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Application and Progress of Chemical Iron Sludge

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ABSTRACT

This thesis summarizes the recycling of chemical iron sludge, draws a conclusion that scrap iron sludge can be used in the fields of preparation of ironmaking raw material, iron oxide pigment, ferric salt and new material, and put forwards that new prospect of cyclic utilization and application of iron sludge in the productive process of preparing metanilic acid with m-Nitrobenzenesulfonic acid makes iron sludge develop in the direction of high added value from low added value and bring favorable economic benefit and social benefit.

Key words: iron sludge, iron oxide pigment, ferric salt, new material

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INTRODUCTION

In the technological process of preparing aromatic amino compounds with many aromatic nitro compounds, iron powder is frequently used as the reducing agent. In the meantime, a mass of industrial waste residue called iron sludge will be produced and it is a kind of pollution source which is difficult to be degraded and disposed. In recent years, with the rapid development of economy, the output of industrial waste residue especially iron sludge is increasing with each passing day. There is a saying that “wastes are misplaced resources”. How to turn “waste” into wealth and improve resource utilization rate has become an urgent demand for the development of society [1]. Forefathers have made relevant explorations and researches on the recycling aspect of iron sludge and already made some progress. This thesis is to make an introduction and summary of the application and progress of chemical iron sludge.

1 Use iron sludge as raw material for ironmaking

Iron sludge has high iron content. The material cost is low and effect is quite good if iron sludge is used as the raw material for ironmaking. Mingcheng Steel Factory in Jilin Province uses iron scurf reduction method to produce aniline and ortho-toluidine and a mass of waste residue of amino compounds is produced accordingly every year. The waste residue is also named as “reduced iron”. With the increasing demand for amino compounds, reduced iron is becoming more and more. In order to protect the environment and eliminate the pollution, Li et al[2] make iron sludge turn into ironmaking material through processing steps such as recycling of metal scrap iron, settling separation of iron sludge, centrifugal filtration, deposition and solidification and the effect is satisfactory. Although the effect of iron sludge as ironmaking material is pretty good, abrasion of machine is quite severe and production efficiency is reduced because there are unreacted reduced iron particles in iron sludge when the machine is running at high speed.

2 Use iron sludge to prepare iron oxide pigment

Ferric oxide series pigments are the first major colored inorganic pigment and the second major inorganic pigment next to titanium dioxide [3]. Comparing with international pigments in the aspect of quality, domestic pigments lag far behind. Under such condition, Technique of making use of iron sludge to prepare ferric oxide series pigments including iron oxide red iron oxide black and iron oxide yellow has an extremely wide application because of advantages such as simple process, complete chromatography and small noxiousness [4].

2.1 Prepare iron oxide red

The molecular formula of iron oxide red is α-Fe_2O_3 and its output takes up 80% of iron series products. Iron oxide red is an important colored pigment and it is widely applied in coloring of oil paint, construction and plastics because of superior light fastness, thermo-stability, alkali-resistance and resistance of atmospheric influence, dirty air and all kinds of alkali. A little iron oxide red can be used in magnetic materials and materials for elements of electronics and telecommunication.

There are two preparation methods for iron oxide red. One dry method (known as high-temperature calcination) and the process is relatively simple. The other one is wet method and there are comparatively more process routes. However, reaction mechanisms of these two preparation methods are basically the same. Iron oxide red up to standard can be produced by both of two methods [5]. Traditionally, iron oxide red produced by iron sheet and scrap iron has a good quality but the technological process takes quite a long time. What is more, costs are high but competitive force is low. Thus, it is necessary to find new raw materials to enhance productivity.

Yang et al[6] have confirmed that industrial iron sludge can be used as raw material after exploration to produce iron oxide red pigment under the circumstance of 60% sulphuric acid concentration after acid-curing oxidization, 1:1.2 mass ratio for sulfuric acid and iron sludge, 800℃ temperature, and 120min reaction time. Moreover, the pigment meets the requirements of coating and oil paint on pigment.

Zhou et al[7] use scrap iron and industrial waste sulfuric acid after production of hydroquinone as the raw material, adopt high temperature dry method to produce iron oxide red through processing steps such as smashing, burdening, calcination, cooling and ball-milling. Its cost is 30% lower than that of conventional methods. Optimal technological condition is confirmed after exploration. Mass fraction of H_2SO_4 is 70% to 80%, mass ratio between iron and sulfuric acid is 1:0.85 to 1:1, calcination temperature is 900℃, and calcination time is 40 to 70min.

