OLI systems, inc.

think simulation | getting the chemistry right

OLI simulation for industrial water treatment

Chemistry, phenomena and unit blocks differentiate Flowsheet: ESP

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The industrial water treatment challenge

Water has and will always be the single-most important human resource. As increasing global population and a changing climate deplete existing water sources, governments have responded by tightening restrictions on water consumption by industrial processes. The *once-through* water usage policy from prior years is now replaced with innovative, water-reuse schemes. At the same time, stringent discharge regulations seek to ensure environmental air and water quality. Industry continues to make strides in improving the air quality of vents and water quality of effluents, and we can expect this trend to accelerate in coming years.

Figure 1 - Wastewater treatment at a petrochemical site

Process simulation is integral in efforts to achieve maximum water reuse and minimum plant emissions. The ability to simulate heat and material balance makes process simulation the cornerstone for designing and optimizing plant operations and discharge. The investment returns to the operator include reducing costs, increasing yields, meeting regulatory limits, and perhaps most important, improves confidence in an engineer's recommendations for treatment schemes.

Current water chemistry simulation capabilities

Despite what has now been over half-a century since the first commercial process simulators were developed, most engineers and scientists developing water-based processes still rely on MS Excel spreadsheets and off-line calculations to complete their work. Compare this to the hydrocarbon-based simulators, where sophisticated process simulation software is available for anything from simple heat balance, to sizing, to cost optimization.

Why the disparity between hydrocarbon-based and water-based simulation

Hydrocarbon-based process simulations commonly define the water stream as simply "H2O", and then the user calculates offline, the effect of the ions and solids in the water. When simulators do include a water chemistry model, the model itself is only as good as the experimental data assembled to validate it, since predicting the properties of water and its constituents without it is impossible.

The challenge of accurately modeling water-based processes

Accurate water-based process simulation can be extremely challenging. Simply put, it is thermodynamically and mathematically difficult to predict the properties of water and its dissolved and precipitating components. As concentrations increases, new phases are likely to form, and the new multi-phase system can have radically different mathematical behavior than the prior state.

Layer on that the variety of chemical mechanisms (adsorption, coprecipitation, nucleation, ion-exchange, oxidation-reduction, precipitation kinetics, etc.) and the engineering processes (membranes, electrolyzers, distillation, deaeration, bioreactors), and a seemingly simple task of predicting the concentration of trace – and possibly toxic – element becomes a seemingly impossible task.

Water-based process simulation, Flowsheet: ESP

A commercial tool is now available that combines the rigors of *electrolyte thermodynamics* with the complexity of industrial water processing.

OLI Flowsheet: ESP (**E**lectrolyte **P**rocess **S**imulation) is an electrolyte-based, mass- and energy-balance process simulator. It is a tool that can model the most demanding of water treatment and water process operation.

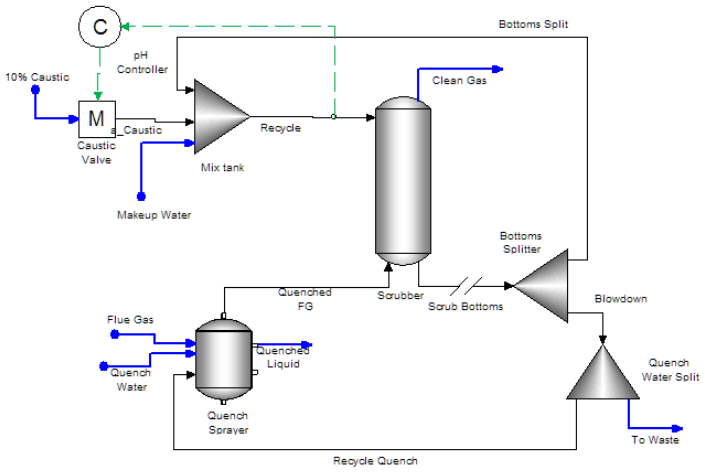


Figure 3 A sample ESP flowsheet

What makes OLI unique

As long ago as 1990, OLI "cracked the code", and created the theory and mathematics needed to predict the chemistry and phase behavior of complex mixtures up to extreme temperatures, pressures and salinities. This combination of thermodynamic theory, thermophysical models, numerical solvers, and databanks is known as the OLI Engine.

