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A global optimization technique for Solid-Liquid Equilibrium calculations: application to calcium phosphate precipitation

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Abstract

Phase equilibrium calculations constitute an important problem for designing and optimizing crystallization processes. The Gibbs free energy is generally used as an objective function to find the quantities and the composition of phases at equilibrium. In such problems, the Gibbs free energy is not only complex but can have several local minima. This paper presents a contribution to handle this kind of problems by implementation of a hybrid optimization technique based on the successive use of a Genetic Algorithm (GA) and of a classical Sequential Quadratic Programming (SQP) method: the GA is used to perform a first search in the solution space and to locate the neighborhood of the solution. Then, the SQP method is employed to refine the solution. The basic operations involved in the design of the GA developed in this study (encoding with binary representation of real values, evaluation function, adaptive plan) are presented. Calcium phosphate precipitation which is of major interest for P-recovery from wastewater has been adopted as an illustration of the implemented algorithm.

1. Introduction

Phase equilibrium calculations constitute an important class of problems in chemical engineering applications and considerable literature has been devoted to global optimization of vapor-liquid equilibrium (Mc Donald and Floudas, 1995) (Lee et al., 1999). Liquid-solid equilibrium modeling is now receiving much attention due to the advent of specialty chemicals, as well as to new constraints such as environmental considerations. An accurate knowledge of such equilibria is particularly of great opportunity for designing and optimizing crystallization processes.

This paper is devoted to calcium phosphate precipitation which has been identified as a major issue. Let us recall that phosphorus can be found under various chemical forms in urban wastewater, which represents about 30 to 50% of the total refusal of P: insoluble or dissolved organic phosphorus, orthophosphates (until 70% sometimes) and condensed inorganic phosphates. In France, the average concentration of phosphorus in domestic wastewater is within the range of 15-25 mg/L, which may strongly vary from day to day, even during day. The P-discharge in aqueous natural environment leads to an excessive development of algae and, generally to a pH increase, thus corresponding to eutrophication. Consequently, the phosphorus reduction in rivers is considered as a key factor of the fight against pollution. The principal legislative tool in Europe for

fighting against eutrophication is the EC Urban Waste Water Treatment Directive (271/91/EEC). This action came into force in 1991 and enabled waterbodies to be classified as Sensitive Areas if they display symptoms of eutrophication.

Calcium phosphate precipitation involves various parameters: calcium and phosphate ion concentrations, supersaturation, ionic strength, temperature, ion types, pH and also time. In fact, the nature of the calcium phosphate precipitate depends on the supersaturation of the various species. More precisely, the co-crystallization of Amorphous Calcium Phosphate (ACP, $\text{Ca}_3(\text{PO}_4)_2$) and DiCalcium Phosphate Dihydrated (DCPD, CaHPO_4) which may occur in the range of pH to be considered has been taken into account in this study (Seckler, 1994).

This paper first presents the development of a simple thermochemical model, enough representative of calcium phosphate precipitation using a Debye-Huckel based approach for activity coefficient modeling. A preliminary study has shown that the initialization problem of classical optimization techniques which may be used (for instance, Sequential Quadratic Programming) is crucial for the robustness of the code. For this purpose, an optimization strategy combining a two-stage approach, i.e. a genetic algorithm for initialization purpose and identification of the search zone followed by an SQP method to refine the solution is proposed in this paper.

2. Chemical equilibrium model for calcium phosphate precipitation

To model the evolution of phosphate conversion rate as a function of pH with respect to ACP and DCPD precipitation, mass and electroneutrality conservation balances have been taken into account as well as the supersaturation relative to each species. During this precipitation, the aqueous species considered are, on the one hand, for phosphoric acid, H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , PO_4^{3-} , and on the other hand, the concentration of Ca^{2+} ion and the corresponding calcium salts.

