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Resourcefulization approaches to pollution control of chromate residues in China

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Abstract—Over 2 million tons of chromate residues as hazardous wastes have been accumulated from chromate production processes during the past more than 30 years in China. Some serious pollution problems have been caused due to no appropriate technology and management. Approaches are reviewed to pollution control of chromate residues by utilizing them as secondary resources in this paper. In addition to legislation for pollution control, chromate residues can be used as raw materials to produce a great diversity of useful industrial products. Strategies are also recommanded for the resourcefulization of chromate residues.

Keywords: chromate residues; resourcefulization; pollution control; China.

STATUS OF CHROMATE RESIDUES POLLUTION AND ITS HARMFULNESS

China has a history of more than 30 years in chromate production. More than 20 factories mainly manufacturing sodium bichromate have been located in 16 provinces or cities. Due to their small production scale and backward technology, these factories, on the average, produced 1 ton of metallic chrome and 1 ton of chromium salt accompanied by 7 and 3–4 tons, of chromate residues respectively. Each year, about 130000 or 140000 tons of chromate residues were dumped in China. As a result, the total piling amount has reached 2 million tons of the total annual discharge of chromate residues (130000 or 140000 tons), only 20000 or 30000 tons were utilized while more than 100000 tons were still piled, most of them were heaped in an open air. What is the worst is that no waterproof and permeating prevention measures were taken in most piling sites. Some enterprises arbitrarily dumped the untreated chromate residues resulting in that chromic dust was discharged in China. As the result of rain washing out and leaching, the Cr(VI) in the dust may permeat down to underground. In China, annual 800000 tons of chromate wastewater are threatening the nearby surface water, underground water and other water sources. For example, the total piling amount of chromate residues from a factory in Shenyang has reached 120000 tons, which has polluted about 3000m^2 area. More than 350000

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tons of chromate tailings stored by Jinzhou Ferroalloy Factory were found to have contaminated 20 km^2 of the underground water with Cr(VI) pollutant and result in 1800 wells of water inedible in 7 villages. A ferroalloy factory in Nanjing dumped annually 4000 tons of chromate residues and has stored 150000 tons of chromate residues, as a result, the Cr(VI) standard of potable water is exceeded by 79 times and 19 times in the inside and outside factory, respectively. A chemical factory of Chongqing has piled 100000 tons of chromate residues along the Jialingjiang River. The water sample taken from downstream 1 km far away from the drain mouth showed that the concentration of Cr(VI) had reached 0.08 mg/L. In Hefei City, the chromate residues from a factory have caused 300m^2 of soil nearly to have been in color of yellow. The highest and lowest content of Cr(VI) have exceeded the standard of potable water by 6000 times and 60 times, respectively. Over the past 20 years, a chemical factory of Qingdao has stored about 300000 tons of chromate tailings and formed a tailing hill that has caused a serious pollution. The hill is getting bigger and bigger because the tailings are adding at a rate of 1000 tons a year. In 1976, by testing the spinach, Chinese chives and coriander planted close to a chemical factory, Chinese researchers found the content of chrome had reached 0.37 mg/kg, 0.74 mg/kg and 0.68 mg/kg respectively. The vegetables became inedible. In the chromate factories, some workers have been found to have had various skin diseases relating to chrome. What is mentioned above elucidated that chromate not only severely contaminated the ecological and living environments but also damaged to the people's health. In the past two decades, total more than 30 million Yuan(RMB) were spent on the tackling of chromate residue, but the problems have not been completely solved. In a word, chromate residue has been a serious public hazard in China and an important environmental problem to be solved urgently.

THE RESOURCEFULIZATION APPROACHES TO DEALING WITH CHROMATE RESIDUES

Formulating laws and standards in order to constraint the expansion of the harmful chromate residues

Since the founding of the People's Republic of China, Chinese Government has issued "Standard for Pollutants Discharge from Chromate Industry" and "Standard for Pollution Control of Chromate Residues (Cr(VI)) from Ferroalloy". Under consolidating the electroplating industry, the relevant branches and local governments also drafted some associated regulations which have taken a restrict effect in controlling the pollution from the chromate and plating industry.

