EXPERIMENTAL DESIGN TO ANALYZE AND OPTIMIZE THE DECHLORINATION PROCESS OF COAL ASH A SHAANXI COAL-FIRED POWER PLANT

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Abstract

Coal is the main structure of China's energy resources. At the same time, coal power generation is the main power supply base in China. Coal contains chlorides, which harm the environment, while building materials are discharged or reused. Therefore, it is necessary to remove chlorine from the waste residue of coal-fired power plants. Moreover, conventional chemical testing methods are limited to detecting representative points and need to provide information about other points. However, results can be obtained for all operational parameters by employing a full factorial design analysis through Design of Experiments (DOE). In this study, a full factorial design of the experimental methods is used to detect the chlorine in the coal-fired coal ash of Shaanxi's coal-fired power plant. The chlorine in the coal-fired power plant ash is removed by calcination. The influence of calcination time and calcination temperature on the chlorine removal rate is studied to find the best method to remove chlorine in industrial production. The results show that calcination has the effect of removing chloride content in the slag of coal-fired power plants, and the two variables of calcination time and calcination temperature are directly proportional to the dechlorination rate. High temperature and long time can increase the removal rate of chloride in the slag of coal-fired power plants.

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According to the removal effect, the best process can be obtained: calcination temperature is 1400°C, calcination time is 2 hours, the removal rate of chlorine is 99.51%, and the residual chloride in the sample is removed. At the same time, achieve full parameter range operation and optimize the dechlorination process accordingly.

Keywords: coal-fired power plant, waste residual, chlorine, calcination

Introduction

According to the 2022 Coal Industry Development Annual Report published by the China Coal Industry Association in 2023, the country's coal production reached a staggering 4.56 billion tons in 2022 (China Coal Industry Association, 2023). In a power plant, when the coal is burned in the furnace, the combustible elements and carbon undergo combustion, while the non-combustible components transform into coal ash (Rafieizonooz et al., 2022). Utilizing industrial waste by-products as substitutes for construction materials can pose environmental risks (Ustaoglu et al., 2021). Moreover, industrial waste materials like coal ash should not present hazards during collection, disposal, and transportation (Kumar & Singh, 2020).

However, it is worth noting that burning one ton of raw coal generates about 250-300 kilograms of residual waste (Lei et al., 2013). Statistics indicate that globally, coal ash production amounts to approximately 750 to 1000 million tons (Wang et al., 2020) . As the primary holder of power plants in Southeast Asia (Kamal et al., 2019), Malaysia generates the region's highest annual output of coal ash. Moreover, developing nations demonstrate heightened environmental consciousness (Rafieizonooz et al., 2016). This necessitates the urgent resolution of the coal ash issue.

Coal naturally contains chlorides, which can pose a risk to the environment when coal waste is disposed of or reused in building materials. Exposure to chloride poses a potential hazard to employees within a facility and the nearby community (Chawla, 2021). Electrolysis and calcination are mainly used to remove solid chlorides domestically and internationally. Under the influence of an electric field (Polder, 1996), researchers such as Yan Yong have shown that electrochemical dechlorination can achieve over 50% removal of chloride ions near the concrete protective layer and steel bar (Yan et al., 2011). This method has not been widely applied in the industry due to its cost and risk. The calcination primarily removes chlorides from cement and other solid materials. It offers a straightforward treatment process and provides favorable results.

This study presents an innovative application of the Design of Experiments (DOE) method to solve the problem of conducting numerous and expensive experiments to optimize the parameters of the calcination process. The Design of Experiments (DOE) is a statistical tool utilized across various systems, processes, product design, development, and optimization applications (Durakovic, 2017). In this study, we will use a generalized full factorial design of experiments as our chosen method.

Methodology

This research studies techniques for analyzing and optimizing suitable parameters for the dechlorination process of coal ash based on The general full factorial experimental design.

1. **The general full factorial design**

The general full factorial experimental design is a widely used approach that enables a systematic investigation of all possible combinations of factor levels.

