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PREPARING POLYMERIZED ALUMINUM-IRON CHLORIDE WITH RED MUD

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Abstract

A new method is proposed for the preparation of polyaluminium ferric chloride (PAFC) with red mud. The dependence of pH of the PAFC on basicity, is discussed and the difference in the products of the process of red mud hydrolysis from products in the process of sodium hydroxide hydrolysis is studied. The results show that basicity increases with increasing pH, the preferred pH value is 3.5, and basicity is up to 85.55%. Comparing the appearance of PAFC with that of crystalline aluminium chloride, polyaluminium chloride by SEM, can indicate that the distribution of materials is not uniform on the surface of PAFC. Energy Dispersive analysis indicates that the content of aluminum, iron, and oxygen accounts for 60.73% in the white areas, 43.95% in the black areas in the process of red mud hydrolysis; whereas the content of aluminum, iron, and elements in the white areas is 49.74%, 23.45% in black areas in the product from sodium hydroxide hydrolysis.

Introduction

Red mud is a waste byproduct generated during the production of alumina from bauxite. Amounts of red mud vary with the different quality and processing of ores containing aluminum. If bauxite is used as starting raw materials, the product of per ton alumina will result in approximately 1 ton of dry red mud, and will produce about 7 tons dry red mud if nephelite is used as the starting raw material. Today, worldwide production of red mud is estimated to be about 150 million tons each year, and production of red mud is more than 4 million tons in China [1]. So red mud occupies largeland areas, and pollutes the environment[2-5]. In order to solve the above problems, various means of utilization of red mud have been suggested by worldwide metallurgy workers, for example, red mud was used as catalyst[6-9], plastics padding[10-11], cement[12], production of castings[13], glass-ceramics[14-15] and so on. Red mud is predominantly a mixture of oxides of iron, aluminium and titanium with relatively smaller amounts of silica and magnesia. Utilizing the components of aluminium and iron in red mud to prepare flocculant-polymerized aluminum-ferric chloride (PAFC) has been reported [16]. The processes is that red mud reacts with Hydrochloric acid, the mixture is filtered, the filtrate is neutralized and hydrolyzed with sodium hydroxide. This process will not only consume a lot of sodium hydroxide, but also the utilization rate of hydrochloric acid is very low and content of byproducts (mostly NaCl) is quite high. Because red mud contains iron oxide, alumina, sodium aluminate and other alkaline substances which can be used to react with aluminum chloride, iron chloride and free hydrochloric acid, replacing sodium hydroxide with red mud to neutralize and hydrolyze the filtrate will save a lot of sodium hydroxide, increase the utilization rate of hydrochloric acid and purity of the products, and cut the cost of production.

Experimental

Materials and Equipment

Waste red mud, hydrochloric acid and sodium hydroxide were used as starting materials. The waste red mud was obtained from Shandong aluminum factory in China. Compositions and content of red mud are shown in Table 1. The equipment is shown in Table 2.

Table 1 Compositions and content of red mud

Composition	Alumina	Iron oxide	Silica	Titania	Others
Content(%)	20.54	26.73	25.21	1.85	25.67

Table 2 names and types of equipment

Names	types
scanning electron microscope	Hitachi S-3400N

Synthetic Principles of PAFC

Alumina(Al_2O_3) and Iron oxide(Fe_2O_3) in waste red mud react with hydrochloric acid to form $[Al(H_2O)_6]Cl_3$, and $[Fe(H_2O)_6]Cl_3$.

$$Fe_2O_3+6HCl+9H_2O \longrightarrow 2[Fe(H_2O)_6]Cl_3 \quad (1)$$

$$Al_2O_3+6HCl+9H_2O \longrightarrow 2[Al(H_2O)_6]Cl_3 \quad (2)$$

The addition of red mud (or alkali) to the filtrate will increase the pH value of system. when the pH value reachs some limit, $[Al(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{3+}$ will hydrolyze to form $H^+$and a series of coordinate ions. The equations are as follow:

$$[Al(H_2O)_6]^{3+} \xrightarrow{OH^-} [Al(OH)(H_2O)_5]^{2+} + H^+ \quad (3)$$

$$[Al(OH)(H_2O)_5]^{2+} \xrightarrow{OH^-} [Al(OH)_2(H_2O)_4]^{+} + H^+ \quad (4)$$

