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Investigation of Fractal Dimension Change in Synthesized $CaSO_4$ Using PSSS

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Abstract

Generally, commercial product of calcium sulfate anhydrous ($CaSO_4$) is synthesized burning gypsum in kiln, in the process that the water is removed from gypsum crystallized by mixing $CaCl_2$ and Na_2SO_4 in aqueous medium. It is possible to change gypsum properties by changing the parameters during crystallization. Also, the differentiation in the structures of the synthesized product can be possible with using additives during the crystallization. The changes in properties of these synthetically produced materials may be investigated instrumentally.

This study examines change of surface fractal dimensions (D_f) of synthesized $CaSO_4$ anhydrate instrumentally. $CaSO_4.2H_2O$ was synthesized by chemical precipitation method in the presence Poly(Sodium 4-Styrene Sulphonate) and measured N_2-physisorption measurements after burning. Fractal dimensions were determined using single N_2-adsorption/desorption isotherms method. For Fractal dimension calculations, the Frenkel–Halsey–Hill (FHH) and the Neimark–Kiselev (NK) methods were used. Taguchi method has been used in evaluation of experimental design for optimization of D_f values.

Keywords: Frenkel–Halsey–Hill, Neimark–Kiselev, calcium sulfate

1. Introduction

It is easily perceived by man that a cube is three-dimensional and the square is two-dimensional. Length, height, thickness, area and volume can easily be calculated in these type materials. However, the materials in the nature are more complex in shape. When calculation of a kidney area is taken into account, more information than length, height and depth information is needed absolutely. The measure of the complexity of this formation is explained by the fractal dimension. In other words, fractal dimension is a measure of the complexity. It is derived from fractus word, which means "broken" in Latin. The entry of this definition into our life was possible by questioning the mathematician Benoit Mandelbrot's coastal length of England. At this point measurement can also be done through the map, or the circumference of the island is measured by help of a meter. Sensitivity can be further increased in this measurement: mm, nm, etc. As the sensitivity is increased, the measurement value will change. This is the result that the length of the measured of a finite piece is infinite can be said [1-7].
Dobrescu et al. reported that since 1984, it was reported that many studies on fractal geometry representing solid surfaces were made. In irregularly shaped materials, the fracture size value is between 2 and 3. D_f=2.0 values, indicate regularity and smoothness and also D_f=3.0 indicate highly irregular surface. The result obtained by using the SEM images in the study conducted and the result obtained by using the adsorption isotherm are very close to each other [5].

If it was easily described, calcium sulphate is a material that is being investigated for its ability to be used in processes such as dehumidification, or due to problems caused by shell formation in heat exchangers [8-9]. In this study, Df values were found by means of a program using adsorption isotherms. Using the Taguchi experimental design, in calcined calcium sulphate production, effect of production factors on fractal dimension has been revealed in the presence of Poly (Sodium 4-Styrene Sulphonate) (PSSS, Mw=1,000,000 g/mol) polymer. It is seen that, in the presence of PSSS, the most effective parameter on the fractal dimension is the $[Ca^{2+}]/[SO_4^{2-}]$ ratio.

Materials and methods

In the experiments, PSSS polymer was added to the calcium chloride solution. The amount of the PSSS was varied between 0.008 to 0.152 g/L. In this study, molecular weight of PSSS polymer was 1,000,000 g/mol and chemicals used were purchased from Sigma-Aldrich. For this study, Taguchi experimental method was selected and in design of experiment, four factors and three levels was used (Table 1). Taguchi L^9 orthogonal experimental design parameters are $[Ca^{2+}]$ concentration, $[Ca^{2+}]/[SO_4^{2-}]$ ratio, temperature, and [PSSS], respectively. The $CaSO_4$ samples were calcined in an oven at 500 °C for 5 hours. Quantachrome, Novatouch Lx^4 was used to obtain Isotherms. D_f values were calculated from using obtained adsorption-desorption isotherms by TouchWin program (Fig. 1-2). Minitab program has been used to generate Taguchi Analyses.

Results and discussion

The response table has been transferred to the Minitab program as it. First and second column were generated from adsorption isotherms, then third and fourth column were generated desorption isotherms. Result of this analysis is shown in Fig.3 and Fig. 4. By Frenkel-Halsey-Hill (FHH) and Neimark-Kiselev (NK) calculations, fractal dimensions obtained from isotherms were used together in Taguchi analysis to understand the common effect. In Table 3, response table for signal to noise ratios is given. according to this table, the order of least effective parameter from the most effective parameter is as follows: $[Ca^{2+}]/[SO_4^{2-}]$ ratio, Temperature (°C), [PSSS] (g/L), and $[Ca^{2+}]$ concentration. In Fig. 3, main effects plot for means on Df value of changing parameters is analyzed Also, main effects plot for SN ratios on Df value of changing parameters is showed. (Figure 4)

Conclusions

There are three major conclusions to be drawn:

-All samples of fractal dimension value were changed by used parameters in the presence of PSSS.