A full factorial design is a collaborative process that effectively examines the interaction between two or more independent variables and their influence on the response (Öztürk & Kavak, 2008). A full factorial design is an appropriate method for examining and evaluating the factors involved in a process with multiple variables (Ridzuan & Al-Mahfadi, 2017). This technique allows for the simultaneous consideration of more than one factor and requires only a limited number of experimental runs (Elarbe et al., 2022).

Implementing a screening full factorial design (FFD) aims to identify the crucial variables that significantly influence a process. This approach reduces the number of experiments required and offers the possibility of investigating several variables simultaneously (Ridzuan et al., 2020).

This study used a full-factorial experimental design to evaluate the operating factors systematically. The main objective of this paper is to investigate the variables that affect the chlorine removal rate, analyze and evaluate the relationship between these variables, and determine the optimal operating conditions for all parameter settings except the experimental test points through an optimization process.

2. Tool and Equipment

The experimental design was created using Minitab software. After planning, the test materials were treated with coal waste, and the chlorine content of the samples was measured and characterized before and after treatment. This analysis aimed to determine the feasibility of the treatment method and the optimum process conditions. The testing equipment is Hebi Wanzhida MF-2000A, as shown in Figure 1.

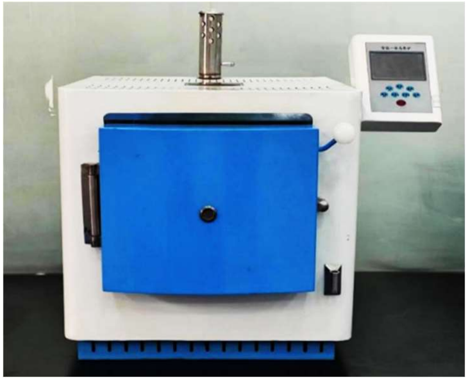

Figure 1 Experimental coal ash heating equipment.

3. Test material

The test material used in this study is coal-fired waste residue in yellow powder obtained from a Chinese coal power enterprise that utilizes supercritical technology. To prepare the test samples, the waste residue is initially crushed using a small swing crusher for 5 minutes, followed by sieving through a 60-mesh sieve to achieve a particle size of 250 μm or less. Following the crushing process, the waste residue is mixed thoroughly to ensure uniformity before removing chlorine.

4. Experimental research methods

In the experimental research methods, the first step is to process coal waste of various qualities to achieve a particle size of less than 250 μm.

After the processing step, Put 10 grams of coal waste crushed to less than 250 μm into a crucible. The crucible is then calcined in a muffle furnace for various periods and fired at a predetermined temperature. After a specific insulation time, the crucible is removed from the furnace and cools naturally at room temperature. Samples are then taken from the calcined material to analyze the chlorine content, and these measurements are used to calculate the chlorine removal rate.

5. **Characterization method**

Measure chloride ions using potentiometric titration, with one measurement for each sample under different parameters, as shown in the table below. In potentiometric titration, the endpoint is determined by observing a sudden jump in the electrode potential, which indicates the titration's completion. Before the endpoint is reached, the concentration of the measured ions in the system changes continuously by several orders of magnitude, leading to an abrupt shift in the electrode potential. Once this jump phenomenon is observed, the content of the tested components can be calculated based on consumption.

6. **Parameters for the Factorial Design**

Table 1 shows the experimental factors considered in the full factorial study: temperature and time. Four levels were established for each factor to achieve the optimum chlorine removal rate. The temperature varied between 800, 1000, 1200, and 1400°C, while the time ranged from 0.5, 1.0, 1.5, and 2.0 hours, respectively.

Table 1 Factor Information.

Factor	Levels	Values
Temperature (°C)	4	800, 1000, 1200, 1400 (°C)
Time (Hours)	4	0.5, 1.0, 1.5, 2.0 (Hours)

7. **Experimental Matrix**

A 4^2 factorial design was employed, resulting in a 16-run experimental plan, where each factor consisted of 4 levels. The experimental matrix and specific data regarding temperature and time are presented in Table 2.