$$[Al(OH)_2(H_2O)_4]^{+} \xrightarrow{OH^-} [Al(OH)_3(H_2O)_3] + H^+ \quad (5)$$

$$[Fe(H_2O)_6]^{3+} \xrightarrow{OH^-} [Fe(OH)(H_2O)_5]^{2+} + H^+ \quad (6)$$

$$[Fe(OH)(H_2O)_5]^{2+} \xrightarrow{OH^-} [Fe(OH)_2(H_2O)_4]^{+} + H^+ \quad (7)$$

$$[Fe(OH)_2(H_2O)_4]^{+} \xrightarrow{OH^-} [Fe(OH)_3(H_2O)_3] + H^+ \quad (8)$$

With the increase of concentration of OH^-, coordinated water hydrolyzes and substances formed will polymerize. Bridge will form between OH^- and OH^-, $[Al(H_2O)_6]Cl_3$ and $[Fe(H_2O)_6]Cl_3$ gradually are converted into dipolymer, tripolymer, finally high molecular weight species PAFC $[Al_2(OH)nCl_{6-n}]m$, $[Fe_2(OH)nCl_{6-n}]m$.

Synthesis Processes of PAFC

Hydrochloric acid was added to waste red mud. It reacted with waste red mud for a period of time, then the mixture of liquid and

solid was filtered and washed, filter liquor and filter cake were obtained. The filter cake then reacted with hydrochloric acid, and was filtered and washed once again. Both filter liquors were mixed, and neutralized and hydrolyzed with either waste red mud or sodium hydroxide. If waste red mud is used to neutralize and hydrolyze the filter liquors, the mixture of liquid and solid will be filtered and filter liquor obtained will be concentrated and dried, and PAFC will be obtained; If sodium hydroxide is used to neutralize and hydrolyze the filter liquors, the solution obtained will be concentrated and dried, and PAFC will be obtained. The production process of red mud neutralization and hydrolysis are shown in figure 1.

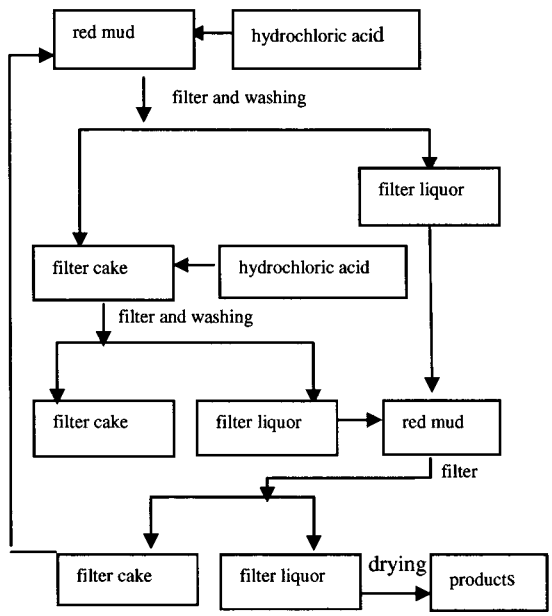


Fig.1 Production process of neutralized red mud

Determining the Basicity of PAFC

One third of the mol ratio of OH^- and Al^{3+} in a sample is called the basicity. Generally, the effects of flocculation increase with the increase of basicity. Firstly, potassium dichromate titration was used to determine content of iron oxide ω_1, and EDTA titration was used to determine content of alumina ω_2. Alumina was used to calculate effective content ω_3, $\omega_3=\omega_2+0.6384\omega_1$, 0.6384 is a factor in which iron oxide was converted into alumina. Then quantitative hydrochloric acid solution was added to the sample of PAFC, sodium fluoride was used to shelter Al^{3+}, sodium hydroxide standard solution was used to titrate above solution. Use equivalent distilled water(no carbon oxide) and hydrochloric acid as blank sample and make the same experiment. The formula of basicity W_4 is as follow:

$$W_4=\frac{(V_0-V)\times C\times 0.01699}{m\omega_3}\times 100\% \qquad (9)$$

V_0—volume (ml)of sodium hydroxide standard solution consumed by blank sample

V— volume (ml)of sodium hydroxide standard solution consumed by sample of PAFC

C---concentration of sodium hydroxide standard solution(mol/L)

m--- mass of sample PAFC(g)