Cui et al[8] use both acid solution oxidation method and dry method to produce iron oxide red with the chemical scrap iron sludge as raw material. First, sulfuric acid is used to steep iron sludge and then the solution is heated to 50℃ with slow stirring. Sulfate liquor in iron-containing mixed valence is produced after sufficient reaction. And then processing steps such as iron powder feeding, filtering and high-temperature calcination are conducted. At last, an analysis of XRD and chemical property is made towards the product to determine the productive rate of iron oxide red product reaches 98.11％.

Besides ordinary iron oxide red, Wang et al [9] also produce high-purity iron oxide red. Industrial scrap iron sludge after production of DSD acid is used as raw material. Iron sludge is dried, smashed and made into serous fluid with water after stirring. And then sulfuric acid and a certain amount of oxidizing agent are added. Reaction under the condition of 80℃ temperature lasts one hour. When pH value of the solution is equal to 3, the reaction is stopped and filtration is done. And then sodium carbonate solution is used to adjust the pH value to 5.0 to 6.0 and filtration is done next. Sodium carbonate solution is added to the filter liquor and filtration goes on to get ferrous carbonate filter cake. A little amount of sodium carbonate solution and deionized water are used to wash up to ferrous carbonate filter cake. And then drying, calcination and smashing are done to get highly purified iron oxide red. Use ration of iron sludge under optimal technological condition is up to 97% which meets the requirements of HG/T2574—1994 Standard for Superior Products on quality.

2.2 Prepare iron oxide yellow

Iron oxide yellow is non-toxic and has good color and wide range of application. The chemical formula of iron oxide yellow is $Fe_2O_3 \cdot XH_2O$ or α-FeOOH. Iron oxide yellow is a kind of high value-added inorganic pigment with excellent light resistance and weather fastness so it is quite popular in the fields of coating, rubber, plastics, stationery and medicine. The preparation methods of iron oxide yellow include peptization method, oxidation style, acid process and alkaline process [10]. Huang et al[11] use iron vitriol dreg of yellow sodium as raw material to make α-FeOOH seed crystal at first and then add weak aqua ammonia to form $Fe(OH)_2$ coating α-FeOOH and finally produce a large number of iron oxide yellow after the oxidization of α-FeOOH seed crystal. These pigments have pretty good mono-dispersity and have no agglomeration. The optimum condition is confirmed through exploration into the optimal technological condition for the preparation of transparent iron oxide yellow. Ferrous sulfate concentration is 40%, alkali ratio is 0.25, 1 L vessel Q is 0.16 to 0.2 m^3/h; seed crystal content is 1%, initial ferrous concentration is 0.40 mol/L, pH value is controlled within 3 to 4, air doss is 0.4 to 0.5 m^3/h, and stirring rate is 700 to 800 r/min。

Zhang et al[12] use industrial iron sludge as raw material to prepare α-FeOOH through processing steps such as acid leaching, de-oxidation, air oxidation and filtration, make an analysis on the influence of factors such as n(NaOH):

$n(FeSO_4)$ and surface active agent to finalize that good products can be produced under conditions of n(NaOH): $n(FeSO_4)$=5, temperature=30℃, and sodium dodecyl benzene sulfonate as the surface active agent and 1h reaction time.

2.3 Prepare iron oxide black

Iron oxide black is mainly used in mosaic floor, wall and artificial marble in construction industry. Iron oxide black can be also used as the coloring agent in plastics industry and rubber industry. Besides, it is applicable to industries of printing ink and oil paint, and it can be used to make iron oxide purple, iron oxide red and γ-Fe_2O_3.

Although iron oxide black prepared by traditional method has high performance, the cost is increasing because more and more raw material is consumed in preparation. Shi et al [13] use scrap iron sludge produced in the iron powder reduction process as raw material to generate iron oxide black, turn iron sludge into iron sludge in solid phase and reduced iron powder which is not fully reacted after composition and filter pressing, and produce pure iron sludge in solid phase through size mixing, sieving, water scrubbing and filter pressing. Finally, iron oxide black produced after drying has good quality meeting relevant national standard.

Patent 102583577A [14] introduces the method of using by-product chemical iron sludge in aminophenol process to prepare iron oxide black. Iron oxide black is mainly produced by sieving and dehydration of iron sludge, adding 2% to 5% $MnCO_3$ and 2% NaCl to thermal treatment furnace, warming under the protection of nitrogen, cooling, washing and drying. By means of this patent, about 1.6 ton chemical iron sludge can be used to get about 1 ton pigments of iron oxide black, bringing enterprises with obvious economic benefit.

Patent CN1415551 [15] adopts physical method to carefully chooses iron sludge and prepare iron oxide black with 70% to 90% content after rouging, drying and smashing. No pollution is caused and less cost is spent by this method so that it has a certain market value.

