

Modeling of the Cadmium Isomorphous Substitution During the Co-Crystallization Process for Cadmium Removal from Wet Phosphoric Acid

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Abstract - The purpose of the present study was to establish an appropriate statistical model to predict and optimize the cadmium isomorphous substitution in calcium sulfate crystal lattice, during to the co-crystallization process for cadmium removal from wet phosphoric acid. Thus, could be useful to find out a good parametrization and optimization to enhance its efficiency. The dataset was referred to the analytical data of the co-crystallization tests for cadmium removal from the wet phosphoric acid. The model was based on the Multiple Linear Regression (MLR), which is one of the most widely used multivariate statistical techniques for determining the relationship between the explanatory (independent) variables and response (dependent) variable. Univariate and Multivariate Descriptive Statistics were first used to provide quick visual summaries of essential data characteristics, and define the number of individual points and variables. The dataset was therefore evaluated by the Principal Component Analysis method (PCA) to emphasize variation and bring out strong correlation between variables. Assumptions of multilinear regression such as, independence, normality, homoscedasticity and linearity were also examined. The data that verify the assumptions were analyzed with multiple regression to elaborate the final model.

Key Words: Cadmium, Phosphoric acid, Co-crystallization, Principal Component Analysis, Multiple Linear Regression.

1. INTRODUCTION

The cadmium removal from wet phosphoric acid still a priority for researchers and the industry. In spite of the fact that health risks associated with cadmium are not a cause for concern, various technologies continue to be researched for the removal of cadmium in phosphate rock and in phosphoric acid, including co-crystallization, ionic flotation, precipitation, solvent extraction, ion exchange and membrane separation. Nonetheless, there is still no proven and economically viable decadmiation technology at the industrial scale. The co-crystallization process as an example seems according to the literature to be promising if its efficiency could be enhanced for considering medium and high cadmium phosphate rocks. The objective of this paper then to establish an appropriate statistical model to predict and optimize the isomorphous substitution of cadmium in

calcium sulfate crystal lattice, during the co-crystallization process for cadmium removal from wet phosphoric acid. Thus, could be useful to find out a good parametrization and optimization to enhance its efficiency.

1.1 Co-crystallization process for cadmium removal from wet phosphoric acid

The co-crystallization process is the most studied and patented technology for the cadmium removal from wet phosphoric acid. The process consists on the co-crystallization of cadmium with anhydrite (CaSO₄) when a concentrated phosphoric acid (50%-54% P₂O₅), including its sludge content, is heated and further treated with calcium phosphate and sulfuric acid. Improvements and intensification of this process were applied and have upgraded the cadmium removal and the P₂O₅ recovery from wet phosphoric acid, saved the heat energy cost and reduced the process design by eliminating the phosphogypsum stream (tank, agitator, pumps and piping)[1]. In fact, the driving force for the cadmium removal by co-crystallization, is the kinetics of the isomorphous substitution of cadmium in calcium sulfate crystal lattice during the recrystallization of calcium sulfate Dihydrate or Hemihydrate to Anhydrite. Accordingly, suitable conditions are required for a high isomorphous substitution kinetics and consequently high efficiency of cadmium removal by co-crystallization. Even though, some impacts still to be challenging, the efficiency needs to be significantly increased for medium and high cadmium phosphate rocks, some caution should be used in applying the value of the cadmium-containing rejects as a way of reducing the costs per ton of P₂O₅ due to the decreasing value of cadmium metal, the cost of disposing of reject material as a hazardous waste, and the production of significant amounts of phosphogypsum with considerable P₂O₅ losses.

1.2 Thermodynamics of the cadmium isomorphous substitution in calcium sulphate crystal lattice

Uptake of Cd²⁺ in calcium sulfate proceeds by isomorphous substitution of Ca²⁺ ions [2]. The degree of uptake is given by the partition coefficient D that takes into account the

competition of Cd²⁺ and Ca²⁺ for the same lattice site in the crystal. D is defined as:

$$D = \frac{[Cd^{2+}]/[Ca^{2+}]_{(solution)}}{[Cd^{2+}]/[Ca^{2+}]_{(Crystal)}} \quad (i)$$

