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## Thermo-kinetic and Physico-Chemical Modeling of Processes Generating Scaling Problems in Phosphoric Acid and Fertilizers Production Industries

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### Abstract

The wet-process phosphoric acid (WPPA) production is generally based on the use of sulfuric acid ( $H_2SO_4$ ) for phosphate ore attack. One of the main issues encountered in this process is related to the uncontrolled formation of mineral deposits at sensitive steps. In the generated complex aqueous systems, the dissolved species and the resulting physicochemical interactions are closely dependent on the variability of both the phosphate rock quality and the operating conditions of the process (40-95 °C;  $H_3PO_4$  and  $H_2SO_4$  concentrations up to 20 mol/kg  $H_2O$ , typically). A collaborative project (CA2PHOS) between OCP and BRGM aims to develop a computational tool dedicated to predict and quantify these mineral deposits in the context of WPPA production. The integrated work presented allows one to gain insight into the understanding of the complex behavior of such systems. It involves specific data such as the activity of water, measured by the hygroscopic method, the density and the chemical composition of the very highly saline aqueous solutions of interest, characteristics of the deposited minerals, and the use of the Pitzer formalism for the thermodynamic modeling of such complex system.

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**Keywords:** Phosphoric acid, Sulfuric acid, Phosphates, Scaling, SCALE2000, Thermodynamics, Pitzer formalism.

### 1. Introduction

Around the world, the upgrading processes for producing phosphates and purified phosphoric acid are primarily based on the use of sulfuric acid ( $H_2SO_4$ ) for acid attack of phosphate rocks. One of the major problems encountered in these wet-process phosphoric acid (WPPA) productions is related to the formation of uncontrolled mineral deposits (scaling/fouling) in sensitive areas of the production units. The optimization of operating conditions requires a better understanding of the formation mechanisms of these undesirable minerals to avoid nuisances like loss of products (i.e. phosphoric acid...), and fouling in reactors, heat exchangers, evaporators, etc. Understanding the key phenomena in the attack of phosphate and in

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the WPPA production steps is real challenge. This unlock allows developing new methods for more efficient valuing of phosphate minerals, allowing scientists and engineers to optimize the operating and the physico-chemical conditions that govern the different units of the process and therefore the whole process.

Based on theoretical, experimental, and practical considerations, the project aimed to extend the capacities of an existing calculation code (SCALE2000) to the complex chemical system of phosphates. SCALE2000 was initially developed by BRGM for addressing scaling risk prediction in applications to geothermal energy and oil production [1-2]. Relying on the Pitzer's approach, this code is dedicated to modeling thermo-kinetic reactions in complex electrolytic and concentrated aqueous solutions.

The current version (V5.0) of SCALE2000 has been specifically redesigned and adapted for a practical use in the field of phosphate industry, with several specific functionalities: i) calculating thermodynamic and physico-chemical properties of systems rich in phosphoric acid (density, water activity, pH ...); ii) determining the conditions of mineral precipitation in sensitive areas of the production facilities; iii) simulating the kinetics of phosphate attack and the chemical reactions involved; iv) generating abacuses, charts and graphs enabling practical visualization of the chemical transformation of phosphates and the reaction steps/paths; v) optimizing the driving upgrading wet-process phosphoric acid, particularly in terms of reactions, using a reliable numerical tool for calculating reactor leaching of phosphates.

The integrated thermochemical database, on which all the thermodynamic calculations rely, has been improved with the sake of consistency, by a critical compilation of data from pilot and industrial studies as well as detailed laboratory measurements of fouling minerals solubility and excess properties for highly saline phosphoric acid aqueous solutions (water activity, density, etc.), mainly acquired in the framework of this project or critically selected in the literature.

## 2. Phosphate industry and scaling/fouling problems

Before its chemical processing, phosphate rock has undergone several operations, namely, mining, milling, the beneficiation (washing, flotation) and finally physical preparation of phosphate to specific profiles according to customer requirements. Throughout the world, when valuation of mineral phosphates is carried out by mean of wet processes, almost the same patterns of manufacturing processes are used. They have essentially four basic unit operations (Figure 1): milling if required, attack reaction and leaching, filtration, and concentration of the dilute acid [3]. These operations differ mainly in the manner of conducting the reaction attack and in the crystalline structure of the calcium sulfate formed. In any case, the aim is to achieve the best possible performance, namely a high yield of product recovery, expressed as  $P_2O_5$ , in a form as close as possible to the commercial quality and with the least cost.

