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A Generic Framework for Modeling, Design and Optimization of Industrial Phosphoric Acid Production Processes

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Abstract

In this work we address the systematic and environmentally efficient design of phosphoric acid production processes through a generic modelling and optimization framework. The employed framework aims to facilitate the design of phosphoric acid production schemes that improve the performance of existing industrial processes while accounting for a number of operating, economic and environmental design options. It is built upon an iterative design strategy, hence allowing the generation and exploitation of useful design insights. Generic process modules are used for the representation of the processes involved in order to facilitate design variability and flowsheet interconnectivity. The beneficial effects of the employed framework are demonstrated through an extensive case study of industrial interest. Designs of improved performance are proposed while the prospect of integrated phosphoric acid production and phosphogypsum utilization is investigated.

Keywords: Phosphoric acid production, phosphogypsum utilization, process design

1. Introduction

Phosphoric acid (PA) is used for the production of a wide range of products such as fertilizers, fodder, food and pharmaceuticals. It is produced in industrial scale when a phosphorous containing mineral reacts with a mixture of sulfuric and phosphoric acids. Existing processes consume increased amounts of energy in order to produce commercially viable PA products, while decreased product recovery is often noticed in industrial practice. Calcium sulfate (phosphogypsum), which is the main by-product of the process, constitutes a major environmental hazard as it is being disposed of in large quantities (up to 4-5 tons of gypsum are produced per ton of PA).

A number of process modeling and design efforts have been reported in published literature [1-3] with the aim to improve the understanding and efficiency of PA production processes. They are largely concerned with process modeling issues and fall short of providing design flexibility as they are explicitly oriented towards the design cases they are expected to emulate. Design issues addressed in such cases mostly focus on the arbitrary investigation of the process behavior caused by the variation of a limited number of operating parameters. The exploitation through optimization of synergies and interactions among the processing components is hardly addressed. The effects in PA production of potential downstream utilization of phosphogypsum have yet to be reported. Clearly, the implementation of generic and systematic process design methods is required for the industrial production of PA in order to explore and identify design targets of optimum performance in a number of operating, economic and environmental indices. In this context, we report on the implementation of a generic design framework that allows highly performing design options to be revealed, is able to account for industrial production requirements and addresses the downstream utilization of phosphogypsum as part of the PA production design problem.

2. Phosphoric acid production and phosphogypsum utilization process

An industrial arrangement commonly utilized for the production of PA consists of a number of CSTR reactors followed by a rotating vacuum filter [4]. During the reaction stage, as the phosphate rock enters the reactors it is attacked by sulfuric as well as recycled PA and converts to phosphoric acid. At the same time, supersaturation of calcium sulfate occurs, leading to gypsum crystallization. The produced slurry is lead to a filter where the solid calcium sulfate crystals are separated from the produced liquid PA. A potential downstream utilization approach of the produced phosphogypsum involves reaction with ammonium carbonate and conversion into ammonium sulfate (useful in fertilizers) and calcium carbonate by-product (utilized downstream as part of a broader process), in a reaction-filtration scheme similar to the PA production process [5]. The described reactions are shown in Eqs. (1) and (2)(n=2,0.5 or 0 for dehydrate, hemihydrate or anhydrate processes, respectively) :

$$3Ca_3(PO_4)_2 \cdot CaF_2 + 10H_2SO_4 + nH_2O \rightarrow 2H_3PO_4 + CaSO_4 \cdot nH_2O + 2HF\uparrow \qquad (1)$$

$$CaSO_4 \cdot nH_2O + (NH_4)_2CO_3 \rightarrow (NH_4)_2SO_4 + nH_2O + CaCO_3 \qquad (2)$$

In such a process arrangement, the conditions of dissolution of the phosphate rock are affected by the recycle rate of the product, which in turn has a significant effect on the development of the calcium sulfate crystals. The number and size of the employed reaction vessels as well as the size and shape of the gypsum crystals affect the performance of the filtering process, which influences the composition and flowrate of the streams recycled to the reactors. Similar intense and complex interactions among solid and liquid components are noticed in the ammonium sulfate production process. As a result, a modeling and design approach is required that is sufficiently flexible and generic to capture all the participating phenomena. It should also account for the entire range of effects caused by such interactions, throughout the production flowsheet during the design stages, in order to obtain high product yields and effectively mitigate the environmental hazards caused by the produced phosphogypsum.

