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The present status and prospect of research on the de-ironing and bleaching technology of kaolin

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Abstract:

The increase of degree of whiteness is an important method for Kaolin growth in value. In this paper, the occurrence of iron in kaolin was briefly described, and the methods of the de-ironing and bleaching technology of kaolin were introduced. The characteristics and the existing problems of all kinds of method were analyzed. Some new green environmental protection technology of the de-ironing and bleaching kaolin were introduced.

Keywords: Thiourea Dioxide, Kaolin, Bleaching, Whiteness degree, Oxidization, Reduction, Green, Environmental protection

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Kaolin is a very important mineral resources, which is widely used in ceramic industry, paper industry, rubber, plastics industry, building materials industry, chemical industry, painting industry etc. China is abundant in kaolin resource, however, most contains much iron and belongs to the inferior one. It can greatly increase the added value of the product and have huge potential economic values if the amount of iron, titanium and manganese is decreased, and the degree of whiteness is increased^[1, 2]. At present, there are some main methods about bleaching kaolin at home and abroad, for example, the physical methods^[3], chemical method^[4-7], and microbial methods^[8], Organic acid methods etc.^[9]

1 Physical method

1.1 flotation method

It depends on the differences between the surface properties of kaolin and iron or titanium mineral when removing the iron and titanium of kaolin with flotation method^[10]. However, the iron and titanium is embedded in kaolin as superfine particle, so it is difficult to achieve the striking effects with one single conventional flotation method. Therefore other new methods have been developed, including carrier flotation, selective agglomeration, two liquids flotation etc. based on the conventional flotation method.

Carrier flotation is that Fe_2O_3 was adsorbed into lime carrier. The carriers, which can not only rely on their own hydrophobicity, but also the hydrophobicity of the collector, could be attached to the bubbles, so carrier foam products containing iron and those with refined ore kaolin are obtained, therefore Fe_2O_3 are separated from kaolin.

The selective agglomeration is by using the properties of dispersion and agglomeration of goethite and kaolin. Goethite will agglomerate near its isoelectric point ($\text{pH}=8.5\sim 9.8$) while it will in dispersion state above or below the pH range. The isoelectric point of kaolin is $\text{pH}=2$. Kaolin will be in dispersion state when $\text{pH} > 2$. Therefore Fe_2O_3 can be separated from kaolin by controlling suitable pH. But it is difficult to control in production owing to the narrow pH range, so far, its practical application have not been reported.

Two liquids flotation is developed from ultra-fine particles flotation. The advantage of ultra-fine particles flotation is that the ordinary equipment and flotation agent can be used, the flotation effect is good: about 70 percent of iron can be removed and the degree of whiteness can arrive above 90 percent, the shortcoming is that the process is complicated.

1.2 Magnetic separation

Kaolin contains a little iron minerals, which mainly are iron oxide, Ilmenite, siderite, pyrite, mica and tourmaline etc. These substances mostly exist in form of ultrafine particles with weak magnetism and if they are removed in normal ways, the separation effect usually is not higher. So the high gradient magnetic separator has been used to remove the magnetic substances. Before conducting magnetic separation, calcination shall be done to oxidize pyrite thus promoting magnetic susceptibility and effects of magnetic separation. High gradient magnetic separator increases magnetic pressure, and the efficiency of removing of iron as well as titanium, however the investment of equipment is so high that normal factories can not afford. Although there exists shortcomings like easy blocking the equipment and high power consumption in this way, yet it has high efficiency of removing of iron and titanium, and still widely used in the soft kaolin field.

2 Chemical method

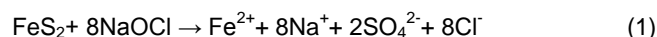
There are three methods of chemical bleaching, namely: oxidation, reduction and oxidation-reduction combined method. Among them reduction is widely used.



2.1 Oxidation method

Oxidation method aims at pyrite and organic impurity containing in kaolin. Kaolin will become gray when containing pyrite and organic impurity. Often it is hard to remove them in the ways of washing by acid or reduction, and at this moment oxidation method is usually adopted^[11].