If the main advantage of the WPPA is its relatively low energetic cost [4], the main drawback is the production of a low-grade acid containing a wide variety of suspended and dissolved organic and inorganic impurities. These impurities must be removed in a series of operations which are often complex and seats of various forms of dirt and solid deposits. Some of these impurities play an important role in the performance of these processes, which must be also source of problems for phosphoric acid manufactures (including manufacturing units of fertilizers). These problems are generally related to fouling and solid deposits at sensitive locations of reactors and pipes in industrial units reducing the availability of facilities, allowing loss of phosphate and increasing the maintenance costs [5].

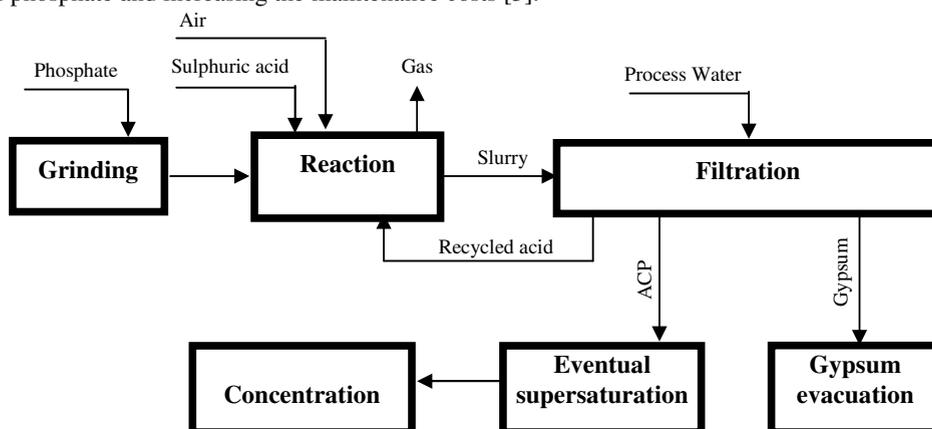


Figure 1- Major unit operations in a manufacturing wet process of phosphoric acid (WPPA).

These impurities, which cause fouling, can be classified into two broad categories [3]:

- *Impurities related to the process itself*, i.e. the reagents used in the process, like sulphuric acid and the process water. The

other impurities, carried by the process water, are generally sodium and chlorine. These chemicals are already contained in the phosphate rock and the introduction of additional quantities with the process water leads therefore to an increased risk of sodium fluorosilicate precipitations and corrosion reactions, especially if the chloride content exceeds 0.1% [6].

• *Impurities from phosphate ores.* There is a great variety of valuable bearing-phosphate rocks. The main impurities include calcium, fluorine, carbonates, chloride, sulphates, magnesium, potassium, sodium, iron, aluminium, organic matter and other trace impurities (mainly heavy metals ...).

In most WPPA, based on historical of the exploitation of these processes at the manufacturing units of phosphoric acid, it appears that: i) in the reaction units, the deposit is mainly composed of hemihydrate ( $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ ), anhydrite ( $\text{CaSO}_4$ ), malladrite ( $\text{Na}_2\text{SiF}_6$ ) and chukhrovite ( $\text{Ca}_4\text{SO}_4\text{AlSiF}_6\text{OH} \cdot 12\text{H}_2\text{O}$ ); ii) in the flash-cooler, mineral phases that are deposited are mainly malladrite and anhydrite; iii) on the surfaces of filter, one finds chukhrovite, gypsum and malladrite and ; iv) on the filter cloths, deposit consists essentially of chukhrovite and barite ( $\text{BaSO}_4$ ).

The deposit that forms at the boilers consists mostly of malladrite which represents about 68% of the deposit. In the heat exchangers and scrubbers, the mineral phase which is deposited is substantially malladrite, representing about 96% of the total deposits.

### 3. Thermodynamic properties of acid solution generated by the attack reactions of phosphates and purification process.