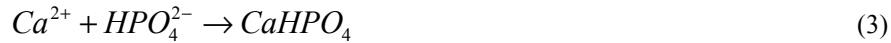
The ACP precipitation equation can be written as follows:



The ACP supersaturation is defined by the β parameter :

$$\beta_{ACP} = \frac{1}{5} \ln \left(\frac{([\text{Ca}^{2+}] \lambda_{\text{Ca}^{2+}})^3 ([\text{PO}_4^{3-}] \lambda_{\text{PO}_4^{3-}})^2}{K_{S_{ACP}}} \right) \leq 0 \quad (2)$$

The DCPD precipitation equation can be expressed as:



The DCPD supersaturation is defined by the following constraint:

$$\beta_{DCPD} = \frac{1}{2} \ln \left(\frac{([\text{Ca}^{2+}] \lambda_{\text{Ca}^{2+}}) ([\text{HPO}_4^{2-}] \lambda_{\text{HPO}_4^{2-}})}{K_{S_{DCPD}}} \right) \leq 0 \quad (4)$$

The different mass balances in the liquid phase include :

- a mass balance for calcium :

$$\begin{aligned} & [Ca^{2+}] + [CaH_2PO_4^+] + [CaHPO_4] + [CaPO_4^-] + [CaOH^+] \\ & = (Ca_{total} - \frac{3}{2}P_{total}X_{ACP} - P_{total}X_{DCPD}) \end{aligned} \quad (5)$$

where X_{ACP} (respectively X_{DCPD}) is the conversion ratio relative to ACP (respectively DCPD) form defined as :

$$X = \frac{P_{Total} - P_{sol}}{P_{Total}} \quad (6)$$

- a mass balance for phosphate :

$$\begin{aligned} & [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] + [CaH_2PO_4^+] \\ & + [CaHPO_4] + [CaPO_4^-] = P_{total}(1 - X_{ACP} - X_{DCPD}) \end{aligned} \quad (7)$$

The electroneutrality requirement gives :

$$\begin{aligned} & [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] + [CaPO_4^-] + [Cl^-] + [OH^-] \\ & = [CaH_2PO_4^+] + 2[Ca^{2+}] + [CaOH^+] + [H^+] + [K^+] \end{aligned} \quad (8)$$

The concentrations of ions and complexes are determined from chemical equilibrium relations (equilibrium constants are given for a temperature of 25°C in molar units) (see table 1):

K_i	A_i	B_i	AB_i	K_i value
K_1	H^+	$H_2PO_4^-$	H_3PO_4	$7.1285 \cdot 10^{-3}$
K_2	H^+	HPO_4^{2-}	$H_2PO_4^-$	$6.2373 \cdot 10^{-8}$
K_3	H^+	PO_4^{3-}	HPO_4^{2-}	$453.942 \cdot 10^{-15}$
K_4	Ca^{2+}	$H_2PO_4^-$	$CaH_2PO_4^+$	$3.908 \cdot 10^{-2}$
K_5	Ca^{2+}	HPO_4^{2-}	$CaHPO_4$	$1.8239 \cdot 10^{-3}$
K_6	Ca^{2+}	PO_4^{3-}	$CaPO_4^-$	$347.536 \cdot 10^{-9}$
K_7	Ca^{2+}	OH^-	$CaOH^+$	$5.8884 \cdot 10^{-2}$
K_w	H^+	OH^-	H_2O	$1.004 \cdot 10^{-14}$

Table 1. Equilibrium constants for the system Ca-PO₄-H₂O $K_i = \frac{(A_i)(B_i)}{(AB_i)}$

The Debye-Huckel model giving the activity coefficient of each species is defined by :

$$\text{Log}_{10} \lambda = -A_{DH} z_i^2 \frac{\sqrt{\mu}}{1 + B_{DH} \alpha \sqrt{\mu}} + C_{DH} \mu \quad (9)$$

$$\text{with } B_{DH} = \sqrt{\frac{2e^2 N_A \rho_o}{\epsilon k_B T}} \text{ and } C_{DH} \text{ is a constant equal to } 0,055 \text{ mol.L}^{-1}.$$

