AA05 - Design and Analysis for the Optimization of Synthesis Technological Conditions of Tricalcium Aluminate Hexahydrate

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Abstract

Tricalcium aluminate hexahydrate (TCA) is widely used as a filter aid during purification of unpolished pregnant liquor within the security filtration, whose physical properties (like particle size, specific surface area and so on) directly affect filter efficiency and filter cloth life. Based on the process of alumina production, TCA was prepared using sodium aluminate solution and hydrated lime. In addition, the effect of caustic soda concentration (N_k), temperature, duration time and C/A molar ratio on TCA particle size and specific surface area were analyzed. At the same time, orthogonal experiments were designed to analyze the influence sequence of various factors, which can provide us with guidance for preparing TCA that meets different requirements.

Keywords: Tricalcium aluminate hexahydrate, particle size, specific surface area, orthogonal experiments.

1. Introduction

Compared with sintering process when dealing with bauxite bearing low silicon, Bayer process has some merits, like simpler process, less energy or production cost and so on, thus about 90% or more alumina and aluminum hydroxide product obtained from Bayer process all over the world [1].

Tricalcium aluminate hexahydrate (TCA) act as an important role within a Bayer refinery, which comes from the reaction between sodium aluminate and lime within the Bayer process. TCA has amount of functions, like reducing soda lost during pre-desilication and digestion process, being used as filter aid. Among above functions, the main role is using as a filter aid, in which it assists with the removal of impurities from polished liquor before the precipitation process and enhances the filtration efficiency, and prolong leaf filter duration time [2-6].

Typically, TCA is prepared by the reaction of lime or slaked lime with sodium aluminate solution, in which spent liquor or polished liquor are usually used as reaction solution. Major reaction equations are as follows [7]:

$$3CaO + 2NaAlO_2 + 7H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O + 2NaOH \quad (1)$$
$$3Ca(OH)_2 + 2NaAlO_2 + 4H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O + 2NaOH \quad (2)$$

Above reactions are idealized, while the actual reaction process is complex. Based on theory analysis and experimental investigation, it can be seen that reaction conditions involved in this synthesis process, like caustic soda concentration (N_k), reaction temperature (T), duration time (ϴ) and C/A molar ratio, will have an influence on the TCA production especially its morphology, which may affect its physical property such as filtration efficiency, leaf filter duration time and so on.

Given the importance of synthesis for TCA on its chemical and physical properties, the impacts of synthesis technological conditions on Tricalcium aluminate hexahydrate were investigated. In addition, based on the theory analysis and orthogonal experiments, the optimization of process conditions was explored.

2. Experiment

2.1 Raw Material

Plant lime (alumina refinery, Shan xi, available CaO 89.26%), spent liquor after precipitation (SLP), cycling liquor (CLP), the total caustic (NT) and caustic soda concentration are expressed in gpl Na_2O. Sodium Aluminate (AO) is expressed as g/l Al_2O_3. The liquor analysis is displayed in Table 1.

Table 1. Composition of various liquor used.

liquor type	NT	AO	NK	ak
SLP	194.19	91.37	162	2.92
CLP	271.46	130.18	228	2.88

2.2 Equipment and Methods

Tests were performed in the laboratory to simulate the preparation of TCA. In order to control reaction temperature and agitation efficiency properly, an oil bath was used during the preparation of TCA (Figure 1).

To obtain the information about particle size distribution (PSD) in the TCA products and evaluate the percentage of particles less than 5μm and average size, Particle size distribution analysis were performed using light scattering equipment (Mastersizer 2000 da Malvern).

To better understand the morphology of TCA product, BET specific surface area was also measured and analyzed based on nitrogen adsorption method.