Generally some strong oxidants (sodium hypochlorite, hydrogen peroxide, potassium permanganate) are used to oxidize pyrite to watersoluble ferrous salt, which can be removed by washing by water. The equation is :



Fe^{2+} is relatively stable in acidic medium, but it can be transformed into ferric iron in alkaline medium. In weakly acidic medium (pH=5~6), sodium hypochlorite has the most activity and oxidative ability. So the method of oxidatively bleaching should be operated in weak acidic medium. And it is always an effective way to add oxalic acid in the solution, and the parameters are generally as follows: pH=5~6, bleach reagent is approximately 1.5 percent, bleach time is 2~3 h at 20~35⁰C. There are some other factors that can influence bleaching effect of this method, for example: the properties of mine, temperature, reagent consumption, concentration of mine, bleaching time and so on^[12].

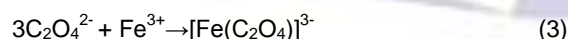
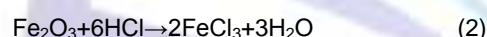
2.2 Reduction method

Iron oxide is common dying impurity in kaolin, and exists in the form of ferric oxidate or iron oxide-hydrate, which are difficult to soluble in water and are not easily be decomposed by dilute acid. In this case, reduction method can be adopted by adding reduction reagent to transform insoluble Fe^{3+} in kaolin into soluble Fe^{2+} , which Fe^{2+} can be removed by water washing.^[13]

The reductive methods of removal of iron includes: acid leaching, reduction with thiourea dioxide, reduction with hydrosulfite, reduction with sodium borohydride, hydrogen reduction method by acid dissolution, and newly-produced hyposulfite, etc.

2.2.1 Acid leaching method

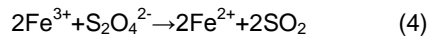
Acid leaching method is to treat kaolin with acid to remove impurity of iron to fulfill the purpose of bleaching kaolin. the hydrochloric acid or sulfuric acid are usually used as extraction agent, or inorganic acid and complex agent as extraction agent when heated^[14-15]. Among the methods bleaching with hydrochloric acid is widely used. The equation of bleaching with hydrochloric acid is as below:



Experimental result shows that iron must be removed when pH is below 2, since it will be insoluble when pH is between 5 and 7. And that the effect of hydrochloric acid with oxalic acid is much better than single one. That is because the complex funtion of oxalic acid will improve the dissolution rate of iron. Although this method is simple, the high - quality kaolin of degree of whiteness above 90 percent is unable to get. And this method need large amount of hydrochloric acid and heated temperature, production environment is poor; the corrosion of equipment is terrible; besides, amount of washing water after acid leaching is large, and the washing could not be thoroughly.

2.2.2 Reduction method with hydrosulfite

Hydrosulfite, called sodium dithionite as well, is a strong reducing agent and widely used in reducing kaolin. The ferric oxide in kaolin is not soluble in water, and neither in diluted acid. In acid medium, hydrosulfite can transformed Fe^{3+} into Fe^{2+} at room temperature, and Fe^{2+} can be leached as it is soluble in water. The equation of the process is as blow:

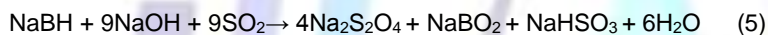


Factors that may influence the process include acidity, temperature, hydrosulfite consumption and so on^[16]. since sodium dithionite decompose into SO_2 and H_2S at a high temperature or in acid medium, thus the effects of bleaching will decrease, and the working conditions are poor because of strong pungent smells. Therefore zinc powder is often added in to help remove iron, the process parameters are: pH=2~4, adding of 7~8 % sodium dithionite.

In practical manufacturing, after Fe^{3+} is transformed into Fe^{2+} by sodium dithionite, product will become yellow again if filtration and washing is not done immediately. Not only reagent is consumed, but also the quality of the products may be affected. So this method demands very strictly. Two main problems must be solved in industrial production, namely: acidity and temperature must be controlled strictly; besides, hydrosulfite is easy aerobic decomposition in air.

