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Integrated Facility for Power Plant Waste Processing

PAULA MANTECA & MARIANO MARTÍN

Abstract In this work a process has been developed for the transformation of gypsum, a byproduct of the desulfurization within coal based thermal plants, into sodium sulphate. The process consists of the synthesis, the crystallization of sodium sulphate and the possibility of producing the hydrated and/or the anhydrous crystal. This section is integrated within the desulfurization unit by processing the residue and regenerating a fraction of the raw material required, $CaCO_3$. The optimal operating conditions for the evaporation and crystals recovery has been computed using a mathematical programming approach. The economics of the process is attractive to produce the anhydrous crystal, 0.21 €/kg with an investment of 36 M€, as well as for the production of the decahydrated sodium sulpahte, 0.06 €/kg and 26 M€ of investment, processing the gypsum of a 350 MW power plant.

Keywords: • Desulfurization • Gypsum • Solvay • Mathematical optimization • Sodium sulfate •

CORRESPONDENCE ADDRESS: Paula Manteca. University of Salamanca, Department of Chemical Engineering, Plz. Caídos 1-5, 37008, Salamanca, Spain e-mail: paulamu@usal.es. Mariano Martín. University of Salamanca, Department of Chemical Engineering, Plz. Caídos 1-5, 37008, Salamanca, Spain e-mail: mariano.m3@usal.es.

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1 Introduction

Power plants are responsible for a fair share of the total power production in any country. The flue gas produced contains a number of pollutants such as SO_2, NOx and a large amount of CO_2. The current regulations limit the emissions of these chemicals. The removal of SO_2 can be performed using various technologies including wet scrubbers, the most used one representing about 85% of all the desulfurizers installed, spray driers, installed in around 12% of the facilities, while 3% use dry injection systems (EPA, 2003) The most common process adds lime and air so that the SO_2 is oxidized and transformed into $CaSO_4$ that precipitates Gypsum from desulfurization could be used in the construction industry. However, the slowdown of the construction industry and the availability of natural product have resulted in an excess of gypsum that represents an environmental challenge due to the large amounts of gypsum that need to be disposed of.

Within the concept of circular economy, gypsum as a waste can be used for the production of sodium sulphate, a product of interest in the pulp and paper industry as well as in the detergents, the glass and the textile industries but also as a raw material for the production of other chemicals such as potassium sulphate, sodium silicate, etc.

In this work, a systematic approach based on mathematical optimization has been performed to design a process that generates sodium sulphate out of gypsum.

2 Process description

The production of sodium sulfate starts with mixing the gypsum and sodium carbonate. While the gypsum is already in the form of fine power, sodium carbonate must be milled for the reaction to take place. The salt particle size is to be reduced to 15 mm (Trendafelov et al., 1995). The reaction takes place at 25°C as follows, obtaining 98% of conversion when using an excess of sodium carbonate.

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4$$

Calcium carbonate precipitates and can be separated using a centrifuge. We can use this precipitate and reuse it to capture SO_2, intensifying the current flue-gas desulfurization process. The presence of residues of sodium carbonate prevent from full recovery of the sodium sulphate. Alternatively, $Ca(OH)_2$ can be used to precipitate the sodium carbonate as calcium carbonate. This alternative is to be evaluated within the design procedure. Next, the solution is sent to a multi-effect evaporator system to concentrate the sulfate and crystallize. The high energy intensity of the process requires integration in the form of a multi-effect evaporation system. Finally, the crystals can be dehydrated in a furnace. Figure 1 shows the flowsheet for the process.

