EUROPEAN ROADMAP OF PROCESS INTENSIFICATION

- TECHNOLOGY REPORT -

TECHNOLOGY: REACTIVE EXTRACTION COLUMNS – HIGH THROUGHPUT & HIGH SELECTIVITY

TECHNOLOGY CODE: 2.2.5

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1. Technology

1.1 Description of technology / working principle

(Feel free to modify/extend the short technology description below)

Reactive extraction is a well-known technique established in the 60-ties for large-scale applications in hydrometallurgy. Most of the applications refer to metal ion ions recovery with liquid ion exchangers in mixer-settler cascades. In order to reduce costs and enhance capacity a significant trend is to use high-throughput columns. This can be achieved using selectors with fast kinetics, nowadays being commercially available (Bart and Stevens, 2004). Recent achievements are with high selective carrier systems in order to obtain optically pure isomers, as is a challenging demand in pharma industry (s. K. Brauch, 2001). The chemistry and the constraints of this selectors and their selector principles are discussed elsewhere (Bart 2005a). In general they are related to ion exchange mechanisms and/or steric interactions with size specific guest-host interactions.

The process and apparatus layout with reactive extraction resembles that of pure physical extraction. However, the mass transfer term is more complex and can be approximated by a apparent transfer coefficient valid in a narrow operation range. A major gap in the prediction of plant performance on mini-plant experiments is when using droplet populance balance models (DPBM) (Bart et al., 2006). This is an enormous advantage, since only small liquid quantities have to be operated on bench-scale supporting fast "time-to-market" concepts. This also was agenda of a DECHEMA-Colloquium "From Single Droplet to Extraction Column – Requirements and New Developments" (s. http://dechema.de/extraktion). There was a further demand from industry in regard to process intensivation with the idea to link DPBM and CFD (Computational Fluid Dynamics) for high precision engineering of industrial scale column design. First attempts in that respect have already been started with solids processing (crystallizations, etc.). Recent works (Drumm & Bart, 2007) have already shown, that local energy distribution serves as a basis for proper description of column hydrodynamics without implications of geometrical constraints (diameter, height, pulsed a rotated internals, etc.).

1.2 Types and “versions”

(Describe the most important forms/versions of technology under consideration, including their characteristic features, differences and similarities)

Centrifugal and non-dispersive membrane extractors are only used in special cases (settling problems, droplet free systems, etc.). The dominating apparatus is the mixer-settler followed by columns (Brand et al., 1978). The latter are increasingly preferred due to their high efficiency at high capacity, at reduced solvent inventory, reduced solvent losses, better turndown and smaller footprint.

The columns are either agitated, to enable better droplet formation and higher mass transfer area, or non-agitated. The latter (s. Fig. 1) are cheaper and simpler, ranging from those with no internals (spray columns) to more complex with packing or trays.

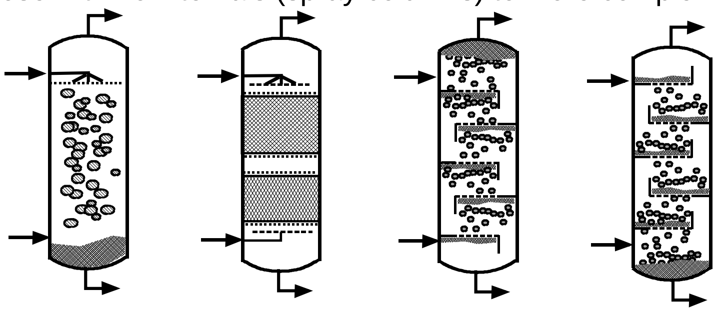

Fig. 1: Non-agitated columns (l.t.r: spray, packed, sieve tray (light) sieve tray (heavy) column)

In non-agitated columns the hydrodynamic of the dispersion is controlled by physical properties and the phase flow rates. In order to decouple the latter and gain more flexibility a number of agitated columns are used (s. Fig. 2). Their efficiency is generally higher with the costs of a more sophisticated design procedure.

