carbon dioxide emissions push energy production towards low carbon energy sources. Two alternatives to fossil fuels are nuclear energy and renewable energy.

Nuclear energy has the potential to supply a convenient base load for electricity generation to national grids. Recent work by Hatch has demonstrated that portable nuclear reactors could be used to power remote industrial sites. Nuclear reactors, however, are not currently suitable for use in commercial transportation, which, according to the World Bank, accounts for 20% of total carbon emissions. In contrast, renewable energy sources are typically intermittent. Lithium-based batteries are promoted as a method to smooth out intermittent electrical supply. This idea has been implemented in the mining industry; Sandfire Resources installed a 10 MW solar generation facility with 4 MW / 1.8 MWh of lithium battery storage at their DeGrussa operation in Western Australia [4]. In addition, demand for lithium-based batteries to power vehicles is currently growing at an exponential rate [5]. This has manifested as an increased demand for lithium, primarily for use in batteries (Figure 1).

Solvent extraction (SX) was first commercialized for the recovery of uranium in the 1950's [6] and is a key processing step in the production of many metals. More recently, SX for recovery of lithium from salar brines has started to become of interest [7]. SX can be used to avoid time consuming and weather dependent solar-evaporation and reduce the capital outlay required for pond construction (~35% of capital costs in Hatch's experience). This has the potential to greatly reduce the cost of lithium refining and production ramp up, predominantly in salar brine applications where 18 –

24 months ramp up is common. The chemistry of novel extraction techniques for uranium and lithium industries is therefore continually being developed in order improve efficiency and to reduce processing costs. Although lithium recovery via SX has yet to be commericalised, there has been pilot work completed to develop the technology for salar brines [8]. SX has also been applied to boron removal in the refining of lithium to generate battery grade lithium products [9].

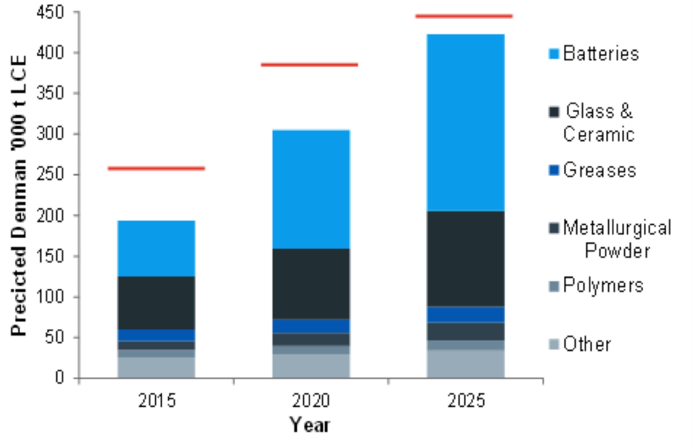

Figure 1: Predicted Lithium Demand by Product Type (Red Lines Represent Predicted Mine Capacity).

In addition to improving the chemistry of solvent extraction circuits, there has been considerable research into optimizing the contact and separation of the two liquid phases. In the uranium industry, both settlers and columns have been used for phase contact in the extract circuit. Columns are suitable to the extract stage [10] due to the particularly fast kinetics of uranium extraction using amines. Despite this, Hatch believes that mixer-settlers are the preferred technology for phase contact due to: (1) the ability to easily alter internal O:A ratios in response to changes in plant chemistry and liquor tenors, (2) the ability to handle larger flows, and (3) less onerous testwork requirements [10-12].

A key aspect of solvent extraction using mixer-settlers is the optimization of the separation of the two liquid phases. Improving the separation efficiency reduces capital costs by reducing the required settling area. It can also improve the quality of the product by reducing entrainment of raffinate into the strip solution. Several innovations for settling and phase separation that can decrease the cost and improve the efficiency of solvent extraction circuits have been proposed and implemented in recent years. Examples include the Hatch distribution array [13], Outotec deep dispersion gate (DDG) [14], and the CSIRO optimized picket fence [15].

Improvements to the solvent extraction of lithium and uranium have the potential to reduce the cost of future electricity generation and supply. There have been many recent advances in the solvent extraction chemistry of these elements as well as in the design of traditional mixer-settlers used in the solvent extraction industry. This paper therefore reviews these advances to provide a summary of the state of the art with references to the authors' experiences.