- While $CaSO_4$ is being synthesized to maximize the Df values; it should be applied the [PSSS] concentration of 0.08 g/L, the $[Ca^{2+}]$ concentration of 0.72 M, reactant ratio of 1, and the temperature of 20 °C then calcined at 500 °C for 5 hours.

- In the presence of PSSS, the most effective parameter on the fractal dimension is the $[Ca^{2+}]/[SO_4^{2-}]$ ratio.

Acknowledgements

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Figure and Table Captions

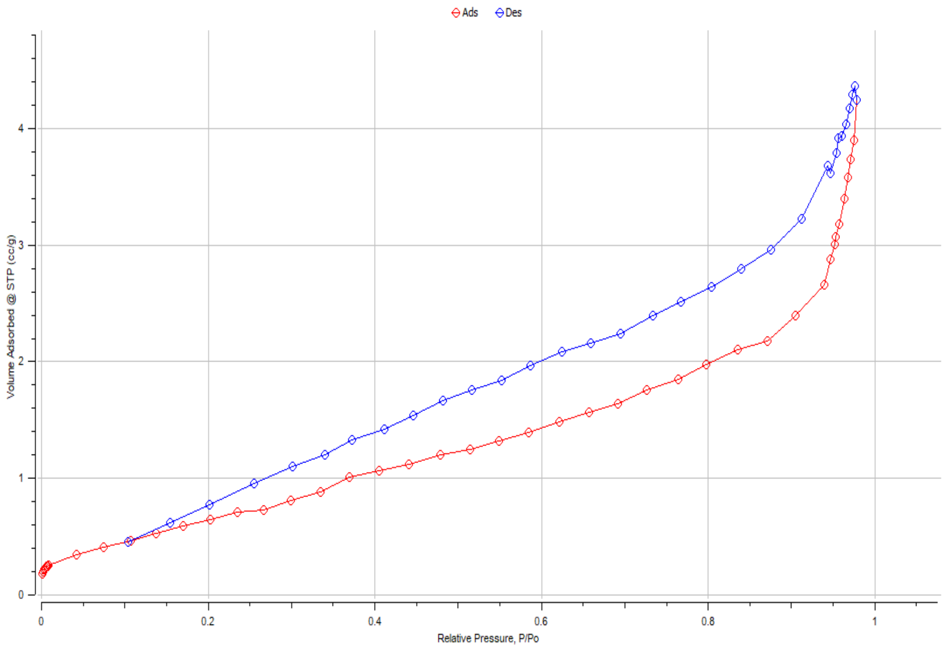

Figure 1. Absorption/desorption isotherm graph

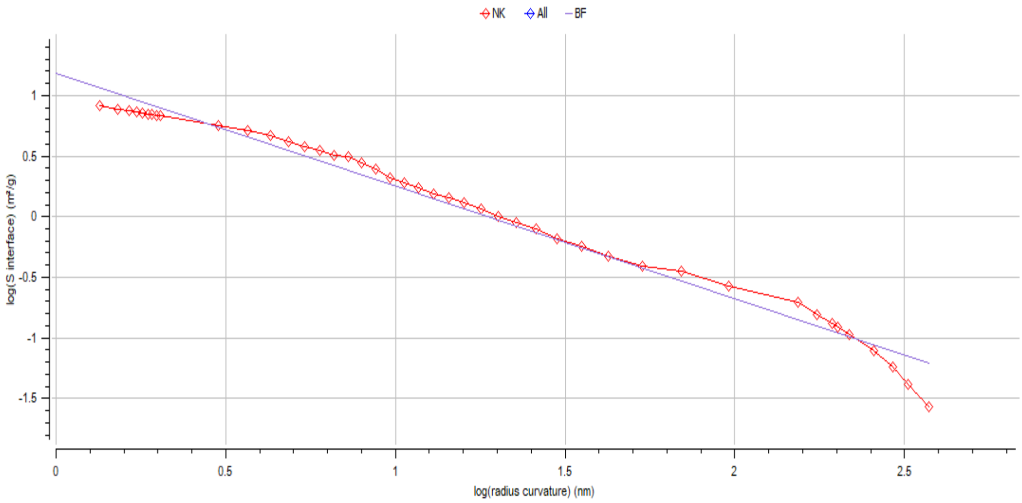

Figure 2. Fractal dimension calculation graph in an isotherm

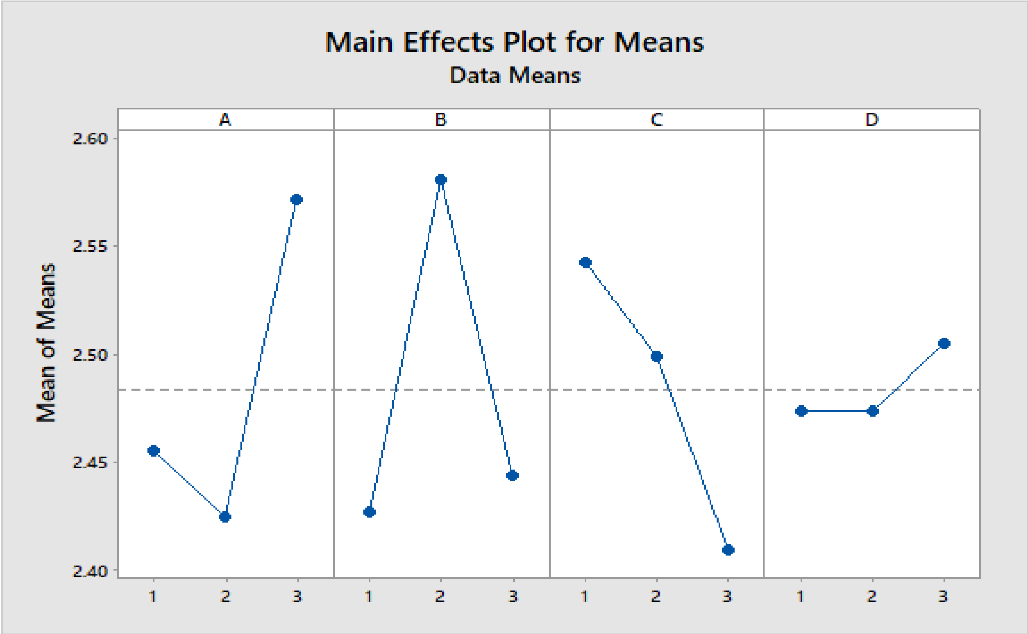

Figure 3. Main effects plot for means on D_f value of changing parameters

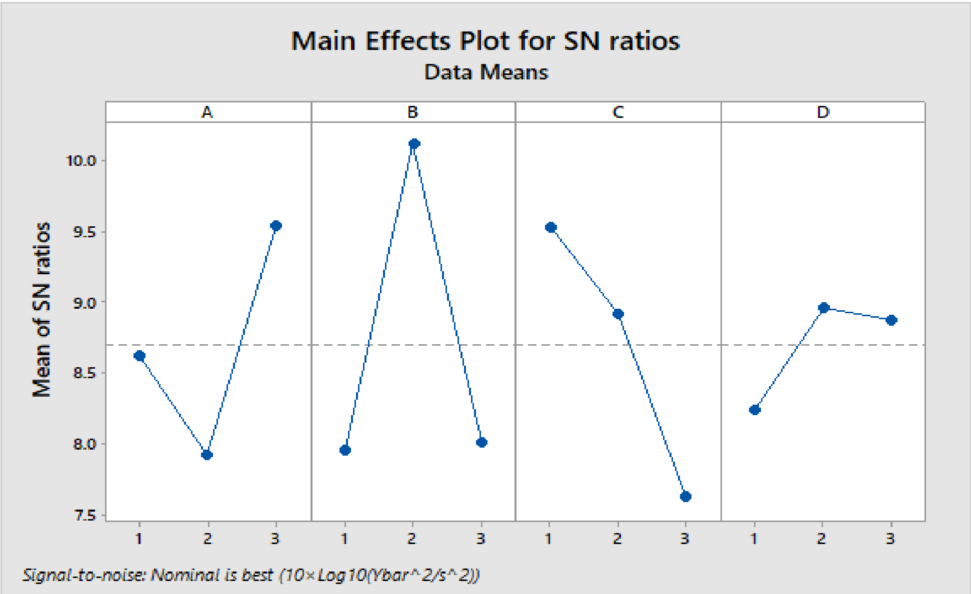

Figure 4. Main effects plot for SN ratios on D_f value of changing parameters

Table1. Taguchi L^9 orthogonal experimental design