A constant D-value implies that the resulting Cd²⁺ concentration in the crystals can be influenced by either the Cd²⁺ or the Ca²⁺ concentration in the solution. Thermodynamically, an expression has been derived for D:

$$D = \frac{\gamma(Ca^{2+})_s}{\gamma(Cd^{2+})_s} * \frac{\gamma(Cd^{2+})_l}{\gamma(Ca^{2+})_l} * \frac{K_{sp}(CaSO_4)}{K_{sp}(CdSO_4)} * e^{(-\epsilon_s/RT)} * e^{(-\Delta f(CdSO_4 \rightarrow CaSO_4)/RT)} \quad (ii)$$

D comprises the activity coefficients γ of Cd²⁺ and Ca²⁺ in the solution (i) and in the solid phase (s), the thermodynamical solubility products of calcium and cadmium sulfate, the energy of elastic lattice deformation ϵ and the free energy required to make a CdSO₄ lattice isomorphous with the corresponding CaSO₄ lattice. The activity coefficients represent in fact the deviation from ideality, which can also be expressed as an excess free energy ($\Delta G = -RT \ln \gamma$). Changes in energy affecting the activity coefficients can thus also be written as an exponent. For pure calcium sulfate $\gamma(Ca^{2+})_s$ equals 1, while $\gamma(Cd^{2+})_s$ is related to the bonding energy of Cd²⁺ in the calcium sulfate lattice. If all parameters in (ii) were known, D could be calculated. Mostly, however, the values of these parameters are not available, which hampers the use of equation (ii) for prediction of the D-value. It is hard to make an a priori prediction of the D-value on basis of (ii), but under certain conditions the effect of some parameters can become visible. For instance, at constant temperature and pressure the exponential terms as well as the solubility product remain constant. If in addition the uptake does not exceed a value of about 1%, the activity coefficients in the solid are also unaltered. In that case, the D-value only depends on the activity coefficients in the solution and thus solely on the solution composition. Although an a priori prediction of D is as said not possible, the observed D-values may be understood by comparing the physical and chemical properties of Cd²⁺ and Ca²⁺. Therefore in table 1, some characteristics of these two ions are listed. The radii of Cd²⁺ and Ca²⁺ are almost equal, enabling replacement of Ca²⁺ by Cd²⁺ without introducing much lattice strain. It is therefore expected that the ϵ term in equation (ii) is small.

Table -1. Comparative properties of Ca²⁺ and Cd²⁺

Properties	Ca ²⁺	Cd ²⁺	Unit	Ref.
Radius (8-coordination)	112	107	pm	[3]
Hydration enthalpy	-1602	-1833	KJ/mol	[4]

Hydration enthalpy sulfate salt	18	52	KJ/mol	[5]
Pitzer constant sulfate salt $\beta^{(0)}$	0.20	0.2053		
$\beta^{(1)}$	2.65	2.62		
$\beta^{(2)}$	-55.7	-48.07		
Solubility of sulfate salt	2.10 ⁻²	6	Mol/Kg	[6]

1.3 Kinetics of the cadmium isomorphous substitution in calcium sulphate crystal lattice

The incorporation of an impurity takes place at the surface. Uptake is therefore mostly influenced by surface processes as growth [2]. The first is that the growth rate is so high that any Cd²⁺ or Ca²⁺ near the crystal surface has an equal chance to become incorporated with equal diffusion coefficients for these two ions, The resulting D value is equal to 1. For Cd²⁺ in calcium sulphate crystal lattice where D is smaller than 1 this means an increase with respect to the equilibrium situation, due to entrapment at the surface. The second situation is equilibrium without growth, but with an exchange of ions between the solid state and the solution. Since this will only occur at a very large time scale, equilibrium partition coefficients can only be obtained by extrapolation to growth rate zero. In practice, D will lie between the thermodynamical value and the value determined by the diffusion rates. The kinetical aspects have long been recognized. In many studies, efforts are made to explain the trapping of impurities as a function of growth rate. For a proper explanation the reactions occurring during growth of the crystals and uptake should be considered for each case separately. By comparing the respective reaction rates of, in this case, Cd²⁺ and Ca²⁺ some prediction of the kinetical behaviour of uptake may be done. The reactions that can be considered are bulk diffusion, adsorption desorption, surface diffusion, transport along a step, bonding at the kink site, or direct attachment from the solution. Since during these reactions dehydration occurs, the reaction rates are somehow related to well-known processes as ligand exchange, dehydration and diffusion

2. MATERIALS AND METHODS

2.1 Approach

As we have described above, the thermodynamics and the kinetics aspects of the cadmium isomorphous substitution in calcium sulfate lattice are complicated and not easy to model phenomenologically. For that reason, in this present study we have focused primarily on statistical modeling as an exploratory approach, to expect finding a good model that allow good prediction and optimization of the cadmium isomorphous substitution in calcium sulfate lattice during the co-crystallization process for cadmium removal from phosphoric acid. The expected model will show how necessary the phenomenological model should be required.