Phosphoric acid ( $\text{H}_3\text{PO}_4$ ) production process generates complex aqueous systems concentrated in phosphates, sulfates, chlorides and other trace elements (cf § 2). The Pitzer formalism [7-8] is dedicated to the highly charged electrolytic systems. It has already been successfully used to study the geochemical behavior of complex solutions like the phosphoric acid systems up to 20 mol/kg<sub>H<sub>2</sub>O</sub> at 25°C [9-15] and the concentrated  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  system for temperatures between 25°C and 250°C and concentrations up to 10 mol/kg<sub>H<sub>2</sub>O</sub> [16-19]. The Pitzer's parameterization has been established for these two fundamental acids for phosphoric acid production.

The purpose of this project was to extend consistently a database containing Pitzer interaction parameters applicable to  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$ -rich acid solutions, following the same methodology as the one developed to deal with the brines stemming from oil fields [1] and brines produced during seawater desalination [2]. Here, the selected parameters make it possible to simulate the geochemical behavior of dissolved species for temperatures ranging between 25 to 100°C and salinity up to 20 mol/kg<sub>H<sub>2</sub>O</sub>, but also the thermo-kinetic behaviors of aqueous, gaseous and solid phases involved in the phosphoric acid production process.

The current version of the extended database makes it possible to take into account the aqueous speciation of phosphorus, the pH of the solution, the water activity, the vapor pressure and saturation state of a group of relevant minerals and gases. The consistency of the database is also evaluated by comparing model results with independent measurements available in the literature, and on pilot production units of phosphoric acid. In the present work, experimental data are also coming from partner laboratory [3].

### 4. The SCALE2000 (V5.0) software

#### 4.1 Main menus of SCALE2000 and the man-machine interface

SCALE2000 is a Microsoft Excel<sup>®</sup> (2003, 2007, and 2010) add-in with its own specific menu bar. This version of SCALE2000 was specifically designed for engineers and technicians of the phosphate industry. Consequently, efforts have been made on the practical aspect and easiness of use of the interface so that the content of the required input datasets rely on parameters and units familiar to persons working in the phosphate industry. The current version (v5.0) accounts for the Na-K-Ca-Mg-Ba-Sr-Fe-H-OH-SO<sub>4</sub>-Cl-H<sub>2</sub>S-SiO<sub>2</sub>-CO<sub>2</sub>-Ac-AcH-Al-F-H<sub>3</sub>PO<sub>4</sub>-H<sub>2</sub>O system under the following conditions: 0.01 < P < 1 bar; 20 < T < 100°C; concentrations up to 20 molal, depending on the studied sub-system (Figure 2).

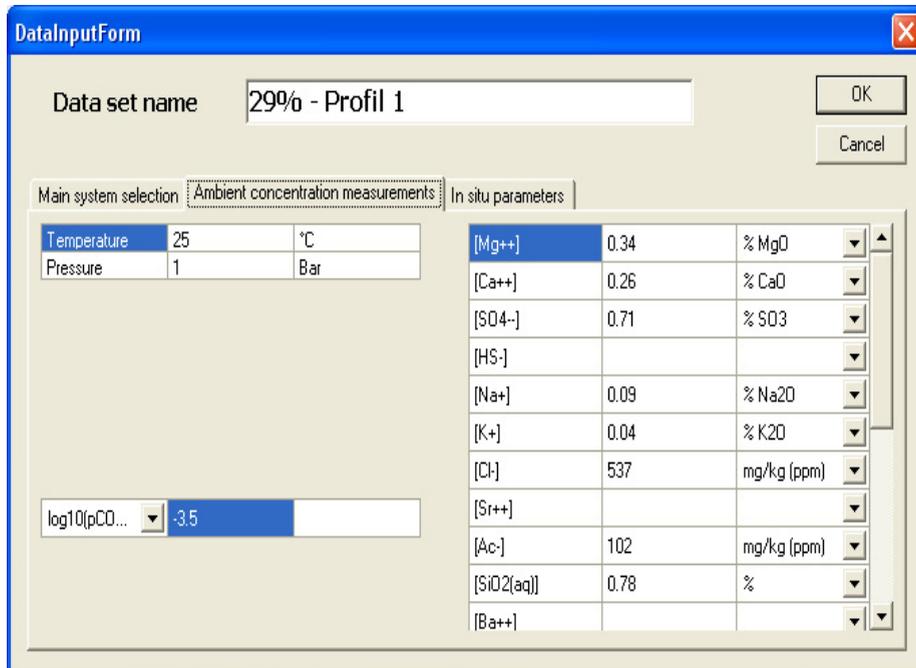


Figure 2 - Welcome page of the SCALE2000 software: limits of use and main available functionalities are listed.