	A	**B**	**C**	**D**
Exp. No.	$[Ca^{2+}]$ (mol/L)	$[Ca^{2+}]/[SO_4^{2-}]$ ratio	Temperature (°C)	[PSSS] (g/L)
Exp 1	0.24	0.5	20	0.008
Exp 2	0.24	1	30	0.08
Exp 3	0.24	2	40	0.152
Exp 4	0.48	0.5	30	0.152
Exp 5	0.48	1	40	0.008
Exp 6	0.48	2	20	0.08
Exp 7	0.72	0.5	40	0.08
Exp 8	0.72	1	20	0.152
Exp 9	0.72	2	30	0.008

Table 2. Response Table

FHH (Adsorption)	**NK (Adsorption)**	**FHH (Desorption)**	**NK (Desorption)**
1.33900	3.06942	2.00249	3.37733
1.71322	3.04303	2.13883	3.33358
1.09386	3.02400	1.93424	3.39597
1.18291	3.01351	2.01280	3.40622
1.22604	3.01469	2.06868	3.43939
1.33420	3.04570	2.00450	3.34570
1.23817	2.95906	2.09806	3.42718
1.80132	3.05254	2.72737	3.41158
1.32860	3.06106	2.29518	3.46083

Table 3. Response Table for Signal to Noise Ratios Nominal is best (10. Log10($Ybar^2/s^2$))

Level	**A**	**B**	**C**	**D**
1	8.625	7.954	9.536	8.240
2	7.919	10.127	8.924	8.969
3	9.545	8.009	7.628	8.881
Delta	1.626	2.173	1.908	0.729
Rank	3	1	2	4