ω_3---content of effective composition (%) (calculated as it was Al_2O_3)

0.01699----Mass (g) of Al_2O_3 equivalent with 1.0 ml NaOH standard solution [C (NaOH)=1.000mol/L]

Results and Discussion

Effect of pH Value of Solution on Basicity of PAFC

Different volumes of sodium hydroxide solution were added to the filter liquors obtained when red mud reacted with hydrochloric acid. The pH value of the filter liquors was adjusted to 1.5, 2.0, 2.5, 3.0, 3.5 respectively. The alumina and iron oxide content was determined for each sample, and then basicity determined. The results of the experiments are shown in Table 3.

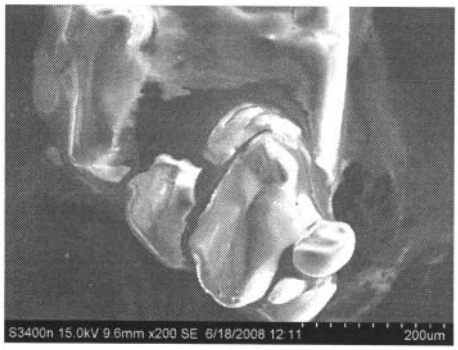
Table 3 Effect of pH on basicity of production

pH	basicity (%)
1.5	5.82
2.0	72.27
2.5	76.35
3.0	80.89
3.5	85.55

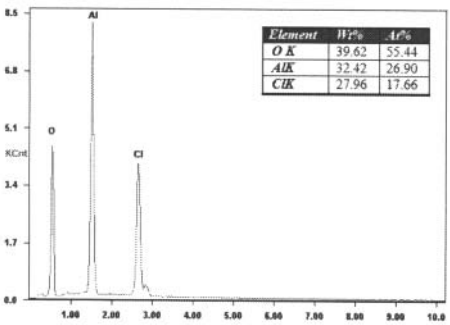
When pH value of solution is between 1.5 and 3.5, the basicity of products increases with the increase in pH of the solution, but for pH value >3.5, the solution will change into a gel. If the pH value of the solution is low, most of the base will be used to neutralize free hydrochloric acid, and the hydrolyzing degree of $AlCl_3$ and $FeCl_3$ should be low, as the contents of hydroxyls are low. Thus basicity of the product is low when the pH value of solution is less than 1.5. When the pH value of solution is more than 2.0, then some of base reacts with $AlCl_3$ and $FeCl_3$, and some of chloride in $AlCl_3$ and $FeCl_3$ is changed into hydroxyls. So basicity of the products increases with the increase of alkalinity. When the pH of the solution is more than 3.5, $AlCl_3$ and $FeCl_3$ will be changed to deposits of $Al(OH)_3$ and $Fe(OH)_3$.

Comparison of PAFC with Aluminum Chloride and Polymeric Aluminum Chloride

In order to determine whether the synthetic products are the target PAFC or not and, simultaneously, determine the composition of the products, crystalline aluminum chloride and polymeric aluminum chloride were chosen to compare with the synthetic products. Their appearance and composition were investigated using scanning electron microscope and energy dispersive analysis. The experimental results are shown in figure 2, figure 3 and figure 4. Conditions for the preparation of the synthetic products were that the liquid-solid ratio of hydrochloric acid to red mud is 4:1, the concentration of hydrochloric acid is 6 mol/L, reaction time is 60 minutes, reaction temperature is about 109°C, the extraction is the second extracting (see fig. 1, pH value of the filter liquors was adjusted to 3.5 with sodium hydroxide solution. The synthetic product- PAFC was obtained after the solution was dried.