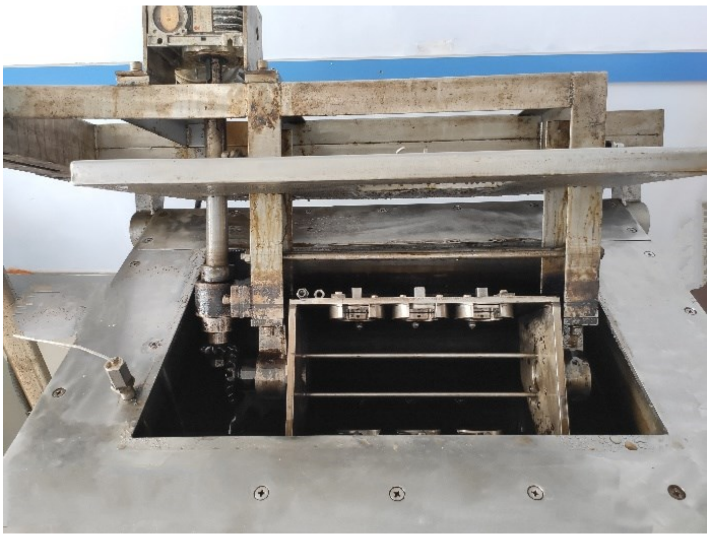

Figure 1. Oil bath equipment.

2.3 Tests

Single impact analysis experiments and orthogonal experiments were conducted respectively, to investigate the effects of synthesis conditions on the TCA properties and bring an effective and simple method to find out the optimal synthesis conditions to match industrial or (and) real need.

2.3.1 Single Impact Analysis Experiments

SPL and CLP were used as sodium aluminate liquor source to prepare TCA respectively, and the effects of their chemical composition and reaction time on particle size distribution (PSD) were investigated, in which duration time(or reaction time) and lime addition (C/A mole ratio) were constant. Detailed preparation conditions are as shown in Table 2.

Table 2. Preparation conditions for TCA.

liquor type	No.	Volume, ml	lime addition, C/A mole	reaction time, h	Temperature, °C
SLP	TCA-1	100	3	1	70
	TCA-2	100	3	1	80
	TCA-3	100	3	1	90
	TCA-4	100	3	1	100
CLP	TCA-5	100	3	1	70
	TCA-6	100	3	1	80
	TCA-7	100	3	1	90
	TCA-8	100	3	1	100

Based on the preparation condition as shown in Table 2, TCA products were obtained, whose physical properties like particle size distribution and specific area were measured and analyzed using corresponding methods as mentioned in section 2.2. Particle size distribution results are shown in Figure 2 and Figure 3.

According to the results of particle size distribution analysis as shown in Figure 2 and Figure 3, done for the TCA samples prepared with spent liquor after precipitation and cycling liquor respectively(ranging from 70 to 100 °C)， it can be seen that average diameter of the particles lies in the range from 2 to 3.5 micrometers based on the d0.5 calculation.

