PROPOSED SYSTEMS IN VIEW OF APPLICATIONS

	System Id	Salt	Solvent	Solute	Investigated propertiy(ies)	Application
	1a	NRS		НС	VLE (solubilities, vaporization of neutral cpds)	<u>Gas storage,</u> <u>Distillation, active ingredient</u> <u>manufacturing</u>
Only fluid Phase Eq	1b	NRS	Protic	HC	LLE (Solute partitioning)	Extraction, purification (hydrometallurgy)
	1c	NRS	Aprotic	НС	LLE (Solute partitioning)	Extraction, purification (hydrometallurgy)
	2a	NRS		AG	VLE (solubilities)	Gas storage /
	2b	RSB		AG	VLE (solutes partitioning)	gas scrubbing / absorption/ geotherma
Fluid Phase +	2c	RSA		BG	VLE (solutes partitioning)	gas scrubbing / absorption
reaction	2d	OrgS	Protic		VLE (all volatiles partitioning)	Separation / stripping
	2e	OrgS	Aprotic		VLE (all volatiles partitioning)	Separation
	2f	RSB	Protic		VLE (vaporization of neutral cpds)	Evaporation (distillation)
Solid Phase no	3a	NRS			ELS (solid appearance condition and amount)	salt purification; water treatment
reaction in the	3b	NRS		HC	ELS (solid appearance condition)	scaling - flow assurance
	3c	NRS	Protic		ELS (solid appearance condition)	scaling - flow assurance
liquid phase	3d	NRS		HC	ELS (solid appearance condition and amount)	crystallisation of active compounds ; flow assurance
Solid phase +	4a	OrgS			Activities, speciation	<u>Batteries</u>
reaction	4b	MOx			ELS, speciation (pH)	Corrosion, catalyst manufacturing
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New energy technologies require the capacity to store large amount of gases. This may E_{e} be natural gas or increasingly hydrogen. It may also be a mixture of hydrogen and methane (hythane).

A very efficient large scale solution is to store these gases in salt caverns that contain an aquifer. This aquifer is a brine, most often containing NaCl.

The solubility of the gas to be stored must be determined, as well as the water content of the gas.

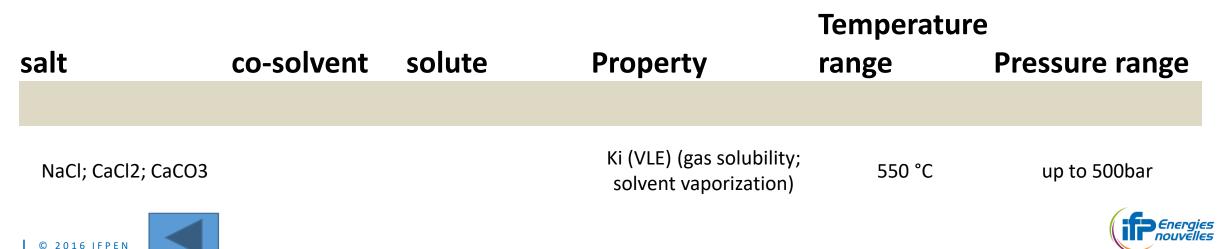
Challenge: Pressure conditions are generally high, and very few data exist with high ionic strength water.

				Temperatur	е
salt	co-solvent	solute	Property	range	Pressure range
NaCl; CaCl ₂	none	H ₂ ; CH ₄	Ki (VLE) (gas; water)	up to 200 °C	200 bar
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In geothermal applications, water is recovered in temperature conditions that may be $E_{E} = D_{E} + D_{E}$ supercritical. In these conditions, salts are soluble in molecular form. When temperature is lowered, new types of vapour-liquid equilibrium can appear, where ions appear in both liquid and vapour phases

Challenge: (1) **Data**: measuring VLE and SLE in high temperature conditions may be a real challenge; (2) most of today's **models** consider that the ionic species remain in the liquid phase. This is no longer true in conditions where water has a very low dielectric constant.



	2b	RSB	ļ	AG	VLE (solutes partitioning)	gas scru	bbing / absorption	
GAS SCRUBBING							N E W	- ENERGIES

In gas treatment technologies, a solvent is used for removing reactive gases. Chemical solvents are much more efficient as they allow a higher solubility of the gas in the solvent, but regeneration issues may then become important (heat needed to recover the gas from the solvent).

