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Toxic Leaching of Heavy Metals in Copper Catalyst Residue

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The authors compared identification standard for hazardous wastes-extraction procedure toxicity of China and Japan and toxicity characteristic leaching procedure of United States to evaluate which is better to identify toxicity characteristic of typical copper catalyst of China. They also studied leaching characteristic of metals in copper catalyst under different pH values. The results showed that pH was a major controlling factor in metal leachability. The metals exhibited a marked increase in leachability at low, while relatively low leachability of these metals were observed at neutral conditions.

Key Words: Copper catalyst, Heavy metal, Leaching characteristic identification.

INTRODUCTION

Copper catalyst is one of the optimal catalysts for methanol synthesis[1,2]. However, as this catalyst has properties of poor thermotolerance, sensitive to sulfur, easy shattered into powder, easy to absorb moisture and easy to be poisoned, its general life cycle scope is only half a year to one year. Sometimes it has to be scrapped for even merely months. When a methanol plant with an annual output of 50,000 tons has emissions of 120 tons spent catalyst annually, the current production capacity of domestic is about 2 million tons with an annual discharge of about 4,000 to 5,000 tons spent catalyst and emissions are still increasing year by year. The disposal of improperly, dead catalyst will bring in great bad effect. Harmful substance dissolving out from heavy metal, after which is leached by rain water and organic acid, will infiltrate to the surrounding soil, surface water and groundwater systems, posing a serious pollution on the local environment and residents' water. But whether the solid waste having potential hazard characteristics or not is determined by means of toxic leaching[3,4]. Up to now, there are many test methods to estimate hazardous wastes-extraction procedure toxicity, but different methods may draw significantly different conclusions[5,6]. Moreover, there are rarely researches on toxic leaching of heavy metals in copper catalyst residue domestic and oversea[7]. Therefore, our group did experiments on toxic leaching of copper catalyst residue with leaching procedure of China, United States and Japan to identify toxicity characteristic, in order to provide scientific basis for environmental impact assessment and pollution control of the methanol production of copper catalyst residue.

EXPERIMENTAL

Inductively coupled plasma atomic emission spectrometry (ICP, OPTIMA2100DV, PE Company, USA), water bath oscillator (Shanghai Yuejin Medical Apparatus Factory), Electronic balance (Electronic Instrument Co. Ltd. of Shanghai Jingtian), vacuum pump with recycled water (Zhengzhou Branch Trade and Industry Co. Ltd.), hydrogen nitrate (AR); ethylic acid (AR); sodium hydroxide (AR); deionized water.

Waste copper catalyst for methanol synthesis was taken from a certain nitrogen fertilizer factory in Henan Kaifeng. It was dark grey particle, random sampling and uniform mixing. After dried and smashed into pieces, it was ball-milled and sieved by 100 holes sieve. Then the particles were divided into a number of parts by quartering with every part of 10 g, as the material of residue metal components analysis and oscillation extraction test.

Leaching procedure: Toxic leaching methods used in this paper included horizontal oscillation, which was employed as solid waste-extraction toxicity in China and toxicity characteristic leaching procedure (TCLP) adopted in the United States and landfill method in Japan. Metal content in leaching solution of copper catalyst residue was determined by ICP. The results of the three leaching procedures of toxicity characteristic were presented in Table-1.

TABLE-1
COMPARISON OF THREE LEACHING PROCEDURES OF TOXICITY CHARACTERISTIC

Country	Liquid/Solid (L Kg^{-1})	Leaching solvent	Leaching method	Leaching time/h	Filter medium
China	10	Deionized water GB/T 6682, second level, pH 5.5-6.5	Horizontal and/or rotary oscillation	8	0.45 µm millipore filter/medium-speed quantitative filter paper
USA	20	pH = 2.88 ± 0.05, adjusted by ethylic acid and deionized water	Rotary oscillation	18	0.45 µm millipore filter
Japan	10	pH = 5.8-6.3, Adjusted by hydrogen nitrate and deionized water	Horizontal oscillation	6	1 µm glass fibre paper

The deionized water was used as leaching agent to leach toxicity of solid waste in China. However, this leaching method had neither illustrated the actual scene of disposal, nor combining with disposal manner of waste, so now it was only adopted as the standard approach of hazardous waste leaching toxic identification, mainly for index of inorganic pollutant. Similar to leaching method in China, Japan employed neutral or soft acid deionized water, which had no buffering capacity as leaching agent as well, while ethylic acid buffer solution with strong acidity was chosen as leaching agent in the USA.