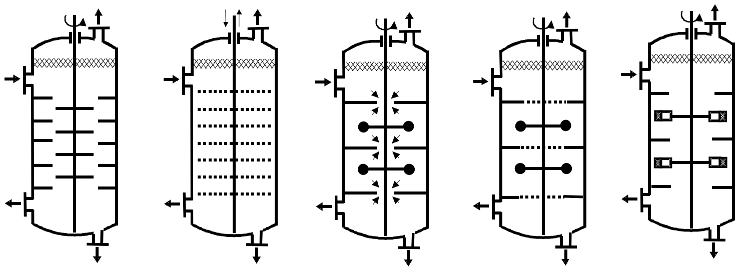

Fig. 2: Agitated columns (l.t.r.: RDC, Karr, Oldshue-Rushton, Kühni, Scheibel extraction columns)

1.3 Potency for Process Intensification: possible benefits

(In Table 1 describe the most important documented and expected benefits offered by the technology under consideration, focusing primarily on energy; CO_2 emission and costs, providing quantitative data, wherever possible. Add other benefits, if needed).

Table 1: Documented and expected benefits resulting from technology application

Benefit	Magnitude	Remarks
Cost-savings	Substantial (> 50 %)	Cost savings results from: • Higher capacity • Smaller solvent inventory • Less entrainment • Smaller footprint • Better turndown
Increased selectivity and better product quality	Substantial (> 50 %)	Selectivity is due use of specific reactive ligands: • Ion exchangers • Chelating ligands • Chiral ligands
Increased savely	No data available	Contrary to mixer-settler columns can be easily fabricated in a casted shell. No organic vapors penetrate the environment.
Environmentally benign	Substantial (> 100 %)	Bad pump-mixer-settler performance can result in entrainment of the total solvent inventory. Phase slip with columns is smaller in magnitudes.
Energy savings	Substantial (> 100 %)	In comparison to distillation, no reboiler heat is necessary. Only pumping and agitation of internals occur. With reactive extraction stripping is with chemicals, in comparison to absorption is also no strip-steam demand.
Less CO_2	No data available	See remarks concerning energy above

1.4 Stage of development

Reactive extraction columns are widely distributed with uranium reprocessing in nuclear industry. In chemical and pharmaceutical industry bigger units are installed and several large reactive units are in the mining and hydrometallurgical field (Bart, 2005b). The state-of-the-art of column design is up till now with widely and extensive pilot-plant operations. However, scale-up from mini-plants is becoming more popular and for high precision engineering the use of CFD and/or population balance modeling is a future challenge.

2. Applications

2.1 Existing technology (currently used)

(Describe technology (-ies) that are conventionally used to perform the same or similar operations as the PI-technology under consideration)

The majority of the operations are with non-reactive systems. With reactive ones the mixer-settler applications are still dominant.

2.2 Known commercial applications

(Is the technology broadly applied on commercial scale? In which process industry sectors is the technology most often applied: large volume chemicals – specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? What is the estimated number of existing applications? In Table 2 provide the most prominent examples of realized applications and provide their short characteristics)

So far commercial applications in the speciality chemical and pharmaceutical industry have not been published openly to a great extent. However there are some reactive extractions column been reported in hydrometallurgy and are state-of-the-art in nuclear reprocessing (T.C. Lo et al., j1983, Thornton, 1992).

Table 2. Industrial-scale applications of the Technology (existing and under realization)

Sector	**Company - Process/Product name/type**	**Short characteristic of application**	**Product-ion capacity/ Plant size**	**Year of appli-cation**	**Reported effects**
Hydro-metall-urgy	INCO	Cu/U separation	Feed: 800 m^3/h	2002	• 10 % less entrainment
	Western Mining	Ni/Co separation		under erection	• 100 % > capa-city

2.3 Known demonstration projects

(Are there any demonstration projects known related to the technology under consideration? In which process industry sectors are those projects carried out: large volume chemicals – specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? In Table 3 provide the short characteristics of those projects.)

No demonstration projects on reactive extraction columns are known.