The function to be minimized is the Gibbs free energy G of the system expressed as a linear combination of the chemical potential of each component in each phase :

$$G = \sum_{i=1}^N \sum_{k=1}^{\pi} n_{ik} \mu_{ik}$$

$$\mu_{iL} = \mu_{iL}(T) + RT \ln([x_i] \lambda_{x_i}) \quad (10)$$

$$\mu_{iS} = \mu_{iS}(T)$$

μ_{iL} (respectively μ_{iS}) represents the chemical potential of the species i in the liquid phase (respectively in the solid phase)

A substitution method has been applied so that the only unknowns of the system are the following concentrations $[Ca^{2+}]$, $[PO_4^{3-}]$, $[H^+]$ and the phosphate conversion rate under DCPD and/or ACP forms. The system has been solved for various concentrations in KOH in order to analyze pH influence on conversion. Since calcium exists in the form of calcium chloride, this concentration has been taken equal to 2 $[Ca^{2+}]$.

To solve the system, the two cases of calcium phosphate precipitation have been dissociated, thus leading to an optimization problem with simultaneously 4 equations and one inequality constraint. They are summarized in table 2. In the former case, DCPD (respectively in the latter case ACP) is the equilibrium component of the system.

	First case	Second case
ACP Supersaturation	0	= 0
DCPD Supersaturation	= 0	0

Table 2. Different cases considered in the optimization method

3. System resolution

Several approaches have been proposed for the computation of the solutions to the phase and chemical equilibrium problem (see the paper of Mc Donald and Floudas (1995) for a review of the different contributions). A typical feature of such problems is that the generation of starting points that are used in the search with conventional optimization methods (for example SQP) is very important to guarantee the success of the optimization procedure.

A preliminary study on the above mentioned example has shown that the only use of an SQP method (SQP package from IMSL library) (Schittkowski, 1986) is very sensitive to the choice of the initial guess and often leads to a failure. Consequently, this work is motivated by the development of a technique for the automatic generation of good starting points. For this purpose, a hybrid optimization method is proposed in this paper: a Genetic Algorithm (GA) is used to perform a first search in the space and to locate the neighborhood of the solution. Then, the derivative driven optimization tool (SQP) is used to refine the solution. Let us recall that Genetic Algorithms (Goldberg, 1989) differ from most classical optimization methods since no assumption about the problem space is required and yet produce a global search. GAs use a guided random search in which many different solutions to a problem are investigated and refined simultaneously to identify near-optimum solutions. A major interest of such methods is that they lead to

reasonable solutions even with a poor initial guess. GA implementation requires the definition of parameters: population generation mode, population size, (i.e., the number of individuals forming a population which must be sufficiently large to create sufficient diversity, in order to cover the possible solution space) crossover probability, mutation rate, survival, crossover and mutation mechanisms. In this paper, the initial population has been selected randomly. Nevertheless, constraint respect at a precision of $5 \cdot 10^{-6}$ is required. Each potential solution, i.e., a real value, has been coded as an haploid chromosome with the so-called “weight box”. The weight box consists to encode each digit of real in 4 bits with respectively the following weights 1, 2, 3, 3 with a precision of 10^{-20} . By lack of place, the choice of weight is not justified here but has been achieved after a sensitivity analysis. For example the real 0.18 is encoded 1000 0111, the zero digit and the point are not encoded. Each chromosome represents the 5 unknowns. The development of the GA involves the following features: a survival rate of 0.6, a mutation rate of 0.4, a number of generations of 100 with 101 individuals in a population (the 101th place corresponds to the ‘niche’ of the best individual kept from a generation to the following one).