2.2 Experimental

The degree of incorporation depends on the kinetics of the isomorphous substitution which depends mainly on the supersaturation. For that, the concentrated phosphoric acid (50%-54% P₂O₅), is heated at 75°C under specific conditions in terms of free sulfate and solid content, and further treated with phosphate rock to adjust the final free sulfate content. The free sulfate content, expressed hereafter as %SO₄²⁻, points out the amount of sulfate ions in excess relatively to the calcium ions. It could be either positive for excess sulfate ions or negative for excess calcium ions. To establish an appropriate statistical model to predict and optimize the isomorphous substitution of cadmium in calcium sulfate crystal lattice, during the co-crystallization process for cadmium removal from wet phosphoric acid, continuous laboratory tests were conducted typically to the process as shown in Fig.1 below, using small reactors of one-liter capacity, filter and raw materials:

- Phosphoric acid industrial grade (52 wt % to 54 wt % P₂O₅).
- Sulfuric acid H₂SO₄ (96 wt %).
- Phosphate rock (31 wt % P₂O₅).

The experiments were based on a phosphate rock sample containing 10 ppm cadmium content, by changing the operating conditions such as P₂O₅ content in the ACP feed, free sulfate and solid contents during co-crystallization steps, and final free sulfate content at the free sulfate removal step. The aim was to generate a big data to model the co-crystallization process, especially the isomorphous substitution of cadmium in calcium sulfate crystal lattice. For each experiment, solid was separated by press filtration to recover the phosphoric acid with reduced cadmium content. The chemical analysis of the P₂O₅ content was carried out by UV/VIS Spectrometry, and the cadmium content by Inductively Coupled Plasma Spectrometry (ICP), the free sulfate was determined by titration with standard barium chloride solution. The calcium sulfate crystallization form was characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

2.3 Methodology

There are many patents concerning the cadmium removal (decadmiation) from phosphoric acid by co-crystallization. For this present study, we have referred to the process [1] given in Fig -1 below:

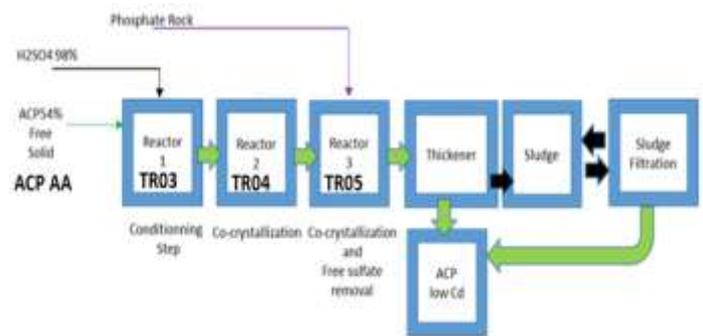


Fig -1: Typical co-crystallization process for cadmium removal from phosphoric acid [1]

The process involves several steps:

- The conditioning step: sulfuric acid (98 wt%) were added to the phosphoric acid (ACP AA) free solid to reach respectively 6 wt% of free sulfate. The working temperature was 70°C.
- The co-crystallization step: cadmium incorporation during hemihydrate/anhydrite co-crystallization. The free sulfate removal step (desulfation): the free sulfate was removed by precipitation using fine phosphate rock within particle size distribution less than 160 µm. The working temperature was about 90°C.

$$\text{CaO (Phosphate)} + \text{SO}_4^{2-} + x\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot x\text{H}_2\text{O} \text{ at } 90^\circ\text{C}$$
 With x equaling 0.5 or 2 depending on working conditions (temperature and P₂O₅ content).
- The desaturation step: after the free sulfate removal step, the treated phosphoric was given an additional residence time for desaturation in order to complete kinetics of reactions and having therefore very lower free sulfate content.
- The solid removal: at the end of the process, the treated phosphoric acid was clarified to separate solids from the phosphoric acid with reduced cadmium concentration. The sludge was filtered by press filter to increase the P₂O₅ recovery and dispose the calcium sulfate solid.

3. RESULTS AND DISCUSSIONS

3.1 Phosphoric Acid Quality

Fig -2 shows the phosphoric acid quality over the time specifically to different steps of the co-crystallization process. The phosphoric acid quality implies %P₂O₅, %Ts (solid ratio), %SO₄²⁻ (sulfate level) and cadmium content.