Table 3. Demonstration projects related to the technology (existing and under realization)

Sector	**Who is carrying out the project**	**Short characteristic of application investigated, including product name/type**	**Aimed year of applicati on**	**Reported effects**
				•

2.4 Potential applications discussed in literature

(Provide a short review, including, wherever possible, the types/examples of products that can be manufactured with this technology)

Reactive extraction first used for uranium production in the "Manhattan"-project (Coleman & Leuze, 1978) came to commercial break-through with selective copper extraction in the 60-ties (Power, 1971). Hundreds of research papers have been published and there exist good reviews on this subject (Bart, 2005, Lo et al., 1983, Thornton, 1992). The potential use for reactive extractions columns is for separation or recovery of:

- Metal ions and salts
- Organic and inorganic acids
- Intermediates
- Pharmaceutics
- Food additives and nutraceutica
- Active pharmaceutical ingredients (API).

3. What are the development and application issues?

3.1 Technology development issues

(In Table 4 list and characterize the essential development issues, both technical and non-technical, of the technology under consideration. Pay also attention to “boundary” issues, such as instrumentation and control equipment, models, etc.) Also, provide your opinion on how and by whom these issues should be addressed)

Table 4. Technology development issues

Issue	Description	How and by whom should be addressed?
Engineering & performance simulations	The design and apparatus performance simulations rely on simplified concepts (dispersion or back mixing model), which not correctly reflects hydrodynamical constraints (geometry, energy input, etc.)	R&D projects carried out at universities in collaboration with equipment manufacturers and engineering firms
Modeling and scale-up methodologies	The scale-up is usually based on extensive pilot work. Miniplant and computer assisted expertise is needed for precision engineering quality	R&D projects carried out at universities in collaboration with equipment manufacturers and engineering firms
Control systems for commercial-scale applications	In-line sensor systems have to be developed, controlling drop size distribution, to adapt automatically to changes in separating conditions	R&D projects carried at the universities in collaboration with particle sensor manufacturers and equipment vendors

3.2 Challenges in developing processes based on the technology

(In Table 5 list and characterize the essential challenges, both technical and non-technical, in developing commercial processes based on the technology under consideration. Also, provide your opinion on how and by whom these challenges should be addressed)

Table 5. Challenges in developing processes based on the technology

Challenge	Description	How and by whom should the challenge be addressed?
Big scale units	The design of reactive columns of big scale (∅ > 1.5 m) is still a challenge due to insufficient scale-up rules. CFD and DPBM methods are modern tools to tackle that problem	The challenge should be addressed in the R&D projects on engineering and design concepts for commercial scale units
Difficult image analysis at high	Droplet distribution sensor systems available are either not exact or need help of an operator	The challenge should be addressed in the R&D

hold-up	during analysis	projects on particle imaging
Control	Proper control, self-adaptive based on process models, to maintain efficiency	Reliable models and control policies have to be developed based on in-line sensors

4. Where can information be found?

4.1 Key publications

(Provide the list of key publications in Table 6)

