A LAB IN YOUR LAPTOP:

OLI SIMULATION FOR HYDROMETALLURGY

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INTRODUCTION

Accurate and reliable simulation of aqueous solution chemistry is a powerful tool for engineers dealing with hydrometallurgical processes. The behaviour of ions in plant solutions is often complicated and counter-intuitive, and practicing engineers do not normally have the resources to evaluate every problem in the laboratory.

OLI provides an easy to use, ready means of predicting the equilibrium behaviour of systems involving aqueous solutions. For a given set of conditions, the OLI engine performs Gibbs Energy minimisation to determine, under equilibrium conditions, the most stable species in solution, solid and gas phases.

After 30 years of development, OLI has the most comprehensive database and solver engine available for simulation of aqueous chemistry. A simple user interface gives power to the non-experts, enabling quick evaluation of process chemistry issues and significant savings in laboratory testing. It does not replace the need for testing, but helps define the test parameters. Rather than re-testing known systems, the user can take advantage of the existing, validated databanks.

This paper seeks to give a simplified, equation–free overview of the application of OLI to hydrometallurgy. There are already numerous papers providing case studies and details of the underlying theory and development. The aim here is to raise awareness and offer engineers some insight into how OLI functions and when it is the right tool for the job.

The basic function of the OLI engine is to combine all known aqueous data into a single, easy to access software program. OLI is based on the belief that predictive modelling of aqueous systems requires that the system be fully speciated. This allows for smoother extrapolation of experimental data with less reliance placed on corrections.

SAMPLE PROBLEM

To illustrate the function of OLI, a simple example problem is taken directly from the OLI user's guide:

What is the pH of a 1M solution of $FeCl_3$?

OLI approaches the problem by developing the full speciation of the system. The water dissociation reaction is always present:

$H_2O = H^+ + OH^-$

The ferric chloride dissolves to form 14 separate species, including the following complexes with the hydroxide ion:

$FeOH^{+2}$, $Fe(OH)_2^{+1}$, $Fe(OH)_3^0$, $Fe(OH)_4^{-1}$, $Fe_2(OH)_2^{+4}$

These complexes shift the water dissociation reaction to the right. The resulting increase in free H^+ ions causes the pH to drop. OLI works out the equilibrium concentration of all the species giving the lowest Gibbs Energy, and provides the answer:

pH = 2.2

The effect of changing concentration, temperature and pressure can be readily evaluated.

The process of aqueous speciation always shifts the water dissociation reaction, in ways that may not be expected. As more components are added, the number of possible species mushrooms and the equilibrium calculations become far more complicated.

AQUEOUS THERMODYNAMICS

OLI can be effectively used without fully understanding the underlying theory, but an appreciation of the fundamentals is useful. This section gives a very brief summary/refresher on the subject for non-specialists. For more details refer to references 1 and 4, downloadable from the OLI website.

Solution chemistry encompasses the chemical equilibria describing

- Ionic dissociation
- Ion pair formation
- Hydrolysis of metal ions
- Formation of metal-ligand complexes
- Acid-base reactions
- Disproportionation reactions

The “Atlas of Electrochemical Equilibrium” was released by Marcel Pourbaix in 1963, with potential-pH diagrams for the elements known at the time. Pourbaix diagrams map out the possible stable phases of an aqueous electrochemical system.

These diagrams are commonly used by hydrometallurgists to identify the likely stable species under given conditions. However, they suffer from several drawbacks. Firstly, they are necessarily based on a single set of conditions of temperature and pressure. Secondly, they are based on a fixed total concentration of a given element. The addition of any metal binding agent may modify the diagram substantially. And thirdly, they only provide the single most stable species at the given Eh and pH. In reality, there are a vast range of stable species at any given point on the diagram.

The key to thermodynamic equilibrium is the Gibbs Energy, or chemical potential. For any thermodynamic equilibrium reaction, the Gibbs Energy of the products is equal to that of the reactants. Gibbs Energy, along with the other principal thermodynamic properties (enthalpy, entropy, heat capacity and volume) can be split into two parts:

- Standard state, a function of temperature and pressure only
- Excess property, a function of temperature, pressure and concentration

The standard-state properties are described by the HKF (Helgeson-Kirkham-Flowers) equations of state. These equations describe the standard state properties of any species in water in terms of seven constants, independent of the data system used to obtain them.

Excess properties are more difficult to model because they depend on the properties of the system, in particular the concentration of the various species present. The excess Gibbs Energy is of most concern with OLI. Gibbs Energy is a function of concentration and activity coefficient. The activity coefficient captures all the non-ideal characteristics of a species, and this is the value that is hardest to predict.

Decades of research have been devoted to the fundamental problem of modelling aqueous activity coefficients in terms of temperature, pressure and concentration. These models generally contain several contributing factors to the excess Gibbs energy:

- Long range electrostatic interactions
- Middle range ionic interactions

- Short range intermolecular interactions

The Debye-Huckel equation, Pitzer extension, Uniquac model and various other models all basically attempt to link activity coefficients with solution concentrations. OLI developed a Mixed-Solvent Electrolyte (MSE) model capable of reproducing speciation, chemical and phase equilibria in the full range of concentrations. The MSE model is now integrated into all OLI products to give the broadest possible range of application.

HYDROMETALLURGICAL DATABASE DEVELOPMENT

A major development program has been underway for several years at the University of Toronto’s Department of Chemical Engineering and Applied Chemistry, in collaboration with OLI. The Aqueous Process Engineering and Chemistry group, led by Professor Papangelakis, is supported by an international consortium of metal producers. The default database is being improved to cover industrially significant processes including high temperature nickel leaching and refining operations.