3 Use iron sludge to prepare ferric salt

3.1 Prepare solid polymeric ferric sulphate

Polymeric ferric sulphate (PFS for short) is a kind of efficient inorganic water depurator and its general formula is $[Fe_2(OH)n(SO_4)_{3-n/2}]_m$, m=f (n). As an inorganic water depurator, polymeric ferric sulphate has advantages such as good coagulation ability and high efficiency, good water quality after purification and has good effect on disposing organic waste water in meat-packing, tanning and printing.

Su et al [16] make a research on solid polymeric ferric sulphate produced by raw materials of industrial iron sludge and sulfuric acid. Polymeric ferric sulphate is prepared by experimental procedures including smashing, soaking, neutralization, oxidization, and filtration. Solid matters produced by this method have high production efficiency and low pollution.

Di et al [17] make use of ions co-precipitation principle to change all Fe^{2+} in iron sludge into Fe^{3+}, add polypropylene phthalein amine to get pure ferric sulfate through filtration and cooling, and then distribute the ferric sulfate to a solution with certain concentration, and finally get PFS sample after polymerization reaction, aging and smashing.

3.2 Prepare solid poly-silicate ferrite

Poly-silicate ferrite (PSF for short) flocculating agent is a kind of inorganic polymer flocculating agent in compound type. It has advantages such as low toxicity, cheap price, no waste emission and friendship with environment so that it has relatively high value in use. Ma et al [18] use iron sludge and sodium silicate as raw materials to prepare poly-silicate ferrite through calcination and excitation. Optimal technological condition is determined through exploration. Iron sludge calcining temperature is 800℃, calcining time is 1h, sulfuric acid concentration is 4 to 5mol/L, liquid-solid ratio (mass ratio) is 4:1, acid leaching time is 2h to 3h, acid leaching temperature is 100℃, ratio of n(Fe) and n(Si) is 2:1, pH value of silicate activation is 3.0, activation time of silicate is 25min, and aging time is 2h.

3.3 Prepare ferrous sulfate

Ferrous sulfate is blue-green monoclinic crystal or particle with no odor and it has wide application in the aspects of water flocculating purification, processing of industrial wastewater, treatment of iron deficiency anemia and coloring agent. Li et al [19] establish a new method for preparation of a hydrated ferrous sulfate with scrap iron sludge and sulfuric acid as raw materials through lab test and pilot plant test. This technique requires no pretreatment for scrap iron sludge in the process of preparing ferric salt. Optional experimental condition is determined through experiment. Sulphuric acid concentration is 22%, solid-to-liquid ratio is 0.25, extraction time is

40min, extraction temperature is 85℃, melting temperature is 90℃ to 95℃, pH value is 0.5 to 1, and reaction time is 30min.

Zhang et al [20] use scrap iron sludge as raw material to prepare $FeSO_4{\bullet}7H_2O$ through processing steps such as acid leaching, reduction and pH value adjustment. A conclusion is drawn through experiment that $FeSO_4{\bullet}7H_2O$ has relatively good crystal in water-ethyl alcohol. Crystal ratio reaches 95% when $FeSO_4$ concentration is 1.41mol/L, ratio of V (ethyl alcohol) and V (water) is 1.5:1.0, and reaction time is 20min. Optimal technological condition is determined. Temperature is no higher than 30℃, pH value is 1.7 to 2.0, 1.7～$FeSO_4$ concentration is over 0.8mol/L, and ratio of V (ethyl alcohol) and V (water) is 1.5:1.0. Products meet the standard of HG/T2935-2000D.

3.4 Prepare ammonium ferric citrate

Ammonium ferric citrate has wide application in the aspects of food, medical and meteorological analysis due to high iron content and good performance [21]. Dong et al [22] use iron sludge as raw material to prepare ammonium ferric citrate and use sulfuric acid to remove hazardous substances in iron sludge. Optional experimental condition is determined. Mass fraction of sulphuric acid concentration is 35%, extraction temperature is 85℃, solid-to-liquid ratio is 0.1:1, and extraction time is 2h. Ferric hydroxide is prepared under conditions of 80℃ reaction temperature and 1h reaction time. And then citric acid and ammonium hydroxide is added to generate the sample. High-purity ferric citrate got through heating concentration, drying and anhydrous ethanol soak meets the requirement of the country on the quality of iron supplement agents.

4 Use iron sludge to prepare new material

The application research fields of iron sludge is expanding constantly from the field of relatively mature preparation of ironmaking material, iron oxide pigment and ferric salt to that of the preparation of iron based new material. Nanometer material, water treatment material and also battery material are involved.