2. Developments in Solvent Extraction Chemistry for Uranium and Lithium

2.1 Uranium Solvent Extraction

Uranium recovery from primary ores is commonly practiced using amine-based solvent extraction reagents, the most common being trioctyl amine (TOA) [6, 16]. Uranium is then traditionally stripped using ammonia [16]. During ammonia stripping there is a risk of precipitating ammonium diuranate in the mixer-settler, causing crud and loss of valuable product. Ammonia must also be recovered from the strip solution to minimize operating costs and to meet stringent nitrogen discharge limits [6, 17]. Further, the stripped amine reagent must be re-protonated before the extract stage and ultimately regenerated in a strong base strip mixer-settler, adding further costs. Research by Hatch has shown that although ammonia strip stages exhibit good phase separation compared with the extract stages, the regeneration stage exhibits very poor phase separation (Figure 2) and hence requires conservative settler specific flux (SSF) rates in design (< 3.5 $m^3/h/m^2$).

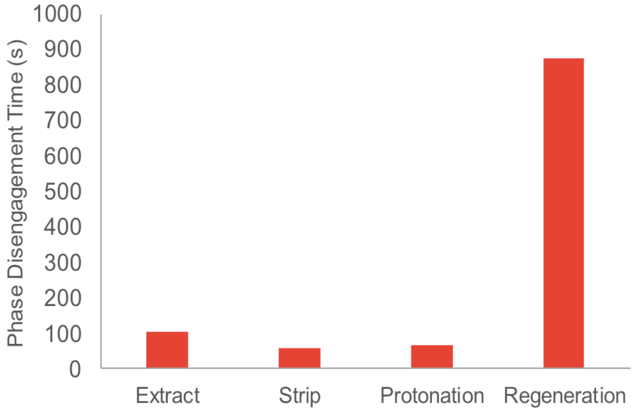

Figure 2: Phase Disengagement Times for Each Circuit from USX Testwork by Hatch.

Alternatives to ammonia stripping of amines that use different stripping chemicals or different organic reagents are being investigated. Different reagents are similarly being promoted for high chloride aqueous feeds due to strong competition between chloride and uranyl sulphate for the extractant. For example, Ballestrin *et al.* [18] combined TOA, TBP and di-2-ethylhexyl phosphoric acid (D2EHPA) in ShellSol 2046 for application to the Uranium One Honeymoon operation. This reagent mixture was able to extract uranium even in the presence of high chlorides. The inclusion of D2EHPA unfortunately increased iron co-extraction into the organic phase. To avoid stripping with ammonia, this system was stripped using sodium carbonate. Tight pH control was necessary to avoid third phase formation and phase separation issues, comparable to those noted for regeneration stages in conventional USX (Figure 2).

Morais *et al.* [19] suggested stripping of TOA with 4 M sulfuric acid to avoid ammonia stripping. Previous researchers have additionally promoted alternative reagents to TOA that can be effectively stripped using sulphuric acid. Zhu *et al.* [20] presented a solvent system containing D2EHPA and the ionic liquid CyphosIL-101. This system resulted in high uranium extraction (85%) at pH 0.5. Although iron co-extraction was acceptable (15%), vanadium co-extraction was particularly high (55%). Strong (4 M) sulfuric acid was required for effective stripping. Dogmane *et al.* [21] similarly researched uranium extraction with Cyanex 272 and subsequent stripping with strong sulfuric acid.

Sulfuric acid-based loaded strip solutions require neutralisation with lime, to generate gypsum, before uranium yellowcake precipitation can occur. Extensive washing of the gypsum would be necessary before disposal to recover uranium in the precipitate. Additionally, the stripping acid is destroyed in the process and cannot be recycled. In response to this, Zhu *et al.* [17] developed a method to recover uranium from strong acid (4 M) with transfer to weak acid (0.5 M) for subsequent neutralisation and yellowcake recovery. This method employs SX of uranium from the strong acid strip using 10% Cyanex 923 and 10% isodecanol. Unfortunately, many stages were required for both extraction (4) and stripping (5), suggesting that a high capital outlay may be required for this process.

Research by Hatch has shown that a strong acid contact with a USX organic phase could be designed at a much higher SSF (> 5 $m^3/h/m^2$) compared with the regeneration stage, thus requiring smaller settling areas and reducing capital costs. If a process for recycling the strong sulfuric acid required for uranium stripping can be successfully commercialized, then this process route appears to be an attractive option for future USX installations.

2.2 Lithium Solvent Extraction

Alternative purification techniques to extract lithium directly from salt lake brines or sulfate-based leach liquors, such as ion exchange or solvent extraction, can improve product quality by generating upgraded lithium solutions before precipitation of the final product. SX is considered a preferred method for lithium extraction over ion exchange, as it is able to treat higher concentrations of lithium (1 – 5 g/L) and higher solution volumes typically encountered in lithium refining.