Table 6. Key publications on the technology

Publication	Publication type (research paper/review/book/ report)	Remarks
Bart, H.-J.: Prozessintensivierung durch reaktive Carrier bei Reaktivextraktion und –sorption. Chem. Ing. Techn. 77 (2005a), 1773-1783	Review	Reactive Carriers
Brauch, S.K.: Int. Regulation of Chiral Drugs, in: Chiral Separation Techniques, G. Subramanian Ed., 319-342, Wiley-VCH, Weinheim, 2001	Review	Chiral Drugs
Bart, H.-J., Stevens, G.: Reactive Solvent Extraction. In: Ion Exchange and Solvent Extraction, M. Kertes, A.K. Sengupta Eds., Vol. 17, 37-82, Marcel Dekker, New York, 2004	Review	General Overview
Bart, H.-J. et al.: Vom Einzeltropfen zur Extrak-tionskolonne. Chemie Ingenieur Technik 78 (2006), 543-547	Review	Hydrodynamics
Brandt, H.W., Reissinger, K.H., Schröter, J.: Moderne Flüssig/Flüssig-Extraktion – Übersicht und Auswahlkriterien. Chem. Ing. Techn. 50 (1978), 345-354	Review	Apparatus Selection
Drumm, C., Bart, H.-J.: Computational Fluid Dynamics – Simulation der Ein- und Zweiphasen-strömung in einer Rotating Disc Contactor-Ex-traktionskolonne. Chem. Ing. Techn. 79 (2007), 68-72	Research Paper	Hydrodynamics
Bart, H.-J.: Extraction Columns in Hydrometall-urgy. Hydromet. 78 (2005b), 21-29	Review	Reactive Columns
Lo, T.C., Baird, M.H.K., Hanson, C. (Eds): Handbood of Solvent Extraktion, J. Wiley & Sons, New York, 1983	Book	Handbook
Thornton, J.D. (Ed): Science and Practice of Liquid-Liquid Extraction, Vol. 1&II, Oxford University Press, Oxford, 1992	Book	State of the Art
Coleman, C.F., Leuze, R.E.: Some Milestone Solvent Extraction Processes at the Oak Ridge National Laboratory, J. Tennessee Acad. Sci., 54 (3) (1978), 102-107	Research Paper	Manhattan Project
Power, K.L.: Operation of the First Liquid Ion-Exchange and Electrowinning Plant. In: Proc. ISEC '71, Vol. II, 1409-1415, Soc. Chem. Ind. (Ed), London, 1971	Research Paper	1st Commercial Reactive Copper Extraction

4.2 Relevant patents and patent holders

(Provide the list of relevant patents in Table 7. Under “remarks” provide, where applicable, the names/types of products targeted by the given patent.)

Table 7. Relevant patents
No specific reactive extraction column patents are known.

Patent	Patent holder	Remarks, including names/types of products targeted by the patent

4.3 Institutes/companies working on the technology

(Provide the list of most important research centers and companies in Table 8)

On extraction columns is a limited number of research groups, which partly tackle reactive processes.

Table 8. Institutes and companies working on the technology

Institute/Company	Country	Remarks
TU Graz (Prof. R. Marr)	Austria	Broad range of research activities
ENSIGC, Toulouse (Prof. G. Casamatta)	France	Focus on column hydrodynamics
TU Kaiserslautern (Prof. H.-J. Bart)	Germany	Broad range of research activities, including scale-up issues
TU Darmstadt (Prof. M. Hampe)	Germany	Focus on mechanism and fundamentals
Universität Dortmund (Prof. E. Kenig)	Germany	Focus on mathematical description
RWTH Aachen (Prof. A. Pfennig)	Germany	Broad range of research activities with focus on mass transfer and thermodynamics
TU Eindhoven (Prof. A. de Haan)	Netherlands	Broad range of research activities with focus on thermodynamics and solvents

5. Stakeholders

5.1 Suppliers and developers

(Provide the list of key suppliers/developers in Table 9)

Several supplies of non-reactive extraction columns are known being potential stakeholders. Very few have experience with reactive extraction columns.

Table 9. Supplier and developers

Institute/Company	Country	Remarks
Batman	Israel	Broad range of experience, focus in hydrometallurgy and inorganic processes (metal separations)

Koch-Glitsch	USA	Physical extraction
Kühni AG	Switzerland	Broad range of experience, flexible, also some reactive applications in chemical and pharmaceutical field
Montz	Germany	Physical extraction
QVF	Germany	Broad range experience in high corrosion applications
Raschig	Germany	Physical extraction
Stahl	Germany	Physical extraction

5.2 End users

(Describe the existing and potential end-users, other than those already listed in Table 2)

Potential group of end users includes companies operating in the fine chemical & pharmaceutical sectors, food additives and nutraceutical products as well as in environmental and hydrometallurgical applications.

6. Expert's brief final judgment on the technology

(maximum 5 sentences)

Reactive column extractors have the potential to be applicable at mini-scale high value products or at big-scale high throughput applications. The particulate bounded hydrodynamics makes apparatus scale-up tedious and costly. Sophisticated design and control concepts relying on CFD, population balance modeling and the usage of reliable in-line sensors should be implemented and developed within the next 5-10 years. Reactive extraction is a extremely flexible and highly selective technology, is environmentally benign and has per se a low power consumption linked with minor CO_2 emissions.