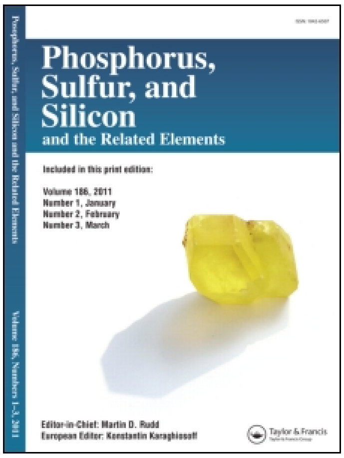


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# MODELLING AND OPTIMIZATION OF THE REMOVAL OF CADMIUM FROM WET-PROCESS PHOSPHORIC ACID

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This paper concerns the removal of cadmium from wet-process phosphoric acid. In order to define the best conditions as well to suggest possibilities for the removal of cadmium the synthesis of phosphoric acid from a natural concentrate containing cadmium oxide was performed in laboratory conditions. A central composite design was performed in order to check the effect on the Cd concentration in the phosphoric acid of the four main factors $\%P_2O_5$, $\%H_2SO_4$, solid/liquid ratio, and temperature. The initial concentration of cadmium was fixed at 1%.

It can be concluded that the amount of cadmium largely depends on the $\%H_2SO_4$ and that cadmium removal can be optimized by working at precise conditions of temperature $\%P_2O_5$, $\%H_2SO_4$, solid/liquid ratio, and temperature.

*Keywords:* Cadmium removal; wet-process phosphoric acid; experimental design

## INTRODUCTION

The manufacture of phosphoric acid with the wet-process has been extensively studied especially since wet-process phosphoric acid forms the raw material for phosphate fertilizer manufacture[1]. Over the last years, due to environmental and safety rules, the amount of cadmium admitted in fertilizers and consequently in commercial phosphoric acid has drastically decreased. Cadmium, which is quite a rare element in the nature, is toxic; when initially contained in fertilizers, it

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follows the food chain and concentrates in the hard tissues of man and other mammals[2].

Various investigations are now concerned with the problem of cadmium removal. The recovery of the cadmium can be attained by the precipitation of insoluble salts, liquid-liquid extraction or the binding to cation exchange resins. Another route is the coprecipitation of cadmium with phosphogypsum formed during the wet process. The main interest of this route is to be able to follow the industrial process without any large modifications of the apparatus or of the industrial operations. The purpose of this paper is to model and optimize the calcium recovery, following an industrial process, taking an account four variables: $\%P_2O_5$, $\%H_2SO_4$, solid/liquid ratio and temperature which all play a major role on the amount of cadmium remaining in the phosphoric acid.

## EXPERIMENTAL



The wet-process consists of the digestion of a natural apatite (close to a calciumfluorapatite $Ca_{10}(PO_4)_6F_2$) by sulfuric acid. In the experiments described here, a cadmium-containing phosphate is modelled using a natural apatite to which tricadmium phosphate $Cd_3(PO_4)_2$ was added. The amount of tricadmium phosphate was calculated in order to obtain 1% of cadmium in the initial solution. This mixture was treated by the stoichiometric amount of sulfuric acid in the conditions of the wet-process, in a solution of phosphoric acid. The liquid/solid ratio, the temperature, the $\%H_2SO_4$ and the initial $\%P_2O_5$ were varied. The slurry was filtered and the phosphoric acid analyzed for both $P_2O_5$ and Cd content.

In these conditions, the solid phase consisted of a mixture of hemihydrate and dihydrate calcium sulfate.

## THE FACTORIAL PLAN

Experimental designs are frequently performed in study of empirical relationships between one or more measured responses and various variables[3,4,5]. In order to optimize the wet process for cadmium removal, an orthogonal central composite plan was set up taking into account the four variables previously mentioned, at five levels, as listed in TABLE I.

