

GIBBS ENERGY MINIMISATION FOR PROCESS SIMULATIONS AND AN EXAMPLE IN URANIUM SOLVENT EXTRACTION

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CONTENTS

1. INTRODUCTION	2
2. THEORY	2
3. HURDLES FOR GIBBS ENERGY MINIMISATION MODELLING.....	4
4. JUSTIFYING AND ENABLING GIBBS ENERGY MINIMISATION.....	4
5. URANIUM SOLVENT EXTRACTION EXAMPLE	6
6. OTHER OPPORTUNITIES FOR GIBBS ENERGY MINIMISATION MODELLING	11

1. INTRODUCTION

Mass and energy balance simulations form an integral part of metallurgical process design, from concept level studies through to detailed design. To build an efficient process plant, that maximises production with least capital and operating costs, an accurate model of the flows and the chemistry involved in the process is indispensable for all but the simplest of processes. For existing operations, a mass and energy balance is essential for optimisation of the existing process. Also, the consequences of proposed modifications to the process can be assessed quickly, before purchasing any new equipment. In an engineering study, a mass and energy balance is usually created at the concept level, with limited detail, and expanded in the later study phases to contain more detail of both the chemistry and the minor process flows. The selection of tank and pond volumes, pipe diameters, materials of construction, power requirement for motors, and most other design parameters rely on accurate predictions of the conditions that the plant will encounter through the life of the resource.

A mass and energy balance model, as with all models, will always be a simplified representation of reality. The level of detail with which a process is simulated need only be enough for the purpose for which it is being created. As an example, the chemical phenomena occurring in the high temperature and pressure soup of an HPAL autoclave need not be modelled unless they are relevant to the design of the autoclave or downstream processes. The precise reaction or mechanism is usually irrelevant in this case, provided the distribution between phases and the oxidation states of the elements is adequately characterised. While valid in many instances, this philosophy is an easy one to apply irresponsibly. When forming a process design criteria, previous experience from engineers will often be agreed upon as the basis for critical design parameters, but these figures may be biased towards similar, but not identical processes, where a critical factor has not been considered that may drastically affect the result. Future phases of work, and testwork, should hopefully decrease the risk associated with this, but in some cases, the outcome could be disastrous. In this case, had the model been more predictive and less biased towards past experiences, alarms warranting investigation may have been triggered much earlier in the process design.

2. THEORY

Gibbs energy (G), is defined as $G = H - TS$, where H and S are enthalpy and entropy respectively and T is temperature. At constant pressure and temperature, chemical reactions are spontaneous in the direction of decreasing G ⁱ. At chemical equilibrium, no reaction is spontaneous, therefore G is at minimum. The equilibrium composition of a mixture of reactants, at a given temperature and pressure, is the mixture of products which produce the lowest value of G . Mass must of course be conserved, so the moles of each element is the same in the reactant mixture as in the product mixture.

The technique of Gibbs energy minimisation to estimate the equilibrium composition for a given set of species is enabled by many process simulation packages, including OLI Systems Stream Analyserⁱⁱ, FactSageⁱⁱⁱ, Aspen Plus^{iv}, METSIM^v and HSC Chemistry^{vi} among many others. The software packages have varied levels of sophistication, with some able to predict the behaviour of non-ideal solutions at elevated temperature and pressure. Gibbs energy minimisation has been used to characterise many pyrometallurgical systems^{vii,viii}. FactSage is now usually favoured for pyrometallurgical calculations due to its comprehensive databases of molten and solid solution phase equilibria. In hydrometallurgy, OLI Systems Stream Analyser is often favoured for its ability to simulate non-ideal behaviour in concentrated solutions of most aqueous chemical species. The application of Gibbs energy minimisation to solvent extraction is limited due to the lack of available data for the enthalpy and entropy of loaded organic species. Several efforts have been made to determine the Gibbs energy of metal complexed organic extractants from experimental data^{ix,x,xii}, but the technique is not usually employed by engineering firms during solvent extraction circuit design or existing circuit simulation.

Solving for minimum Gibbs energy is an example of a constrained optimisation problem, for which there are many computational methods available. A simple method of minimising Gibbs energy is described elsewhere^{xii}. This method is used by HSC Chemistry to approximate the equilibrium composition of a mixture of selected components. As an example, for the assumed gas species: CO_2 , H_2O , CH_4 , O_2 , CO and H_2 , reacting 1 mol of O_2 with 1 mol of CH_4 at 500°C and 1 bar produces the mix of species shown in Table 1. The product mixture is calculated without needing to define any chemical reactions.