Challenge: Many different types of reacting salts can be used, including organic salts, for which very few data exist.

The enthalpy of reaction and vaporization of the gas is a key piece of information in these processes, since it determines the global energy efficiency.

The loss of solvent through vaporization is often badly studied. This vaporization strongly depends on the speciation in the aqueous phase.

				Temperatur	е
salt	co-solvent	solute	Property	range	Pressure range
amine salts; NaOH; KOł	l Amine	CO ₂ ; H ₂ S; SO _x ; NO _x	Ki (VLE) (gas solubility; solvent vaporization); enthalpies	140 °C	up to 100 bar
			charpies		





EXTRACTION	1b	NRS	Protic	HC	LLE (Solute partitioning)	Extraction, purification	ERGIES
	1c	NRS	Aprotic	HC	LLE (Solute partitioning)	Extraction, purification	



The objective of extraction processes is to ensure that a solute passes from one liquid phase to another. One of the liquid phases is often aqueous; but sometimes two aqueous phases are created by adding polymeric material (Aqueous Two Phase System).

Example:

Liquid-liquid extraction is used for separating individual metals in hydrometallurgical processes. The pH is typically modified and depending on that property, the reaction equilibria will shift and thus improve or decrease the extracting power of a given solvent.

Challenges: Most of the operations take place at 20-40 °C but for specific safety studies, extrapolation of data are needed from 40 to 100-120 °C leading to major uncertainties.

salt	co-solvent	solute	Property	range	re Pressure range
U, Pu Li, Co, Mo, (for battery c catalyst recycling)	HNO₃, Tributyl or Phosphate; C12 alkane		Ki(VLLE)	20-120 °C	around 1 atm





Example:

Alcohols and acids are removed from a fermentor that contains alcohol, water, organic acids and a pH buffer (typically NaOH, KOH or NH₃OH). The volatility of the compounds strongly depends on the pH as a consequence of the speciation of the acid.

Challenge: data exist for some acids; often determined at low concentrations (pKa). No data exist for higher molecular weight acids. In addition, when the concentration is large, non-idealities need to be considered in the liquid phase which means that a model needs to be used. No data exists for these high molecular weight material.

				Temperature	}
salt	co-solvent	solute	Property	range	Pressure range
NаОН; КОН; NН₃ОН	alcohols (ethanol, propanol)	organic acids	Ki (VLE) (solute; water)	50 °C	1-2 bar



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ACTIVE	INGREDIENT MA	NUFACTUF	RING		NEW ENERGIES							
	1a NRS	нс	VLE (solubilities, vaporiz neutral cpds)	ation of <u>Gas storage,</u> distillation	. • • •							
Alkali hydroxides are commonly used during batch reaction steps for the production of active ingredients. NaCl as well as complex polyatomic salts, like phenolates, can be formed as intermediates. The reaction mixture is further processed, requiring e.g. a distillation (batch or continuous) for a solvent exchange or the distillative separation of residual water. For this purpose, in particular knowledge on the VLE of the solvents as well as the solubility of the salts in different solvent mixtures is of interest.												
	e: The large variety of ntribution method or			· · · · · · · · · · · · · · · · · · ·								
	Temperature											
salt	co-solvent	solute	Property	range	Pressure range							
	Various organic											

e.g. Phenolates, solvents (alcohols, phenolates VLE, SLE NaCl, NaOH, KOH OMAC, etc.)

10 - 1013 mbar

ACTIVE INGREDIENT DEVELOPMENT

3d	NRS	μс	ELS (solid appearance condition	crystallisation of active	
Ju	NIN3	ne	and amount)	compounds; flow assurance	

Apart from the process design, in the development phase of new active ingredients, the solubility of complex polyatomic molecules in different buffer and salt solutions is required. These information are of interest in particular in an early development phase, requiring highly predictive models. Depending on the pH, the API might exist in different ionized forms.