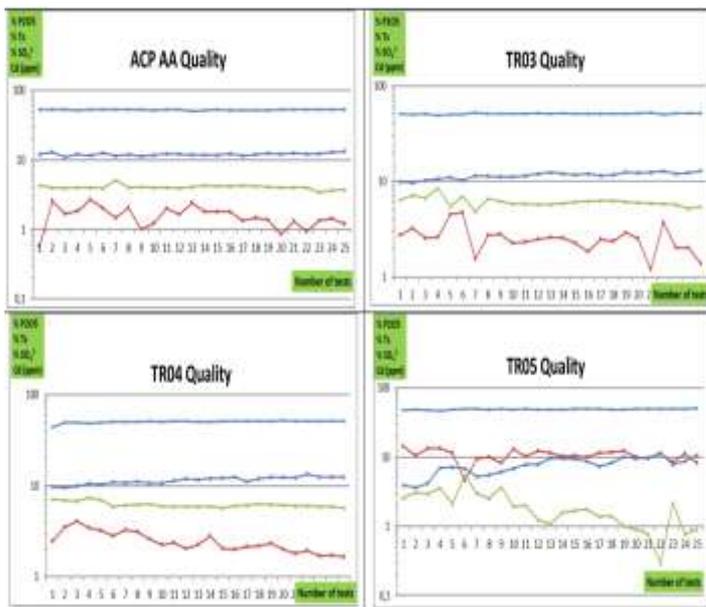


Fig -2: Phosphoric acid quality by step of the co-crystallization process

3.2 Data Analysis

3.2.1 Univariate Descriptive Statistics

It describes patterns found in univariate data include central tendency (mean, mode and median), dispersion (range, variance, maximum, minimum, quartiles (including the interquartile range)), and standard deviation [7]. Fig -3 shows several graphical methods used in our case, to provide quick visual summaries of essential data characteristics. It concerns Dispersion Diagram Plot, Density Trace Plot, Box Plot, and Q-Q Plot. These graphs provide information about dispersion, ranges, shapes of distributions, extreme values (outliers), relationships between different datasets, and trends (increasing, decreasing, and cyclic).

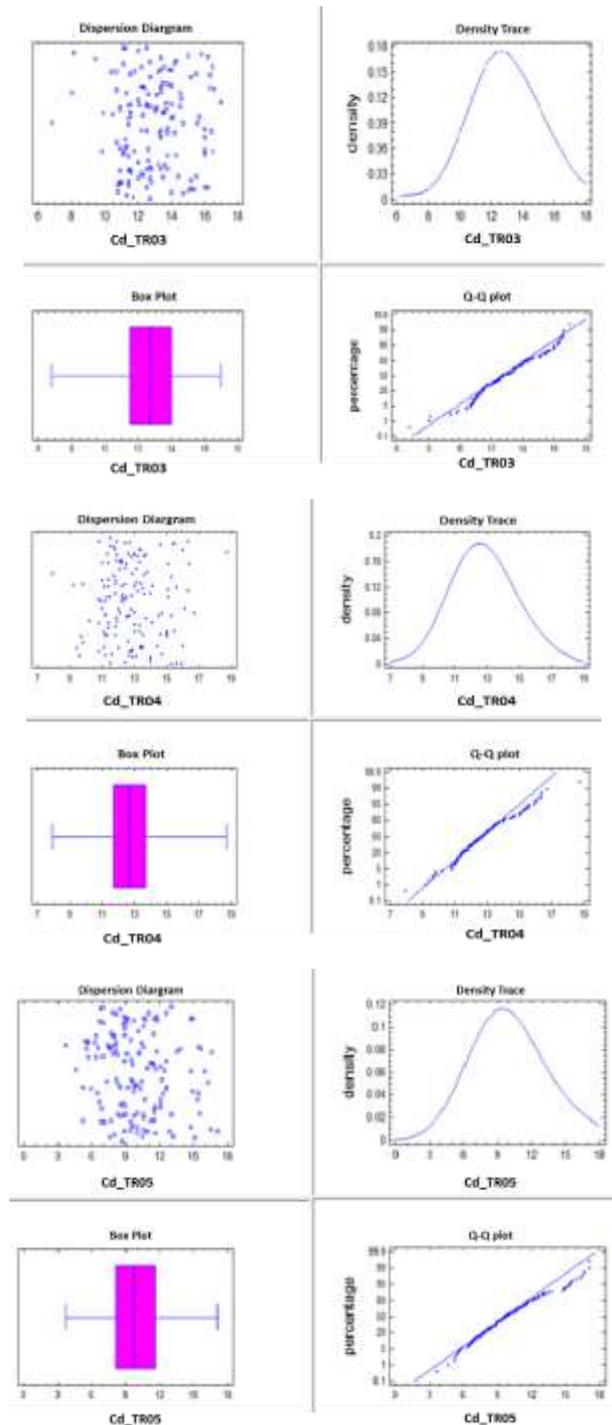
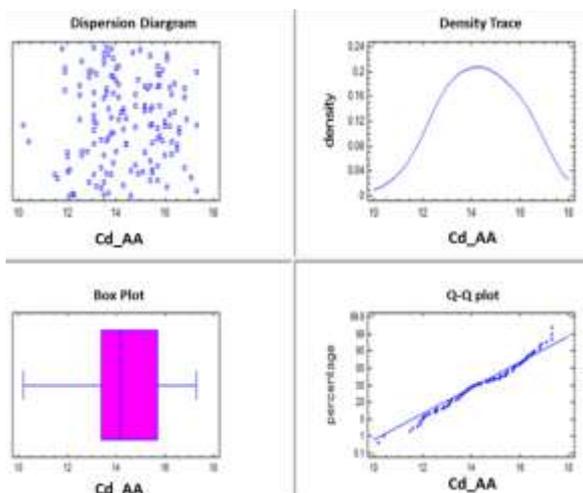