Product	mol
CO ₂	0.575674
H ₂ O	0.766929
CH ₄	0.342603
O ₂	9.01E-28
CO	0.081723
H ₂	0.547865

Table 1: Simplified product composition calculated by HSC Chemistry when reacting 1 mol of CH₄ with 1 mol of O₂ at 500°C and 1 bar

In this example, soot (graphite, C) is omitted as a possible reaction product so it is ignored in the calculations. Had it been included, the resulting product composition would have been significantly affected. Comparison of the predicted compositions, with soot allowed and without soot allowed is shown in Table 2.

Product	Without Soot (mol)	With Soot (mol)	Difference (%)
CO ₂	0.575674	0.542709	6%
H ₂ O	0.766929	0.842541	10%
CH ₄	0.342603	0.297331	13%
O ₂	9.01E-28	1.03E-27	15%
CO	0.081723	0.072041	12%
H ₂	0.547865	0.562797	3%
C (solid)	-	0.08792	-

Table 2: Product composition calculated by HSC Chemistry when reacting 1 mol of CH₄ with 1 mol of O₂ at 500°C and 1 bar, with and without soot formation allowed

It is therefore extremely important to know which species are likely to form when setting up an HSC Gibbs minimisation problem as incomplete speciation may give erroneous results.

It is also possible to calculate the isenthalpic product temperature and equilibrium composition by using the StreamH function in HSC's Excel Add-In in conjunction with Excel's goal seek function to set the product enthalpy to equal the reactant enthalpy. For example, if 1 mol of CH₄ and 1 mol of O₂ is reacted with 5 mol of H₂O gas, with each reactant at 25°C, for constant enthalpy, the product temperature is 1059°C and the product mixture is shown in Table 3.

Product	mol
CO ₂	0.629898
H ₂ O	5.370102
CH ₄	2.15E-07
O ₂	1.91E-12
CO	0.370102
H ₂	1.629897

Table 3: Simplified product composition calculated by HSC Chemistry when reacting 1 mol of CH₄ with 1 mol of O₂ and 5 moles of H₂O at constant enthalpy (reactants at 25°C, products at 1059°C) and 1 bar

3. HURDLES FOR GIBBS ENERGY MINIMISATION MODELLING

The modelling of chemical reactions in metallurgical process models is usually based on either testwork data, or some form of previous experience. Predictive tools such as Gibbs energy minimisation ('free energy' minimisation: FEM) are infrequently used in metallurgical process plant design. There are two main reasons for this:

- There is less likelihood, or at least a lower perception of likelihood, of errors being made when testwork data is used. It is hard to argue with experimental data and past experience.
- The cost, or perception of cost, both in man-hours and to project schedule, associated with complex simulation methods is often prohibitive in metallurgical studies.

The first reason is clearly a valid one. The complex suite of chemical species encountered in hydrometallurgical process streams will often behave in unexpected ways. The solubility of calcium in mixed sulphate solutions at varied pH, for example, has long been the bane of process engineers encountering gypsum scaling in places where they wouldn't have hoped to see it. Pyrometallurgists encounter molten, immiscible phases containing many more than the three or four elements usually shown on conventional phase diagrams. Trace elements can affect the melting point of each phase. The relationships between phase equilibria, for molten systems containing more than four elements are difficult to predict. It is no wonder that when a mining company employs an engineering consultancy to develop a mass and energy balance model of their future or existing process plant, testwork, or existing plant data generally settles the nerves more than the predictions of a computer-savvy engineer.

The second, cost related reason, why FEM is not often used for metallurgical process plant design, is explored in the following section.

4. JUSTIFYING AND ENABLING GIBBS ENERGY MINIMISATION

There are many instances when the chemistry involved in a metallurgical process can be accurately predicted from first principles, especially when thermodynamic equilibrium can be assumed:

- Gas phase reactions at elevated temperature will often be at chemical equilibrium and the behaviour will often be close to ideal. Here, FEM can be used to predict the gas composition accurately.
- The composition of many aqueous streams in hydrometallurgical refineries is often limited to a small number of elements due to selectivity in upstream solvent extraction or ion-exchange processes. The chemistry of such chemical systems may be well documented in the literature, and accurately predictable by such tools as OLI Systems Stream Analyzer, FactSage, or HSC Chemistry.
- The extraction and stripping of metals by solvent extraction can in simple cases be accurately predicted by FEM, if the entropy and enthalpy of the extractant and the metal complexed extractant molecule is known, or can be calculated from literature data.

- The selective complexation of metal ions to ligands such as ammonia or cyanide can also be predicted by FEM.
- Many vapour / liquid equilibrium systems are accurately characterised in the literature and can be simulated with accuracy for a range of temperatures and pressures.