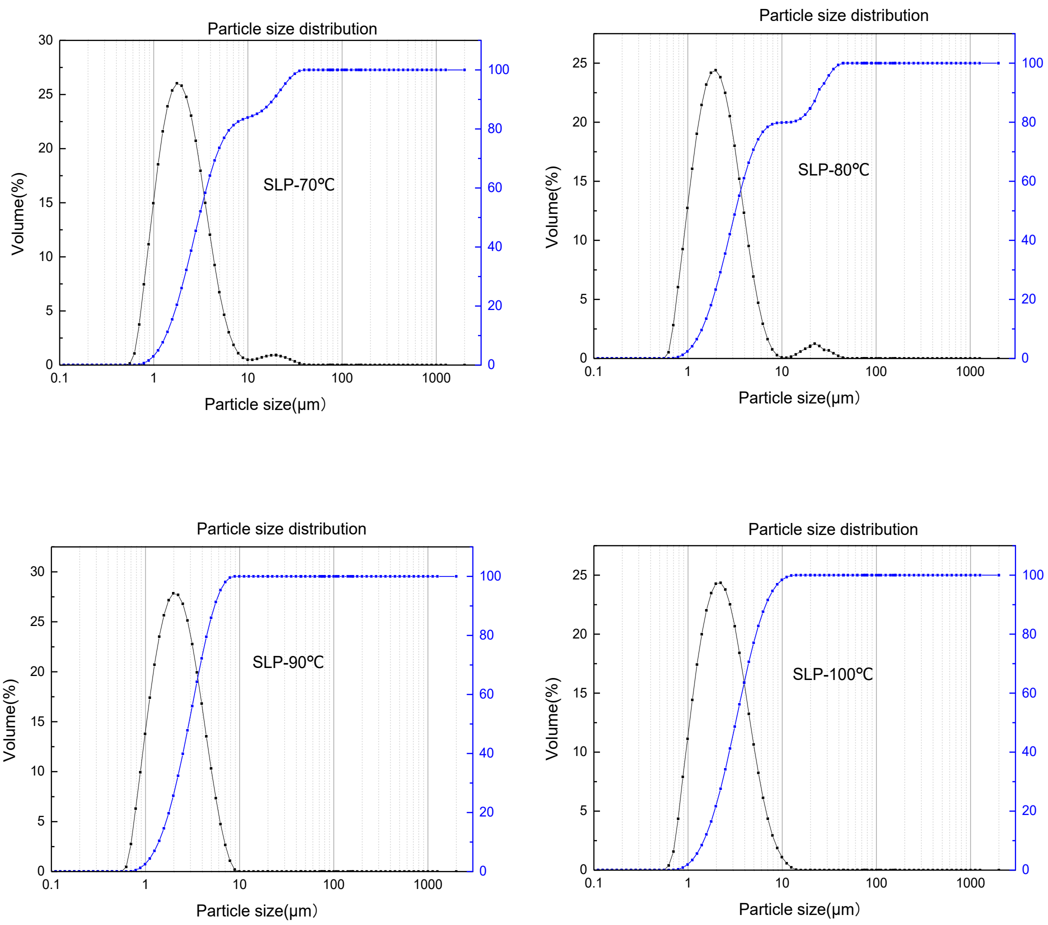

Figure 2. Particle size distribution of TCA prepared from SLP (70~100 °C).

From Figure 2, it can be seen that synthesis temperature (T) indeed affect the particle size distribution of TCA product, in which average diameter has bigger trend with ɵ increasing, which is also corresponding to Figure 3. However, compared with Figure 3, two peak phenomenon occurs at 70 and 80 °C in Figure 2. Based on the vertical and horizontal analysis, the reason may be the results of reaction lying in the specific synthesis condition including liquor system, reaction temperature and so on, which needs further study in next research. In addition, the results of TCA product from CLP are better than that from SLP, based on PSD as indicated by the adsorption efficiency.