Historical research into solvent extraction of lithium focused on using TBP with ferric chloride as a co-extractant [22, 23]. The use of ferric chloride as a co-extractant poses several operational problems, not least a requirement to acidify the entire process stream to avoid hydrolysis of the ferric ion. This would be a significant additional expense. In treatment of sulfate-based leach solutions of lithium-bearing minerals, the addition of ferric chloride to the process would increase the required bleed to avoid high levels of recirculating chloride. Further, to avoid third phase formation, highly polar diluents with low flash points, such as methyl iso-butyl ketone [24, 25], have been used, which would require additional design complexity for nitrogen blanketing to reduce fire risk.

To avoid the use of ferric chloride, other researchers have promoted the use of fatty alcohols for lithium recovery. Examples include the use of butanol [26] and octanol [27]. Processes promoting fatty alcohols were not adopted by the industry, presumably due to high solubility of the alcohol in the aqueous phase, and relatively low separation factors (< 3) of lithium over sodium, calcium and magnesium [26].

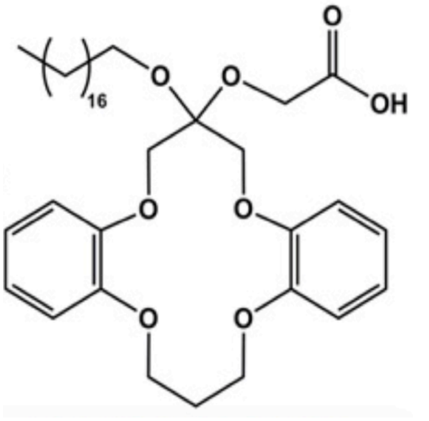

Figure 3: Functionalized Crown Ether used for Lithium Recovery

In response to these historically proposed techniques for lithium solvent extraction, Pranolo *et al.* [28] developed a solvent extraction process using commercially available reagents and diluents. The process was based on the extraction of lithium using trioctyl phosphine oxide (TOPO) and a beta-diketone dissolved in benzene [29]. Pranolo *et al.* [28] propose using LIX 54 (a commercial beta-diketone) and Cyanex 923 (a branched, liquid version of TOPO) dissolved in ShellSol D70 (100% aliphatic diluent). The lithium-sodium separation factor was 1500 at 1 g/L lithium and 80 g/L sodium. Extraction was carried out at pH 11 in 3-4 stages. Stripping was carried out using 0.5 M HCl in 2 stages. This method of selectively recovering lithium using commercially available solvent extraction reagents is believed to be a promising advancement in the lithium refining industry.

The most recent research trend for lithium recovery has targeted ionic liquids. Although many of these systems are not yet commercially applicable, they have the benefits of very selective lithium extraction. Further, ionic liquid diluents have negligible vapor pressures and hence greatly improved health and safety characteristics. Crown ethers (Figure 3) are particularly attractive for lithium recovery as the size of the cavity can be tuned specifically for a lithium ion. Combining these two concepts, Torrejos *et al.* [2] report the application of a functionalized crown ether (Figure 3) dissolved in Cyphos IL 109 that offers separation factors of lithium over sodium of 2000. Although these ideas are still in their infancy, they are exciting developments that have the potential to improve the efficiency of lithium refining.

3. Developments in Phase Separation

Mixer-settlers are popular for phase contact because the degree of extraction of target metal and impurities can be easily controlled via three variables: (1) the residence time, (2) the agitation power, and (3) the phase volume ratio. In Hatch's experience, the operational benefits of mixer-settlers are also significant. These include ease of inspection of the mixer and settler units and ease of access for crud removal and sampling.

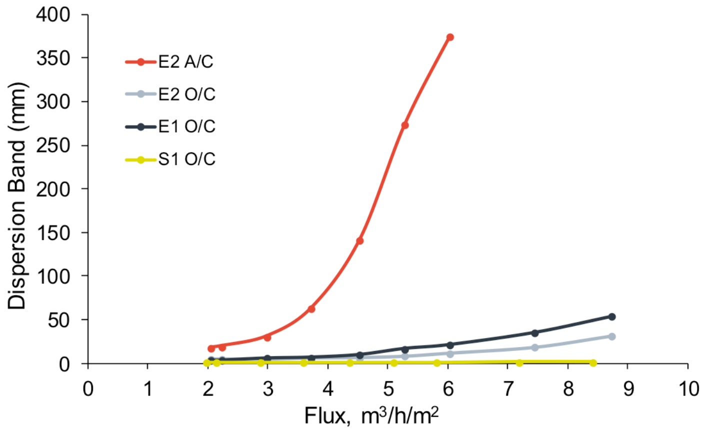

Figure 4: Dispersion Band Height for USX Stages at Varying SSF

One disadvantage of mixer-settlers is that during mixing a homogenous dispersion is created that must be separated. Phase separation rates differ depending on the two phases being mixed, kinetics and energy put into creating the dispersion. The rates of phase disengagement will therefore be different between extract and strip, and within each of their respective stages. This means that different mixer settlers should not always be sized at the same flux rate. This philosophy has been applied by Hatch previously to the design of uranium [10] and boron solvent extraction plants. Laboratory data collected comparing the settler flux rates versus the height of the dispersion band at the weir end of a test settler demonstrate the significant differences in achievable flux rates for different SX conditions (Figure 4).