Fig -3 Univariate Descriptive Statistics of the datasets

From the graphs:

- The Box Plot shows that there are no outliers points in the datasets.
- The Q-Q Plot (Henry plot) shows that the datasets represents a normal distribution.

Specifically to the Dispersion Diagram Plot (Scatter Plot), it is found that:

- The cadmium contents in the phosphoric acid (ACP AA) are scattered between 12 to 17 ppm, which is also confirmed by the Density Trace Plot where all the points are concentrated at an average of 14 ppm.
- The cadmium contents at the TR03 step are little dispersed between 11 to 16 ppm, with an average of 13 ppm.
- The cadmium contents and average at the TR04 step still the same like the TR03 step.
- In the TR05 step, the cadmium contents are less dispersed than the previous steps, they are scattered between 5 and 15 ppm with an average of 10 ppm.

3.2.2 Multivariate Descriptive Statistics

Multivariate Descriptive Statistics employs vectors of statistics (mean, variance, etc.), which can be considered an extension of the univariate descriptive statistics [8].

• Mahalanobis Distance:

The Mahalanobis Distance method shows that 10 individuals points must eliminated by considering them as outliers points.

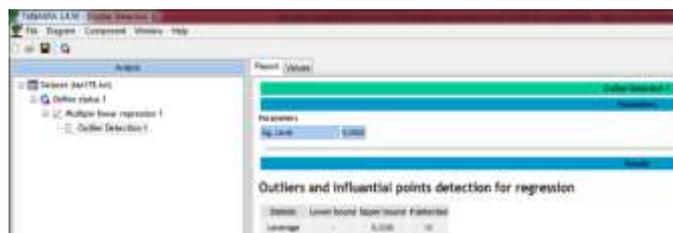


Fig -4: Outliers detection by Mahalanobis Distance method

• Box Plot:

From the Box Plot in Fig -5 below, it is shown that the cadmium content has decreased from ACP AA to TR05. The steps TR03 and TR04 display the same behavior in term of cadmium content trend.

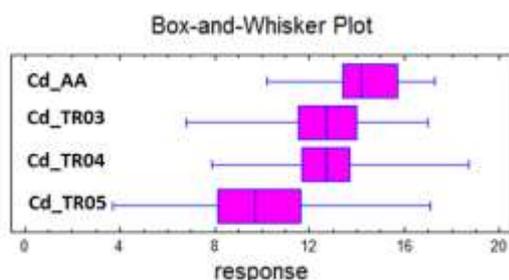


Fig -5. Central tendency display by Box-and-Whisker Plot

Consequently, we have reduced the number of individual points of the dataset, and have selected 4 parameters which are %P₂O₅, %Ts (solid ratio), %SO₄²⁻ (sulfate level) and cadmium content for modeling the isomorphous substitution

behavior during the cadmium co-crystallization in calcium sulfate crystal lattice.