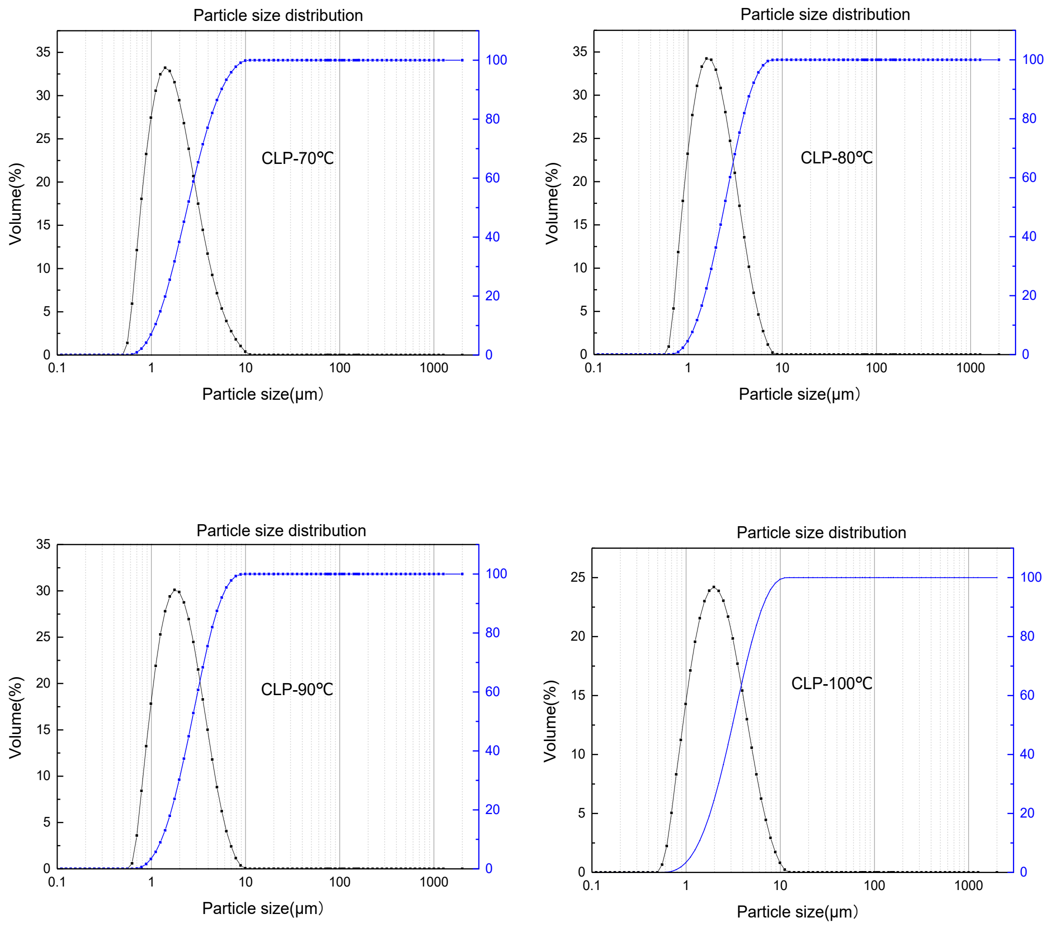

Figure 3. Particle size distribution of TCA prepared from CLP (70~100 ℃).

Specific area results are as shown in Table 3. According to Table 3, it can be seen that specific area of TCA product prepared from SLP and CLP become larger with synthesis temperature increasing. Analysis of specific area results combined with particle size distribution results from Figure 2 and Figure 3 demonstrates that the morphology of TCA product is not full core, because of specific area results are contrary to particle size distribution results of TCA product, which need further study in next research. In addition, the results of TCA product from SLP are better than that from CLP, based on specific area (S_{BET}) as indicated by the adsorption efficiency, which is contrary to above conclusion.

Table 3. Specific area for TCA prepared from SLP and CLP.

SLP	No.	TCA-1	TCA-2	TCA-3	TCA-4
	S_{BET}, $m^2\ g^{-1}$	7.18	5.70	4.02	3.18
CLP	No.	TCA-5	TCA-6	TCA-7	TCA-8
	S_{BET}, $m^2\ g^{-1}$	4.17	3.16	2.77	5.58

2.3.2 Orthogonal Experiments

In order to investigate optimal synthesis condition of TCA product, orthogonal experiments were designed, where synthesis temperature, duration time and lime addition were selected as variables.

According to the design principle of orthogonal experiment, L_9 (3^4) orthogonal table[8] was adopted, and each factor identifies three levels (Table 4). Tests were conducted.

Table 4. Design of Orthogonal Table L_9 (3^4).

Exp. No.	temperature, °C	duration time, h	C/A, mole
1	60	0.5	2
2	60	1.0	3
3	60	1.5	4
4	75	0.5	3
5	75	1.0	4
6	75	1.5	2
7	90	0.5	4
8	90	1.0	2
9	90	1.5	3

According to above designed experiment, $d_{0.5}$ and S_{BET} were selected as objective functions respectively, corresponding results are shown in Table 5 and Table 6 respectively.

Table 5. Experimental scheme and analysis results based on $d_{0.5}$.

Exp. No.	A	B	C	$d_{0.5}$, µm
1	1	1	1	3.75
2	1	2	2	3.33
3	1	3	3	1.00
4	2	1	2	2.61
5	2	2	3	10.00
6	2	3	1	5.93
7	3	1	3	3.97
8	3	2	1	2.98
9	3	3	2	1.87
K1	8.08	10.33	12.66	
K2	18.54	16.31	7.81	
K3	8.82	8.80	14.97	
k1	2.69	3.44	4.22	
k2	6.18	5.44	2.60	
k3	2.94	2.93	4.99	
R	3.49	2.50	2.39	
factor order: degrade trend	A B C			
optimal scheme	A1B3C2			

According to the range comparison based on $d_{0.5}$ in Table 5, the results demonstrate that R_A>R_B>R_C, thus the order of each factors from primary to secondary is A (temperature), B (duration time), C (lime addition, C/A).