Challenge: The large variety of possible compounds will necessitate some predictive approach (group contribution method or other kind of property – structure relationships) to extrapolate the data





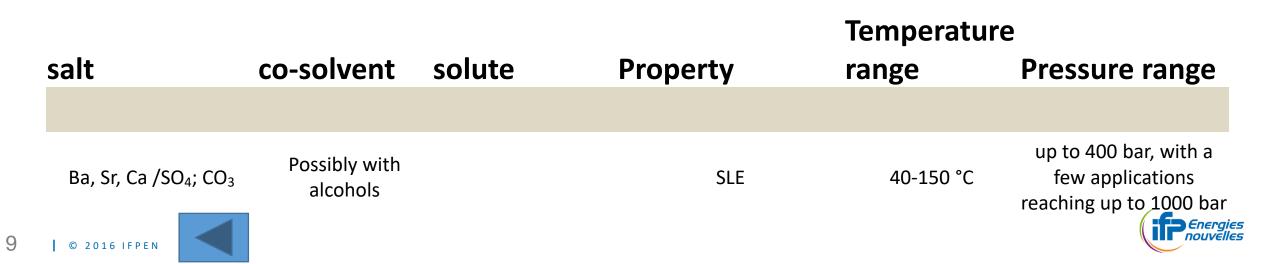


NEW ENERGIES

FLOW /	ASSURA	NCE			NEW	<u>e</u> nergies
3d	NRS		HC	ELS (solid appearance condition and amount)	<u>crystallisation</u> of active compounds ; flow assurance	
E a martin		:	and the second states			EleTher

Formation water typically contains a wealth of ions, which could lead to precipitation of salts at suitable conditions and/or upon mixing with aqueous streams of different compositions. It is important to be able to use limited available data for simple systems and conditions away from those of interest, to develop models that can predict the behaviour of more complex systems and their blending. Common ion effects, effect of ratio of anion/cation, differences with respect to ion valence, are thought to be crucial for the behaviour of these systems.

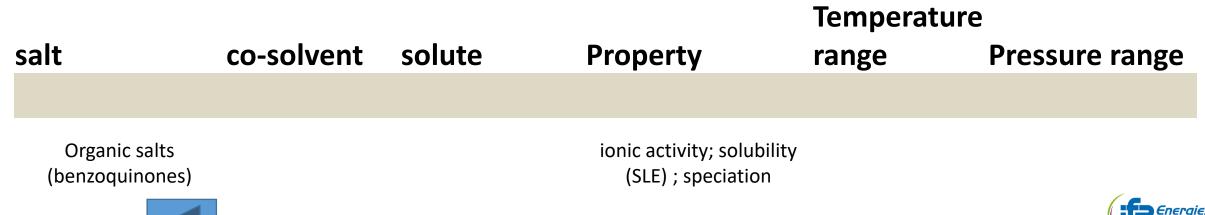
Challenge: How would BaSO₄ or SrSO₄ behave at different ratios of the ions, different conditions, and at the presence of CaCO₃? How does Total Dissolved Solids affect the model? Can we increase confidence on how we transfer knowledge from simple systems to more complex ones?



E	BATTER	RIES						N	EW	ENEI	RGIES	
	4a	OrgS			Activities, speciation		Batteries					
F	atteries	require a	high e	nergy intensity	meaning a high	content	of ionic	snecies	Yet	in	EleTh	her

Batteries require a high energy intensity, meaning a high content of ionic species. Yet, in aqueous media, the voltage is limited by the decomposition voltage of water. As a consequence, there is an active search for electrolytic media based on organic species, that still dissolve as ions in water. The redox potentials of these products are needed, hence the formation properties and the ionic activity coefficients. Examples are quinones in water. How can we increase confidence on the prediction of dielectric constant for such systems?

Challenge: Very few data exist for (1) solubility; (2) speciation; (3) activity coefficients and (4) formation properties of these organic salts. Everything needs to be done.

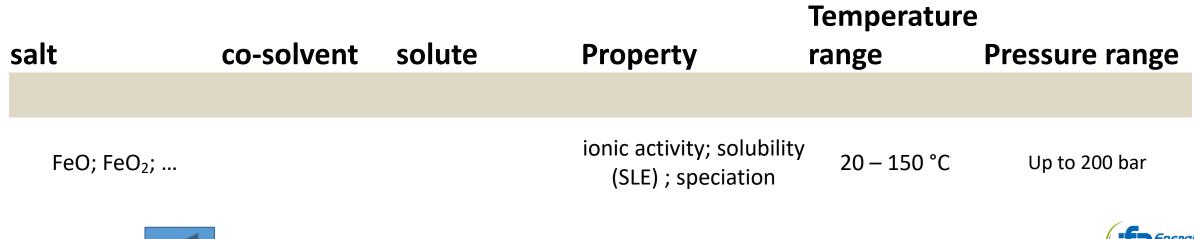




CORROSIO	N			N E W	ENERGIES
4b M	Ox	ELS, speciation (pH)	<u>Cor</u> ma	rrosion, <u>catalyst</u> nufacturing	EleTher

Corrosion is essentially a redox chemical reaction between a solid and a liquid. This means that the species activity as well as their crystallization tendency must be modeled simultaneously.

