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DETERMINATION OF THE CALCIUM SULFATE HEMIHYDRATE CONTENT BY REGRESSION ANALYSIS USING THE INITIAL SETTING TIME

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Abstract: In this paper, we randomly select 75 sets data of calcium sulfate hemihydrate (CSH) content and initial setting time, and the traditional test method of CSH and analyses initial setting time was used by complexometric titration. So the close relationship between them was studied in depth, which classification fitting data to be analyzed by regression analysis. The result shows that this regression analysis method can accurately determine CSH content in modified industrial by-product gypsum. The determination method has the advantages of simplification and rapid operation. As well as, the XRF quantitative analytical method was used to test the CSH content, which verified the accuracy of regression analysis method. The results also show that this method has high accuracy, and can simplify the traditional experimental process. The method developed is easier and more convenient and has broad prospects in application.

*Keyword: G*ypsum, Modified, Setting time, Regression analysis

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1. INTRODUCTION

Currently, there are many kinds of industrial by-product gypsum, among which phosphogypsum is representative. However, the real resource utilization of phosphogypsum is very low. Most of them are in-situ stockpiling, which not only occupies a large amount of land, but also brings serious safety and environmental pollution problems[1-3]. This has become an important factor restricting the sustainable development of phosphorus chemical industry. Therefore, the comprehensive utilization of industrial by-product gypsum is of great significance. Strengthening the research and development of key technologies and building a number of large-scale industrial demonstration projects with high value-added utilization have become the key tasks of comprehensive utilization of industrial by-product gypsum in the future.

Before comprehensive utilization of by-product gypsum, for example phosphogypsum, it must be pretreated by high temperature calcination or vacuum high pressure modification[4-6]. The phosphogypsum was modified into hemihydrate gypsum, so various building materials were prepared by utilizing its hydraulicity. So the key index to measure the quality of modified phosphogypsum is the content of calcium sulfate hemihydrates (CSH). The higher the content of CSH, the better the performance of hemihydrate gypsum is. Therefore, the detection of CSH content is a necessary item. At present, EDTA chemical titration is the traditional method for the determination of CSH. This process is cumbersome and complex, which makes it difficult for many modified gypsum enterprises to monitor the content of CSH. In this paper, we randomly chose 75 sets data of CSH content by complexometric titration, from the gypsum companies over an 18-month period. In these researches, the close relationship between the content of CSH and the initial setting time was studied. The exact relationship between the initial setting time and the content of CSH was obtained through data fitting. In addition, this method can simplify the traditional experimental process, and also has high accuracy, convenient operation and great application value.

2 MATERIAL AND METHODS

2.1 RAW MATERIALS

The modified phosphogypsum was phosphogypsum calcined at 600℃ for 2-3 hours to obtain effective hemihydrate gypsum which can turn into a hydraulic binding material, and using phosphate fertilizer plant to provide modified phosphogypsum in Chongqing, China.

2.2 TRADITIONAL METHODS

The CSH content was determined according to Chinese standard YY/ T 1118-2001[7]. The titration principles and processes are as follows.

(1) Principles

The content of CSH was determined by complexometric titration, as Ca^{2+} forms a stable chelate complex with EDTA. The principle of replaceable titration was used to analyze the measurement and indicate the end-point.

$$CaSO_4 \bullet 1/2H_2O + H^+ \rightarrow Ca^{2+} + HSO_4^- + 1/2H_2O$$

(2) Test process

a. Standard solution preparation and calibrating

The benchmark reagent of zinc oxide that burned to constant weight in a high temperature furnace at 800 ºC, wetted with a small amount of water, dissolved in 2mL hydrochloric acid (1+4) solution, and added with 100mL water. The pH of the solution was adjusted to 7-8 with ammonia solution (1+9), and added with 10mL of ammonia-ammonium chloride buffer solution A (1000mL≈10) and 5 drops of chromium black T indicator solution (5g/L). The solution was titrated with the prepared EDTA solution until the solution changed from purple to pure blue. At the same time, blank test was done. The concentration of EDTA standard titration solution was as follows:

$$C(\text{EDTA}) = m \times 1000/(M \times (V_1 - V_2))$$

where, *C*-EDTA standard solution concentration, mol/L;

m- mass of zinc oxide, g;

V_1-volumic numbe of EDTA, mL;

V_2- blank experiment's volumic numbe of EDTA, mL;

M-molar mass of zinc oxide (81.39), g/mol.

The calibration results are shown in Table 1.