Modifications to the settler itself can improve the separation characteristics of the two phases. If settling performance can be improved by modifying the settler, thus flattening the curves in Figure 4, then smaller setting areas can be used, or in existing circuits, additional throughput achieved. Computational fluid dynamic (CFD) modeling has recently been used in the solvent extraction industry to test these settler modifications without construction of a test settler. Research by the CSIRO has further demonstrated that CFD models can predict real settler performance with sufficient accuracy to allow design and screening of proposed improvements [15].

Hatch has exploited CFD modeling over a number of years to improve setter design. Similarly, the CSIRO (Australia) has also applied CFD modeling to propose modifications to the design of a picket fence for a copper SX operation. The outcomes of some of this modeling are presented here as changes to settler design that improve phase separation in solvent extraction circuits, and thus reduce required settling area and ultimate capital costs of new projects. In existing operations, application of these principles can reduce operating costs, increase throughputs and improve the SX plant operability.

3.1 Feed Distribution

The Hatch feed distribution array [13] incorporates sets of panels arranged across the width of the settler. The number of sequential panels in each set and the number of sets of panels will depend on the particular application. Typically, two sets of two panels can achieve even distribution of the feed flow across the settler width. The multiple arrays encourage coalescence much like a picket fence.

This technology is currently being applied to a copper solvent extraction circuit where the redesign of the current picket fence is required to reduce entrainment at a given flux and therefore increase settler throughput. Variation in design combined with careful positioning of each array results in even distribution of flow to the settler. Even distribution of the created dispersion and parallel flow can then be achieved with minimal dynamic head loss avoiding upgrading of pump mixers.

3.2 Organic Weir

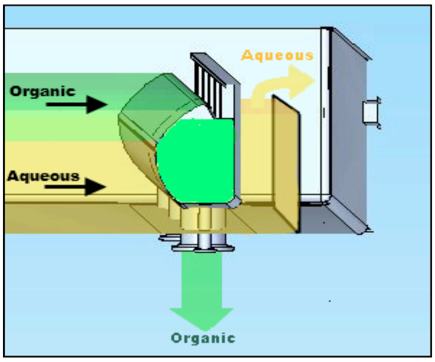

Figure 5: Hatch 'Bull Nose' Phase Splitter

Plant observation and measurement combined with CFD modelling have been utilised to develop improvements to the organic weir. The conventional vertical organic weir was observed to induce a recirculation in the organic phase at the weir end of the settler. This increases horizontal and vertical velocity in the organic phase, significant increasing entrainment. These problems are duplicated in the typical aqueous discharge arrangement.

The Hatch bull nose phase splitter (Figure 5) can be integrated into the organic launder. It presents a convex ‘bull nose’ profile to the separating phases with the apex positioned at the interface [30]. This profile prevents the formation of recirculating flow patterns in both separating phases, thereby reducing fluid velocities and hence entrainments.

4. Conclusions

There have been many recent developments in the chemistry of solvent extraction of both lithium and uranium, two key elements for the modernization of the energy industry. The drawbacks of conventional stripping of uranium loaded organic phases with ammonia can be avoided by stripping with strong (4 M) sulphuric acid. For this to be successful, a method for the recovery of uranium from the loaded strip solution must be developed. Recent advances in this area, using solvent extraction to transfer uranium from strong to weak acid, are promising. There have similarly been improvements in the solvent extraction of lithium. The most commercially relevant option recovers lithium using a mixture of LIX 54 and Cyanex 923 dissolved in a high flashpoint aliphatic diluent.

In addition to improvements in solvent extraction chemistry, the solvent extraction of lithium and uranium will benefit from recent improvements in settler designs. Application of CFD modelling to the design of settlers has resulted in innovations in settler internals that can increase the achievable flux and therefore reduce the required settling area and SX plant capital outlay. Examples of these internals include the Hatch distribution array, the Outotec deep dispersion gate, and the Hatch bull nose organic weir.

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