Table 2 Experimental matrix for the 4^2 designs for the extraction.

StdOrder	RunOrder	PtType	Blocks	Temperature (°C)	Time (Hours)
1	1	1	1	800	0.5
2	10	1	1	800	1
3	4	1	1	800	1.5
4	12	1	1	800	2
5	9	1	1	1000	0.5
6	15	1	1	1000	1
7	13	1	1	1000	1.5
8	3	1	1	1000	2
9	8	1	1	1200	0.5
10	16	1	1	1200	1

Table 2 Experimental matrix for the 4^2 designs for the extraction. (cont.)

StdOrder	RunOrder	PtType	Blocks	Temperature (°C)	Time (Hours)
11	5	1	1	1200	1.5
12	2	1	1	1200	2
13	11	1	1	1400	0.5
14	14	1	1	1400	1
15	7	1	1	1400	1.5
16	6	1	1	1400	2

Results

The experimental design examined the impact of calcination temperature and calcining time on chlorine removal. Specifically, the chlorine removal was assessed at temperatures of 800, 1000, 1200, and 1400°C and for durations of 0.5, 1, 1.5, and 2 hours, respectively.

The chlorine content in the initial sample was determined using potentiometric titration, and the results are presented in Table 3. Based on the analysis, the chlorine content was 4.53%.

Table 3 Analysis results of chlorine content in coal waste residue.

Number	T-1	T-2	T-3
Chlorine content (%)	4.52	4.53	4.53
Average value (%)		4.53	
Range (%)		0.01	
Relative range (%)		0.22	

Calcination effect under 800°C temperature: The samples were calcined at 800°C for 0.5, 1, 1.5, and 2 hours, respectively. The chlorine content of the samples was determined, and the dechlorination rate was calculated. The test results are shown in Table 4 and Figure 2.

Table 4 Removal of chlorine from different calcination times at 800°C.

Number	Calcination temperature (°C)	Calcination time (Hours)	Chlorine content (%)	Dechlorination rate (%)
C-1-1	800	0.5	4.117	9.12
C-1-2	800	1	3.840	15.23
C-1-3	800	1.5	3.782	16.52
C-1-4	800	2	3.704	18.23

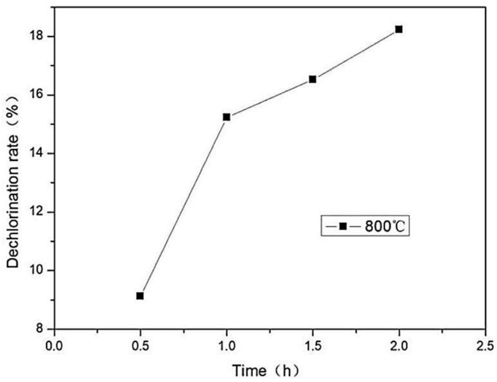

Figure 2 The effect of 800°C on chlorine removal time.

According to the experimental data, the chlorine removal rate increases with the calcination time at 800°C calcination. The dechlorination rate was 18.23% after a calcination time of 2 hours.

Calcination effect under 1000°C temperature: The samples were calcined at 1000°C for 0.5, 1, 1.5, and 2 hours, respectively. The chlorine content of the samples was determined, and the dechlorination rate was calculated. The test results are shown in Table 5 and Figure 3.

It can be concluded that the effect of chlorine removal is improved at different times under calcination at 1000°C. The chlorine removal rate is over 60%, increasing with the increase of calcining time. The chlorine removal rate was 75.36% after calcining for 2 hours.

Table 5 Removal of chlorine from different calcination times at 1000°C.