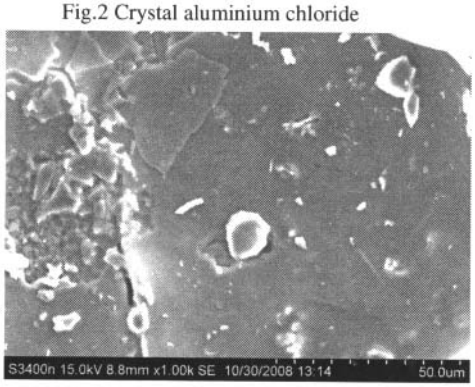
(a) SEM of crystal aluminium chloride



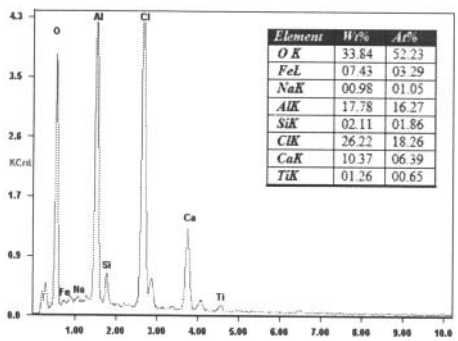
Element	Wt%	At%
O K	39.62	55.44
AlK	32.42	26.90
ClK	27.96	17.66

(b) Energy spectrum of crystal aluminium chloride

Fig.2 Crystal aluminium chloride



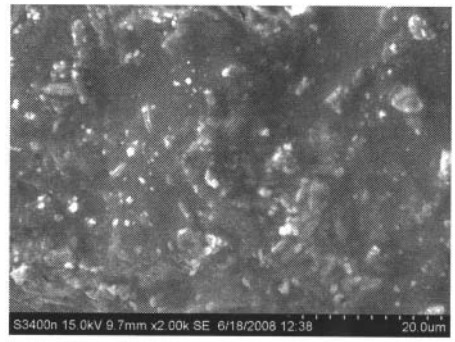
(a) SEM of polyaluminium chloride



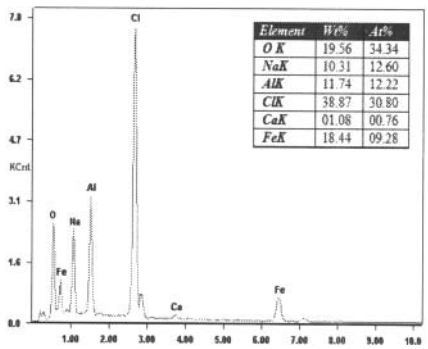
Element	Wt%	At%
O K	33.84	52.23
FeL	07.43	03.29
NaK	00.98	01.05
AlK	17.78	16.27
SiK	02.11	01.86
ClK	26.22	18.26
CaK	10.37	06.39
TiK	01.26	00.65

(b) Energy spectrum of polyaluminium chloride

Fig.3 Polyaluminium chloride

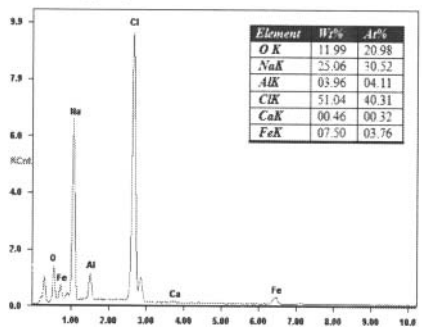


(a) SEM of PAFC



Element	Wt%	At%
O K	19.56	34.34
NaK	10.31	12.60
AlK	11.74	12.22
ClK	38.87	30.80
CaK	01.08	00.76
FeK	18.44	09.28

(b) Energy spectrum of white areas of PAFC



Element	Wt%	At%
O K	11.99	20.98
NaK	25.06	30.52
AlK	03.96	04.11
ClK	51.04	40.31
CaK	00.46	00.32
FeK	07.50	03.76

(c) Energy spectrum of black areas of PAFC

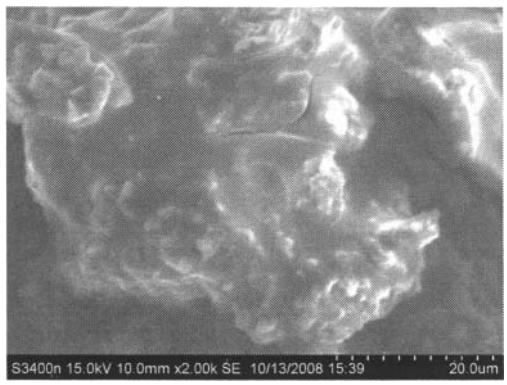
Fig.4. PAFC of pH=3.5 with sodium hydroxide neutralisation.