3. Modeling and optimization framework

3.1. Iterative design strategy

The employed bi-level iterative strategy of Fig. 1 targets both the efficient development of a comprehensive process model as well as the systematic exploitation of this model in order to develop highly performing process schemes. The first level addresses the effective development of a realistic process model using generic process modules (described in section 3.2). The modules are represented by an inclusive set of equations in order to realize the unit operations taking place in the phosphoric acid production flowsheet regardless of the process task they represent. Process models can be developed that will be evaluated based on available industrial/experimental data. The evaluation will allow the identification of those model features that provide valid results, while features resulting to poor model performance will become the target for further improvement. As a result, the model can gradually evolve based on the generated insights, maintaining a balance between necessary design detail and model-related calculation complexity. This is of particular importance as the developed model is then used in order to propose designs that improve the performance of existing PA production processes. At this stage, the processing components, represented by the employed modules, are interconnected by an all-inclusive network of process streams. A set of objective functions and constraints is utilized representing the desired design targets and the process flowsheet is subjected to optimization using a number of design variables such as the topology of the process stream network, the addition or removal of processing tasks and the stream flowrates distribution, to name a few. In this respect all the synergies and interactions among the different design elements that affect the decision making process are accounted for. The employed framework allows further design iterations to be performed, hence capitalizing on the gained knowledge by incorporating it yet again in process design, if necessary.

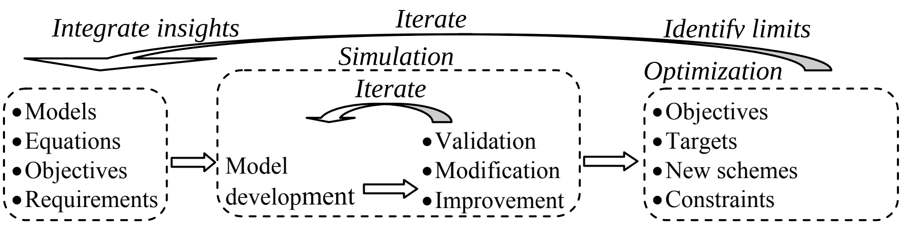

Figure 1: Iterative modeling, design and optimization strategy

3.2. Process representation through generic process modules

The process modules employed for the representation of the utilized processing comopnents are based on the RMX unit concept proposed by [6]. A schematic representation of the process module concept within a generic flowsheet is presented in Fig. 2. A certain module consists of compartments in different phases (*p* and *l*) that exchange mass. Inlet streams of a certain phase enter compartments of the same phase through the preceding mixers, while outlet streams are distributed to the flowsheet through the splitter following each compartment. A generic implementation of the mass balances in the system is shown in Eqs. (3a,b) representing the mixer and splitter mass balance, respectively and (4) representing the compartments mass balance. The term $F_{n.i-1,p,c}$ (with n=2) represents the flowrate of a component c entering a module i(part of a set of modules *SEM*) in phase p(part of a set of phases *SEPH*), while $F_{n.i,p,c}$ represents the flowrate of component c leaving the module. The $SF_{i,p,c}$ term is the side feed flowrate of component c in phase p of the mixer preceding module i and $SFR_{i,j,p}$ is the split fraction of a stream leaving the splitter following a module j and entering the mixer preceding module i. The term *SP* stands for side product (defined similarly to *SF*) while X, a and M stand for conversion degree, stoichiometric coefficient and molecular weight, respectively (*LR* is the limiting reactant). Finally, the term $MT_{i,p,l,c}$ represents the mass transfer operation between the modules and must be defined explicitly, depending on the mass transfer type considered (i.e. diffusion, phase change etc.)