Among this analysis section, $d_{0.5}$ was selected as evaluation index, besides the aim of this value is small. Thus, the evaluation value is the smaller the better. According to the range analysis results, among this synthesis condition, the best scheme is A1B3C2, namely reaction temperature is 60 °C, duration time is 1.5 h and A/C is 3(mole/mole).

Table 6. Experimental scheme and analysis results based on S_{BET}.

Exp. No.	A	B	C	S_{BET}, $m^2\ g^{-1}$
1	1	1	1	7.72
2	1	2	2	6.74
3	1	3	3	10.00
4	2	1	2	3.93
5	2	2	3	8.39
6	2	3	1	5.54
7	3	1	3	9.89
8	3	2	1	1.00
9	3	3	2	2.84
K1	24.46	12.16	14.26	
K2	17.87	16.13	13.51	
K3	13.72	18.38	28.28	
k1	8.15	4.05	4.75	
k2	5.96	5.38	4.50	
k3	4.57	6.13	9.43	
R	3.58	2.07	4.92	
factor order: degrade trend	C A B			
optimal scheme	A1B3C3			

According to the range comparison based on S_{BET} in Table 6, the results demonstrate that $R_C > R_A > R_B$, thus the order of each factors from primary to secondary is C (lime addition, C/A, mole) , A (temperature), B (duration time). Among this analysis section, S_{BET} was selected as evaluation index, besides the aim of this value is large. Thus, the evaluation value is the larger the better. According to the range analysis results, among this synthesis condition, the best scheme is A1B3 C3, namely reaction temperature is 60 °C, duration time is 1.5 h and A/C is 4 (mole/mole).

3. Conclusion

This research aims to explore the effects of synthesis conditions on the Tricalcium aluminate hexahydrate, including sodium aluminate solution, reaction temperature, reaction time and lime addition. It also brings in a method to analyze the interaction among synthesis factors to find out the best reaction condition matching different real needs.

Using Orthogonal experiments, interaction effects among different factors can be obtained. Besides, different evaluation index may bring different optimal synthesis scheme, namely $d_{0.5}$ was selected as evaluation index corresponding to A1B3C2 (reaction temperature is 60 °C, duration time is 1.5 h and A/C is 3(mole/mole)). While S_{BET} was selected as evaluation index corresponding to A1B3C3 (reaction temperature is 60 °C, duration time is 1.5h and A/C is 4 mole/mole).

Appendix A. Nomenclature

TCA	Tricalcium aluminate hexahydrate
NK	caustic soda concentration
NT	total caustic
SLP	spent liquor after precipitation
CLP	cycling liquor
gpl	gram per litre
PSD	particle size distribution
S_{BET}	specific area

4. References

1. Yang Zhongyu, Alumina production technology, Beijing: *Metallurgical Industry Press*, 1993.
2. S.C.A. França, P.F.A. Braga, J. Aldi, J. Moraes, A.J.P. Borges, Some Aspects of Tricalcium Aluminate Hexahydrate Formation on the Bayer Process, *Light Metals 2010*, 63-66.
3. R. P. Mahoney and L. Connelly, Bayer Liquor Polishing, *Light Metals 1993*, 85-88.
4. S. L. Barham, S. U. Khan, J. T. Malito, and W. J. Rennick, Optimization of Tricalcium Aluminate for Enhanced Bayer Liquor Filtration, *Light Metals 2000*, 111-116.
5. N. Mugnier, P. Clerin, and J. Sinquin, Industrial Experience of Polishing Filtration Performance Improvement and Interpretation, *Light Metals 2001*, 33-39.
6. S.P. Rosenberg, D. J. Wilson, and C. A. Heath, Some Aspects of Calcium Chemistry in The Bayer Process, *Light Metals 2001*, 19-25.
7. L.J. Andermann, G.J. Pollet, The Manufacture of Tricalcium Aluminate, *Light Metals 2003*, 476-482.
8. Phillip J Ross. Taguchi techniques for quality engineering: loss function, orthogonal experiments, parameter and tolerance design, McGraw-*Hill,* 1988.