Imagine having, in a single tool, the ability to predict oxidation-reduction, surface complexation, ion exchange, precipitation, boiling point elevation, density, thermal conductivity, mineral phase saturation, pH, and other industrial-critical properties. And, doing so over a wide range of temperatures, pressures, and compositions. The OLI Engine is one-of-a-kind technology and available to any user, regardless of their simulation platform.

The chemical thermodynamics is dynamic enough to a range of systems, from oilfield produced water to boiler feed water, to fine chemical purification. The unit operations range from the simple mix and separates to membrane separation, reactive distillation, to rate-limited surface reactions. Below is a short list of applications that can be modeled rigorously with Flowsheet: ESP.

Autoclaves	Flue gas desulfurization	Steam generation
Chemical distillation	Gas sweetening and regeneration	Stripper applications
Claus plants	Membranes	Syngas purification
Cooling towers and cycle-up	Chemical recovery and purification	Clay-resin fixation
Evaporative crystallization	Desalination	Lime softening
Multi-stage evaporation	Pond evaporation	Wastewater treatment

OLI is masterful in developing out-of-the-box solutions for important process chemistry systems. Using a common chemistry base: Na, K, Mg, Ca, Sr, Ba, Al, Fe, and NH_4 cations and Cl, F, SO_4, NO_3, CO_3, and HCO_3 anions, OLI has created a domain of solid phases, adsorption reactions, redox reactions, speciation, and physical properties that clients need to solve the most challenging water treatment problems. Some of recent advances are in:

- Potash mining and processing
- Lithium recovery from Salars
- Pollutant chemistry: arsenic, selenium, mercury (cadmium, planned)
- Natural systems: fulvic and humic acids, surface complexation and adsorption
- Silica removal during lime softening

Flowsheet: ESP

OLI developed ESP Process in 1992, the first steady-state process simulation tool designed specifically for environmental applications. In 2017, OLI rolled out an advanced and updated version of that seminal software.

Flowsheet: ESP simulates the expected operations; mixing, separating, evaporating, condensing, etc., and then goes one step further: chemical kinetics, membrane separation, ion exchange, reactive distillation, and mass-transfer limited column processes. All of this within an electrolyte environment. The adjacent image is a single effect, seawater evaporator. The change in composition, boiling point, and precipitate formation (including double salts) is integral to the simulation.

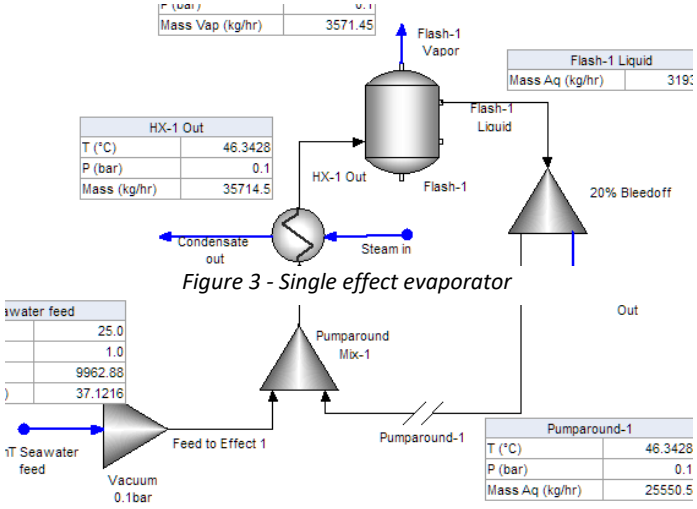


Figure 3 - Single effect evaporator

Essential phenomena and processes for water treatment

Electrolyte processes in natural and industrial systems are recognized for their mechanistic complexity, and our understanding of them continues to evolve.