2.2.3 Reduction method with sodium borohydride

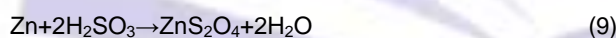
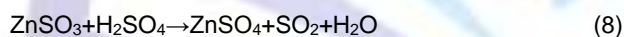
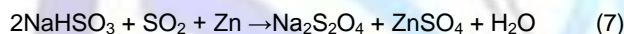
Sodium borohydride method is that the sodium borohydride reacts with other reagent to form hydrosulfite to bleach kaolin^[17], the process is: add the mixture of sodium borohydride and sodium hydroxide into slurry when pH is between 7.0 and 10.0, then sulfur dioxide was introduced, adjust pH to 6~7, which will help produce the largest amount of sodium dithionite, then adjust pH to 2.5~4.0 with sulphuric acid or SO_2 . After all steps above, reaction of bleaching is beginning. The equation of producing sodium dithionite is as below:



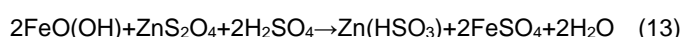
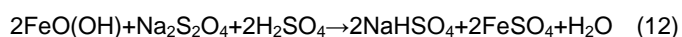
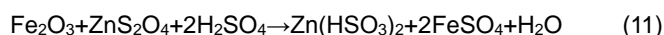
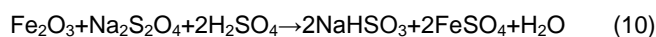
This method is actually bleached with sodium borohydride in nature, but it's very inactive when pH is 6~7. After pH is lowed, it will react with slurry of kaolin immediately so that the decomposition of sodium borohydride is avoided. Even though sodium borohydride is a strong reducing agent, it's extremely expensive, and the industrialized rate is not high because its high cost.

2.2.4 Reduction method with newly-produced liquid dithionite

add sodium bisulfite solution into slurry and put the slurry into a container with zinc. Essentially, reducing agent is the newly-born bisulfite zinc^[18,19]. The main reaction, when pH of the solution is adjusted, is:



The newly-produced dithionite(sodium bisulfite, bisulfite zinc)are very strong reducing agent, the equation of dithionite and iron oxide is below:



FeSO_4 , produced by the reaction above, is soluble and can be removed in subsequent treatment processes, thus colored iron oxide was removed and kaolin was whitened.



Hydrosulfite is expensive (about ¥ 12 yuan per kilogram) while NaHSO₃ in the method of newly-produced liquid dithionite is cheap (about ¥ 0.5 yuan per kilogram), which makes that expense of this way accounts for 33~50 percent of method of hydrosulfite. But however, this way hasn't been widely applied because of the problem of zinc ions polluting our waste water.

2.2.5 Hydrogen reduction method by acid dissolution,

Active metal, such as Zn power or Al power as reduction agent, displaces the hydrogen of acid solvent, which consists of hydrochloric acid, sulfuric acid, and oxalic acid. The newly-produced hydrogen is to transform insoluble Fe into soluble Fe²⁺, and Fe²⁺ was removed from the filtrate.

For those coal - series kaolin that contains large amount of iron (more than 2.1 %) and has low degree of whiteness (less than 70), only in this way can the degree of whiteness be increased to its limit.

2.3 Oxidation - reduction method

Some impurities of kaolin are complicated since iron exists in many valences. Satisfying effect can not be achieved if single oxidation or reduction method is adopted. In that case, method of oxidation - reduction can be used. It is that the organics and pyrite were first oxidized and removed with strong oxidants NaClO and hydrogen peroxide, then with sodium dithionite as reduction agent, the remaining ferric oxidate, such as Fe₂O₃, is transformed into Fe²⁺, to achieve the aim of bleaching.