Number	Calcination temperature (°C)	Calcination time (Hours)	Chlorine content (%)	Dechlorination rate (%)
C-2-1	1000	0.5	1.444	68.12
C-2-2	1000	1	1.242	72.58
C-2-3	1000	1.5	1.198	73.56
C-2-4	1000	2	1.116	75.36

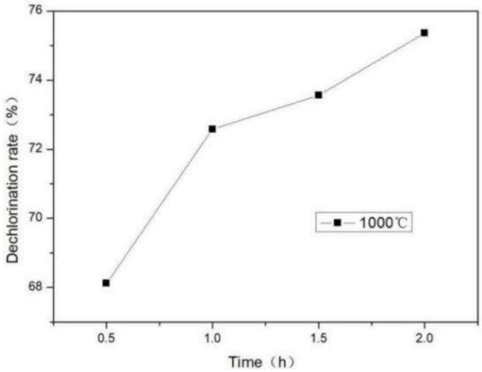

Figure 3 The effect of 1000°C on chlorine removal time.

The impact of calcination at 1200°C was assessed by calcining the samples for durations of 0.5, 1, 1.5, and 2 hours. Subsequently, the chlorine content of each sample was measured to determine the dechlorination rate. The results of this experimentation are presented in Table 6 and Figure 4.

Table 6 Removal of chlorine from different calcination times at 1200°C.

Number	Calcination temperature (°C)	Calcination time (Hours)	Chlorine content (%)	Dechlorination rate (%)
C-3-1	1200	0.5	1.349	70.21
C-3-2	1200	1	1.112	75.45
C-3-3	1200	1.5	0.971	78.56
C-3-4	1200	2	0.908	79.96

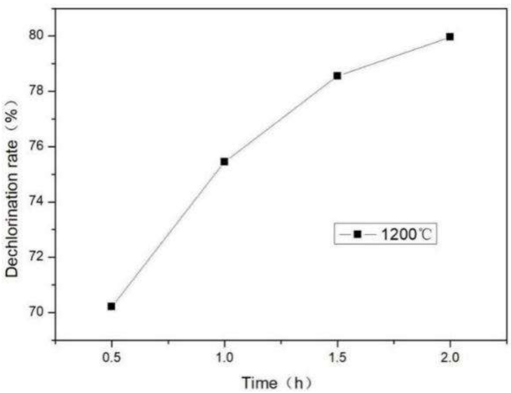

Figure 4 The effect of 1200°C on chlorine removal time.

The test data conclude that under the calcination conditions at 1200°C, chlorine removal efficiency increases at different times. The removal rate of chlorine is above 70%, increasing with the increase of calcination time.

Calcination effect under 1400°C temperature: First, the samples were calcined for 0.5, 1, 1.5, and 2 hours, respectively, at 1400°C. The chlorine content of the samples was determined, and the dechlorination rate was calculated. The test results are shown in Table 7 and Figure 5.

Table 7 Removal of chlorine from different calcination times at 1400°C.

Number	Calcination temperature (°C)	Calcination time (Hours)	Chlorine content (%)	Dechlorination rate (%)
C-4-1	1400	0.5	0.427	90.57
C-4-2	1400	1	0.217	95.21
C-4-3	1400	1.5	0.050	98.89
C-4-4	1400	2	0.022	99.51

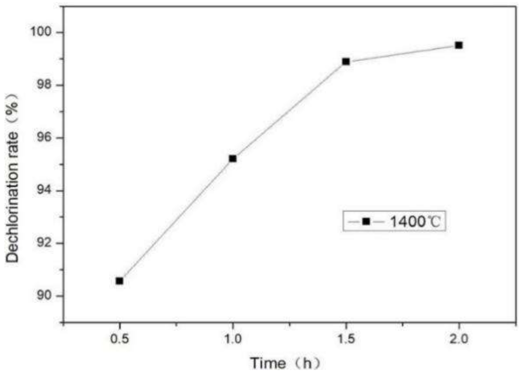

Figure 5 The effect of 1400°C on chlorine removal time.

The test data conclude that under the calcination conditions at 1400°C, chlorine removal efficiency increases at different times. The removal rate of chlorine is above 90%, increasing with the increase of calcination time.

Discussion

1. Influence of calcination temperature and time

The main reasons why increasing the calcination temperature and prolonging the calcination time can reduce the chlorine content in coal ash are that high temperature and sufficient calcination time facilitate the decomposition and volatilization of chlorides in coal.