Challenge: Few data exist in extreme conditions (e.g. high CO₂ or H₂S pressures, or in the presence of impurities that may affect the reaction -dissolved oxygen).

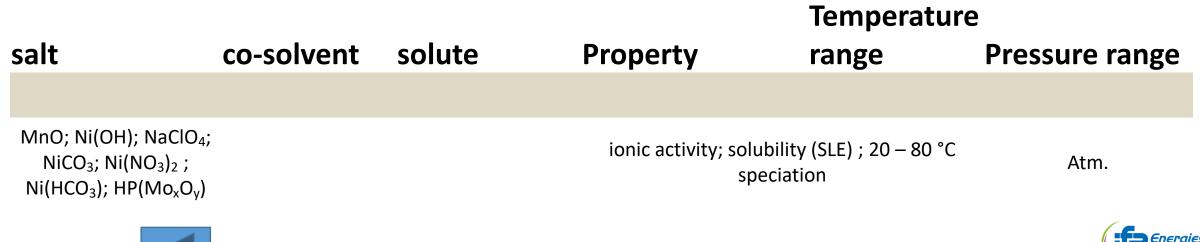




С	ATALY	ST MAN	N E W	ENERGIES			
	4b	MOx		ELS, speciation (pH)	<u>Corrosion, cat</u> manufacturin	_	
							Elether

Catalyst manufacturing is based on the deposition of well-controlled metallic oxides on a support. In order to make sure that the correct oxide is being deposited, it is essential to control precisely the speciation in liquid phase as a function of pH and temperature condition.

Challenge: Considering the high concentrations, an adequate model must be available to describe non-idealities, in addition to reactive equilibrium. Several solid phases may co-exist, and making sure that the correct one is deposited is a challenge.



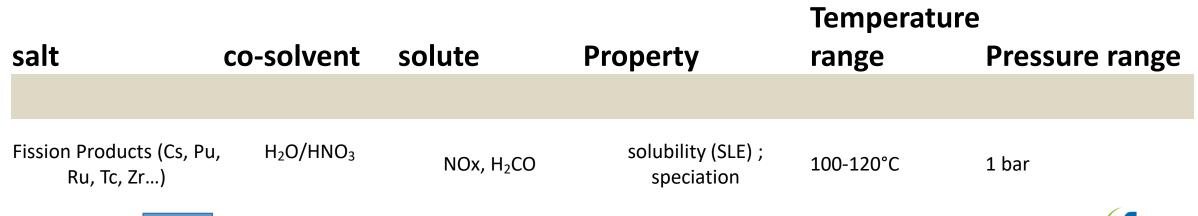


NUCLEAR WASTE TREATMENT

NEW ENERGIES

The High Liquid Level Waste Concentration collects and concentrates the high liquid wastes which EleTher contain most of the activity of the fuel. Due to the number of elements in the liquid solution, speciation is a big challenge that could help to achieve a better management of the corrosion of the boiler and to understand the development of fouling which results in reduced thermal capacity. In addition a chemical reaction between HCOH and HNO₃ producing NO_x takes place in the boiler.

Challenge: No tool exists capable to describe the large amount of reactions that occur in high concentrated solution.





SALT PRODUCTION

NEW ENERGIES



Pure salt products are often obtained as a solid that precipitates as a result of a chemical reaction. However, many reactants may coexist in the aqueous phase, and it is essential that the correct solid is precipitated.

Industrial example:

- Precipitated Calcium Carbonate (PCC) is a high value product that can be recovered from marble wastes. It is produced by adding CO2 to a CaO rich aqueous solution.

Challenge: Several solid phases can precipitate. In order to model this correctly, there is a need to parameterize both the aqueous phase thermodynamic up to high salt concentration, and the solid phase(s) formation properties. Both have an impact on the results. Only limited data is available.

salt	co-solvent	solute	Property	Tempera range	ture Pressure range
CaCO3; CaO		CO2	solubility (SLE) ; speciation	??	??