• Student Test :

The Student test summarized in table 2 below, investigates statistically the variation in cadmium content through the different steps of the co-crystallization process. The test results are proven and fit well with the co-crystallization process philosophy of cadmium removal.

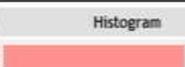
Table -2: Student Test of the cadmium content variation

	ACP AA	TR03	TR04	TR05	
Number of individuals	N	150	166	169	168
Mean	μ	14,3	13	12,9	10,3
Standard Deviation	σ	1,53	2,07	5,13	1,43
Hypothesis	H ₀ (μ ₁ =μ ₂ =μ _{avg}) Vs H ₁ (μ ₁ >μ ₂)				
Considering Statistical Significance α = 5%					
t Calculated	6,31		0,48	5,68	
t Critical Value	1,96				
Test Result	H ₁ (μ ₁ >μ ₂)		H ₀ (μ ₁ =μ ₂ =μ _{avg})	H ₁ (μ ₁ >μ ₂)	
Interpretation	The Cadmium content decrease from ACP AA to TR03 is statistically proven		No cadmium decrease in TR04	The Cadmium content decrease from ACP TR04 to TR05 is statistically proven	

3.3 Principal Component Analysis (PCA)

To emphasize variation and bring out strong patterns in dataset, we have used the Principal Component Analysis method [9]. So, considering the 4 parameters already selected (%P₂O₅, %Ts (solid ratio), %SO₄²⁻ (sulfate level) and cadmium content (expressed as Me)) and specifically to all process steps (ACP AA, TR03, TR04 and TR05), table 3 gives the number of axes and the variation per each axis. The first three axes will explain 69.42% of the total inertia of the cloud data. The correlation circle below in Fig.6 shows that the cadmium content values (Me) are correlated with the horizontal axis.

Table -3. Principal Component Analysis of datasets

Axis	Eigen value	Difference	Proportion (%)	Histogram	Cumulative (%)
1	9.483779	7.173378	47.42 %		47.42 %
2	2.310401	0.221387	11.55 %		58.97 %
3	2.089014	0.583404	10.45 %		69.42 %
4	1.505611	0.467920	7.53 %		76.94 %
5	1.037691	0.021015	5.19 %		82.13 %

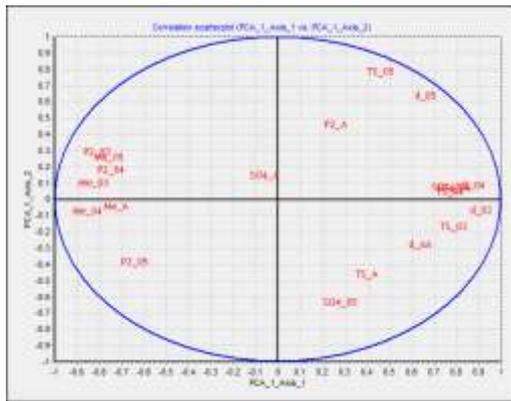


Fig -6: Correlation circle of the PCA

It is clear that the first factor (Axis 1) is negatively correlated with decreases in cadmium (Me_AA, Me_03, Me_04 and Me_05) and with decreases in %P₂O₅ (TR03, TR04 and TR05). However, it is positively correlated with increases in SO₄_TR03 and SO₄_TR04. The cadmium contents are positively linked which makes sense since the process is continuous, so each step depends on the previous one. It is also found that the cadmium content depends on the SO₄_TR03 and SO₄_TR04, that also makes sense since the cadmium isomorphous substitution in calcium sulfate crystal lattice is improved by the sulfuric acid excess.

3.4 Data Modeling

3.4.1 Multiple Linear Regression (MLR)

Multiple Linear Regression (MLR), also known simply as multiple regression, is a statistical technique that uses several explanatory variables to predict the outcome of a response variable [10]. The goal of Multiple Linear Regression (MLR) is to model the linear relationship between the explanatory (independent) variables and response (dependent) variable. In essence, multiple regression is the extension of ordinary least-squares (OLS) regression that involves more than one explanatory variable. The Formula for Multiple Linear Regression is :

$$y_i = \beta_0 + \beta_1 x_{i1} + \beta_2 x_{i2} + \dots + \beta_p x_{ip} + \epsilon$$

Where, for i=n observations:

y_i : dependent variable

x_i : explanatory variables

β₀: y-intercept (constant term)

β_p: slope coefficients for each explanatory variable

ε: the model's error term (also known as the residuals)