Table 1 Calibration results for EDTA standard titration solutions

Parallel samples	ZnO/g	V1/mL	V2/mL	C(EDTA)/ mol/L
First sample	0.1501	36.91	0.05	0.05003
Second sample	0.1501	36.93	0.05	0.05000
Third sample	0.1501	36.92	0.05	0.05002
Average				0.05002

b. Preparation of reagent

Methyl red indicator solution: methyl red of 0.1 g was weighed, dissolved by adding 7.4 mL of sodium hydroxide solution (0.05 mol/L), diluted to 200 mL by adding water, and shaken well.

Calcein indicator solution: 0.1g of calcein was weighed, added with 10g of potassium chloride, and grinded evenly.

Potassium hydroxide test solution: potassium hydroxide of 6.5g was weighed and dissolved with water, and the solution reached a constant volume of 100 mL by adding water, and shaken well.

Copper reagent (1mg/mL): sodium diethyldthiocarbanate of 0.1g was weighed and dissolved with water, and the solution reached a constant volume of 100 mL by adding water, and shaken well.

Mixed solution of EDTA and ammonium chloride: 6.75 g ammonium chloride, 0.0616 g magnesium sulfate, and 0.093 g EDTA were weighed, dissolved with 65 mL ammonia water, diluted to 100 mL by adding water, and shaken well.

Chromium black T indicator: 1.25 mg mordant dyeing 11 and 11.25 mg ammonium ammoniate were weighed and dissolved with methanol, and the solution reached a constant volume of 100 mL by adding methanol, and shaken well.

c. Preparation of test solution

Three samples of 75 cm^2 hemihydrate gypsum were separately taken from the same batch of samples and placed in evaporating dishes. They were dried in a drying oven at 105 ºC to reach constant weight and weighed accurately (accurate to 0.0001g). They were all placed in flasks containing 200 mL of water and 10 mL of hydrochloric acid, heated and shaken until the gypsum dissolved. The solutions were neutralized with ammonia water (5 mol/L) and filtered with 10 mL ammonia buffer solution (pH=10). The fabric was washed with water, and the washing water was incorporated into the filtrate. The filtrate was diluted to 500 mL with water (note: the fabric was kept for use). The filtrate was absorbed for 50 mL to add to a 250 mL conical bottle, and neutralized with hydrochloric acid (2mol/L).

d. Complexometric titration

The test solution was taken for 20 mL, added to a suitable conical bottle, mixed with 5 mL the mixed solution of EDTA and ammonium chloride, added with 1 mL copper reagent, added with 0.25-0.30 mL chrome black T indicator, titrated with EDTA standard solution from wine red to blue till reaching the titration end-point.

2.3 OTHER TEST METHODS

a. Initial setting time

The initial setting time of CSH was determined according to Chinese standard "Common Porland Cement"(GB 175).

b. X-Ray Fluorescence (XRF)

Smash the samples and the grind them to the extent that they can sieve through the 200 mesh sieves. The powder was then vacuum dried and tested using XRF.

3 RESULTS AND DISCUSSION

This research randomly chose 75 sets data of the initial setting time and CSH content by complexometric titration, from the industrial by-product gypsum disposal companies, and the test results are presented in Table 2 and Table 5.

3.1 CLASSIFICATION ANALYSIS

3.1.1 Initial setting time greater than 7.8min

(1) Simple equation finishing

In accordance with the author's working experience of many years, the initial setting time equal to 7.8 min was chosen for dividing data between two separate analyses. So, the measured values of the initial setting time greater than 7.8min (CSH content less than 82%) were presented in Table 2.

Table 2 Measured values of the initial setting time greater than 7.8min (CSH content<82%)

Initial setting time /min	Calcium sulfate hemi-hydrate content /%	Initial setting time /min	Calcium sulfate hemi-hydrate content /%	Initial setting time /min	Calcium sulfate hemi-hydrate content /%
14.1	78.6	13.8	78.4	9.9	80.8
8.1	81.2	11.3	79.6	8.2	81.3
13.3	79.8	7.1	81.4	10.9	80.9
8.4	80.7	10.9	80.4	8.6	81.1
11.4	80.1	9.6	80.5	8.1	81.4
8.0	81.9	7.9	81.5	11.0	80.9
9.2	80.9	13.5	79.1	8.1	81.8
12.8	79.6	14	77.1	11.5	79.9
14.9	78.8	8.0	81.9	8.1	81.5
8.0	81.6	12.9	79.8	13.8	78.9
12.4	79.3	8.4	81.3	8.1	81.0
11.1	80.7	13.9	78.7	8.9	80.8