1. Use of chromate residues as additives for smelter industry

Chromate residues can be served as a substitute for dolomite and limestone in iron-smelting. During smelting pig iron, dolomite and limestone must be added so as to clear calcium and silicate, that is make residues. Experiments proved that replacing dolomite and limestone by

chromate residues was available. For example, Suzhou Steel Plant took the simple sinter in a furnace of 84 cubic meter and consumed 1000 tons of chromate residues. Tonghua Iron-Steel Plant and Fushun Iron-Steel Plant used 6270 and 3400 tons in the furnace of 250 cubic meter respectively. Nanjing Ferroally Factory and Jinzhou Ferroally Factory have taken a series of successful industrial tests. These tests reflect as follows:

The fact that calcium (CaO), and Magnesium (MgO) present in chromate residues are nearly equal to those in dolomite and limestone makes this replacement available.

Cr(VI) may be completely disoxidated and detoxicated through being smelted in furnace.

Due to the rise of chromic content in pig iron, the mechanical property, the hardness, the rub fastness and the fastness to erasion of pig iron are strengthened and are popular highly with users.

In case of producing 1 ton of pig iron, about 600kg chromate residues will be consumed. According to this rate, if the total annual chromate residues were put into iron-smelting, it only could meet the needs of 180000 tons of iron. In short, this is an ideal approach to utilization of chromate residues.

2. Bright prospects for using chromate residues as the stain of emerald green glass

While 1 ton of chromate compound being produced, 3 or 4 tons of chromate residues are turned out. The total amount of chromate residues over the years has reached 2 million tons. At the same time, it is increasing at the rate of 130000 or 140000 tons per year. If the chromate residues were not treated, it would be highly harmful because of the toxication of Cr(VI). The chemical factories in Tianjin and Shenyang and the Qingdao Red Star Chemical Factory have processed the chromate residues into powder that contains 4-6% of chrome. The powder is certainly up to the quality standard for glass stain. Consequently, glass factories not only got the cheap stain but also produced the beautiful dark green glass which is popular with users. Qingdao Red Star Chemical Factory has set up a production line with an annual output of 4000 tons of glass stain. If the stain is sold in the price of 70 Yuan (RMB) per ton, the gross profits will reach 40000 Yuan (RMB). This approach may increase economic profit together with eliminating the pollution of chromate residues.

This approach has many superiorities:

Cr(VI) can be reduced to Cr(III), which attains detoxification and eliminates the chromate residues pollution.

It is possible to save on raw materials and reduce production costs. If we used the chromate minerals imported from abroad, we would spent 500 Yuan (RMB) per ton. But if we chose the chromate residues, it would only cost 30 Yuan (RMB) of processing fee for a ton. The chromate residues containing CaO and MgO can serve as a substitute for dolomite and limestone in the process of glass. In the case of replacement, 100 kg of dolomite and 80 kg of limestone will be

saved for the output 1 ton of glass. This substitute can efficiently reduced the production costs.

Using chromate residues as glass stain is popular with workers because the method is simple and practical in technology and makes the material easily mix even.

That chromate residues take the place of chromate mineral in the glass production produce the glass in gay color and in improved quality. This is a significant approach to treat the chromate residues.

3. To make light aggregate or ceramsite from chromate residues

At the present time, adding chromate residues into the process of light aggregate or ceramsite to make up light concret is a good means because the weight of buildings can be cut off greatly, particularly for the higher buildings. The technologies of making ceramsite have been well developed. The ceramsite made from chromate residues has a characteristic of low weight and efficient strength which can save transport power and expenses.

From the point of view of environmental protection, the ceramsite made from the high-temperature treatment of chromate residues did not contain Cr(VI). As a product of reducing, the chromic compound(Cr(111)) exists in ceramsite in a fixed form while the ceramsite is packed and closed in conceret and is cut off from the environment. It is evident that making ceramsite from chromate residues can give rise to the better and more reliable environmental effect. In addition, the technique that chromate residues replace (or partly replace) cobble in producing concret is worth adopting and spreading. No doubt, the technique has paved a board road for the treatment of chromate residues.