According to figure 2(a), figure 3(a) and figure 4(a), the appearance of the synthetic product is much different from that of crystal aluminum chloride and similar to that of polymeric aluminum chloride. The surface of the crystalline aluminum chloride is smooth, and the distribution of materials is uniform. Distribution of materials is not uniform on the surface of PAC and PAFC. The white and black areas occur on their surface. According to the energy spectrum of white areas in figure 2(b), figure 3(b)and figure 4(b), crystalline aluminum chloride contains only Al, Cl, and O; polymeric aluminum chloride contains traces of Fe, and Na in addition to Al, Cl, and O; PAFC contains high levels of Fe, Na in addition to Al, Cl, O. The appearances and compositions of white areas show that the white areas should be PAFC. Comparing compositions of white areas in figure 4(b) with that of black areas in figure 4(c), the content of Fe, and Al in the white areas are more than that of Fe and Al in the black particles. Fe and Al in

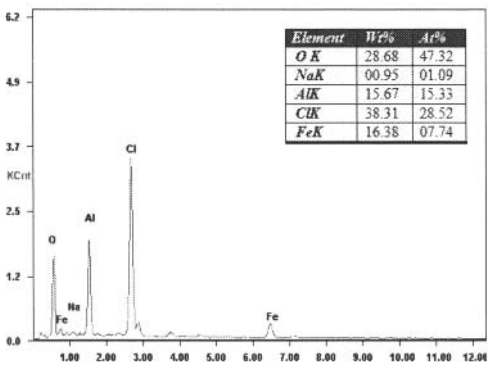
the white particles account for 30.18%, but is only 11.46% in black particles.

The effect of Neutralizing approach and Hydrolysis on the Appearance and Composition of PAFC

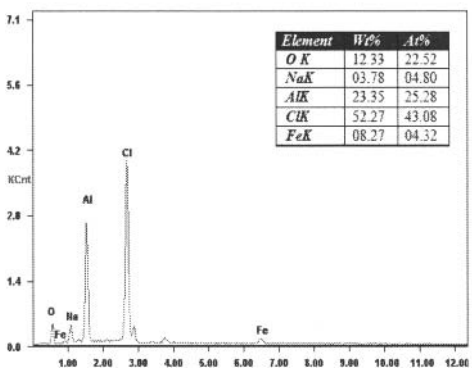
Red mud was leached with Hydrochloric acid, the filter liquor was neutralized and hydrolyzed to pH=3.5 with red mud. The results of the experiment are shown in figure 5.



(a) SEM of PAFC



(b) Energy spectrum of white areas of PAFC



(c) Energy spectrum of black areas of PAFC

Fig.5 PAFC with pH value 3.5 in process of red mud neutralizing

According to figure 5(a), the distribution of materials of PAFC obtained in process of red mud neutralizing is more uniform than that in process of sodium hydroxide solution in the figure 4(a). The white areas of materials are quite large in figure 5(a). Comparing figure 5(b) with figure 4(b), content of Al, Fe and O in PAFC obtained in process of red mud neutralizing is higher than that in process of sodium hydroxide neutralizing. The content of Al, Fe and O is 60.73% in the former, and 49.74% in the latter. The content of Na is 0.95% in the former, and 10.31% in the latter. The results indicate that the content of PAFC obtained in process of red mud neutralization is higher than that in the process of sodium hydroxide neutralization in the chosen white areas. The content of by-product NaCl is lower in the former than in the latter in the white areas. Comparing figure 5(c) with figure 4(c), the content of Al, Fe and O in PAFC obtained in the process of red mud neutralization is higher than that in process of sodium hydroxide neutralization in the black areas.The content of Al, Fe and O is 43.95% in the former, and 23.45% in the latter. The content of Na is 3.78% in the area analysed in figure 5(c), and 25.06% in figure 4(c), which also indicates that content of PAFC obtained in process of red mud neutralization is higher than that in process of sodium hydroxide neutralization in the chosen black areas, and the content of by-product NaCl is lower in the former than in the latter in the darker areas.

The composition of the material in figure 5(c) can indicate whether compositions of the black areas in figure 5(a) are PAFC or not. The proportion of Fe and Al is 29.6%. Subtracting the proportion of the atoms of Na from that of atoms of Cl gives 38.28%, which indicates each Al (or Fe) can bond with 1.3 Cl atoms. The residual atoms (Cl) were hydrolyzed into hydroxyl (-OH). The analysis above shows that compositions of the black areas in figure 5(c) are PAFC, in addition to a little by-product NaCl.

