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Study on treatment and recycling of mercury from waste mercury catalysts in China

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Abstract

CCP PVC production is the unique technology in China that consumes most mercury with annual consumption of nearly 10,000 t, about 70% of them entering waste mercuric chloride catalyst. The main supply of mercury for CCP PVC industry includes the production of primary mercury and recycling of waste mercuric chloride catalyst. The production of primary mercury will be constrained and phased out after the Minamata Convention on Mercury going into effect. Therefore, the recycling of waste mercuric chloride catalysts will be an important supply source of mercury before the phasing out of mercury in CCP PVC industry. Based on the investigation of current status of CCP PVC production and recycling of waste mercuric catalysts industry, this paper analyzes mercury content of waste mercuric chloride catalysts and mercury recycling rate of waste mercury catalyst recycling industry, and estimates less than 50% of cyclic use of mercury in CCP PVC industry. In view of low cyclic use rate of mercury and excessive production capacity of the industry, this paper puts forward policy recommendations in the following three areas such as strict implementation of mercury destiny reporting system, stricter management of environmental access conditions and demonstration and extension of close loop circulation mechanism of mercury.

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Keywords: waste mercury catalysts, treatment and recycling of mercury, China

CCP PVC production is the unique technology in China with the biggest consumption of mercury. As the catalyst for the process of synthesizing VCM by acetylene and HCl, mercuric chloride catalyst is employed in large amount in CCP PVC industry. It is turned into waste mercury catalysts in the production process due to drop and final loss of activity because of factors such as mercury sublimation and poisoning. At present, this industry discards waste

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mercury catalysts as many as about 15,000 t each year, containing several hundred tones of mercury with relatively high value for recycling and reuse. Therefore, recycling and disposal of waste mercury catalyst becomes a relatively mature industry in our country.

The Minamata Convention on Mercury was adopted by the international communities in 2013 and is expected to go into effect as of 2016. The Minamata Convention on Mercury requires prevention and control the whole cycle risks of the production, use, release and waste of mercury. The CCP PVC production is the key mercury consumption technology subject to the regulation of the Convention. Although the Convention does not set a specifically phasing out deadline, it requires that all parties should ban the construction of new primary mercury mines after the Convention going into effect and close all primary mercury mines within 15 years. Mercury supply in China mainly comes from the production of primary mercury. The regulation of the Convention on primary mercury means the control of the source of mercury supply for CCP PVC production. Therefore, the recycling and treatment of waste mercury catalysts will become an important source of mercury supply before the phasing out of mercury consumption by CCP PVC industry in our country. Our country should strengthen the management of recycling of waste mercury catalysts, raise recycling rate of mercury, and minimize mercury release and secondary pollution in mercury recycling process.

1. Waste mercury catalyst recycling and treatment technology and mercury release

1.1. Key processes for recycling and disposal of waste mercury catalysts

Mercury in waste mercury catalysts mainly exists in the form of mercuric chloride, with small amount of reduced elemental mercury at the same time. The following three processes could be employed for recycling and treatment of waste mercury catalysts: recycling metal mercury by distillation, recycling mercuric chloride by oxygen-control dry distillation method and regenerated mercuric chloride catalyst by chemical activation method.

Recycling of metal mercury by distillation is a traditional mercury reclamation process for waste mercury catalysts, mainly including the processes such as chemical retting, roasting and condensation. Mercuric chloride in waste mercury catalysts is turned into mercury oxide through chemical retting. Metal mercury is obtained after the processes such as roasting and condensation. The transformation degree of mercuric chloride determines the mercury recycling rate [1].

Oxygen-control dry distillation method is a new technology that recycles $HgCl_2$ and active carbon in waste mercury catalysts. Applying the fact of coking temperature of activated carbon higher than that of sublimation temperature of $HgCl_2$ and the theory of easy sublimation of $HgCl_2$ at high temperature, we put dried waste mercury catalyst in an airtight furnace that could rotate and adjust temperature. The mercuric chloride in the feed will turn into vapor. We could extract it by a gas extraction device, strongly cool it into solid particles and then recycle them.

With the prerequisite of no separation of activated carbon with mercuric chloride in waste mercury catalysts, chemical activation method employs chemical method to reactivate active carbon, eliminates accumulated carbon and catalyst poisoning, and then adds appropriate amount of addictive and active substance based on the requirement for mercuric chloride content in catalyst product-mercuric chloride to achieve the reclamation or generation. The process flow is as the follows: firstly remove mechanical impurities (such as iron fillings, screws, stones and wood block) in waste mercury catalysts and fine waste mercury catalysts by manual selection (or machine selection) and screening, then put it in an activator for chemical activation, followed by production according to normal mercury catalysts production process.

The investigation results show that at present, most enterprises employ the technology of recycling metal mercury by distillation method. Only a few enterprises employ oxygen-control dry distillation method. There is not any enterprise that employs chemical activation method.

1.2. Mercury release in the recycling and disposing process

All processes of metallic mercury recycling technology by distillation method will release mercury at different degrees. Figure 1-1 shows the release path. In the chemical dipping process, waste mercuric catalysts firstly is dipped in alkaline solution, then heated and dried by high temperature vapor, turning mercuric chloride into