4. To make tanning agents from chromate residues

Chromate residues is $Cr(OH)SO_4$ that can tan hides. The main processes can be stated as follows: the first is mixing $Cr(OH)_3$ waste slags with sulphuric acid in a ratio of 1.1–1.5 and heating. The second is analysis

$$Cr\ (OH)_3 + H_2\ SO_4 \longrightarrow Cr(OH)SO_4 + 2H_2O,$$

for chromium (as $Cr_2\ O_3$), basic radical degree (i.e., alkalinity, %) and pH value and adjusting these values to accord with the specifications. The third is putting it into effect in tanning hides.

Because the iron and copper are harmful to tanning agents, the sources of chromate residues should be selected and the foreign matter such as iron and copper should be lowered as much as possible so as to guarantee the quality of tanning agents. The leather tanned by the chromic tanning agents has been up to the national standard in many indicators. The chromic tanning agents not only completely replaced chromium, alum, sodium but also saved a great deal of foreign currency and reduced the tanning cost by 30%.

5. To make catalyst from chromate residues

A large amount of catalyst is needed for use in the process of synthetic ammonia (as nitrogenous fertilizer). The components of catalyst consist of 50–60% of Fe_2O_3, 5.3–6.8% of Cr_2O_3 , 17–20% of MgO, 0.5–0.7% K_2O and some CaO and graphite. The density, facet, catalytic activation, thermal stability and mechanical hardness of catalyst should accord with a certain standards. For example, the content of sulfate should be under the level of 1.0%. Sulfate and other easily dissolved impurity in the slags should be firstly washed and cleared, then the specified amount of MgO and KOH will be added into the slags according to some analysis results. In the end, a series of processes such as milling, making granule, drying, mixing graphite, pressing sheet and roasting will be put into use to turn out sheet-catalyst. If the slags contain chromate compound, first of all, it is necessary to clearly wash away the ferrous compound and the chromic oxyhydroxide through many processes such as acid dissolve (1:3 H_2SO_4), precipitating neutralization (adding ammonium carbamate), heating and self-cooling, precipitating, washing sulfate and drying and so on. Then the process for producing common catalyst will be taken to turn out the catalyst. But this catalyst is not appreciate to the process of synthetic ammonium that takes the natural gas as materials.

6. To make dyestuff and coating

The chromate slags got from electrolysis can be put into effect in making red iron oxide paint which contains specified amount of Fe_2O_3 that can enhance the hardness of paint film. If the red iron oxide point contains Cr_2O_3, its hardness, weathering-resistance and fastness to erosion will be enhanced.

The chromate slags got by Barium Salt Process can be used in making barium-based lead chrome yellow that makes up the inside-wall or outside-wall coating. The process has a better economic efficiency but has a very complicated technology.

7. To make magnetic materials

The best material for making magnetic materials is the chromate slags produced by Ferrite Process, though other chromate slags is available. China was successful in making the type Mx–400 magnetic bar of middle-wave antenna (a kind of manganese stibium ferrite). In the content of the magnetic materials, Cr_2O_3 is under the level of 4%. The process is as follows: first is taking content-analysis for the drying chromate ferrite slags; the second is mixing materials in the ratio of 63.3% of Fe_2O_3, 9.5% of ZnO, 23.2% of $MnCO_3$, and 4% of Cr_2O_3; the last is ball-grinding, firing beforehand, secondly grinding, form-processing and sintering in the temperature of 1270–1300°C.

The magnetic bar made in the process mentioned above is better in main indicators such as magnetic conductivity and Q value. In addition, the type Mx–2000 magnetic bar has been made successfully.

8. To make polishing paste

If the reducing agent is sodium disulfite ($NaHSO_4$) and hydrazine, the chromate slags contain few iron and can be used in the production of green polishing paste. While the chromate slags got by means of electrolysis or ferric sulfite can be used in producing red polishing paste.

The process of making green polishing paste can be elucidated as follows: first is drying and burning the slags that contain $Cr(OH)_3$ at the temperature of 650–1200°C (about 12 hours) to get the green Cr_2O_3.

$$2Cr(OH)_3 \longrightarrow Cr_2O_3 + 3H_2\,O.$$

The second is putting paraffine (20%), beeswax (3%) and stearin (7%) into container to bake in low-grade, the third is adding the powdered Cr_2O_3 (70%) and approciated kerosene, in the end, taking agitation, modeling and cooling to get the green polishing paste which can be used in polishing many high-hardness metals such as stainless steel, chrome and hard alloy.