The experimental matrix was formed by 31 experiments randomly carried out (TABLE II) The first 16 experiments belong to a $2^4$ factorial plan; the next 8

TABLE I Different levels of the four studied variables

| *variables* | $X_1$ | $X_2$ | $X_3$ | $X_4$ |
|---|---|---|---|---|
| −2 | 20 | 24.0 | 14.5 | 70 |
| −1 | 25 | 24.5 | 15.0 | 75 |
| 0 | 30 | 25.0 | 15.5 | 75 |
| +1 | 35 | 25.5 | 16.0 | 85 |
| +2 | 40 | 26.0 | 16.5 | 90 |

With: $X_1$: $\%P_2O_5$
$X_2$: $\%H_2SO_4$
$X_3$: temperature
$X_4$: solid/liquid ratio



experiments were performed at the distance $\alpha$ from the center; finally, 7 experiments were placed at the center of the orthogonal plan[6].

Table II also reports the results of the amount of cadmium in the phosphoric acid for each experiment.

At first, the same value for the amount of cadmium in the final phosphoric acid was obtained for the seven experiments at the center of the plan, this confirms the very good reproducibility of this method[7,8].

Using a computer and a special software an estimated equation of the model can be calculated and gives the amount of cadmium (Q) as a function of the four variables:

$$Q = 125.71 + 15X_1 + 41.67X_2 - 11.67X_3 + 11.67X_4 + 5.66(X_1)^2 + 15.66(X_2)^2 + 20.66(X_3)^2 + 5.66(X_4)^2 - 2.5X_1X_2 - 27.5X_1X_3 + 2.5X_1X_4 - 17.5X_2X_3 + 2.5X_2X_4 - 32.5X_3X_4 \quad (1)$$

Variables $X_1$, $X_2$ and $X_3$ present a positive effect on Q. The amount of cadmium increases with $\%H_2SO_4$, $\%P_2O_5$ or temperature. In contrast the liquid/solid ratio presents a negative effect. But the effect of these factors is not very important except the $\%H_2SO_4$. In, to a level of confidence of 95%, the equation of the model can be simplified to:

$$Q = 125.7 + 41.67\,X_2 - 32.5\,X_3X_4 \quad (2)$$

It is only necessary to retain the effect of the $\%H_2SO_4$ and the interaction between the solid/liquid ratio and the temperature.

TABLE II The thirty-one experiments of the central compositer plan, and the results design

| *N°* | $X_1$ | $X_1(\%)$ | $X_2$ | $x_2(g/l)$ | $X_3$ | $x_3(g/128ml)$ | $X_4$ | $x_4(°C)$ | *Amount [Cd] ppm* |
|---|---|---|---|---|---|---|---|---|---|
| 1 | – | 25 | – | 24,5 | – | 15 | – | 75 | 40 |
| 2 | + | 35 | – | 24,5 | – | 15 | – | 75 | 80 |
| 3 | – | 25 | + | 25,5 | – | 15 | – | 75 | 120 |
| 4 | + | 35 | + | 25,5 | – | 15 | – | 75 | 280 |
| 5 | – | 25 | – | 24,5 | + | 16 | – | 75 | 200 |
| 6 | + | 35 | – | 24,5 | + | 16 | – | 75 | 200 |
| 7 | – | 25 | + | 25,5 | + | 16 | – | 75 | 200 |
| 8 | + | 35 | + | 25,5 | + | 16 | – | 75 | 240 |
| 9 | – | 25 | – | 24,5 | – | 15 | + | 85 | 80 |
| 10 | + | 35 | – | 24,5 | – | 15 | + | 85 | 280 |
| 11 | – | 25 | + | 25,5 | – | 15 | + | 85 | 240 |
| 12 | + | 35 | + | 25,5 | – | 15 | + | 85 | 320 |
| 13 | – | 25 | – | 24,5 | + | 16 | + | 85 | 120 |
| 14 | + | 35 | – | 24,5 | + | 16 | + | 85 | 160 |
| 15 | – | 25 | + | 25,5 | + | 16 | + | 85 | 240 |
| 16 | + | 35 | + | 25,5 | + | 16 | + | 85 | 200 |
| 17 | −2 | 20 | 0 | 25 | 0 | 15,5 | 0 | 80 | 80 |
| 18 | +2 | 40 | 0 | 25 | 0 | 15,5 | 0 | 80 | 160 |
| 19 | 0 | 30 | −2 | 24 | 0 | 15,5 | 0 | 80 | 80 |
| 20 | 0 | 30 | +2 | 26 | 0 | 15,5 | 0 | 80 | 240 |
| 21 | 0 | 30 | 0 | 25 | −2 | 14,5 | 0 | 80 | 280 |
| 22 | 0 | 30 | 0 | 25 | +2 | 16,5 | 0 | 80 | 80 |
| 23 | 0 | 30 | 0 | 25 | 0 | 15,5 | −2 | 70 | 120 |
| 24 | 0 | 30 | 0 | 25 | 0 | 15,5 | +2 | 90 | 120 |
| 25 | 0 | 30 | 0 | 25 | 0 | 15,5 | 0 | 80 | 120 |
| 26 |  | 30 | 0 | 25 | 0 | 15,5 | 0 | 80 | 120 |
| 27 | 0 | 30 | 0 | 25 | 0 | 15,5 | 0 | 80 | 120 |
| 28 | 0 | 30 | 0 | 25 | 0 | 15,5 | 0 | 80 | 120 |
| 29 | 0 | 30 | 0 | 25 | 0 | 15,5 | 0 | 80 | 120 |
| 30 | 0 | 30 | 0 | 25 | 0 | 15,5 | 0 | 80 | 120 |
| 31 | 0 | 30 | 0 | 25 | 0 | 15,5 | 0 | 80 | 120 |