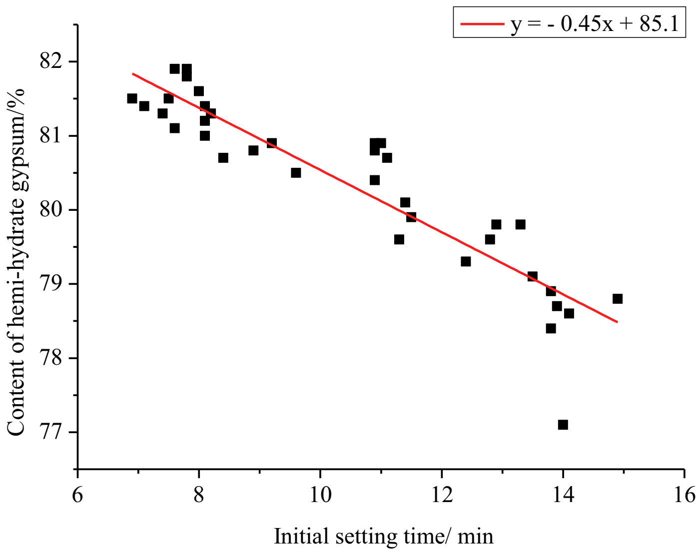

Fig.1 Linear regression model (simple equation finishing) between initial setting time and CSH content (initial setting time greater than 7.8min)

Table 3 Calcium sulfate hemi-hydrate content of simple equation fitting

Initial setting time /min	14.1	9.6	11.3	8.0	10.9	7.9	8.1	12.8	8.9	8.0	12.4	8.2	11.5	8.1	12.9
Calcium sulfate hemi-hydrate /%	78.6	80.5	79.6	81.9	80.4	81.5	81.4	79.6	80.8	81.6	79.3	81.3	79.9	81.4	79.8
Simple equation fitting /%	78.8	80.8	80.0	81.5	80.2	81.6	81.5	79.3	81.1	81.5	79.5	81.4	79.9	81.5	79.3
Difference value	0.2	0.3	0.4	0.4	0.2	0.1	0.1	0.3	0.3	0.1	0.2	0.1	0	0.1	0.5
Relative error /%	0.25	0.37	0.50	0.49	0.25	0.12	0.12	0.38	0.37	0.12	0.25	0.12	0	0.12	0.63
Relative error average value /%	0.273														

The 15 sets of initial setting times greater than 7.8min (calcium sulfate hemi-hydrate content less than 82%) were randomly selected, and the data was fitted and a simple equation fitting formula was obtained. The fitted value, difference and relative error are shown in Table 3. From the simple equation fitted data in Table 3, and the finishing data in Fig.1, the fitted formula by the simple equation fitting was: $y = -0.45x + 85.1$, where x is the initial setting time, and y is the calcium sulfate hemi-hydrate content . According to the simple equation fitted value, difference and relative error, then calculated the relative error average value is only 0.273%, and the error range is far below 5%, which indicates that it meets the requirements of regression analysis with regard to hemi-hydrate gypsum content tests.

(2) Quadratic equation finishing

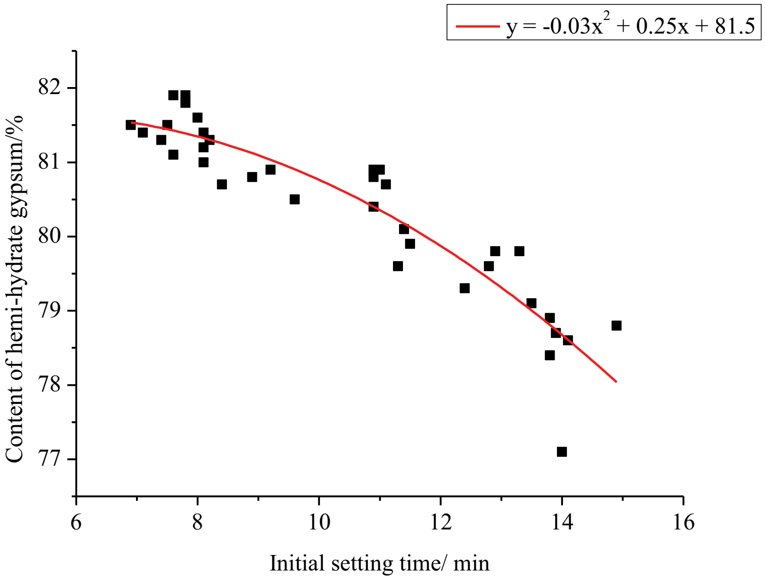

Fig.2 Linear regression model (quadratic equation finishing) between initial setting time and CSH content (initial setting time greater than 7.8min)