9. To make calcium magnesium phosphate fertilizer

In the production of calcium magnesium phosphate fertilizer, apatite ($Ca_5F(PO_4)_3$) is key material and serpentine ($3MgO.2SiO_2.2H_2O$) is flux. In consideration of the chemical component of chromate residues, researchers found it could partly replace the serpentine in the production of phosphate fertilizer. Changsha Chromate Factory and the Synthetic Chemical Factory of Xiangfan collaborated with Hunan University in studying the application and the spread of the process for phoshate fertilizer in the flux of chromate residues. This study applied the nonspherical chromate residues as flux into the furnace. Through a series of experiment, Changsha Environmental Mornitoring Station found chromate residues could be detoxicated completely ($Cr^{6+} < 1PPm$) and did not cause the secondary pollution and could reduce the fluorine in the furnace tail gases. Consequently, the chromate factories and phosphate fertilizer factories could gain better economic and environmental benefits. These experiments also showed the optimal amount of chromate residues added is 10–15%, i.e., producing 1 ton of fertilizer consumes 100–150 kg of chromate residues. This will eliminate greatly the chromate residues. It is evident that using chromate residues as flux is available and can guarantee the quality and quantity. The operation of furnace is normal and stable. Adopting the semi-processed chromate residues as flux can lower the melting point of the materials in furnace and increase the fluidity and have brought the effect of decreasing coke ratio and increasing output and reducing the fertilizer cost. In brief, using chromate residues in making the phosphorate fertilizer may not only bring the better environmental and social effect but also gain a good economic effect. The fertilizer has a good effect and keeps remains under standard and is popular with peasants and has a good sale.

10. To make cast-stone from chromate residues

Making process is as follow: the first is mixing 30% of chromate residues, 20% of silica

sand, 45% of soot and 3–5% MgO; the second is smelting the mixture at the temperature of 1500°C; then casting crystallizing (in 900°C), cooling. Xincheng Chemical Factory produced annually 10000 tons of cast-stone and consumed 3000 tons of chromate residues.

TACKLING AND STRATEGIES FOR THE RESOURCEFULIZATION OF CHROMATE RESIDUES IN CHINA

To deepen understanding and strengthen guidance and administration

The leaders at all levels should constantly deepen the understanting of the significance of tackling and strategies for the resourcefulization of hazardous chromate waste and sincerely regard the prevention of chromate residues and environmental protection as a strategic take which will benefit the nation and the people as well as the future generations. So long as we try to make laws and regulations and strengthen administration and stick to the principle of "three at the same time" and take the road of "priority of prevention, combination of prevention and tackling and integrated tackling", the pollution from chromate residues will be minimized.

Planning the tackling of chromate residues

At the same time of planning the location of chromate production, the present and long-run plan for chromate control and tackling should be made. What is more important is to implement the investment plan so as to carry out the tackling plan in a planned, stepped and aimed way. Such planning will do good to the establishment and development of the chromate residues treating factories.

To draft the effectively economic and technological policies

Because the chromate production is an indispensable trades in Chinese industrial sectors, the pollution of chromate residues must be controlled. With a view to assuring both the development of chromate production and the pollution tackling of chromate residues, it is necessary to draft the effectively economic and technological policies which can encourage the tackling. These policies comprise the aspects relating to concentrated production, centralized tackling, giving full play to the superiority of the professional and large-scale factories, process innovation the renewal of equipment and other relevant preferential policies consist of price, taxes and supply of raw material and so on. Sticking to practice these policies will do good to chromate production and gain better tackling effect.

STRENGTHENING SCIENTIFIC RESEARCH AND RAISING TECHNOLOGICAL LEVELS

For the approaches to tackling and resourcefulization of chromate residues, attention should be paid to such aspects as the systematic process including producing and utilization and treatment, the economic and technological policies, the pollution control technology and equipment,

the integrated development and utilization and the resourcefulization. Firstly, we should enlarge the technological exchange at home and abroad, and constantly raise the scientific and technological levels so as to attain automation, systematization and standardization, and achieve multi-step use and high efficiency. Secondly, we should try to finalize the production and popularize the technology and achieved the full resourcefulization of chromate residues. In the end, we will solve the problems of chromate residues and obtain the social, economic and environmental benefits.