In each of these cases, FEM can be used to produce mass and energy balance data with confidence of accuracy. Validation from testwork and previous experience should still remain an important part of the review process, but in this way, there are two sets of data arrived at independently, that can be compared for consistency: a calculated set and an anticipated set. FEM generates a new, independent set of information. If the predicted values don't agree with the anticipated values from previous projects, further investigation may discredit the anticipated values which could otherwise have been accepted unchallenged. Conversely, if the Gibbs model proves to be incorrect, the lessons learnt by explaining the deficiencies in the predictive model could prove invaluable to the project by increasing the fundamental knowledge of the engineers involved.

The two software packages most commonly used in industry until 2007 for steady state metallurgical mass and energy balance models were SysCAD (ProBal), and METSIM. Typically, a new model would be created from scratch for every metallurgical plant modelled in either of these packages. While there are many similarities in technology between process plants around the world, every process plant in the world is unique, due to subtle variations in ore body mineralogy. Setting up a model in both METSIM and SysCAD generally first involves setting up the thermodynamic data of chemical species to be encountered in the process. The model structure (tanks, reactors, chemistry etc) would be constructed after this. While it is possible to copy sections of a model from one model to another, when a new model has similarities to an old model, the time and difficulty involved often makes it seem easier to rebuild the model section from scratch. The implications of this are that if a complex, predictive model is built for one process plant, it would usually be rebuilt from scratch for every subsequent process plant to use the same technology. The inefficiencies of such a situation would decrease the appeal of such a model.

IDEAS (Bronze) is a modelling package, similar in many ways to both METSIM and SysCAD. Chemical species are defined, then the model's structure is built. The model can output stream information to Excel in much the same way as SysCAD and METSIM. One point of difference between the packages is copy and paste functionality. IDEAS allows you to select parts of a model and duplicate them, either in the same or in a different model. If the chemical species in the different models aren't identical, there may be difficulties in copying the chemical reactions or some of the settings in the model structure relating to chemical species or elements, but overall, duplicating past work is made significantly easier by the IDEAS software. It follows that if a complex, predictive model is constructed in IDEAS, it is relatively easy to distribute it into as many subsequent models as desired. This reduces the cost impact of the development of predictive models in metallurgical simulations. A section of a model, with complex controls or predictive algorithms, can be built, and stored in a library of complex models, to be used as needed for future studies without significant rework. Time spent on improving the graphic user interface, or other features to improve the usability for future clients, can now be cost effective because the work need not be repeated again at a later date.

METSIM already contains an FEM object. It uses the Gibbs data entered in the component properties library. Most of the components in the METSIM component library already have Gibbs correlations, but the author recommends that they be validated with another source such as HSC Chemistry before being applied with confidence. In some instances accuracy in a tight temperature range may be desired, so the broad correlations applied to components in METSIM may need "tweaking" for higher accuracy at the desired temperature. The METSIM FEM object operates quickly and accurately, both for adiabatic calculations and for isothermal mode (with calculated enthalpy loss or gain). Chemical reactions do not need to be specified. The object instead solves for the minimum free energy, constrained to the chemical components defined in the model, with conservation of mass for all elements.

IDEAS does not currently have the capacity to do FEM calculations, however as chemical component data can be imported from HSC Chemistry, all the data required to do this already exists in the software, so there is scope for future programming to allow this to happen if there is a need in the industry. It is possible to run FEM models through IDEAS indirectly, by linking IDEAS to Excel through continuous dynamic data exchange (DDE), where a spreadsheet has been set up using HSC Chemistry's Gibbs minimisation array user-function through the HSC 6 Excel Add-In feature. This method is not ideal, because reaction chemistry is still required and links between output composition setpoints and chemical reaction extents need to be established. The benefit with IDEAS however, as previously mentioned, is that after setting the model up once, it need not be repeated in the future.

For single point, or simple correlations that do not require integration into a full mass and energy balance model, the software packages: FactSage for pyrometallurgical processes, or OLI Stream Analyser for hydrometallurgical processes, can be used to calculate the equilibrium in complex, non-ideal multiphase systems. Output data from these packages can also be used to develop simplified correlations to be used in a full mass and energy balance model in another package like METSIM, IDEAS or SysCAD.

5. URANIUM SOLVENT EXTRACTION EXAMPLE

Solvent extraction is the most common extraction route for uranium from sulphuric liquor. One of the most common organic extractants used for the extraction of uranium is Alamine® 336, an octyl / decyl tertiary amine manufactured by Cognis^{xiii}, usually diluted in kerosene.

Estimating the effect of operating parameters such as the organic to aqueous flow ratio, pH, uranium concentration, extractant concentration, etc, on the equilibrium of the system, is usually achieved by a testwork program. Such testwork requires representative samples of the aqueous uranium feed liquor and usually several weeks of laboratory testing. The benefit of a generic model that could predict to reasonable accuracy the behaviour of a solvent extraction circuit operating under a wide range of conditions is evident. Unfeasible circuit options could be eliminated during the early phases of a desktop study before any money was spent on testwork. Multiple flowsheet scenarios could be examined quickly at low cost. For existing operations, the model could be of use for troubleshooting, or for examining the likely effect of modifications to process parameters before trialling them in reality.