Table 4 Calcium sulfate hemi-hydrate content of quadratic equation fitting

Initial setting time /min	14.1	9.6	11.3	8.0	10.9	7.9	8.1	12.8	8.9	8.0	12.4	8.2	11.5	8.1	12.9
Calcium sulfate hemi-hydrate /%	78.6	80.5	79.6	81.9	80.4	81.5	81.4	79.6	80.8	81.6	79.3	81.3	79.9	81.4	79.8
Simple equation fitting /%	79.1	81.1	80.4	81.6	80.6	81.6	81.6	79.8	81.3	81.6	79.9	81.5	80.4	81.6	79.7
Difference value	0.5	0.6	0.8	0.3	0.2	0.1	0.2	0.2	0.5	0	0.6	0.2	0.5	0.2	0.1
Relative error /%	0.63	0.75	1.0	0.37	0.25	0.12	0.25	0.25	0.25	0	0.76	0.24	0.63	0.25	0.12
Relative error average value /%	0.393														

A quadratic equation fitting formula was obtained from the fitting analysis of the 15 sets of initial setting times greater than 7.8min (calcium sulfate hemi-hydrate content less than 82%). The fitted value, difference and relative error are shown in Table 4. From the quadratic equation fitted data in Table 4, and the finishing data in Fig.2, the fitted formula by the quadratic equation fitting was: $y = -0.03x^2 + 0.25x + 81.5$, where x is the initial setting time, and y is the hemi-hydrate gypsum content. According to the quadratic equation fitted value, difference and relative error, the relative error average value is only 0.393%. Although, the error range is far below 5%, but, this error is higher than the previous simple equation fitted value of 0.273%. Therefore, it is very clear from the results that when the hemi-hydrate gypsum content under 82% and initial setting time greater than 7.8 min, the optimum formula is the simple equation fitting $y = -0.45x + 85.1$, where x is the initial setting time, and y is the hemi-hydrate gypsum content, which can calculate the hemi-hydrate gypsum content quickly than the traditional test.

Comprehensive analysis Table 3 and Table 4, the measured values of CSH content of simple equation and quadratic equation fitting were all calculated, it shows that the relative error average value is very low using the simple equation fitting than the quadratic equation fitting. So, it is necessary to classify and analyze the 75 sets data with the demarcation point at 82% CSH content.

3.1.2 Initial setting time less than 7.8min

(1) Simple equation finishing

The measured values of the initial setting time less than 7.8min (CSH content greater than 82%) were presented in Table 5.

Table 5 Measured values of the initial setting time less than 7.8min (CSH content>82%)

Initial setting time /min	Calcium sulfate hemi-hydrate content /%	Initial setting time /min	Calcium sulfate hemi-hydrate content /%	Initial setting time /min	Calcium sulfate hemi-hydrate content /%
7.0	82.7	7.8	82.3	7.1	82.4
6.4	84.3	6.5	83.3	5.1	84.7
5.3	84.6	4.8	85.4	6.0	83.7
4.2	86.9	6.6	83.9	4.0	86.9
4.9	86.3	4.1	86.6	6.9	82.6
7.2	82.4	6.3	84.1	5.9	83.9
6.1	84.4	6.8	82.7	4.1	86.7
5.8	85.1	6.1	83.4	5.9	84.0
7	82.9	4.6	85.6	7.0	82.4
6.9	83.4	6.0	83.7	7.3	82.3
5.4	85.5	5.7	84.1	5.8	83.9
6.5	82.9	7.2	82.1	6.7	83.6
6.4	83.1	6.0	83.8	5.8	84.2