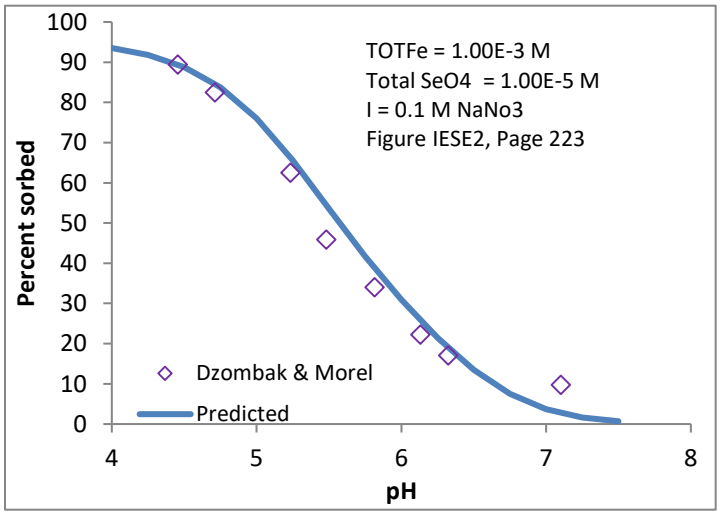


Figure 4 - Selenate adsorption on hydrous ferric oxide. OLI Predictions vs. data published in Dzombak and Morel (1990).

Surface complexation

Selenium removal is through a combination of redox and adsorption reactions. Modeling this quantitatively requires an understanding of selenium thermodynamics and surface complexation mechanisms. This is the chemistry OLI strives to understand.

The image to the left is the predicted selenium adsorption onto ferric oxide, a common adsorbent. Similar reactions exist for arsenic, mercury, and other pollutants. Surface complexation is essential to the water purification process.

Complex mineral phases

A basic, two-salt system can produce many unique solid phases. Adding a third salt can double the number of potential phases and increase their complexity (i.e., double and triple salts). Predicting each phase is important as T, P, and composition change, since it impacts directly, product yield and process optimizing. This requires that the thermodynamic of all phases be quantified.

The adjacent image is the plot of lead solubility in a water-sulfuric acid solution. The six-order-of-magnitude solubility change and the tortuosity of the solubility curve is an indication of the complexities associated with predicting accurately toxic metals like lead.

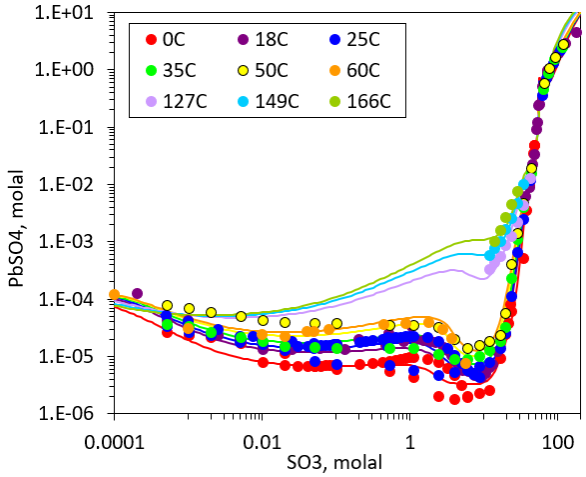


Figure 4 - Lead Sulfate Solubility in Sulfuric Acid

Ion exchange

Exchangeable sites on resins and clays directly affect cation concentrations. The *Selectivity Coefficient*, which governs the exchange reaction, varies with temperature, pH, salinity, and speciation. The ion exchange function embedded in OLI captures these essential factors, making predictions mechanistic in nature.

Kinetics

Kinetic reactions are process and condition dependent and predicting the functional form and rate coefficients of kinetic reaction remain an empirical operation. To accommodate the variety of rate expressions possible for any number of chemical reactions, OLI provides an open-architecture kinetic tool that users can develop using their lab and field data.