The chlorine in coal ash mainly includes chlorine introduced during coal-fired power generation processes, such as waste residues brought in during flue gas treatment and capture, which are difficult to volatize under low-temperature conditions. Additionally, there are chlorides inherently present in coal, albeit in small amounts, that are also hard to decompose at low temperatures. The melting and boiling points of common chlorides are as follows: $MgCl_2$ has a melting point of 714°C and a boiling point of 1412°C; NaCl has a melting point of 801°C and a boiling point of 1465°C; KCl has a melting point of 770°C and a boiling point of 1420°C. When the calcination temperature is too low, the chlorides in coal ash do not completely decompose, resulting in the continued presence of substances like chloric acid with high chloride ion content, leading to excessive chloride ion levels in coal ash. Increasing the calcination temperature can promote the more thorough volatilization and decomposition of chlorides in coal ash, forming chlorine gas or other volatile chlorides, which are subsequently emitted with the flue gas, thereby reducing the chlorine content in coal ash. It can be concluded from this study. The influence of the calcination temperature on the dechlorination rate can be divided into two stages. Before 1000°C, the chlorine removal rate increases to about 70%, from 1000 to 20% when the chlorine removal rate is low. It is pointed out that the higher the chlorine removal rate is, the reaction temperature should be at least 1000°C Celsius. This shows that increasing the calcination temperature can increase the chlorine removal rate, but the effect is not apparent within 1000°C. When the temperature reaches 1400°C, the chloride removal rate exceeds 90%; as the calcination time increases, it is close to 100%. All the standards for residues in coal-fired power plants are met at this temperature.

Sufficient calcination time ensures that chlorides in coal have ample time to decompose and volatize. Maintaining a certain calcination time at high temperatures allows the decomposition reaction of chlorides to proceed more completely, further reducing the chlorine content in coal ash.It can be concluded from this study. If the calcination time is less than 0.5 hours, the reaction time is insufficient, and the chlorine removal rate is low. When the calcination time was increased from 0.5 hours to 1 hour, the chlorine removal rate increased significantly. It reached the most significant increase, indicating that the reaction time should exceed 1 hour.

2. Regression Equation

By deriving the regression equation, we can determine the regression equation for the dechlorination rate at varying calcination temperatures of 800, 1000, 1200, and 1400°c. the resulting regression equations are detailed in Table 8.

Table 8 Shows the regression equation of the dechlorination rate under different calcination temperatures.

Temperature	
800	Dechlorination rate = 7.639 + 5.709 Time
1000	Dechlorination rate = 65.269 + 5.709 Time
1200	Dechlorination rate = 68.909 + 5.709 Time
1400	Dechlorination rate = 88.909 + 5.709 Time

3. Influence of calcination temperature

Considering temperature and time, the effect of different calcination temperatures on the dechlorination efficiency can be determined by examining the chlorine removal rate at various calcination temperatures. The test results at different calcination temperatures for 0.5, 1, 1.5, and 2 hours, respectively, are shown in Table 9 and Figure 7.

Table 9 Shows the dechlorination effect under different calcination temperatures.

Calcination temperature (°C)	Dechlorination rate (%)			
	0.5 (Hours)	1 (Hour)	1.5 (Hours)	2 (Hours)
800°C	9.12	15.23	16.52	18.23
1000°C	68.12	72.58	73.56	75.36
1200°C	70.21	75.45	78.56	79.96
1400°C	90.57	95.21	98.89	99.51

Table 9 and Figure 6 show that the chlorine removal rate increases as the calcination temperature increases. Increasing the surface temperature can effectively improve the chlorine removal rate.

Before 1000°C, the chlorine removal rate is 1000°C, and the chlorine removal rate has increased from the previous 20% to about 70%. When the calcination temperature was increased from 1000°C Celsius to 1200°C, the chlorine removal rate increased slightly. This is consistent with the theory that the melting point of chlorides is 1000°C, and the boiling point is 1200°C. After more than 1200°C, a large amount of volatile chlorine volatilizes in the phase, increasing the chloride removal rate. When the temperature reaches 1400°C, the chloride removal rate is over 90%.

