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Tool and Workflow for Systematic Design of Reactive Extraction for Separation and Purification of Valuable Components

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Introduction

Rare-earth metals like La(III), Nd(III), Eu(III), or Y(III), recycled from electronic waste in the context of urban mining, can be separated and purified utilizing reactive extraction. Process design then aims at optimal selection of reactive extractant, diluent, possible additional components, equipment type, internals structure as well as all process parameters. This requires a deep understanding of the CHEMISTRY of the underlying complexations as well as ENGINEERING expertise on extraction-process as well as equipment design.

To solve this design task, a tool was developed based on cascaded option trees, which combines the expertise from both sciences. Process design is on the one hand supported by a prototypic work flow and on the other hand by systematically structured and quantitative information on the underlying thermodynamics. The method is also applicable for extraction of diluted components from aqueous solutions as encountered in fermentation broth in the context of bio-economy.

The process

It is assumed that in a general process as shown in Figure 1 first the metals are leached from a solid starting material, possibly after dismantling the urban waste, crushing, and grinding. The choice of these preliminary steps as well as the leaching acid can already be based on the option-tree method. The focus here shall be on the extraction step. Therefore, it is assumed that a suitable acid has been found. After the extraction, typical steps are the re-extraction to regenerate the extractant and to access one separated fraction in an aqueous phase as well as precipitation.

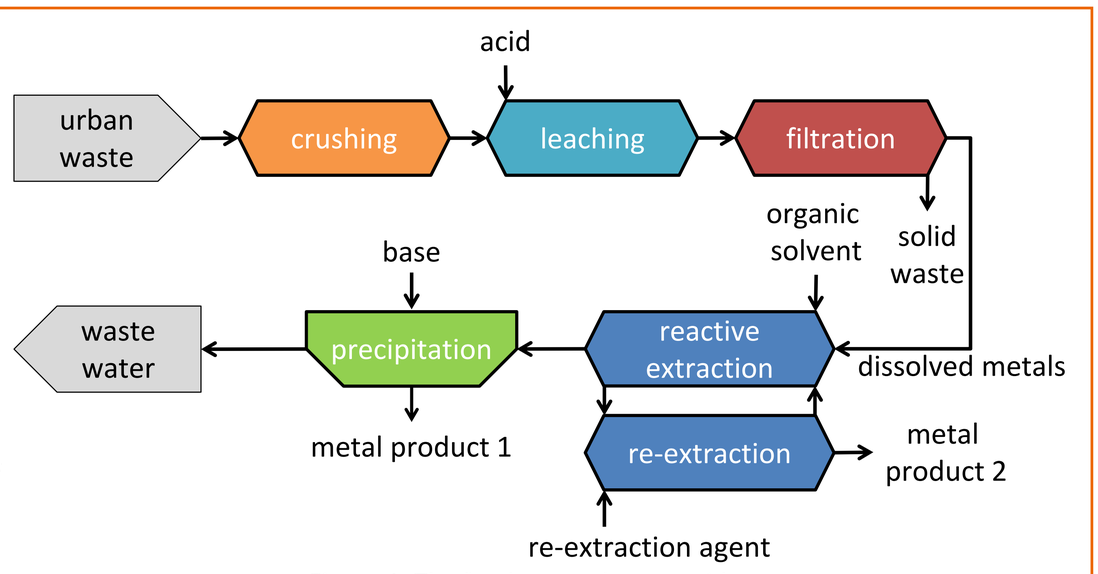

Figure 1. The fundamental process idea

Cascaded Option Trees

The cascaded option-tree methodology had been proposed previously to support design of new processes based on experience in cooperation projects with industry [1]. As starting point for an options tree for a specific separation-process design task, the options for that separation process on a coarse level of detail are collected as well as the basic criteria that have to be fulfilled. For each of the options it is then evaluated, to which degree the individual criteria are fulfilled, which is recorded in a corresponding matrix. The first criteria evaluated should be those that are most restrictive. The result of this evaluation can be coded with colors or symbols. Green or a '+' indicate that the option meets the criterion, while yellow or '0' show that the option would work for the criterion regarded, but some challenges like higher cost or more process effort are foreseeable. If an option does not fulfill a criterion, this is indicated with red or '-'.