Carbon adsorption

Hydrophobic adsorption of organics onto carbon surfaces is a planned mechanism in OLI. The basic fundamentals to model this reaction already exist, and empirical models can be created for the user. Within the next few years, OLI will plant this empirical reaction on more firm thermodynamic footing, making it another process that users can model properly.

Reverse osmosis

The current standard for modeling RO is to use a fixed permeability for an element group, regardless of their speciation or ion size. The more accurate method is to compute the speciation of each component in solution, and based on salinity and temperature, compute their hydration radius. These essential mechanisms are part of the RO membrane unit operation in Flowsheet: ESP.

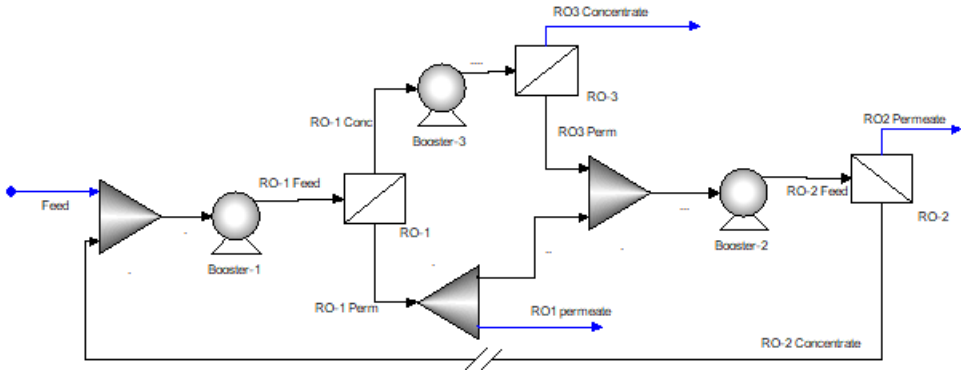


Figure 6 - RO unit operations within Flowsheet: ESP

Furthermore, incorporating the species' diffusivity and electrical mobility transforms the existing empirical approach of RO modeling to a mechanistic tool. Lastly, by taking a mechanistic-speciation approach, it is now possible to predict from first principles the fouling factor and concentration polarization effects on performance. OLI has an ambitious plan over the next several years to expand this mechanistic membrane processes into NF, UF, FO, and ED.

LLE and solvent extraction for electrolytes

Effective design of solvent extraction (SX) units relies on the thermodynamic understanding of metal speciation and its complexation with the extracting agent. Competing reactions between metals and the extracting agent also need to be predicted, so that metal recovery can be optimized.

