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Chemical Synthesis and Properties of A New Collector for Solid Waste Phosphogypsum

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Abstract: Harmless treatment and resource utilization of phosphogypsum are of great significance for environmental protection and promoting the sustainable and healthy development of phosphorus chemical enterprises. This paper introduces the policy environment, main impurities and collector types of phosphogypsum in China and the research status at home and abroad.

Keywords: Flotation, Collector, Keywords impurity, Research status at home and abroad.

1. Introduction

1.1. Research Background

Phosphogypsum is a kind of typical industrial by-product gypsum, which is a solid waste produced by phosphate rock in the production of phosphoric acid and a by-product of chemical products. At present, phosphogypsum is mainly produced from the following three processes: (1) wet phosphoric acid production of calcium-magnesium phosphate and mono-ammonium phosphate process; (2) wet phosphoric acid production process of calcium hydrogen phosphate, calcium dihydrogen phosphate and phosphate; (3) The wet process of producing phosphoric acid from phosphate rock in China.

Wet phosphoric acid is the main process to produce high concentration phosphoric acid from sulfuric acid and phosphate rock, and a large amount of phosphogypsum solid waste is produced in the process of acid production. According to statistics, the production of 1 ton of phosphoric acid (calculated by P2O5-) by wet phosphoric acid produces 4.5-5.0 tons of phosphogypsum.

Due to the rapid development of the wet phosphoric acid industry, the amount of phosphogypsum accumulated is considerable. At present, the global cumulative emissions of phosphogypsum are about 6 billion tons, and it is expected that the total storage of phosphogypsum will increase to 2 times the existing between 2025 and 2045, while the stock of phosphogypsum in China has exceeded 700 million tons, with an annual increase of about 80 million tons, and the production is mainly concentrated in the Yangtze River Economic Belt. However, for the new production of phosphogypsum every year, the market can not do "eat dry squeeze clean", pile is still the main way of disposal of excess phosphogypsum. However, the discharge and accumulation of phosphogypsum will cause serious damage to the ecological environment, not only pollute the groundwater resources, but also cause the waste of land resources.

In 2016, The State Council issued the Action Plan for Soil Pollution Prevention and Control, which put forward strict requirements for soil management. The emphasis is on the development concept of "innovation, coordination, green, open and sharing", and it is clearly pointed out that the treatment of industrial waste such as phosphogypsum should be increased. In January 2019, the General Office of the National Development and Reform Commission issued the Notice on Promoting the Development of Industrial Agglomeration for the Comprehensive Utilization of Bulk Solid Waste, which indicated that the resource utilization of industrial gypsum should be promoted and the intensive development of the resource utilization industry of industrial gypsum should be encouraged. In October, the Ministry of Finance issued the "Announcement on the Value-added Tax Policy on the Comprehensive Utilization of Resources", which announced that from September 1, 2019, taxpayers selling self-produced phosphogypsum comprehensive utilization products can enjoy the VAT collection and refund policy. In March 2021, the National Development and Reform Commission issued the "Guiding Opinions on the Comprehensive utilization of bulk solid Waste", saying that during the "14th Five-Year Plan" period, phosphogypsum should continue to promote the use of phosphogypsum in the production of cement and new building materials and other fields, and on this basis explore new ways to use phosphogypsum, and develop phosphogypsum products with high added value. Traditional low value-added phosphogypsum products have been unable to meet the current market demand, high value-added, green and sustainable phosphogypsum products are the future trend.

1.2. Solid waste phosphogypsum

Phosphogypsum takes calcium sulfate dihydrate as the main phase, and its appearance is mostly gray and white. The form and content of impurities in phosphogypsum depend on the property of phosphate rock and the production process of phosphoric acid, and there are some differences in phosphogypsum from different sources. The main impurities in phosphogypsum are phosphoric acid and phosphate, silicon dioxide, fluoride and organic pollutants. In addition, some phosphogypsum contains some metal impurities, and in some areas phosphogypsum also contains trace radioactive elements or rare earth elements. The discharge and accumulation of phosphogypsum seriously damaged the ecological environment, not only polluted the groundwater resources, but also caused the waste of land resources.

According to the physical characteristics of the impurities in phosphogypsum, the impurities can be divided into three categories: the first type is soluble impurities; The second type of refractory impurities; The third category is radioactive impurities. Among them, soluble impurities are the most harmful to the environment, which penetrate into the soil with rain and pollute the environment. For insoluble impurities, the effect is relatively weak. The content of insoluble impurities is high and the types are different.