Then, the menus of SCALE2000 offer the possibility to select different types of calculations: i) aqueous speciation of the dissolved species, saturation indices of minerals, partial pressure of gases (CO<sub>2</sub>, H<sub>2</sub>S, SiF<sub>4</sub>, etc.); ii) precipitable masses of one or more minerals previously identified as supersaturated with respect to the aqueous solution; iii) mixing of two aqueous solutions having contrasted physico-chemical properties; iv) kinetics of dissolution and precipitation of minerals according to an adapted kinetic law from the transition state theory (TST); v) series of reactors which allow accounting simultaneously for flow rate and mixing effects into part of a typical phosphoric acid production flow-sheet, determining the accumulation of deposits with time throughout the whole chain and; vi) abacuses representing various key parameters evolution (mineral solubility, gas pressure, water activity, etc.) as a function of P<sub>2</sub>O<sub>5</sub> concentration, temperature, etc. [20].

#### 4.2. Input data of SCALE2000

The input data are the physico-chemical parameters of the brines (pH, T, P, pCO<sub>2</sub>, pH<sub>2</sub>S, Na, K, Ca, Mg, Sr, Ba, Fe, SO<sub>4</sub>, HS, and SiO<sub>2</sub> concentrations, total alkalinity, total dissolved carbon,...), acquired by routine measurements on the field and industrial plants and by complementary chemical analyses performed in laboratory (Figure 3).



(a)

The screenshot shows a software window titled "DataInputForm" with a blue border and a close button in the top right corner. The window contains the following elements:

- Data set name:** A text box containing "29 % - Profil 1".
- Buttons:** "OK" and "Cancel" buttons are located in the top right corner.
- Navigation tabs:** "Main system selection", "Ambient concentration measurements", and "In situ parameters". The "Ambient concentration measurements" tab is currently selected.
- Ambient concentration measurements table:**

Temperature	25	°C
Pressure	1	Bar
- In situ parameters table:**

[Fe <sup>++</sup> ]		
[NH <sub>4</sub> <sup>+</sup> ]		
[N <sub>2</sub> (aq)]		
[CH <sub>4</sub> (aq)]		
[Al <sup>+++</sup> ]	0.31	% Al <sub>2</sub> O <sub>3</sub>
[F <sup>-</sup> ]	1.55	%
[PO <sub>4</sub> <sup>---</sup> ]	29	% P <sub>2</sub> O <sub>5</sub>
[Fe <sup>+++</sup> ]	0.28	% Fe <sub>2</sub> O <sub>3</sub>
[Li <sup>+</sup> ]		
[Br <sup>-</sup> ]		
- log<sub>10</sub>(pCO<sub>2</sub>)...**: A dropdown menu showing "-3.5".

(b)

Figure 3 - Example of a typical ACP 29 % data formatted in the « Input Data Menu » of SCALE2000 (V5.0).

#### 4.3 The "Precipitable masses" menu

The "Precipitable masses" item is used to compute the changes in fluids composition in relation with the saturation state of minerals. It computes the saturation indices of all minerals and then calculates the masses that must be precipitated or dissolved to restore the thermodynamic equilibrium of the minerals - aqueous solution system.

These calculations can be done on two types of fluids: either with a fluid taken directly from the analysis results (see Figure 3), either with a fluid resulting from a mixing computation of two end-members (via the Mixing menu). Before running the computation, potentially reactive minerals must be selected in the list by checking the corresponding item.

#### 4.4. The "Kinetics" menu

This option (*Kinetics*) allows the simulation of precipitation/dissolution of selected mineral phases now including a kinetic law relying on the Transition State Theory [21].

Figure 4 –Example of a typical calculation parameter set for the “kinetics” menu.