## OPTIMISATION OF CADMIUM REMOVAL AND DISCUSSION

It is concluded from the analysis of the factorial plan that, in fact, only the $\%H_2SO_4$ is a significant factor. Temperature can be seen not to be a significant factor to control the amount of cadmium in the wet-process.

In order to minimize the amount of cadmium in the final phosphoric acid, it is possible to plot the curves of the isoreponses. These curves, obtained with the previous equation (1) define the optimum conditions of the experimental area[9,10,11]. Figures 1, 2 and 3 plot the isoresponse curves giving the the

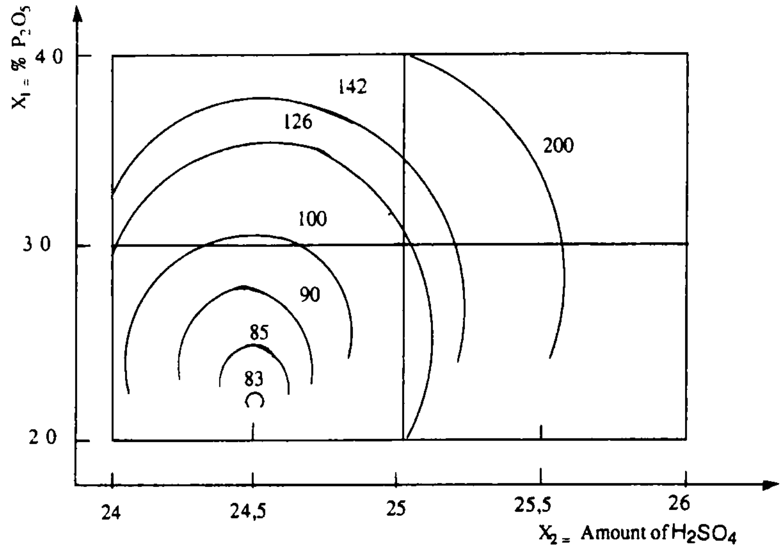


FIGURE 1 Isoreponse curves: % $H_2SO_4$ and % $P_2O_5$.

% $H_2SO_4$, which is the main variable, versus the three other variables: % $P_2O_5$, solid/liquid ratio and temperature. The optimum conditions corresponding to the minimum value of the cadmium content can be defined in each case.