1.2.1. Phosphorus-containing impurities

Impurity phosphorus can be divided into three kinds according to the existence form of phosphorus in phosphogypsum, which are soluble phosphorus, insoluble phosphorus and eutectic phosphorus. Among them, soluble phosphorus has the greatest influence on the performance of phosphogypsum. The main component of soluble phosphorus is phosphoric acid, which is ionized in solution, and water-soluble phosphorus mainly exists in the form of H3PO4, H2PO4-, HPO42- and PO43-. Soluble phosphorus is easy to form insoluble calcium salts with calcium ions, and calcium salts hinder the hydrolysis of dihydrate gypsum, which seriously affects the further hydration of phosphogypsum. At the same time, the hydrogen ions ionized by phosphoric acid reduce the pH of the surrounding environment, and the acidic soil environment is not suitable for the growth of some plants and microorganisms. Groundwater can also be affected by acidic environment, so that the pH of domestic water is reduced, affecting the life of humans and other organisms. In addition, phosphorus-containing compounds flow into lakes with rainwater, causing eutrophication of water bodies, causing red tides, and destroying the balance of ecological environment. The existence forms of insoluble phosphorus in phosphogypsum are Ca3(PO4)2 and FePO4, of which the content of Ca3(PO4)2 is relatively high, about 1.2%, and the distribution of insoluble phosphorus is relatively concentrated, mainly distributed in phosphogypsum with relatively large particles. The physicochemical characteristics of insoluble phosphorus are stable, and the influence on the physical properties of phosphogypsum is very small and can be ignored. Eutectic phosphorus is the solid solution produced when HPO42- replaces SO42- enters the crystal lattice of calcium sulfate.In the hydration process of phosphogypsum building materials, eutectic phosphorus significantly reduces the hydration rate of gypsum, decreases the supersaturation of dihydrate gypsum, coarses the gypsum crystal, loosens the structure, reduces the strength of building materials and cement, and affects the condensation of gypsum. During the hydration process of gypsum, eutectic phosphorus precipitates from the lattice into soluble HPO42-, and the ionized PO43- from HPO42- combines with Ca2+ in solution to form insoluble Ca3(PO4)2. Insoluble calcium phosphate covers the surface of the crystal to prevent further hydration of gypsum, resulting in reduced strength of gypsum. The ionized hydrogen ions reduce the pH of the slurry, which will not only corrode the machinery and equipment, but also powder and frost the surface of the dried product.

1.2.2. Fluorine containing impurities

According to the form of fluorine in phosphogypsum, it can be divided into two types, namely soluble fluorine and insoluble fluorine. The soluble fluorine is mainly NaF, and the insoluble fluorine is mainly CaF2 and Na2SiF6. The fluorine in phosphogypsum is mainly transferred from phosphate rock, phosphate rock after sulfuric acid acid hydrolysis, phosphate rock in 20%-40% fluorine inclusion in phosphogypsum. The effect of soluble fluorine on phosphogypsum is mainly to weaken the interaction force between phosphogypsum molecules, so when the content of soluble fluorine in phosphogypsum reaches a certain degree, the compressive and flexure strength of phosphogypsum will be reduced.

1.2.3. Organic Impurities

Phosphogypsum contains certain organic matter, which mainly comes from the phosphate rock itself and the organic catalytic reagent added in the acid hydrolysis process of phosphate rock. The organic catalytic reagent components are mainly ethylene glycol methyl ether acetate, isothiocyanomethane and so on.

1.2.4. Heavy metals, radioactive impurities

Heavy metal ions and radioactive substances in phosphogypsum are issues that need to be concerned about, its content is about 0.05%-0.2%, heavy metal ions are Cd, Cu, Zn, Pb and so on. The distribution of heavy metals in soil is affected by phosphogypsum pile, and the farther away from phosphogypsum pile, the lower the heavy metal content is. The radioactive substances in phosphogypsum are mainly hydrogen, radon, etc. The radiation emitted by these elements during nuclear decay forms aerosols with fine dust particles, and inhalation of these particles causes harm to the human body.

1.3. Collector

The collector is a flotation agent that changes the hydrophobicity of the mineral surface and makes the floating ore particles adhere to the bubble. The most important class of flotation agents. It has two basic properties: (1) it can be selectively adsorbed on mineral surfaces; (2) It can improve the hydrophobic degree of the surface of the mineral, so that it is easy to adhere to the bubble, thus improving the buoyancy of the mineral.

1.3.1. Fatty acid collector

Fatty acid collector is the most used collector for phosphate rock flotation, which includes fatty acid derivatives.

Fatty acid modifiers, etc. The mechanism of interaction between fatty acid collector and mineral surface includes reversible adsorption and irreversible adsorption. The essence of irreversible adsorption is electron transfer, co-ownership or exchange between adsorbent and atom on mineral surface. The conventional fatty acid collector has a strong ability to collect ores, but the selection of minerals will be relatively poor, and the corresponding regulator and inhibitor are generally used in flotation. The solubility of fatty acids is very low at low temperature, which is not conducive to the dispersion of the agent in the pulp. If necessary, the fatty acids can be modified to generate corresponding salts and enhance the solubility.

1.3.2. Fat amine collector

Fatty amines are the most commonly used cationic collectors in phosphate rock flotation. There are many kinds of amine collectors, but according to the chemical molecular structure, it is basically divided into primary, seasonal, tertiary and secondary amine salts. In the pulp, ionization can occur and ionize -NH3+ cation. This positively charged ammonium ion will adsorb on the surface of the mineral to form a film, making the surface of the mineral hydrophobic and floating up to achieve the purpose of sorting.