The purpose of the work described in this paper is to demonstrate that a relatively simple model can be prepared in Microsoft Excel combined with HSC Chemistry software, using few experimental correlations gathered from the literature, that can predict the behaviour of uranium in an Alamine® 336 solvent extraction circuit at any pH, to a degree of accuracy high enough for preliminary design work, based on Gibbs energy considerations alone.

Justification for the speciation selection, and the method used to approximate the thermodynamic data required for Gibbs energy minimisation modelling is presented in the following sections.

5.1 AQUEOUS SPECIATION

There are numerous chemical species present, both in the aqueous and organic phases, during the loading and stripping of uranium, that affect the performance of the solvent extraction process. All such species should be taken into account to improve the reliability of the model. The predicted speciation, present in sulphate solutions of uranium with ammonia and sulphuric acid used for pH control, was determined using OLI Stream Analyser software. The H⁺ databank was used and redox chemistry was excluded. The aqueous species considered are shown in Table 4.

H ₂ O	(UO ₂) ₂ (OH) ₂ ²⁺	OH ⁻
UO ₂ SO ₄	(UO ₂) ₃ (OH) ₅ ⁺	SO ₄ ²⁻
H ₂ SO ₄	H ⁺	UO ₂ (SO ₄) ₂ ²⁻
NH ₃	HSO ₄ ⁻	UO ₂ ²⁺
UO ₂ (OH) ₂	NH ₄ ⁺	UO ₂ OH ⁺
NH ₄ SO ₄ ⁻	SO ₃	

Table 4: Aqueous species present in H₂O / UO₂SO₄ / H₂SO₄ / NH₃ system

The database included with HSC Chemistry 6.1 includes enthalpy and entropy data for all components in Table 4 except NH₄SO₄⁻. The OLI results suggest that this specie is a major constituent so the component was added to a custom HSC database and enthalpy and entropy of formation data were approximated from results obtained by OLI. The estimated HSC database parameters for NH₄SO₄⁻ are:

$$H = -1042.4 \text{ kJ/mol}$$

$$S = 127.7 \text{ J/(mol.K)}$$

The parameters for NH_4SO_4^- may not be correct, but they result in similar predicted concentrations of NH_4SO_4^- in the HSC Gibbs calculations for the system being examined at both 25°C and 50°C and thus are fit for the current purpose.

HSC version 6.0 and above has an Excel Add-In feature that allows equilibrium calculations to be set up in Excel. It is a relatively simple model based on an early Gibbs minimisation technique^{xiv}, that uses the enthalpy and entropy data from the HSC database to estimate equilibrium composition at a given temperature and pressure. Currently, there is no way of incorporating activity coefficients into the model, but Outotec is currently working on including this in future versions of the software. By using Excel, this allows the flexibility of using the “goal seek” feature to achieve target pH (approximated as $-\log[\text{H}^+]$) by adjusting H_2SO_4 or NH_3 input to the system. Equilibrium compositions at any pH can thus be estimated.

Results from OLI were validated against HSC by comparing the outputs for a 0.1M solution of UO_2SO_4 with trace NH_3 , with H_2SO_4 adjusted to achieve 3.0 for $-\log[\text{H}^+]$ in the HSC output. The results are presented in Table 5. Note that HSC cannot predict the activity of the H^+ ion, so calculated “pH” from HSC data is only approximate.

HSC Species	Input mol	HSC Output mol	OLI Output mol
$\text{H}_2\text{O}(\text{l})$	5.55E+01	5.55E+01	5.55E+01
$\text{UO}_2\text{SO}_4(\text{a})$	1.00E-01	8.42E-02	6.01E-02
$\text{H}_2\text{SO}_4(\text{l})$	4.69E-04	2.70E-15	2.14E-17
$\text{NH}_3(\text{a})$	1.00E-07	5.78E-14	4.03E-14
$\text{UO}_2(\text{OH})_2(\text{a})$		4.01E-09	3.37E-09
$(\text{UO}_2)_2(\text{OH})_2(^{+2}\text{a})$		2.69E-04	5.40E-04
$(\text{UO}_2)_3(\text{OH})_5(^+\text{a})$		3.35E-07	2.31E-07
$\text{H}^+(\text{a})$		1.00E-03	1.33E-03
$\text{HSO}_4^-(\text{a})$		5.38E-04	7.64E-04
$\text{NH}_4^+(\text{a})$		9.96E-08	9.28E-08
$\text{NH}_4\text{SO}_4^-(\text{a})$		4.12E-10	7.23E-09
$\text{OH}^-(\text{a})$		1.03E-11	1.33E-11
$\text{SO}_4^{2-}(\text{a})$		6.51E-03	2.06E-02
$\text{UO}_2(\text{SO}_4)_2(^{-2}\text{a})$		4.62E-03	9.48E-03
$\text{UO}_2(^{+2}\text{a})$		1.06E-02	2.92E-02
$\text{UO}_2\text{OH}^+(\text{a})$		5.96E-05	7.24E-05
pH		unknown	3.009
$-\log [\text{H}^+]$		3.000	2.877