$$F_{n\cdot i-1,p,c} = SF_{i,p,c} + \sum_{j=1}^{SEM} SFR_{i,j,p} \cdot F_{n\cdot j,p,c} \; (a), \quad SP_{j,p,c} = (1 - \sum_{i=1}^{SEM} SFR_{i,j,p}) \cdot F_{n\cdot j,p,c} \; (b) \quad (3)$$

$$F_{n\cdot i,p,c} = F_{n\cdot i-1,p,c} + F_{n\cdot i-1,p,c^{LR}} \cdot X_i \cdot \frac{a_{c,i,p}}{a_{c,i,p}^{LR}} \cdot \frac{M_c}{M_c^{LR}} + \sum_{l=1}^{SEPH} MT_{i,p,l,c} \tag{4}$$

A major characteristic of the employed representation is the design flexibility that it provides. Reactive or non-reactive, multi- or single-phase units can coexist in the same flowsheet regardless of the process task they represent, while recycle and bypass streams as well as side feed and side product options can be implemented in any of the participating process modules. Recycles and bypasses can also be implemented between different phases, provided that a phase change operation (an additional module) is included (in this case it is omitted to maintain Fig.2 clarity).

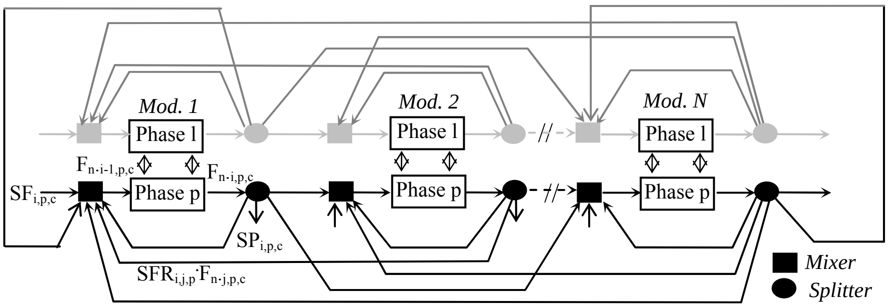

Figure 2: Process flowsheet of generic process modules and connectivity options

4. Industrial case study

Actual operating data are provided by an industrial user in order to suggest potential improvements for a single-stage dehydrate PA production process. The process flowsheet (Fig. 3) consists of two CSTR reactors (Mod. 1 and 3) followed by a filter (Mod. 4). Slurry and vapor are the two phases considered for the reactors, while the separated solid gypsum is considered as the second phase in the filter. The phosphate rock and sulfuric acid raw material as well as water required for the filter operation are introduced as side feed streams. Part of the produced PA is recycled to Mod. 1 and 3. The dashed-line modules represent additional processing tasks that will be considered in order to investigate different design options for the existing process structure in the performed case studies. Design equations for the PA and ammonium sulfate process models are available in [1-5].

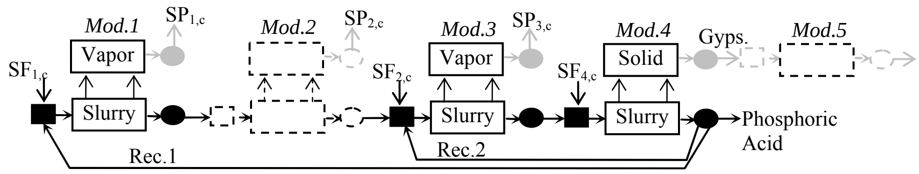

Figure 3: Existing industrial phosphoric acid production flowsheet and potential design options

The PA product is diluted mainly in water and intensive evaporation is required in order to produce a commercially viable product. Furthermore, the gypsum by-product must be converted to ammonium sulfate in order to alleviate the associated environmental hazards. As a result, the objective is to maximize the amount of PA and ammonium sulfate produced (this option is used in the fourth design case) while minimizing the amount of water in which the product PA is diluted. Optimization constraints are associated with desired limits imposed by industrial requirements such as gypsum dilution in solid phase outlet stream, sulfuric acid content in product stream and operating conditions. Stochastic optimization is used in the form of Simulated Annealing (SA)[7], as it has been proven beneficial in several separation/reactive separation [6,7] design problems. We first validate the developed model against the available industrial data and then investigate four design cases of interest to industrial users.