Application to Reactive Extraction

As first step the different extractants are considered. From the chemical perspective, the hardness or softness of the ions to be separated and the hardness or softness of the extractant can be used as a framework for systematically sorting and interpreting the extraction results. In principle it is assumed that hard metal ions are best extracted by hard extractants, and soft metals by soft extractants. The hardness of a metal ion is defined as the arithmetic mean of the electron affinity and the ionization potential. The extractants which are O-, N-, or, P-donors are called hard extractants and those which are S-, F-, or Cl-donors are called soft extractants. Additionally, the extractants are sorted according to their decreasing pK values. This results in a matrix is obtained, which systematically characterizes the equilibrium constants as shown for some selected extractants and ions in Table 1.

		extractant			
		Cyanex 272	Cyanex 302	Versatic 10	DEHPA
	pKa	6.37	5.63	5.17	3.24
metal ion	hardness				
--	eV	pK			
Fe^{3+}	15.3		0.9	1.75	0.5
Cu^{2+}	9.5	1.75-3.6	< 0	4	2.8
Zn^{2+}	9.0	1.8-2	1.5	5.5	0.75-1.5
Ni^{2+}	8.5	5.75-6.2	6.5	6.4	5
Co^{2+}	8.2	4	3.9	6.6	4

Table 1. Extraction of cobalt and nickel as an example

This table is then used in a first step to evaluate the different options for extractants. Since metal ions need to be separated, in the illustrative example cobalt and nickel, the difference in their pK should be considerable, if a separation with few equilibrium stages is desired. Further critical criteria are then systematically evaluated for the extractants as shown in Table 2. Option trees are then applied also to find optimal choices for further parameters and fundamental characteristics of the process: diluent as shown in Table 3, complexing agent, possibly modifier in case of third-phase formation, pH of extraction and re-extraction, concentration of extractant, type of extractor, operating conditions of the extractor, etc. One advantage of the option trees is that the criteria can be evaluated based on different methods. First choice is available and reliable information from the literature, other options are modeling and simulation, expert knowledge and finally also own experimental results. This includes also drop-based modelling and simulation of extractors as well as mixer settlers, for which the basis can be obtained by lab-scale experiments [2, 3].

Thus, the criteria include not only the basic chemical properties of the system but directly consider parameters, which are relevant for the technical performance. This is also shown in Table 3 in the last column, where the ease of phase separation is regarded. Usually this criterion should not be analyzed as last criterion, because it often imposes the harder restrictions. Here, due to the COVID-19 pandemic, this parameter could not yet be evaluated and is thus left for evaluation in the near future.

		criteria								
overall evaluation	diluent	sufficient solubility in extractant	density difference between phases	low viscosity	intermediate surface tension	low solubility in water	non toxic	resistance to degradation	cost; economy	ease of phase separation
0.86	kerosene	1	1	1	1	1	0	1	1	
-1.00	carbon tetrachloride	1	1	1	1	0	-1			
-1.00	benzene	1	1	1	1	0	-1			
0.57	toluene	1	1	1	1	0	0	1	0	
0.71	xylene	1	1	1	1	1	0	1	0	
0.86	biodiesel	1	1	0	1	1	1	1	1	
-1.00	chloroform	1	1	1	1	-1				

Table 3. Option tree for diluent

overall evaluation	extractant	criteria: separation possible	criteria: easy extraction	criteria: stripping efficiently possible
1	Cyanex 272	1	1	1
0.67	Cyanex 302	1	1	0
-1	Versatic 10	-1		
0.67	DEHPA	0	1	1

Table 2. Option tree for extractant

Conclusions

It is obvious that the method of cascading option trees is very transparent. At each point in the process development it is very clear, which options still exist, which are the best options available, and why. The method does not only allow to choose the best option, but also second-best options are directly visible.

It turns out that the workflow is identical for different separation tasks, the thermodynamic data apply generally and the option trees can very well be reused for other separations. Thus, an overall workflow, prototype option trees and the basic tables on molecular and thermodynamic properties have been developed as a sound basis for optimal extraction-process and equipment design. The option-tree methodology has been applied to the separation of rare-earth and transition metals from waste, to phosphorous recovery from sewage sludge and several separations in cooperation with industry, mostly in the context of bio-based processes.

References

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