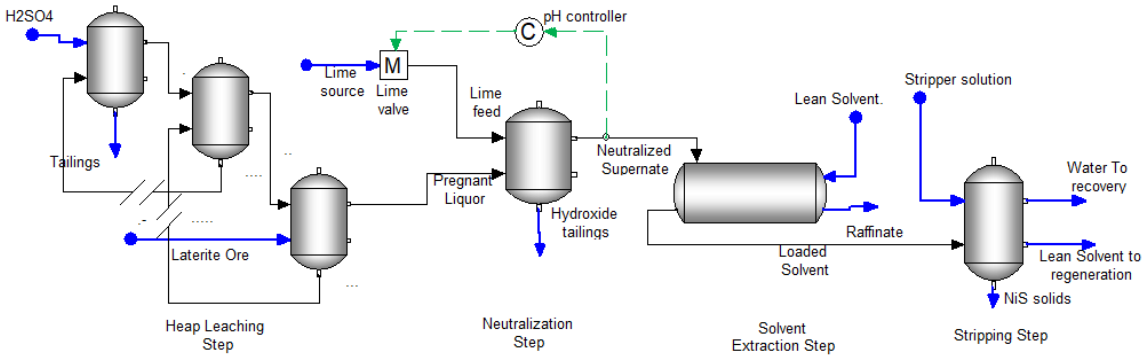


Figure 7 - Solvent extraction of nickel from Laterite ore

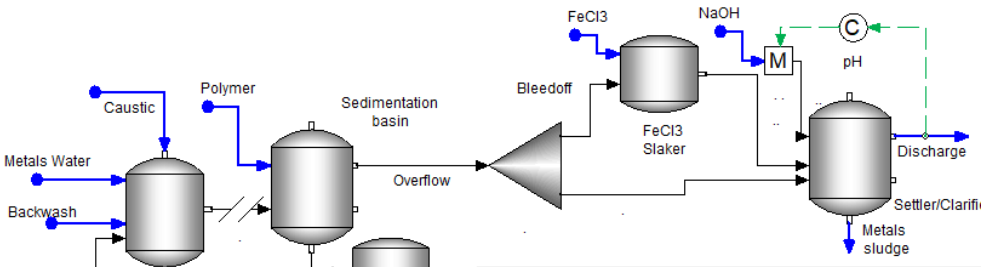
The chemical reactions contributing to SX is well within OLI technology capabilities. Specialized databases can be developed to contain the various extracting agents and solvents that are used in this process. The planned development of electrowinning (EW) within Flowsheet: ESP will complete the simulation circuit, enabling the complete separation process to be modeled mechanistically.

Target applications

The fundamental thermodynamic mechanisms described earlier enable the simulation of a very large range of applications. Below are some examples of applications that can be accurately simulated using OLI's Flowsheet: ESP product

Heavy metal removal from waste water

Removal of arsenic, selenium, lead, and other heavy/toxic metals from waste water via adsorption with water treatment absorbents is quantifiable. The image below is an example of a solvent extraction process where water containing Co^{+2}, Cu^{+2}, Ni^{+2}, and $Pb^{+2}$are removed by adsorption onto hydrous ferric oxide. All metal concentrations are reduced by several orders of magnitude.



Metals Water		Overflow		Discharge	
pH	3.0	pH	8.9998	pH	7.99925
Co(+2) (mg/L)	4.68389	Co(+2) (mg/L)	3.39727e-3	Co(+2) (mg/L)	4.55766e-6
Cu(+2) (mg/L)	0.327992	Cu(+2) (mg/L)	1.7905e-4	Cu(+2) (mg/L)	6.82733e-10
Ni(+2) (mg/L)	10.5888	Ni(+2) (mg/L)	2.07912e-6	Ni(+2) (mg/L)	1.15288e-9
Pb(+2) (mg/L)	0.0279994	Pb(+2) (mg/L)	0.0278795	Pb(+2) (mg/L)	7.49346e-8

Figure 8 - Adsorbing pollutants onto hydrous ferric oxide in a water-treatment plant

Cooling towers

Cycle-up in cooling tower applications is an opportunity to reduce costs and to decrease a company's environmental footprint. The resulting salinity increase, solids buildup, and properties changes are all predictable, even up to zero-liquid discharge conditions. Chemical requirements and engineering modifications needed to meet any regulatory requirement or company goals can be predicted using electrolyte simulation software.