Below, we give specifically to each dependent variable the MLR results containing the model coefficients, the analysis of variance (ANOVA), the analysis of residuals, the global results and the final statistical model:

Table -4: MLR of Dependent Variable Cd_TR03

Attribute	Coef.	Std.	t-Statistic	P-Value
CONSTANT	13.2405	0.724849	18.2748	0.0000
TS_AA	-0.531108	0.103183	-5.14726	0.0000
Cd_AA^2	0.0120375	0.002617	4.59958	0.0000
(SO4_TR03-SO4_TRA)	-0.597337	0.009611	-6.18196	0.0000
(TS_TR03-TS_AA)	-0.548831	0.008917	-6.10375	0.0000

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Regression	353.354	4	88.3385	83.34	0.0000
Residual	143.099	135	1.05999		
Total	496.453	139			

Initial Regression Conditions		Re-evaluated Regression Conditions (Linearity, Independence, Normality, Equal variance)	
R ²	0.711758	0.900047	
Adjusted R ²	0.703217	0.897577	
Sigma Error	1.02956		
Mean absolute error	0.692989		
Durbin-Watson statistic	1.09704 (P=0.0000)		

Model of Cd_TR03

$$Cd_TR03 = 13.2405 - 0.531108 * TS_AA + 0.0120375 * Cd_AA^2 - 0.597337 * (SO4_TR03 - SO4_AA) - 0.548831 * (TS_TR03 - TS_AA)$$

The output presents the results of fitting a Multiple Linear Regression model to describe the relationship between Cd_TR03 and 4 independent variables. Since the P-value in the ANOVA table is less than 0.01, statistically there is a significant relationship between the variables at the 99% confidence level. The test results for residuals (errors) was positive, so some atypical points were removed to improve the R².

Table -5: MLR of Dependent Variable Cd_TR04

Attribute	Coef.	Std.	t-Statistic	P-Value
CONSTANT	23.6813	3.83986	6.16723	0.0000
Cd_TR03	0.596242	0.0398702	14.8546	0.0000
P2O5_AA	-0.412348	0.0468242	-8.99133	0.0000
Cd_AA	0.245899	0.0445868	5.51906	0.0000

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Regression	322.651	3	107.55	249.70	0.0000
Residual	58.5781	136	0.430721		
Total	381.229	139			

Initial Regression Conditions		Re-evaluated Regression Conditions (Linearity, Independence, Normality, Equal variance)	
R ²	0.846344	0.912075	
Adjusted R ²	0.842954	0.909895	
Sigma Error	0.656294		
Mean absolute error	0.506984		
Durbin-Watson statistic	1.35254 (P=0.0000)		

Model of Cd_TR04

$$Cd_TR04 = 23.6813 + 0.596242 * Cd_TR03 - 0.412348 * P2O5_AA + 0.245899 * Cd_AA$$

The output presents the results of fitting a Multiple Linear Regression model to describe the relationship between Cd_TR04 and 15 independent variables. Since the P-value in the ANOVA table is less than 0.01, statistically there is a significant relationship between the variables at the 99% confidence level. The tests results for residuals (errors) are

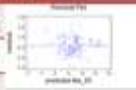
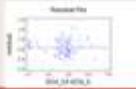
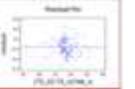
positives, so some atypical points were removed to improve the R².

Table -6: MLR of Dependent Variable Cd_TR05

$$- 0,0821001*(SO4_TR05*Cd_AA) - 0,0629848*((TS_TR03 - TS_AA)*Cd_AA) + 0,43350*Cd_AA^2 - 0,678078*(SO4_TR03 - SO4_AA)$$

Attribute	Coef.	Std.	t-Statistic	P-Value
CONSTANT	-95,2698	22,4511	-4,24343	0,0000
P2O5_AA	3,34181	0,708453	4,71705	0,0000
Exp(Cd_AA)	-2,6866E-7	6,27079E-8	-4,28431	0,0000
(P2O5_AA*Cd_AA)	-0,205686	0,0467431	-4,40034	0,0000
(SO4_TR05*Cd_AA)	-0,0821001	0,00943504	-8,70162	0,0000
((TS_TR03-TS_AA)*Cd_AA)	-0,0629848	0,00909764	-6,94486	0,0000
Cd_AA^2	0,433501	0,0050998	8,62648	0,0000
(SO4_TR03-SO4_AA)	-0,678078	0,135782	-4,99461	0,0000