5. Results and discussion

We develop the phosphoric acid (PA) production process model and compare the simulation results with the available industrial data in terms of key process stream flowrates. The relative difference between calculated and industrial data are in the range of 0.01-4.5%. This is in agreement with modeling data presented in [1] and shows a close match between model calculated and industrial data. Proceeding to the investigation of potentially improved design options for the available process the following cases are addressed:

In case 1 we add a reactor (Mod.2) in the existing process structure with a volume identical to that of Mod. 3 and only use the split fractions of streams Rec.1 and Rec.2 as design variables. Results in Table 1 show that the PA mass fraction increases compared to the base case (industrial process) due to increase in the flowrate of the produced PA as well as reduction in the water flowrate. The addition of the reactor is therefore beneficial, because the increase in the residence time reduces the unreacted PA quantity. Case 2 considers the split fractions of all slurry phase recycle and bypass streams shown in Fig. 2 as design variables, together with the volume of the reactor represented by Mod. 2. Results show an improvement in the PA mass fraction mostly due to the reduction of the water flowrate in the product stream. This is achieved in a significantly lower reactor volume than the volume of case 1, but through a complex process structure with multiple active recycle and bypass streams. It is concluded that the addition of a reactor in the existing process is worthwhile if properly integrated within the flowsheet.

Table 1. Optimization results

	Case 1	Case 2	Case 3	Case 4	Base case
PA in product (%)	33.8	37.6	33.5	31.7	31.5
PA flowrate (tn/hr)	20.090	20.147	16.857	19.146	19.147
Water flowtare (tn/hr)	39.261	32.101	33.474	39.829	40.204
Reactor (Mod. 2) vol. (m^3)	250	156	-	-	-
Total filter surface (m^2)	-	-	46	-	63
Vacuum pressure (kPa)	-	-	32	-	40

Case 3 considers the addition of a filtering process (Mod.2) between the two reactors (Mod.1 and 3) of the existing process. Part of the PA produced in Mod.2 is recycled to the first reactor (Mod.1), while the rest is fed to Mod.3. The split fractions of the recycle streams (including Rec.1 and 2) are considered as design variables, together with the filter surface and the vacuum pressure applied in both filters (Mod.2 and 4). Results show an increase in the PA mass fraction compared to the base case, which is realized through reduction in the product water flowrate as well as in the product PA flowrate. While reduced water flowrate indicates lower evaporation energy requirements, reduced PA flowrate indicates reduction in the plant capacity. The total utilized filter surface is

significantly reduced implying that the installation of two smaller size filters might be beneficial. It can be concluded that reducing the plant output capacity might be beneficial if considered in conjunction with the considerably reduced evaporation energy and filtering investment cost requirements. However, such a case should be further investigated using economic terms in the objective function.
Finally, in case 4 we investigate the option of integrated PA and ammonium sulfate production as a means of effectively utilizing the produced phopshogypsum. Mod.5 of Fig. 3 is considered as a single phase ammonium sulfate production reactor in order to incorporate the phosphogypsum conversion design drive within the PA production flowsheet. Design variables in this case are the split fractions of recycle streams Rec.1 and 2, as well as the ammonium carbonate flowrate (raw material) and the volume of the ammonium sulfate reactor. The obtained result is similar to the industrial PA process in terms of PA mass fraction, although the slightly reduced product water flowrate implies further improvement capacity through extensive integration of the flowsheet. At the same time, 98.5% conversion of gypsum is achieved, which agrees with the pilot plant case reported in [5] and almost completely transforms the undesired by-product into a useful product. On the other hand, the ammonium carbonate to gypsum ratio is 98%, improved from the reported experimental 105% [5].

6. Concluding remarks

The implementation of a systematic and flexible framework was reported to facilitate the modeling and design of PA production processes. The framework is built upon a bi-level iterative strategy that targets both the development of efficient PA process models and the identification of optimally performing process schemes. Generic process modules were used that provide an efficient representation of the processing tasks comprising the flowsheet as well as a comprehensive interconnectivity among the processing components. The performed case study proposed PA production schemes that improve the performance of a real-life industrial process and can be considered for implementation or further investigation by industrial users. At the same time, the phosphogypsum utilization problem was considered as part of the PA production flowsheet, with results providing the incentives for further exploration of potential design schemes. As this is ongoing work, we intend to further investigate the insights generated through the proposed designs from an industrial user perspective as well as to explore more design cases with respect to phosphogypsum utilization.

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