1.3.3. Amphoteric collector

As phosphate rock is more and more difficult to select, fatty acid collectors can not meet the requirements of selection, research workers through research, so that amphoteric collectors are widely used in phosphate rock flotation. Amphoteric collector with two functional groups, cationic functional group and anionic functional group, in different pH, can ionize different ionic functional groups, according to the ore properties to adjust the pH to meet the separation requirements, so amphoteric collector can adapt to a wide pulp pH. The amphoteric collector can be well dissolved in the pulp at room temperature, which solves the problem of poor water solubility of fatty acid collector.

2. Research Status at Home and Abroad

At present, a variety of cationic amine collectors, including amides, ether amines, fatty amines, polyamines and quaternary ammonium salts, have been independently researched and developed at home and abroad. In the reverse flotation of phosphate rock, cationic collector is mainly used to remove silicate minerals, which can dissociate -NH3+ in water, in a certain pH range, -NH3+ can effectively capture quartz. In the process of flotation, cationic amine collectors usually have a series of problems such as high viscosity, poor water solubility, low temperature resistance and poor selectivity. GE Yongzhong et al used GE-609, a cationic amine collector developed by themselves, as a desiliconization collector and applied it to a middle and low grade phosphate rock in Yichang, Hubei, a high silicon and high magnesium collophanite in Hubei and a low grade collophanite in Anyuan to carry out experimental research on the double reverse flotation process, and obtained good beneficiation indicators. The problems of high viscosity, poor water solubility and weak selectivity of cationic reverse flotation foam were solved successfully. Guo Fang et al. found that coarse-grained silicate minerals could be removed by scrub, while fine-grained silicate minerals could be removed by reverse flotation. Compared with ether amine salt or quaternary ammonium salt, alkyl amine salt could better remove silicate minerals by flotation.Li Ying used the self-developed C12Giy collector to study the adsorption mechanism of C12Giy on the surface of quartz, dolomite and collophosphite. MS8.0 software was used to conduct molecular dynamics simulation, calculate the surface binding energy of the collector and the three minerals, and elaborate the adsorption mechanism of the collector in detail.

In flotation, the amine collector and mineral are generally semi-micellar adsorption. In order to enhance the semi-micellar adsorption of amine collector, the combination of amine collector and industrial miscella alcohol or fatty acid surfactant can be used. The composite collector forms parallel adsorption on the surface of the mineral particles, and its non-polar groups can be associated with each other, thus increasing the adsorption amount of the collector on the mineral surface, making it easier to float in contact with bubbles, so as to achieve better flotation effect.

Amphoteric collector is a heteropolar organic compound with both anion and cationic functional groups in its molecular structure. By adjusting the pH of the pulp, the electrical property of the agent can be changed. When the solution is acidic, the agent is charged positively. When the solution is alkaline, the reagent is negatively charged. When the solution is at the isoelectric point, the surface of the reagent is not charged. The amphoteric collector has different advantages in the separation process of phosphate rock. Yang Jie et al. found that sodium N-dodecyl-β-aminoacetate as phosphate rock collector has the characteristics of good water solubility, low temperature resistance, foaming ability and selectivity, etc. The application of sodium N-dodecyl-β-aminoacetate to the middle and low grade silica-calc collophosphine in Qingping, Sichuan Province has obtained ideal indicators. Fatty acid collector is the most typical representative of anionic collector. When used as flotation collector, fatty acid collector has the characteristics of strong collecting ability, poor selectivity, little water solubility, and not easy to disperse in water. Often the use of heating can achieve a better separation effect, which increases the cost of dressing. According to the characteristics of traditional fatty acid collectors, domestic scholars mainly focus on the composition and modification of fatty acid collectors. Zhou Xian et al. used oleic acid as test raw material to synthesize fatty acid methyl ester sodium sulfonate (MES) through esterification, sulfonation and other reactions. By comparing the flotation performance of oleic acid and MES, it was found that MES was more water-soluble, more selective and more resistant to hard water than oleic acid, and using it as a flotation collector could greatly reduce the amount of regulator. Huang Qimao et al. used industrial rapeseed oil scraps as experimental raw materials and modified them through saponification and acid hydrolysis reactions. The test results showed that the modified agent was significantly better than the unmodified fatty acid collector in terms of water solubility, selectivity and dosage.

3. Conclusion

From this point of view, we need to strengthen the research and practice of comprehensive utilization technology and methods of phosphogypsum to improve its utilization rate and product quality; At the same time, enterprises and scientific research units should strengthen joint research and development of new technologies and methods to further tap and make good use of this precious resource, so as to promote the green and sustainable development of phosphate fertilizer industry. On the basis of this research, our team synthesized an amphoteric collector. Through the self-made infrared spectrum, we found that the product structure has amino and carboxyl functional groups, which indicates that the final product meets the expected design.Moreover, we also observed the raw phosphogypsum ore and the flotation concentrate samples by metallography, and observed the impurity content and distribution in the same position through different magnifications. It was found that most of the mineral impurities and fine slime attached to the surface of calcium sulfate grains were eliminated after flotation, which greatly improved the whiteness of phosphogypsum.

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