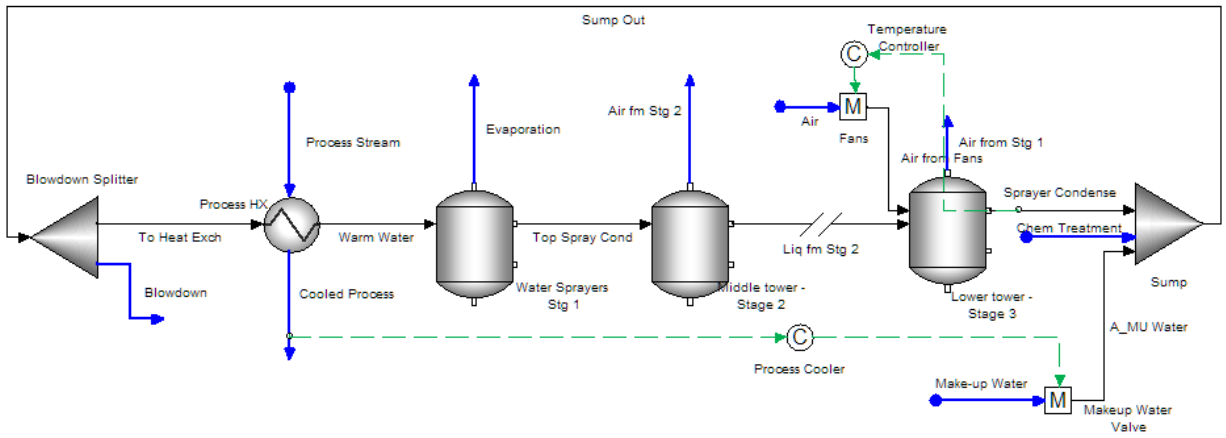


Figure 5 - Modeling a cooling tower in three stages and testing cycle-up conditions

Lime softening and silica removal

The standard lime softening operation relies on acid-base and precipitation reactions. When silica removal is a goal, then the mechanism extends to temperature effects and surface complexation reactions. It is now possible to predict silica removal from process water. Silica can adsorb onto magnesium hydroxide or can precipitate as a magnesium silicate. Both reactions can be computed. Furthermore, measurement of other adsorbing species like borate, can be used as markers to evaluate the overall MgO slaking process.

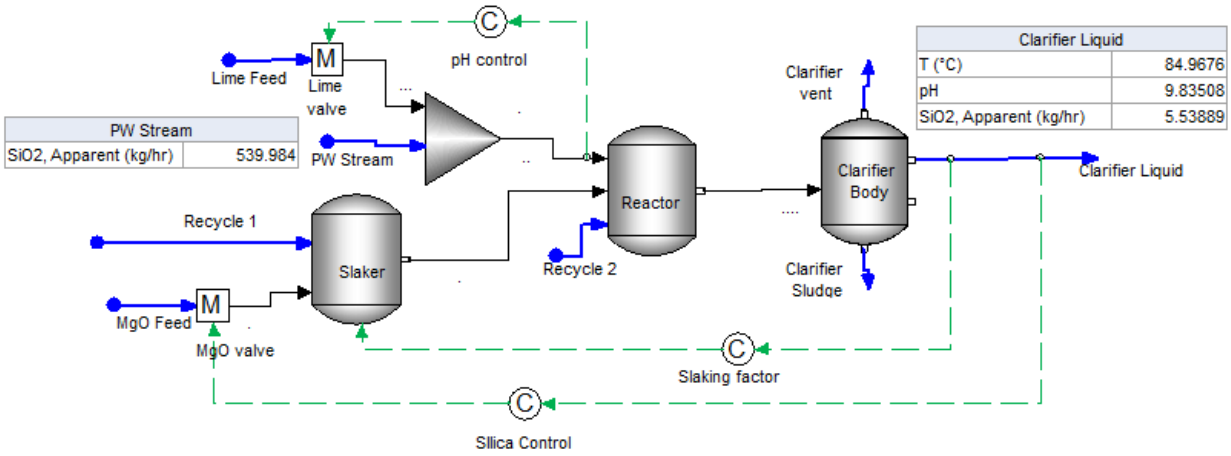


Figure 6 - Lime softener with silica removal and borate adsorption adjustments

New Frontiers

The chemical requirements needed to model membranes, settlers, ion exchange and other units are out of reach for traditional simulators. There was literally no flowsheet simulator available a year ago to model rigorously these chemical processes across industrial and environmental conditions.

OLI Flowsheet: ESP is a breakthrough flowsheet simulator that combines rigorous, state-of-the-science electrolyte chemistry, advanced surface mechanisms, transport properties, and kinetics. This pioneering tool replaces previous estimates and best guesses with accurate calculations.

For more Information

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