Table 5: OLI and HSC predicted aqueous species for 0.1M UO_2SO_4 at approximately pH = 3

The concentration of aqueous SO_3 calculated by HSC was erroneously high. OLI predicts it to be present in very low concentrations under all solvent extraction pH conditions. This specie has thus been excluded from the HSC model. The results in Table 5 show that the HSC Gibbs energy minimisation model agrees reasonably well with OLI for all other species and is thus suitable for an approximation of the aqueous phase behaviour.

5.2 ORGANIC SPECIATION

Unlike the aqueous phase, which contains common, well characterised species, Alamine® 336 and the organic complexes present during uranium loading and stripping are not well characterised. Enthalpy and entropy data for trinonylamine (N,N-dinonyl-1-nonanamine) is included in the HSC 6.1 database. While Alamine® 336 is a mixed octyl / decyl ternary amine (R3N), it will be assumed that Alamine® 336 has the same properties as trinonylamine due to their similar molecular structure. All complexed forms of Alamine® 336 will be assumed to be complexed forms of trinonylamine.

The species listed in Table 6 are the assumed constituents and data for these species are required to model the organic phase. The kerosene diluent is assumed to have the composition of decane for simplicity, but remains an unreactive component so this assumption does not affect results.

The majority of the available literature data is for experimental results at 25°C. To model the effect of temperature, both enthalpy and entropy data would be required. The model created in this current study is limited to 25°C so Gibbs energy is reduced to being a function of component enthalpy only.

$C_{10}H_{22}$	Kerosene
R_3N	Alamine® 336
R_3NHHSO_4	Protonated Alamine® 336 bisulphate
$(R_3NH)_2SO_4$	Protonated Alamine® 336 sulphate
$(R_3NH)_2UO_2(SO_4)_2$	Alamine® 336 uranyl complex #1
$(R_3NH)_4UO_2(SO_4)_3$	Alamine® 336 uranyl complex #2

Table 6: Assumed organic speciation

5.2.1 Acidification

Before the extraction stage, the amine is acidified with sulphuric acid, according to reactions (1) and (2) to ensure that no contaminating anions are loaded onto the organic prior to uranium extraction.



Reactions (1) and (2) produce two distinct acidified organic species, that are present in varied proportions depending on the equilibrium conditions. Reaction (1) is also responsible for the stripping ability of concentrated sulphuric acid on loaded organic.

The acid loads onto the organic as pH is decreased. Below a certain pH, the acid saturates the organic and the proportion present in the aqueous phase increases. The distribution of acid between the aqueous and organic phase was studied by Yakubu and Dudeney^{xv}. For the Gibbs minimisation model to accurately predict the acidification behaviour of Alamine® 336, two species: $C_{27}H_{57}NHHSO_4(l)$ and $(C_{27}H_{57}NH)_2SO_4(l)$ were added to a custom HSC database and enthalpy data for both species was adjusted until the Gibbs model output was as close as possible to the Yakubu and Dudeney results. The results are presented in Figure 1, where acid in organic is the sum of molar concentrations of both acidified organic species from (1) and (2) and acid in aqueous is the sum of the sulphate, bisulphate and undissociated H_2SO_4 .