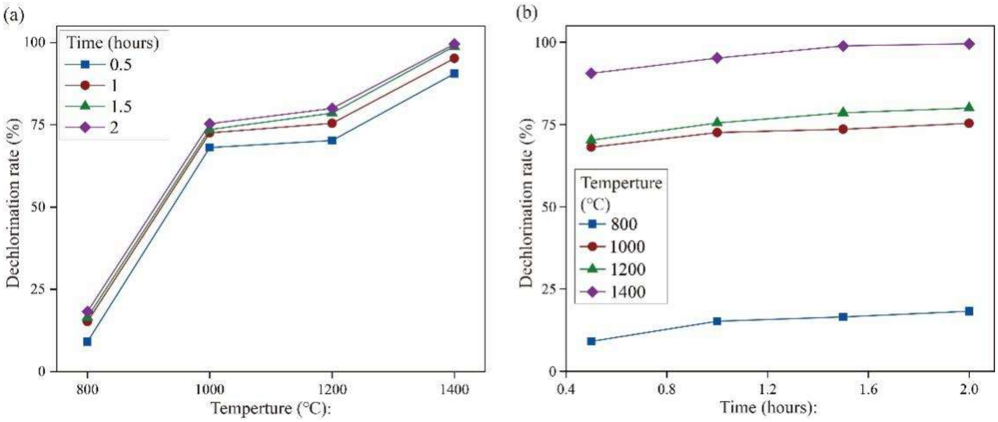

Figure 6 Interaction plot for temperature (a) and for time (b) on dechlorination rate.

4. Full parameter range operation

Conventional chemical testing methods are usually limited to taking samples and analyzing representative points, which may not capture the whole picture of the system. However, obtaining results for all operating parameters is possible using a full factorial design analysis in the Design of Experiments (DOE).

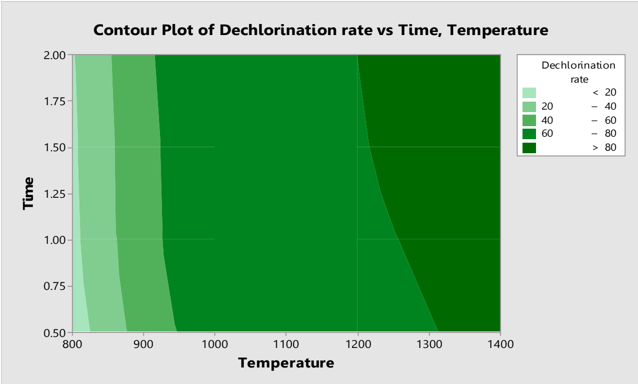

Figure 7 Full parameter range rendering from contour plot for temperature and time on dechlorination rate.

From the observations in Figure 7, a clear pattern can be derived: lighter colors correspond to lower 531 ichlorination rates, while darker colors indicate higher 531ichlorination rates within the entire parameter range. Manufacturers can use this information and their desired 531 ichlorination rate to determine the appropriate operating conditions from the graph.

Conclusion

The calcination method removes the chloride content in the slag from coal-fired power plants. The chloride removal rate depends on the calcination temperatures and times. If you change these two variables, the 532 ichlorination rate can change.

The calcination time is directly proportional to the 532 ichlorination rate in the slag of the coal-fired power plant, but the calcination time is slightly different. At different calcination temperatures, the 532 ichlorination rate increases with increasing calcination time. Within a specific time, the growth rate has changed. The calcination temperature is directly proportional to the chloride removal rate in the slag of coal-fired power plants. The two factors can be checked directly via the calcination time and temperature. High temperatures and a long time can increase chloride removal in the slag of coal-fired power plants. Depending on the removal effect, the best process can be achieved: The calcination temperature is 1400°C, the calcination time is 2 hours, the chlorine removal rate is 99.51%, and the residual chloride in the sample is removed.

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