4.1 Prepare nanometer material

As a new-type material, nanometer iron oxide has wide application in the aspects of magnetic memory material, magnetic liquid and function material due to its unique magnetism. At present, solid phase method, vapor phase method, liquid phase precipitation method and oxy-reduction precipitation method are frequently used to prepare nanometer iron oxide.

Xu et al [23] use chemical iron sludge as raw material to get α-FeOOH through processing steps such as reaction with sulfuric acid, suction filtration reduction and standardization, take α-FeOOH as drive body and add defined amount of Fe^{2+} to adjust pH value to 9 to form precipitation solution. Nanometer iron oxide is finally got through ebullition, 4h reflux, centrifugal separation and drying. Optional experimental condition is determined through exploration. Phase inversion temperature is 80℃, inversion time is 2h, pH value is 9, and R is equal to $n(Fe^{3+})/n(Fe^{2+})$ and 1.75. Nitrogen protection is required in the earlier stage of preparation by this method. There are disadvantages such as long reaction cycle, heterogeneous particles and harsh reaction condition. Li et al [24] use hydrogen peroxide as oxidizing agent to determine the optional experimental condition through orthogonal experiment. pH value is 11, reaction temperature is 75℃, reaction time is 3h, and hydrogen peroxide dosage is 0.5ml. Under such technological conditions, productive rate of nanometer iron oxide is up to 95.89%, overcoming previous disadvantages.

4.2 Prepare water treatment material named sponge iron

Sponge iron is also named direct reduction iron (DRI) for short [25]. Sponge iron becomes a kind of popular new-type water treatment material due to advantages such as many micro-pore and high activity and it has better reducing capacity than ordinary iron powder. At present, domestic industrialization methods of production include down draft kiln method, cold consolidation pellet rotary kiln method, one-step rotary kiln method and XSH-A method.

Sun et al [26] use iron sludge generated in the process of producing DSD acid as raw material to develop sponge iron, a kind of water treatment material. DSD acid is also named Maurer's acid and it is a kind of important dye intermediate. Optimum condition for preparation of conventional sponge iron is determined through experiment. Carbon charging rate is 27%, reaction time is 16min, and reaction temperature is 1160℃. Metallization ratio of iron sludge for sponge iron prepared under such condition is over 90%.

4.3 Prepare materials for li-ion batteries

$LiFePO_4$ is regarded as an ideal anode material for lithium-ion battery due to its advantages such as high-energy density, high security, long life and little pollution [27]. Wu Z J et al[28] use iron sludge after recycling by carbon-thermal and magnetic separation to synthesize $LiFePO_4/C$. Chang et al[29] make use of dissolution-precipitation process to recycle iron in the state of $FePO_4\cdot 2H_2O$ from iron sludge and use $FePO_4\cdot 2H_2O$ as raw material for synthesizing $LiFePO_4/C$. The experiment improves the electrochemical performance of $LiFePO_4/C$ through analysis of iron sludge by virtue of inductively coupled plasma (ICP) for short. X=2, i.e., $FePO_4\cdot 2H_2O$ is calculated through thermogravimetric analysis (TGA for short) of prepared $FePO_4\cdot XH_2O$. The experiment also draws XRD graph and SEM graph for $LiFePO_4/C$ synthesized by $FeSO_4\cdot 7H_2O$ and iron sludge as raw material respectively and then makes a comparison to prove both two are olivine-type in pure phase in orthorhombic crystal system, particles are different in size and distributed among 100 to 200nm uniformly. Because $LiFePO_4/C$ produced by iron sludge as raw material contains beneficial impurity elements such as Mg, Co, Cr and Ni, it has relatively high cycling stability and rate capability.

5 New prospect of application of iron sludge

This thesis makes a general survey of the application and progress of iron sludge. It is involved with the fields of ironmaking material, iron oxide pigment, ferric salt and new material, and improves the utility value of iron sludge. In addition, Klausen et al [30] find that the combination of Fe^{2+} in free state and iron oxide can rapidly reduce nitrobenzene compounds. Klausen name this reduce system as surface binding iron reduce system. Because iron sludge container a large number of iron oxides and a small number of iron scraps, it can be realized to explore the reduction of m-Nitrobenzenesulfonic acid through combination of iron sludge and Fe(II). This method not only finds a new train of thought for the application of scrap iron sludge, but also initiates a new idea for disposing the organic pollutant of m-Nitrobenzenesulfonic acid. Research shows that using Fe^{2+}, the load of iron sludge, as the reducing agent to prepare metallic acid is more economical and causes less pollution than iron powder reduction method, catalysts hydrogenation and electrolysis revivification process. It is expected that this new method will have bigger space for development and utilization in the near future.

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