3. Micro – bioleaching technology

Thiobacillus ferrooxidans is utilized to remove iron when the harmful impurity is pyrite in some nonmetallic minerals, which is a new processing technology of minerals^[20]. Its obvious merit is low investment and cost, small energy consumption, and less environmental pollution. The processing technology of minerals by microorganism includes micro – bioleaching technology and that of flotation technology by microorganism. The research of micro – bioleaching technology is earliest and its development is very fast. It is a new leaching way that can damage lattice and dissolve useful component based on the interaction between microorganism and minerals^[21]. Although it has less pollution in this method, yet it is of long period, higher cost, covers an area of large, and it is easy to get influenced by weather conditions.

The above-mentioned method that is used to bleach kaolin has its own unique advantages, but there exists many obvious shortcomings. In this article, some new green environmental protection technologies of bleaching kaolin were introduced. .

4 New environmentally-friendly technologies of bleaching kaolin

4.1 Bleaching kaolin with thiourea dioxide

Thiourea dioxide (TD) is called formamidine sulfinic (FAS), and its chemical formula is HO₂SC(NH)NH₂, which is a odorless, and non-toxic kind of white powder. Thiourea dioxide itself is neither oxidability nor reducibility, however it may change into its isomer formamidine sulfinic when heated in alkaline medium, then results in its decomposition into sulfoxylate with strong reducibility. The reduction potential of sulfoxylate is higher than that of hydrosulfite. So thiourea dioxide is used as reducing agent. The equation is as below:



Fe³⁺ of kaolin was reduced to Fe²⁺ by sulfoxylate, then complexing agent react with it, to produce a new soluble complexing agent, and Fe²⁺ can be removed by water washing and enhanced the reductive bleaching of kaolin.



Thiourea dioxide is a new green replacement of hydrosulfite. It is safe to store, easy to operate, convenient to transport and has high reduction potential as well as thermal stability. It is non-toxic, odorless, environmentally-friendly without pollution to environment. So thiourea dioxide as reducing agent has been widely used in bleaching mineral and printing machinery.

Since thiourea dioxide has no capacities of oxidation or reduction itself, only when heated in alkaline medium can it be used as reduction agent, and the chosen temperature shall be above 70°C. Thiourea dioxide hasn't been widely used in bleaching kaolin because the process bleaching kaolin is basically performed at room temperature.

In order to make thiourea dioxide technology used in bleaching kaolin widely, the author thinks that a new reduction accelerator should be found, so that thiourea dioxide can associate with accelerator to bleaching kaolin jointly, and then a new environmentally-friendly process that is fit for kaolin should be found out to improve the existing routings, the degree of whiteness and grade of kaolin can be upgrade, and what is more, to search for a way of bleaching kaolin with thiourea dioxide to break out of the dependence on high temperature and strong alkaline condition.

4.2 Bleaching kaolin with thiourea dioxide activated by lanthanum nitrate catalyst

The essence of thiourea dioxide decomposition into sulfoxylate is the process of C-S bond cleavage, but only when heated in strong alkaline condition can it be generated easily which is the main reason thiourea dioxide technology has not been widely used in bleaching kaolin. Some literature reports that a new green technology of whitening kaolin, that in weak alkaline conditions and room temperature, thiourea dioxide activated by lanthanum nitrate catalysts, was found. Since the outermost electrons of rare earth element are similar because of its 4 f electronic characters, so the rare elements with higher ability of oxidation and high charge can be easy to form strong bond with carbon and easy to obtain or loss electrons to accelerate reaction so that C-S bond of thiourea dioxide can be cleaved without high temperature, and then fast decomposed into sulfoxylate, which played a large part in whitening kaolin. The elements of La, Ce, Pr, Nd, Sm are common rare earth element, and often we use their nitrates.

It is reported that effects of bleaching kaolin with thiourea dioxide activated by lanthanum nitrate catalysts is remarkable good [22]. When concentration of mine slurry is 20 percent, the pH is 8, dosage of thiourea dioxide is 0.6 percent, reaction time is 120 minutes, and dosage of lanthanum nitrate as catalyst is 0.2 percent, the degree of whiteness of kaolin can get above 90 percent after being bleached just at normal temperature, the degree of calcined whiteness is 92 percent, and the amount of iron oxide decrease to 0.78 percent from 1.17 percent. Degree of whiteness and calcined whiteness can reached I grade quality standard for material of kaolin used in papermaking industry and ceramics industry respectively. This new green technology of whitening kaolin, that in weak alkaline conditions, thiourea dioxide activated by lanthanum nitrate catalysts can break out of the dependence on high temperature and strong alkaline condition, and will not produce acid waste water, meanwhile, the decomposition product of thiourea dioxide is urea, which would not increase chemical oxygen demand (COD) and biological oxygen demand (BOD), therefore this method is a green environment-friendly technology.