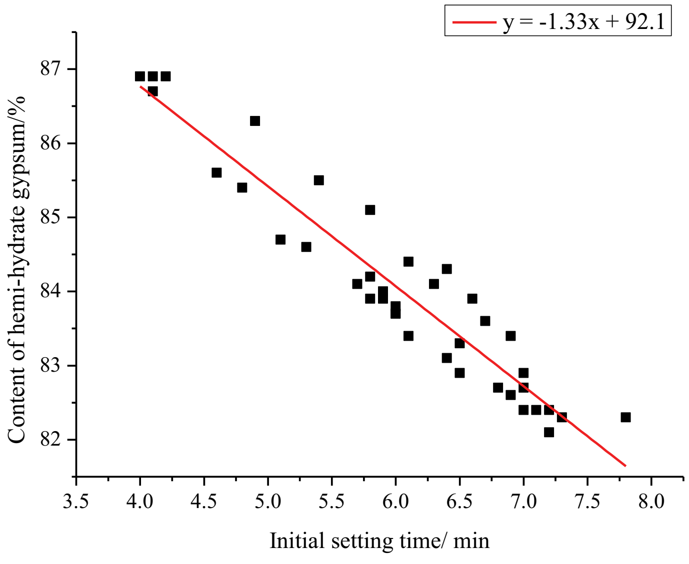

Fig.3 Linear regression model (simple equation finishing) between initial setting time and CSH content (initial setting time less than 7.8min)

Table 6 Calcium sulfate hemi-hydrate content of simple equation fitting

Initial setting time /min	7.0	6.3	4.8	4.2	7.8	7.2	4.0	5.4	6.4	5.8	6.0	4.9	5.1	6.7	6.8
Calcium sulfate hemi-hydrate /%	82.7	84.1	85.4	86.9	82.3	82.4	86.9	85.5	83.1	84.2	83.7	86.3	84.7	83.6	82.7
Simple equation fitting /%	82.8	83.7	85.7	86.5	81.7	82.5	86.8	84.9	83.6	84.4	84.1	85.6	85.3	83.2	83.1
Difference value	0.1	0.4	0.3	0.4	0.6	0.1	0.1	0.6	0.5	0.2	0.4	0.7	0.6	0.4	0.4
Relative error /%	0.12	0.48	0.35	0.46	0.72	0.12	0.12	0.70	0.60	0.24	0.48	0.81	0.71	0.48	0.48
Relative error average value /%	0.458														

The 15 sets of initial setting time less than 7.8 min (calcium sulfate hemi-hydrate content less than 82%) were randomly selected. A simple equation fitting formula was obtained from the fitting analysis results. The fitted value, difference and relative error are shown in Table 6. From the simple equation fitted data in Table 6, and the finishing data in Fig.3, the fitted formula by the simple equation fitting was: y = -1.33x + 92.1, where x is the initial setting time, and y is the hemi-hydrate gypsum content. According to the simple equation fitted value, difference and relative error, the relative error average value is only 0.458%, and the error range is far below 5%, which indicates that it meets the requirements of regression analysis with regard to hemi-hydrate gypsum content tests.

(2) Quadratic equation finishing

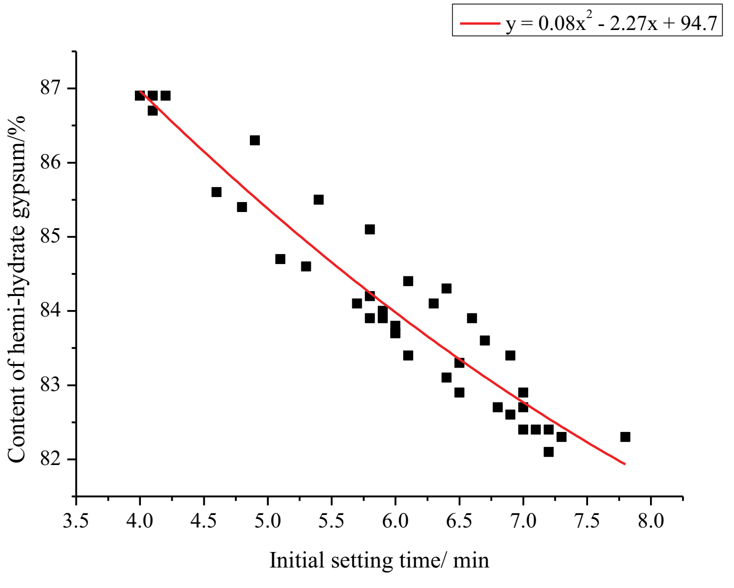

Fig.4 Linear regression model (quadratic equation finishing) between initial setting time and CSH content (initial setting time less than 7.8min)