As initially proposed by Goldberg (1989) and followed by several authors (Costa and Oliviera, 2001), the penalty function method has been used to take into account the constraints in the optimization procedure. Actually, the fitness function (F) involves the objective function (Gibbs free energy) and the penalty terms (p) denoting the equality ($h_l(x)$) and inequality constraints ($g_k(x)$) violations.

$$F = -G - pC \quad (11)$$

$$C = \sum_{k=1}^p \left[\max \{0, g_k(x)\} \right]^2 + \sum_{l=1}^m \left[h_l(x) \right]^2 \quad (12)$$

The penalty coefficients have been adjusted to have a same order of magnitude for both terms G and pC.

In table 3, the Gibbs free energy and the evolution of the penalty terms obtained, on the one hand, after a GA run and on the other hand, at the end of the GA+SQP phase are presented. At step 2 of procedure, the SQP method is initialized by the best solution (i.e. best individual) found by the GA.

	Gibbs free energy (J/mol)	Penalty term
Initialization for GA process	-6236.95	$5 \cdot 10^{-6}$
Best solution obtained by GA used as an initialization for SQP process	-4573.10	$1.2 \cdot 10^{-7}$
Best solution found by SQP	-5425.07	10^{-32}

Table 3. Gibbs free energy and penalty term evolution values under the resolution method influence

4. Conclusions

In this paper, a hybrid optimization tool combining a Genetic Algorithm and an SQP method has been developed and tested on an Solid-Liquid-Equilibrium based calculations. This two-level strategy leads to very efficient search: the GA has been able to provide good starting points for the subsequent SQP method (even if the user has provided rough starting points), thus favoring the local search. Calcium phosphate precipitation which is of major interest for P-recovery from wastewater has been adopted as an illustration of the procedure. More precisely, the co-crystallization of ACP (Amorphous Calcium Phosphate) and DCPD (DiCalcium Phosphate Dihydrated) which may occur in the range of pH to be considered has been taken into account. The generic feature of the optimization strategy presented in this study finds a widespread application for solid-liquid equilibrium calculations.

References

- Costa, L., Oliviera, P., Evolutionary algorithms approach to the solution of mixed integer non-linear programming problems, *Computers and Chemical Engineering*, Vol. 25, pp.257-266, 2001
- Goldberg, D.E., *Genetic algorithms in search, optimization and machine learning*. Massachusetts: Addison-Wesley, 1989
- Lee, Y.P. Rangaiah, G.P., Luus, R., Phase and chemical equilibrium calculations by direct search optimization, *Computers and Chemical Engineering*, Vol. 23, pp. 1183-1191, 1999
- Mc Donald, C.M., Floudas, C.A., Global optimization for the phase and chemical equilibrium problem: Application to the NRTL equation, *Computers and Chemical Engineering*, Vol. 19, N° 11, pp. 1111-1139, 1995
- Schittkowski, K., NLPQL: A FORTRAN subroutine solving constrained non-linear programming problems, (edited by Clyde L. Monma), *Annals of Operations Research*, Vol.5, pp.485-500, 1986
- Seckler, M.M., Calcium phosphate precipitation in a fluidized bed, Ph.D. Thesis, Technische Universiteit Delft, 1994

Nomenclature

- e = electronic charge ($= 1,602177 \cdot 10^{-19}$ C)
- k_B = Boltzmann constant ($= 1,380658 \cdot 10^{-23}$ J.K⁻¹)
- N_A = Avogadro number ($= 6,022136 \cdot 10^{23}$ mol⁻¹)
- T = temperature (K)
- z_i = charge number of ion
- ϵ = solvent dielectric constant ($\epsilon = \epsilon_r \cdot \epsilon_0$)
- ϵ_0 = vacuum permittivity ($= 8,854187 \cdot 10^{-12}$ F.m⁻¹)
- ϵ_r = relative solvent dielectric constant
- λ = ion activity coefficient
- ρ_0 = solvent density (kg.m⁻³)
- μ = solution ionic strength (mol/L)