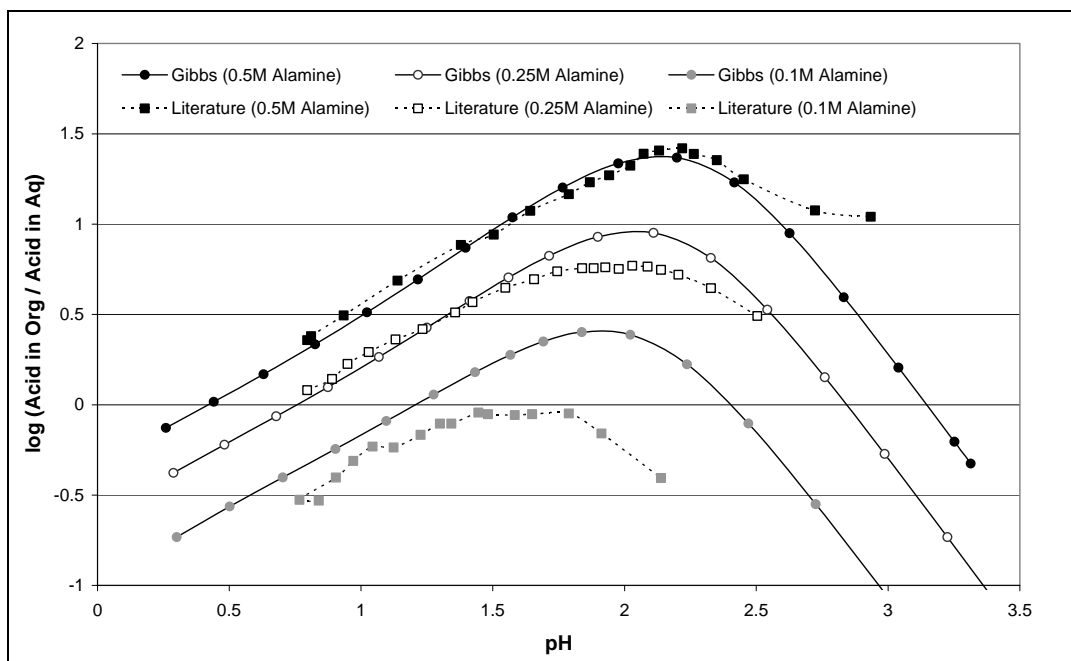
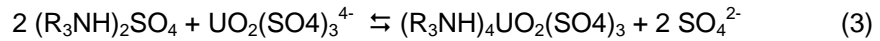


Figure 1: Comparison of Gibbs minimisation model and literature data for the acidification of Alamine® 336

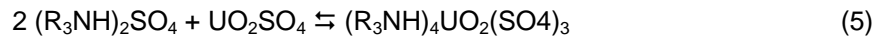
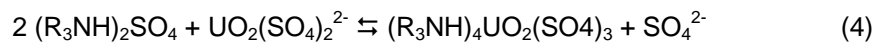
The results show good agreement at low pH but deviate at higher pH, especially at the lowest Alamine concentration of 0.1M.

5.2.2 Uranium extraction

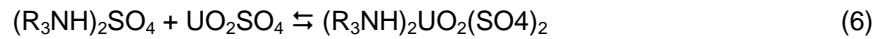
Uranium is loaded onto Alamine® 336 as an anionic complex. It has been demonstrated¹³ that there are two predominant uranyl complex species present in the loaded organic: $(R_3NH)_4UO_2(SO_4)_3$ and $(R_3NH)_2UO_2(SO_4)_2$. The predominant complex was found to be $(R_3NH)_4UO_2(SO_4)_3$ under most uranium extraction conditions, implying that 4:1 Alamine® 336 : uranium molar ratio is required for near-complete extraction. It is interesting to note that the existence of the aqueous anionic species $UO_2(SO_4)_3^{4-}$ is questionable^{xvi,xvii} so the formation of $(R_3NH)_4UO_2(SO_4)_3$ appears unlikely to follow reaction (3).



Mechanism (4) or (5) appears most likely.



Similarly, for the formation of $(R_3NH)_2UO_2(SO_4)_2$, the reaction mechanism is likely to follow (6).



The species $(C_{27}H_{57}NH)_2UO_2(SO_4)_2(l)$ and $(C_{27}H_{57}NH)_4UO_2(SO_4)_3(l)$ were added to a custom HSC database. Uranium extraction data from the Yakubu and Dudeney study^{xv} was plotted for a range of Alamine® 336 concentrations vs pH. The enthalpy parameters for $(C_{27}H_{57}NH)_2UO_2(SO_4)_2(l)$ and $(C_{27}H_{57}NH)_4UO_2(SO_4)_3(l)$ were varied, until the Gibbs model most closely approximated the experimental results. The results are presented in Figure 2.