Table 7 Calcium sulfate hemi-hydrate content of quadratic equation fitting

Initial setting time /min	7.0	6.3	4.8	4.2	7.8	7.2	4.0	5.4	6.4	5.8	6.0	4.9	5.1	6.7	6.8
Calcium sulfate hemi-hydrate /%	82.7	84.1	85.4	86.9	82.3	82.4	86.9	85.5	83.1	84.2	83.7	86.3	84.7	83.6	82.7
Simple equation fitting /%	82.7	83.6	85.6	86.6	81.9	82.5	86.9	84.8	83.1	84.2	84.0	85.5	85.2	83.2	83.0
Difference value	0	0.5	0.2	0.3	0.4	0.1	0	0.7	0	0	0.3	0.8	0.5	0.4	0.3
Relative error /%	0.12	0.59	0.23	0.31	0.49	0.12	0	0.82	0	0	0.36	0.93	0.59	0.48	0.36
Relative error average value /%	0.360														

The 15 sets of initial setting times less than 7.8 min (calcium sulfate hemi-hydrate content less than 82%), and detailed fitting analysis its proceeds, so the fitted value, difference and relative error are shown in Table 8. From the quadratic equation fitted data in Table 7, and the finishing data in Fig.4, the fitted formula by the simple equation fitting was: $y = -0.08x^2 - 2.27x + 94.7$, where x is the initial setting time, and y is the hemi-hydrate gypsum content. According to the quadratic equation fitted value, difference and relative error, the relative error average value is only 0.360%. Although, the error range is far below 5%, but, this error is far below the previous simple equation fitted value of 0.458%. So it is very clear from the results that when the initial setting times less than 7.8min (calcium sulfate hemi-hydrate content less than 82%), the optimum formula is the quadratic equation fitting $y = -0.08x^2 - 2.27x + 94.7$, where x is the initial setting time, and y is the hemi-hydrate gypsum content, which can calculate the hemi-hydrate gypsum content quickly than the traditional test. Comprehensive analysis Table 6 and Table 7, the measured values of calcium sulfate hemihydrate content of simple equation and quadratic equation fitting were all calculated, it shows that the relative error average value is very low use the quadratic equation fitting than the simple equation fitting.

3.2 VALIDATION ANALSIS

To verify the correctness of this method, we compare the results of traditional method, linear fitting and XRF (after the calculation) in the Table 8 and Table 9.

Table 8 Results of traditional method, linear fitting and XRF(initial setting time > 7.8min)

NO.	Traditional Method	Linear Fitting/%	XRF Method/%	Difference Value/%	
1	78.6% (14.1min)	78.8	79.1	0.2	0.5
2	80.7% (8.4min)	81.3	80.9	0.6	0.2
3	81.3% (7.4min)	81.8	82.3	0.5	1.0

Table 9 Results of traditional method, linear fitting and XRF(initial setting time < 7.8min)

NO.	Traditional Method	Linear Fitting/%	XRF Method/%	Difference Value/%	
1	84.3% (6.4min)	83.4	84.9	0.9	0.6
2	86.9% (4.1min)	86.7	88.1	0.2	1.2
3	85.5% (5.4min)	84.8	86.6	0.7	1.1

The calcium sulfate hemihydrate contents tested by XRF were presented in the Table 8 and Table 9. Compare with the linear fitting method, it can be concluded that when the initial setting time is greater than 7.8min, the average values of the difference are 0.43 and 0.57, respectively. When the initial setting time is less than 7.8min, the average values of the difference are 0.60 and 0.97, respectively. It is thus obvious that our linear fitting results are very similar to the XRF method. This indicates that the analysis can accurately determine the CSH content in modified industrial by-product gypsum by regression analysis using the initial setting time. The determination method has the advantages of simple and rapid operation.

3.3 TESTING PROCESS

As shown in Fig.5, the testing process of our method mainly included two steps, the first stage was determined the normal consistency of by-product hemihydrate gypsum, and the second stage was the initial setting time test. According to the test results, and then put them into the formula, the CSH content can be quickly calculated.

Fig.5 Regression analysis calcium sulfate hemihydrate content testing process

4 CONCLUSIONS

The study can accurately determine the CSH content in modified industrial by-product gypsum by regression analysis using the initial setting time. The determination method developed has the advantages of simple and rapid operation. The results obtained can be summarized as follows:

(1) Actual values of the initial setting time under 7.8 min were fitted, and the content of hemi-hydrate gypsum in phosphogypsum can be determined using the simple equation express: $y = -0.45x + 85.1$, where x is the initial setting time, and y is the hemi-hydrate gypsum content.

(2) Actual values of the initial setting time greater than 7.8 min were fitted, and the hemi-hydrate gypsum content can be determined using the quadratic equation express: $y = 0.08x^2 – 2.27x + 94.7$.

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LIST OF FIGURES AND TABLES:

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