By default, all the required kinetic parameters for the 51 mineral phases included in the current SCALE2000 database are defined based on data found in the literature. However the user has the possibility to modify these default parameter values within the appropriate table of the “kinetic parameter” box (Figure 4). Once all the parameters of the problem are defined and the calculation is performed, all the results can be visualized with various figures representing key and relevant variables evolution (precipitated – dissolved masses of minerals, partial pressure of gases, pH, etc.) with time for the selected temperatures of interest.

#### 4.4. The “Mixing” menu

This option (*Mixing*) is used to simulate the mixing between two brines or two solutions and the impact in terms of aqueous concentrations and gaseous partial pressures variations, temperature, and potential reactivity (scaling or attack) with respect to a selected set of mineral phases. This could be used, for instance, to assess the chemical effect of mixing two brines originating from two parts of an actual industrial flow sheet. At the end, results are visualized with appropriate figures representing key variables (pH, partial pressures of gases, saturation indexes, amount of precipitated or dissolved minerals) as a function of the mixing rate (from 0 to 100% of end-member #1). The major advantage of this option is the ability to simulate, for example, the potential effects of mixing between brines emerging from a reactor and flowing into another initially containing a mixed composition of water, as might be the case in the concentration loop. Moreover, this option can also simulate a scenario of warming or cooling of given brine: it suffices to define two end members of identical composition but with different temperatures; SCALE2000 then calculate the mixing temperature in proportion to the chosen mixing ratio and the corresponding speciation (taking into account the possible effects of precipitation and dissolution).

#### 4.4. Examples of calculations carried out with SCALE2000

Detailed aqueous speciation of phosphoric acid already published by Cherif et al. (2002) [15] is well reproduced by SCALE2000 (Figure 5). The detailed aqueous speciation of electrolytic saline solutions is the key step for reproducing physical and chemical properties (e.g., water activity ...) density and saturation vapor pressure of highly saline phosphoric acid solutions [22] are also accurately reproduced by SCALE2000 (Figure 5). These abacuses are of major importance for operational parameter control and the ripening/advancement steps of the processes.

