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Experimental study on molten salt oxidation of high salt content pharmaceutical residue

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Abstract

The pharmaceutical residues from chemical synthesis pharmaceutical industry often contain some alkali salts due to the widely use of alkali salts in the manufacturing process, the waste management of such is a significant challenge. Generally, the residues are disposed by landfill and incineration. However landfill is unsustainable and the incineration's efficiency is effected by furnace slag-bonding during combustion, that affects the widely use of incineration. On the other hand, molten salt oxidation is an efficient, flameless thermal process, has the inherent capability of destroying organic constituents of wastes while retaining the inorganic constituents in the molten salt. Therefore, a new access is proposed by disposing the residues using molten salt oxidation. A high salt content pharmaceutical residue that contains 28.82wt% Na has been selected as the sample. Molten salt oxidation experiments have been conducted in a lab-scale molten salt reactor using a ternary salt $(Li,Na,K)_2CO_3$. The experimental parameters investigated here are the temperature of molten salt and the excess air factor. The concentrations of the CO, NO_x and SO_x in the off-gas are monitored on-line. Results show that the concentration of CO decreases with temperature increasing, especially at temperature higher than 600℃. The SO_x in the off-gas has been detected rarely, irrespective of the operating conditions. When the temperature is below 700℃, the concentrations of NO_x in the off-gas are under 200ppm, but as the temperature reached 700℃, due to the nitrite in salt bath begins to decompose, the concentration increases dramatically, suggests the operating temperature should below 700℃ in order to suppress the emission of NO_x. Compared to the temperature's role, the effect on the residue's oxidation of the excess air factor is relative small. In the drained salt no char has been found and the XRD analysis shows that the main content of the salt is still $(Li,Na,K)_2CO_3$. The results of our study show molten salt oxidation is a promising alternative technology for the disposal of high salt content pharmaceutical residues from the chemical synthesis pharmaceutical industry, and it may be also suitable for other high salt content residues from the fine chemical industry, however, more research is needed to verify this possibility.

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1. Introduction

China has one of the largest pharmaceutical industries in the world which yields thousands of tons of pharmaceutical drugs that bring many benefits to human society every year [1] .An unintended consequence is that the pharmaceutical industry also produces much more wastes: waste water, waste gases and waste solids. Unlike the waste water and waste gases have designated places to go, and often can be managed well, the situation is less certain for the waste solids, especially in the chemical synthetic pharmaceutical industry[2].

An important proportion of the waste solids is pharmaceutical residues generated by chemical synthetic pharmaceutical industry. Owing to the residue of the active pharmaceutical ingredients (APIs) in the residues, as well as many of the raw materials used in the pharmaceutical production are harmful both to human beings and environment, these pharmaceutical residues are hazardous wastes and listed as HW02 in the national hazardous waste list. As hazardous wastes, the residues from the chemical synthetic pharmaceutical industry are detrimental to the environment and public health, if inadequately managed. To make situation worse is the huge quantities of these residues. In 2013, the chemical pharmaceutical industry yields 2.71 million ton of active pharmaceutical ingredients, according to the first national pollution census of industry pollution emission coefficient, 0.126-0.454 ton of hazardous residues is produced when a ton of drugs is yielded, which means the production of the hazardous residues is between 341 to 1,230 thousand ton in 2013. What's more, for the residues come from the chemical synthetic pharmaceutical industry, due to the widely use of alkali salts in middle process during the production of drugs, the residues often contain high content of alkali salts.

The customary treatment means of pharmaceutical residues are landfill and incineration [2]. But after the residues are considered as hazardous wastes, the residues should be treated properly before being filled in the landfills. And as the landfills are becoming fulfilled and places suitable for new landfills are becoming less. And the leachates contain the active pharmaceutical ingredients (APIs), the antibiotics and the metabolites of the pharmaceutical drugs from the landfills also pollute the underground water near the landfills [3]. The disadvantages of landfill disposal limit the use of landfill when treating the residues. Incineration is an effective thermal treatment that has many advantages, such as high reduction of mass and volume of the waste, the organic constituents can be completely oxidized under high temperatures, the pathogens and toxins in the wastes can be destroyed efficiently, the heat value of the waste can be recover. However, like every coin have two sides, incineration also has some disadvantages: the generation of hazardous fly ashes that are rich in heavy metals, the acid gases like SO_x, NO_x, and HCl in the off-gas, other toxic substances (especially PCDD/Fs) are produced, too [4]. These hazardous products and toxins have negative effects on the spread use of incineration. And perhaps the most serious drawback an incinerator faces when treating a high salt content pharmaceutical residue is the furnace-slagging problem as the residue contains high content of alkali salts which have low melting points.

As the residues are produced more and more as a result of the high development of the chemical synthetic pharmaceutical industry in China, it is imperative to develop an alternative treatment that can disposal the residues economically and environmental-friendly.

Molten salt oxidation (short as MSO) is a thermal, flameless process which has the inherent capability of destroying organic constituents in wastes efficiently, and retaining the inorganic constituents in the salt bath in the meantime[5-7]. During a molten salt oxidation process, the wastes are introduced into a molten salt bath together with oxidant air. And the flameless oxidation reaction occurs beneath the melt surface, the carbon and hydrogen are eventually oxidized to CO_2 and steam. The heteroatoms, including sulfur, nitrogen and halogens are converted into acid gases, like SO_x, NO_x and HX (X refers to halogens), which are scrubbed and absorbed efficiently by the alkali melt salt, if the contact time between the acid gases and carbonate salts is enough. The inorganic constituents such as salt and metal oxides are retained in the salt bath. The off-gas leaves the reactor contains fine entrained salt particles needs to be filtered before being discharged to the off-gas treatment equipment[5, 6]. MSO has been tested for the disposal of PCB-contaminated waste oils and solvents, chlorinated solvents, explosives and propellants, ion-exchange resins, PBDEs, plastics, chemical warfare agent sarin and so on, and very high destructive efficiencies have been reported [5, 6, 8-16].When compared to incineration, MSO has several advantages:

- 1). The operating temperature is hundreds of degrees lower than that of incineration, when using a ternary salt eutectic (33.3wt%Li_2CO_3: 33.4wt%Na_2CO_3: 33.3wt%K_2CO_3), the reaction temperature can be as low