$$Na_2SO_4 \cdot 10H_2O \rightarrow Na_2SO_4 + 10H_2O$$

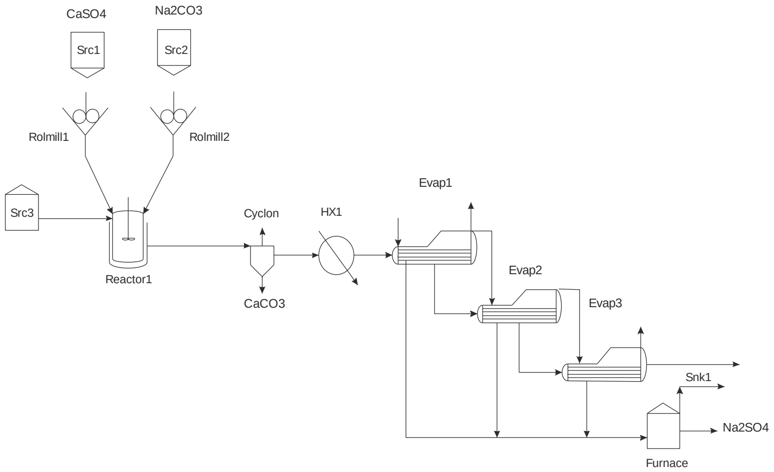

Figure 1: Process flowsheet.

3 Design procedure

The first consideration to comment about is related to the difficulty of crystallizing $Na_2SO_4 \cdot 10H_2O$ in presence of $Na_2CO_3 \cdot 10H_2O$. They both can precipitate together since their solubility is similar. However, note that the presence of the carbonate in the solution is due to the excess provided to reach the 98% conversion reported in the literature. Therefore, the concentration is low. Two alternatives are considered. First, the precipitation of the carbonate in the form of $CaCO_3$ using $Ca(OH)_2$. A preliminary study was carried out comparing the additional profit due to the total recovery of the sulfate. The second alternative consists of recovering the sodium sulphate until both are in the same concentration since the solubility of both, $Na_2SO_4 \cdot 10H_2O$ and $Na_2CO_3 \cdot 10H_2O$ is similar. Two non linear programming (NLP) problems are solvede per alternative. Each one has around 500 variables and 315 eqs. The objective function is a simple profit given as eq. (1)

$$Z=P_{Na2SO4} \cdot fc_{(Na2SO4)} -(P_{GN}) \cdot (Q('Furnace1')+Q('HX1')+Q('Evap1')) -P_{CaOH2} \cdot fc_{(CaOH2)} \quad (1)$$

The second step in the design of the process is related to the number of evaporators. The larger the number of effects, the higher the steam economy. The trade-off is the investment cost. A NLP optimization problem is set up for systems consisting in 1, 2, 3 and 5 evaporator effects. The size of the problem reaches up to around 900 variables and 600 variables when five effects are used using an objective function as given by eq. (1)

4 Results

4.1 Process synthesis

A preliminary study was carried out comparing the additional profit due to the total recovery of the sulfate versus assuming the losses of sodium sulfate in the solution. The high cost of $Ca(OH)_2$, the fact that only an additional 10% recovery of crystals and that gypsum is currently a waste, does not recommend the use of $Ca(OH)_2$.

Next, NLP's optimization problems are set up for systems consisting in 1, 2, 3 and 5 evaporator effects. As expected, the heat load associated decreases with the number of effects while the investment increases but it reaches a plateau which results in the selection of 5 effects.

4.2 Process operation

The design procedure yields a process that consists of the mixing of the reactants, the synthesis, the recovery of calcium carbonate and the crystallization of the sodium sulphate. The first unit only evaporates water and no sulphate is recovered. The second one recovers 7% of the total sulfate and the last three affects almost recover 30% each. The recovery increases as we progress on the number of effects.

The power consumption adds up to 1.2 MW, while the thermal energy corresponds to 40.9 MW with 20% consumed in heating up the solution, 35% in the evaporators system and the rest to dehydrate the sulfate.

4.3 Economic evaluation

The equipment cost is estimated by performing a short-cut sizing of the units involved such as mills, reactor, heat exchanger and multi-effect evaporator system and furnace. The factorial method (Sinnot, 1999) is used to estimate the investment in 36 M€. The raw materials cost account for 2.9M€/yr, utilities add up to 9.7 M€ /yr and labor represents 0.4 M€ /yr. As a result, the production cost results in 0.21 €/kg. Typical costs of sodium sulphate are below 0.2 €/kg (Valmet, 2015). Therefore, renewable sodium sulphate is competitive with regular sodium sulphate.

If hydrated sodium sulphate is sold as such, the price decreases due to savings in water removal at the furnace, around 4.5 M€/yr, and the fact that the product contains water. The facility investment cost without the furnace adds up to 26M€. As a result the production cost decreases down to 0.06€/kg

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