Conclusions

(1) Red mud can be used as a starting material to prepare PAFC.
(2) The basicity of PAFC increases with increasing pH, and the preferred pH value is 3.5.
(3) Comparing the appearance of PAFC with that of crystalline aluminium chloride and polyaluminium chloride by SEM can indicate that the distribution of materials is not uniform on the surface of PAFC. The Energy Dispersive spectrum can be used to analyze the composition of PAFC.
(4) The Energy spectrum indicates that the content of PAFC obtained in the process of red mud neutralization is higher than that in the process of sodium hydroxide neutralization; the content of by-product NaCl is lower in the former than in the latter. Process of red mud neutralizing is better than process of sodium hydroxide neutralizing.

References

1. JIANG Yijiao, NING Ping, "An overview of comprehensive utilization of red mud from aluminum production", Environmental Science and Technology, (2003), 26(1), 40~42.
2. R. A. A. Blackman, K. W. Wilson "Effects of red mud on marine animals", Marine Pollution Bulletin, (1973) 4(11) 169-171.
3. S. Baseden, D. Grey, "Environmental study of the disposal of red mud waste", Marine Pollution Bulletin, (1976), 7(1), 4-7.

4. Shaobin Wang, H.M. Ang, M.O. Tadé, "Novel applications of red mud as coagulant, adsorbent and catalyst for environmentally benign processes",_Chemosphere, (2008), 72(11), 1621-1635.
5. Ekrem Kalkan, "Utilization of red mud as a stabilization material for the preparation of clay liners", Engineering Geology, (2006), 87(3-4), 220-229.
6. Cakici A I, Yanik J, Uçar S, Karayildirim T, Anil H, "Utilization of red mud as catalyst in conversion of waste oil and waste plastics to fuel", Journal of Material Cycles and Waste Management, (2004), 6(1), 20~26.
7. Juan J. Llano, Roberto Rosal, Herminio Sastre, Fernando V. Díez, "Catalytic hydrogenation of anthracene oil with red mud", Fuel, (1994) 73(5), 688-694.
8. Jale Yanik, Md. Azhar Uddin, Kazuo Ikeuchi, Yusaku Sakata, "The catalytic effect of Red Mud on the degradation of poly (vinyl chloride) containing polymer mixture into fuel oil", Polymer Degradation and Stability, (2001), 73(2), 335-346.
9. Jorge Álvarez, Salvador Ordóñez, Roberto Rosal, Herminio Sastre, Fernando V. Díez, "A new method for enhancing the performance of red mud as a hydrogenation catalyst", Applied Catalysis A: General, (1999), 180(1-2), 399-409.
10. Singh B，Gupta M. "Surface treatment of red mud and its influence on the properties of particulate-filled polyester composites", Bulletin of Materials Science, 1995，18（5）: 603-621.
11. Soo-Jin Park, Dong-Il Seo, ChangwoonNah, "Effect of Acidic Surface Treatment of Red Mud on Mechanical Interfacial Properties of Epoxy/Red Mud Nanocomposites",_Journal of Colloid and Interface Science, (2002), 251(1), 225-229.
12. Maneesh Singh, S. N. Upadhayay, P. M. Prasad, "Preparation of special cements from red mud", Waste Management, (1996), 16(8), 665-670.
13. Nilza Jústiz-Smith, Vernon E. Buchanan, Gossett Olive. "The potential application of red mud in the production of castings", Materials Science and Engineering A, (2006) 420(1-2), 250-253.
14. Jiakuan Yang, Dudu Zhang, Jian Hou, Baoping He, Bo Xiao, "Preparation of glass-ceramics from red mud in the aluminium industries", Ceramics International, (2008), 34(1), 125-130.
15. Vincenzo M. Sglavo, Stefano Maurina, Alexia Conci, Antonio Salviati, Giovanni Carturan, Giorgio Cocco, "Bauxite 'red mud' in the ceramic industry. Part 2: production of clay-based ceramics", Journal of the European Ceramic Society, (2000), 20(3), 245-252.
16. ZHANG Lingfen, HUANG Jianfang, MO Yazh, "A study on the preparation of polymerized aluminum ferrum chloride from red mud"._Water Purification Technology 1998,(03):2~4.