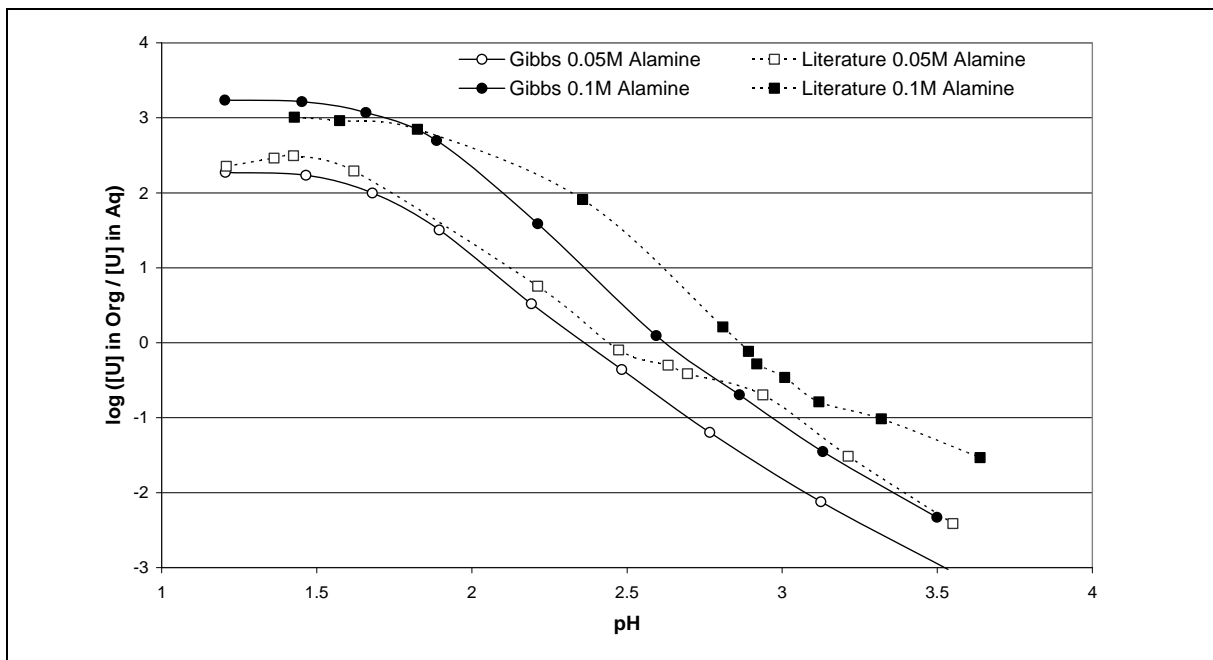


Figure 2: Comparison of Gibbs minimisation model and literature data for the uranium loading behaviour on Alamine® 336

The Gibbs model agrees reasonably well with the literature data although the Gibbs model predicts lower than anticipated uranium loading at pH > 2.

5.2.3 Testwork validation

A testwork program was recently completed for a uranium mining client. The pregnant leach solution is exceptionally clean of contaminant metal anions, so this testwork was considered ideal for the validation of the Gibbs model. The extraction isotherms from the testwork were compared with predicted results from the Gibbs model, comprised of the aqueous and organic species defined in Sections 5.2.1 and 5.2.2.

Extraction isotherms were prepared for three concentrations of Alamine® 336 with varying initial U_3O_8 concentration in aqueous feed. The organic solutions were made up using fresh Shellsol, isodecanol and Alamine® 336. Each isotherm was prepared using eight equilibrium points by varying the organic to aqueous ratio.

The individual data points for each series were calculated using the Gibbs model, using goal-seek in Excel to achieve the target pH (assuming $pH = -\log[H^+]$) for each data point by adjusting sulphuric acid in the feed. The testwork and Gibbs model isotherms are presented in Figure 3 although axis values are hidden due to confidentiality constraints.