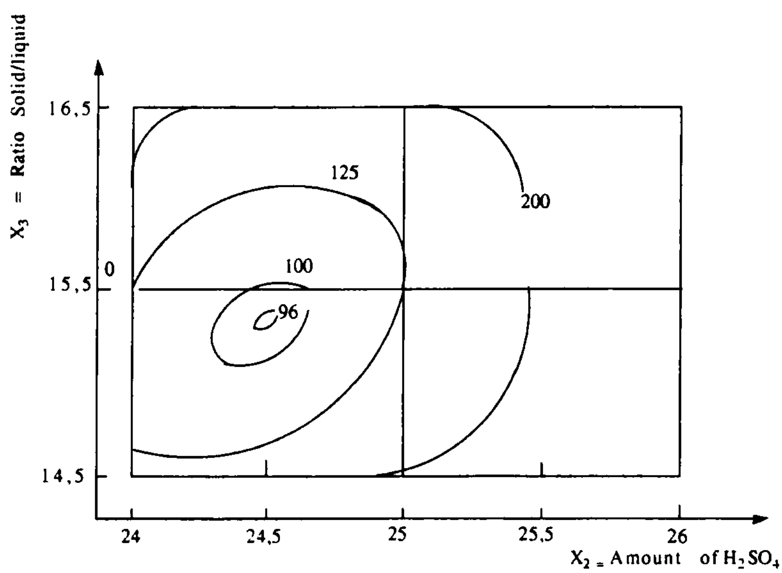


FIGURE 2 Isoreponse curves: % $H_2SO_4$ and solid/liquid.

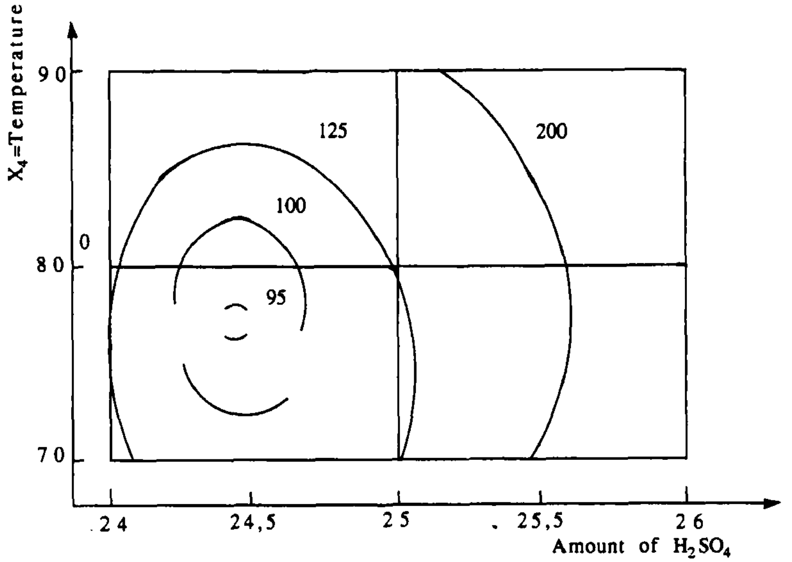


FIGURE 3 Isoreponse curves: % $H_2SO_4$ and temperature.



Finally, the optimum range for the four variables is:

$X_1$: $\%P_2O_5$ :20–25%
$X_2$: $\%H_2SO_4$ :24.5%
$X_3$: solid/liquid ratio :117.2–121.1 g/l
$X_4$: temperature :75–80°C

In these conditions the amount of cadmium in the phosphoric acid is limited to 80 ppm, the initial concentration of cadmium being 10 000 ppm, i.e. more than 99% of cadmium was eliminated from phosphoric acid. Nevertheless it is quite difficult to extend these results to the industrial process: (i) first, in the wet-process, the initial concentration of cadmium is low (100–500ppm) and certainly equilibrium phenomena different from this case (10 000ppm) occur; (ii) secondly, the $\%P_2O_5$ in the final phosphoric acid (20%) is to low for an industrial process. So, other experiments must be performed to more accurately model the phosphoric acid wet-process.

Nevertheless this work shows the value of modelling and of the use of the experimental plans. It also shows, in a very accurate manner, the influence of slight variations of the industrial conditions in the wet-process on the cadmium removal.

## CONCLUSION

The removal of cadmium ions from industrial phosphoric acid was studied using a central composite orthogonal design. The response surface equation for cadmium removal was established. From this equation, it is possible to forecast the best conditions of treatment to obtain a well defined final acid.

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