4.3 Thiourea dioxide and chloride aluminium on kaolin for new bleaching process

Major constituent of kaolin is $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. Owing to the lamellar structure of kaolin [23], aluminum ion is usually vacant, which the lamellar was negatively charged and is easy to adsorb cation. For Fe^{3+} , Al^{3+} and Fe^{2+} , the order of the adsorption ability is: $\text{Fe}^{3+} > \text{Al}^{3+} > \text{Fe}^{2+}$. So theoretically when thiourea dioxide is added to make the adsorbed Fe^{3+} by lamellar was reduced into Fe^{2+} and chloride aluminium is added, the adsorbed Fe^{2+} by lamellar can be easily replaced by Al^{3+} and then get into the solution, to attain the goal of bleaching kaolin. For cost analysis, Let's take one ton of kaolin that contains 0.24 percent of iron for example. The cost of whitening kaolin by thiourea dioxide-aluminum chloride is approximately ¥110



yuan, while the cost of dealing by Sodium dithionite-oxalic acid is about ¥243 yuan. In fact, sodium hyposulphite has strong capability of decomposition, therefore in production we need to increase additional more reagent consumptions if taking this way to deal with kaolin, thus the costs of running sodium hyposulphite have also correspondingly increased; instead of sodium hyposulphite technology, if thiourea dioxide and chloride aluminium on kaolin for bleaching process was adopted, the cost is much lower than traditional ways, and quality of the products was better since the decomposition product of $(\text{NH}_2)_2\text{CSO}_2$ is combined with lamellar of kaolin, which make the distance between lamellar increases and its viscosity increase, to enhance the grade of the kaolin. Comparison with traditional ways, it has lower cost, and better effect of removing iron in this method.

4.4 Bleaching Kaolin with Thiourea Strengthened by Ultrasonic

The essence of this way is to increase degree of whiteness of kaolin by the increase of ultrasound frequency, ultrasound power as well as the bleaching time. Compared with the degree of whiteness of raw ores, this method increases 6 per cent points, and attains the effect of bleaching kaolin of heating method and dosage of thiourea dioxide is reduced, and bleaching time is decreased. Meanwhile, ultrasound have a high activating reaction on the thiourea, and has remarkably increased the rate of reaction^[24].

4.5 Extraction method

Extraction method is not use sulfuric acid or hydrochloric acid, neither hydrosulfite. So it is an environment friendly way, but the cost is high.

5 Conclusions

Although there is the intensified research on whitening kaolin, yet, ideal methods required more study and explore. The present existing methods all have their own advantages, however, these methods have obvious drawbacks, too. The advantages of physical methods were simple process and low cost, but the increase of degree of whiteness is limited because this method is only separated mineral and organics from kaolin. The advantages of the chemical methods is high degree of whiteness, but the corrosion of equipment is terrible, which is caused by strong acid, alkali and high temperature; Also, the wasted water produced in the process of water washing do great harm to environment. The advantages of the biological method is green and less environmental pollution, but it is of long period, higher cost, covers an area of large, and it is easy to get influenced by weather conditions, so it is not fit for industrial production. Therefore the selection of new bleaching process with low investment, lower cost, less energy consumption, no pollution to environment is the developing direction of Kaolin, especially the technology of bleaching kaolin at room temperature. We shall explore a new and environmentally friendly processing method that is fit for kaolin and improve and modify the present process to increase the degree of whiteness and grade of kaolin, and make the technology of whitening kaolin to break out of the dependence on high temperature and strong alkaline condition and is widely used in industry bleaching kaolin.

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