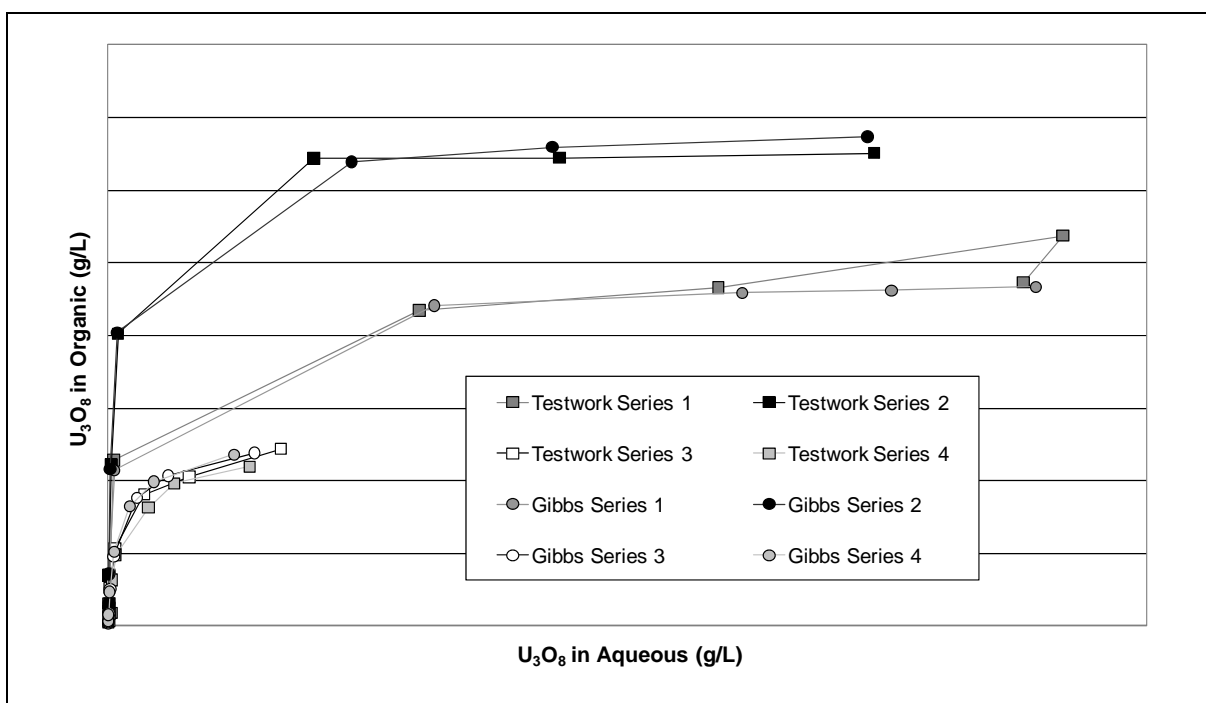


Figure 3: Testwork and Gibbs minimisation extraction isotherm results

The predicted isotherms agree exceptionally well with the testwork results for all testwork series. By using relatively little literature data, it has been possible to create a generic solvent extraction model for the solvent extraction of uranium by Alamine® 336. Testwork extraction isotherm results were predicted to high accuracy by the Gibbs model.

Gibbs energy minimisation could be used during the early phases of an engineering study, to generate first-pass isotherm predictions before the execution of a testwork program. Such a model could be developed for other solvent extraction systems, using other extractants, with predictive speciation for more than one metallic loading element.

For an existing solvent extraction plant, operating with a consistent leach solution composition, the Gibbs model could be improved by customising it for the plant conditions. Specie thermodynamics could be adjusted to increase the model's accuracy for a specified leach solution. The more accurate model could be used to evaluate plant "what if" scenarios quickly and at low cost.

6. OTHER OPPORTUNITIES FOR GIBBS ENERGY MINIMISATION MODELLING

6.1 REDUCTION OF SULPHIDE ORES BY SYNGAS

Coal or other hydrocarbon fuels can be decomposed in a gasifier to produce a gas containing large proportions of H_2 and CO. This "syngas" could be used for the reduction of metal sulphide concentrate in a fluid-bed. The decomposition of the hydrocarbon in the gasifier can be assumed to be at equilibrium and can hence be modelled by FEM. For hydrocarbon FEM modelling, Aspen Plus is often used, however in this example, it is desirable to optimise the syngas composition and temperature for downstream metallurgical requirements. METSIM or IDEAS would therefore be selected as the ideal modelling package. The gasification and downstream metallurgical process would be simulated in an integral model.

The reduction of sulphide ores by H_2 and CO is not an equilibrium process. The solid phases present in the reduced ore will not be at thermodynamic equilibrium. The gas phase however will be near equilibrium while at the temperatures encountered in the fluid bed. Known solid phase reaction extents could be hard coded into the model, with the resultant offgas equilibrated by the FEM object, improving the energy balance of the model.

6.2 ACID PLANT SIMULATIONS

One of the example models provided with METSIM is a Lurgi sulphuric acid plant model that makes use of the FEM object to simulate the acid plant converter stages. Modelling the converter section of an acid plant requires FEM to calculate the SO_2 to SO_3 conversion during each stage. The heat balance of an acid plant is critical to the sizing of the coolers.

6.3 NICKEL SMELTING AND CONVERTING

There are many excellent papers in the literature about using Gibbs energy minimisation to calculate furnace thermodynamics for nickel smelting and converting. Tan and Neuschütz^{viii} developed a complex model for the smelting of high-grade nickel matte, for the Outokumpu flash-smelting process and the INCO flash-smelting process. The model considers 16 elements and the activity coefficients of the components are derived from literature data. Model predictions agree exceptionally well with measured data. Kellogg^{xviii} developed a model for the thermochemistry of nickel matte converting which uses Margules parameters to model non-ideal solution thermodynamics for the Ni-O, Ni-O-S and Ni-Fe-O-SiO₂-CaO systems.

The use of these types of models in engineering studies remains limited. Typically, a simple METSIM model, with rudimentary and highly simplified reaction chemistry is used to develop a mass and energy balance. The benefit of having a comprehensive Gibbs energy minimisation furnace model, to evaluate the effect of process changes could be enormous for existing operations. Metal losses, offgas SO_2 content, and fuel consumption could be optimised more effectively. The reduction of greenhouse gas emissions has never been as relevant as it is today. Decreasing fuel consumption will aid smelter operations to meet their increasingly stringent greenhouse gas emission targets as well as reduce their operating cost.

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- ^v <http://www.metsim.com/>, 1 September 2009.
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