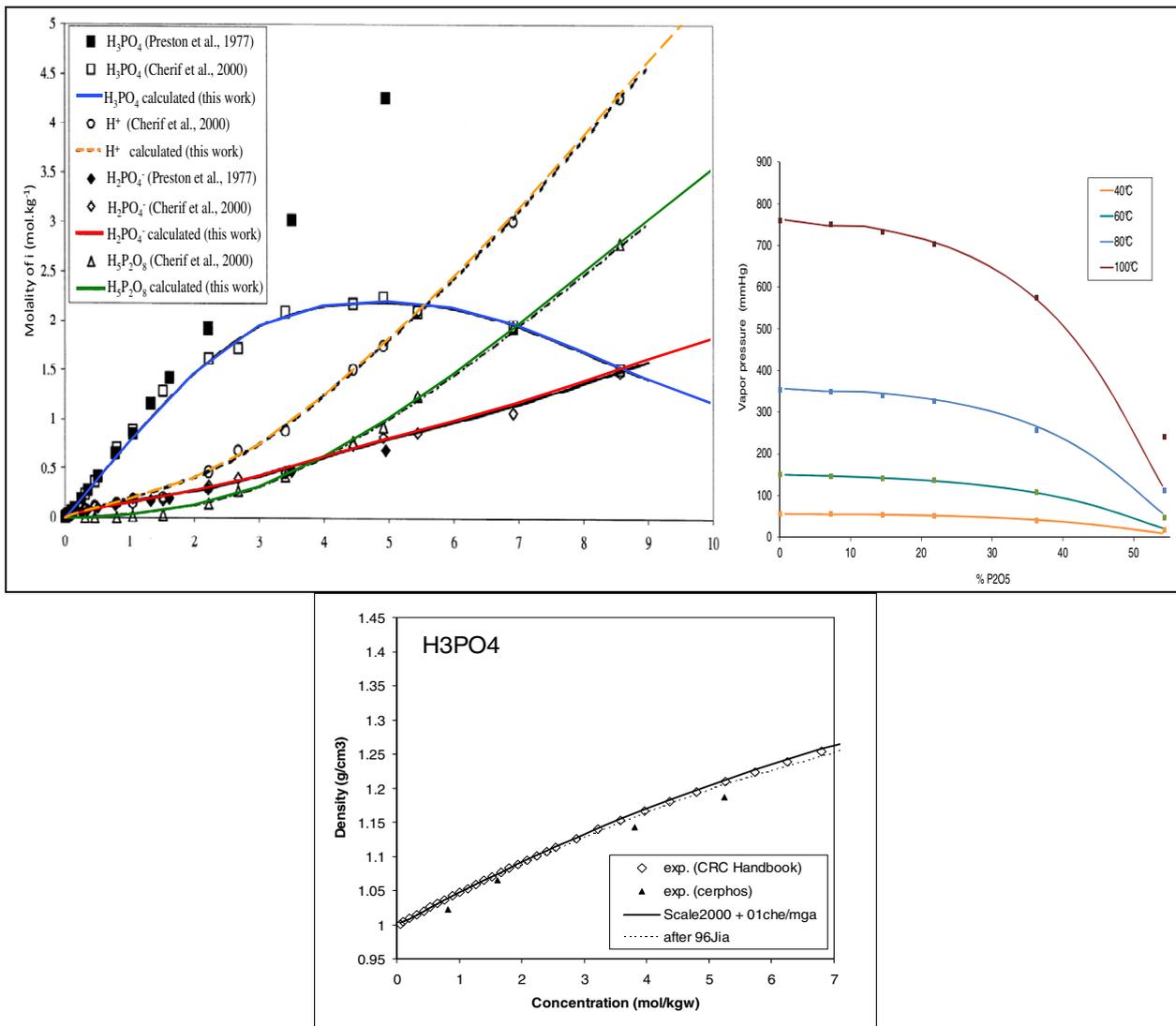


Figure 5 - Typical calculations for phosphate industry obtained with SCALE2000 (V5.0): detailed phosphoric acid speciation ( $H_3PO_4$ ,  $H_2PO_4^-$ ,  $H_5P_2O_8$ ) on the upper left figure, practice abacuses at several temperatures using the « Abacuses Menu » on the upper right figure and density of concentrated aqueous phosphate solutions on the lower figure.

**5. Performances and limits of the current version (V5.0) of SCALE2000**

The last version of SCALE2000 has been optimized in terms of pure computational performance as well as in accuracy of the results produced. On the other hand, we have integrated in the SCALE2000 database the most consistent Pitzer interaction parameter sets that were available from the literature or from experimental work carried out in the framework of this project. Furthermore, though most of the key interaction parameters included in the SCALE2000 database were established and validated against experimental solubility measurements, the geochemical system considered is quite large and some interaction parameters are still missing (no data at all available in the literature). This lacking of data makes some limitations of the effectiveness of the calculations. Finally, the ‘holes’ in the SCALE2000 database will be progressively filled as new experimental data will be made available among the scientific community. That is why, beyond this project, this work has to be considered as still in progress and opening very interesting perspectives to optimize new phosphoric acid processes.

## 6. Conclusion

The wet-process phosphoric acid (WPPA) production is generally based on the use of sulfuric acid for phosphate ore attack. The generated complex and highly saline aqueous systems and the resulting physicochemical interactions are closely dependent on the variability of both the phosphate rock quality and the operating conditions of the process. The computation tool (SCALE2000) dedicated to predicting and quantifying the undesirable mineral deposits in the context of WPPA production allows one to gain insight into the understanding of the complex behavior of such systems. In the framework of the global methodology of studying the scaling problems, observations at the pilot scale and on the industrial units have shown that for a given temperature, the risk of mineral deposits increases with the overall concentration of  $P_2O_5$  [20]. These observations were used as guidelines to check the consistency of thermodynamic database. Detailed aqueous speciation of phosphoric acid, brine density, pH (not shown) etc. already published is well reproduced by the adapted SCALE2000 version (V5.0). The current version (v5.0) accounts for the Na-K-Ca-Mg-Ba-Sr-Fe-H-OH-SO<sub>4</sub>-Cl-H<sub>2</sub>S-SiO<sub>2</sub>-CO<sub>2</sub>-Ac-AcH-Al-F-H<sub>3</sub>PO<sub>4</sub>-H<sub>2</sub>O system under the following conditions:  $0.01 < P < 1$  bar;  $20 < T < 100$ °C; concentrations up to 20 molal.

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