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Regression	795,422	7	113,632	44,19	0,0000
Residual	339,416	132	2,57133		
Total	1134,84	139			

Initial Regression Conditions		Re-evaluated Regression Conditions (Linearity, Independence, Normality, Equal variances)	
R ²	0,700912	0,825954	
Adjusted R ²	0,685052	0,815172	
Sigma Error	1,60354		
Mean absolute error	1,28445		
Durbin-Watson statistic	1,13435 (P=0,0000)		

Model of Cd_TR05

$$Cd_TR05 = -95,2698 + 3,34181 * P2O5_AA - 2,6866E-7 * Exp(Cd_AA) - 0,205686 * (P2O5_AA * Cd_AA) - 0,0821001 * (SO4_TR05 * Cd_AA) - 0,0629848 * ((TS_TR03-TS_AA) * Cd_AA) + 0,433501 * Cd_AA^2 - 0,678078 * (SO4_TR03-SO4_AA)$$

An examination of the Multiple Linear Regression analysis make it clear that our multiple regression model is useful and make sense. By considering Cd_TR05 as a critical part of the global model, as it displays the final cadmium content after the isomorphous substitution in calcium sulfate crystal lattice, it appears that in the presence of the TS_TR03 and TS_TR03, the independent variables P2O5_AA, SO4_TR03, Cd_AA, SO4_TR05 are significantly good predictors for Cd content. Since the P-value in the ANOVA is less than 0.01, statistically there is a significant relationship between the variables at the 99% confidence level. The model's degree of explaining the variance the dependent variable (response) Cd_TR05 was found to be R²=0.83. Considering these coefficients and other statistical parameters, and comparing to our understanding of the cadmium isomorphous substitution in calcium sulfate crystal lattice, during the co-crystallization process for cadmium removal from wet phosphoric acid, it can be said that the model makes satisfactory prediction of the cadmium removal. For future work, it might be recommended to study how a phenomenological model, can be developed to describe the isomorphous substitution of cadmium, in the way to improve the model prediction and consider medium and high cadmium cases.

The output presents the results of fitting a Multiple Linear Regression model to describe the relationship between Cd_TR05 and 7 independent variables. Since the P-value in the ANOVA table is less than 0.01, statistically there is a significant relationship between the variables at the 99% confidence level. The tests results for residuals (errors) are positives, so some atypical points were removed to improve the R².

4. CONCLUSIONS

The fitted Multiple Linear Regression model for predicting the cadmium isomorphous substitution in calcium sulfate crystal lattice, during the co-crystallization process for cadmium removal from wet phosphoric acid, is given specifically to each process step by:

$$Cd_TR03 = 13,2465 - 0,531108*TS_AA + 0,0120375*Cd_AA^2 - 0,597337*(SO4_TR03 - SO4_AA) - 0,548831*(TS_TR03 - TS_AA)$$

$$Cd_TR04 = 23,6813 + 0,596242*Cd_TR03 - 0,412348*P2O5_AA + 0,245899*Cd_AA$$

$$Cd_TR05 = -95,2698 + 3,34181*P2O5_AA - 2,6866E-7*Exp(Cd_AA) - 0,205686*(P2O5_AA*Cd_AA)$$

REFERENCES

- [1] K. Samrane, R. Boulif, D. Dhiba, A. Bouhaouss, "Improvements and intensification of industrial co-crystallization process for cadmium removal from wet phosphoric acid", International Journal of Engineering Sciences & Research Technology, 7(10), 152-163, October 2018.
- [2] G.J. Witkamp, "Crystallization of calcium sulfate and uptake of impurities", Delft 1989
- [3] J.E. Huheey, Inorganic Chemistry, Harper and Row, New York, 1975
- [4] Y. Marcus, Vhem. Soc. Far. Trans. I, 83 339-49, 1987
- [5] P. Vieillard and H.D. Jenkins, J. Chem. Res, (M) 3701-69, 1986
- [6] K.S. Pitzer and G. Mayorga, J. Sol. Chem, 3 539-46, 1974
- [7] A. C. Tamhane, D. D. Dunlop, "Statistics and Data Analysis", 1st edition, 2000.
- [8] J. T. McClave, and Sincich, Statistics (10th edition), 2006.
- [9] J. Jacquard, R. Turrisi, "Interaction effects in multiple regression", 2nd edition, 2003.
- [10] N. R. Draper, and S. Harry, "Applied Regression Analysis", 3rd edition, 1998.

BIOGRAPHIES

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