Papangelakis and Azimi (Ref 3) offer three reasons why chemical modelling in hydrometallurgy is essential:

- To understand and explain the process limits
- To be more predictive outside the range of available data
- To develop predicting the chemistry of hydrometallurgical solutions of varying compositions and temperatures

A methodical strategy has been developed to develop model parameters for the MSE databank. The strategy involves firstly determining solubility and thermodynamic properties for a binary system. Solubility data for ternary systems is then developed. A validation stage is then used to examine the predictability of the parameters on multi-component systems.

OLI PRODUCT SUITE

- OLI StreamAnalyzer – the general purpose OLI database and solver engine for surveys and single point calculations. Calculations include boiling points, dew points, vapour fractions, precipitation points, titration curves and solubility surveys.
- ESP (Environmental Simulation Program) – The OLI steady-state process simulator. This was developed for environmental applications but can be used for any aqueous chemical process.
- Corrosion Analyser – Elemental and alloy metal oxidation and reduction reactions are used in a predictive thermodynamic model to identify the causes of corrosion.
- ScoreAnalyzer – An add-on to StreamAnalyzer, it is mostly used in oil and gas production to analyse scaling tendancies.
- Alliance Engines – OLI provides a link to flowsheet simulators such as UniSim, Aspen and IDEAS.

RANGE OF APPLICATION

The OLI model is subject to several limitations, listed in the table below.

Temperature	-50 to +300 deg C
Pressure	0 to 1500 atm
Mole fraction of water (in liquid phase)	0.65 to 1.0

In addition, the system must be covered in the OLI databank. Regressions have been done for a vast number of binary systems plus over 100 ternary systems. For most common systems it is safe to assume the regression has been done, but a lower accuracy can be expected with unusual systems.

There are numerous reviews available of the electrolyte solution models. Put simply, the further we get into high temperatures, high concentrations, multi-component and supercritical systems, the less is understood of the physical principles. However, there is substantial progress being made and the available models cover many practical problems encountered in industry.

OLI has been applied to a range of industrial applications, including:

- Environmental: Treatment of gases, wastewater chemical wastes
- Separation processes: Crystallisation, distillation, desalination, bioseparation
- Electrochemical processes: Electrolysis, corrosion
- Supercritical technology
- Oil and gas
- Hydrometallurgy

These processes cover a wide range of chemical compositions and conditions, as well as a numerous physical phenomena. The databank continues to grow as more and more applications are found.

Aqueous solution chemistry can be described by equilibrium thermodynamics. Dissociation and complexation are very fast reactions and kinetics is not likely to be an issue. However, reactions involving solids, whether precipitation or leaching, are generally much slower than reactions within the aqueous phase. OLI does not deal with reactions kinetics, but can accurately describe the conditions within the solution (i.e. internal equilibrium) at a point in time, while there are slower leaching/precipitation reactions going on in the broader system.

CASE STUDIES

There have been numerous case studies published in the technical literature. A few examples relevant to nickel hydrometallurgy are summarised below:

GYPSUM SOLUBILITY

Several papers have been published dealing with calcium sulphate hydrates. The chemical behaviour of gypsum is variable and difficult to predict with respect to solution conditions. Several rules of thumb are used to predict behaviour in water, but moderate concentrations of other metals will confound the rules.

Gypsum scale is a well known problem in hydrometallurgical plants, particularly in neutralisation circuits. A hard, crystalline deposit may stick to the surface of tanks, pipes and other equipment, with significant loss of efficiency and capacity, and downtime to remove scale.

OLI has been used to accurately model gypsum scaling behaviour over a wide range of temperature and concentrations. A relationship between fouling rates and process conditions has been developed, which is the key step in minimising fouling rates.

NICKEL LATERITE HIGH PRESSURE ACID LEACHING

Pressure acid leaching of nickel laterites involves a complex set of dissolution and precipitation reactions. The rate of nickel dissolution depends strongly on the pH at the operating temperature, while the acid consumption depends on the nature of the precipitation reactions.

OLI has been extensively applied to determine the solution speciation and precipitation products, and the effect on pH and acid consumption.

The study by Liu et al (5) focussed on the solubility of aluminium, and effect of process conditions on the precipitation of sodium and hydronium alunite. OLI was used to evaluate equilibrium constants for the Al-Mg-Ni-Fe-SO_4 system, and explain the impact of acid, magnesium and aluminium on alunite precipitation.

Another study (6) focused on the solubility of hematite in pressure acid leaching. Iron is basically leached as goethite and precipitated as hematite. Under these conditions, the solubility of hematite decreases with increasing temperature. The relationship is complicated by the presence of other ions in solution. OLI was successfully used to model the solubility of hematite in leach solutions at temperatures of 230 – 270C.

OXYGEN SOLUBILITY – POX LEACH

OLI was used to predict the solubility of oxygen in acidic zinc sulphate solutions, at temperatures from 25 – 250C (Ref 3). The relationship between solubility and temperature, zinc concentration and acid concentration were determined by experiment and compared against OLI predicted values. In each case, close agreement was reported.

IN CONCLUSION

OLI is a powerful tool for chemical modelling in hydrometallurgy. Reagent requirements, impurity levels, solution speciation, scaling tendencies are all understood in terms of solution chemistry and are computed in terms of ore composition and temperature. Its range of application is growing due to an ongoing research effort to expand the database, particularly for hydrometallurgical processes.

No simulation package can eliminate the need for laboratory test programs; OLI is limited to thermodynamics and cannot predict rates of leaching or precipitation reactions. However, it can be used to better focus test programs on site specific issues and avoid re-testing of known systems. The savings in cost and time of pilot programs can be substantial.

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