ICP running parameter: Radio frequency power 1.3 kw, sample size 1.50 mL min^{-1}, plasma gas flow 1.5 L min^{-1}, auxiliary gas 0.2 L min^{-1}, gas flow of atomizer 0.80 L min^{-1}, reading delay 60 s.

Experiment on effect of pH on leaching toxicity in heavy metals: Leaching agent included deionized water system of different pH prepared by 1 mol min^{-1} nitric acid and sodium hydroxide and buffer system of diverse pH confected by glacial acetic acid and sodium hydroxide. As for common industrial solid wastes, buffer system was compound by 5.7mL glacial acetic acid, 500 mL distilled water and 64.3 mL sodium hydroxide (1 mol min^{-1}), then diluting to 1 L with ultimate pH of 4.93 ± 0.05. After that, weigh some prepared solid waste and add water into polyethylene plastic bottle. Put the mixture on oscillator with oscillating frequency of min^{-1} and amplitude of 40 mm. After oscillated for 6-18 h, the mixture had to be stirring for 16 h. Then filtrate was filtered out by vacuum pump, passing through 0.45 µm and 1 µm respectively.

RESULTS AND DISCUSSION

Analysis of major physicochemical index: Analysis indicated that CuO, ZnO and Al_2O_3 were main components of copper catalyst waste residue. The CuO and ZnO were the active component and Al_2O_3 was auxiliaries with graphite as carrier. In addition, there was a handful of metallic oxide, such as Fe_2O_3, *etc.* (Table-2).

Results of leaching toxicity in three different leaching methods: Three leaching methods to leach toxicity in solid waste of China, Japan and the USA were all adopted to identify toxicity characteristic of copper catalyst and the results were shown in Table-3.

TABLE-2
COMPOSITION OF COPPER CATALYST

Component	CuO	ZnO	Al_2O_3	Fe_2O_3	Graphite and other undissolved substance
Mass fraction (%)	42.5	36.7	6.2	0.2	14.4

TABLE-3
RESULTS OF TOXICITY CHARACTERISTIC LEACHING PROCEDURE OF COPPER CATALYST

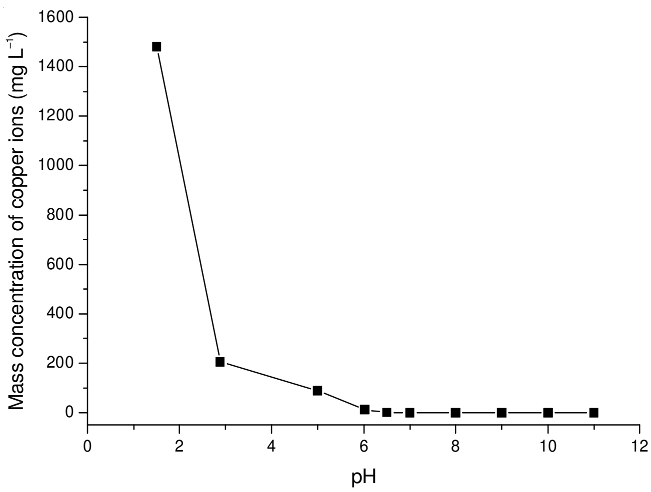
Items		Horizontal oscillation of China		TCLP of the USA	Toxic leaching test of Japan
		Measured value	Upper limit	Measured value	Measured value
pH		6.50		2.88	6.02
Heavy metal	Cu	1.795	100	204.58	9.48
	Zn	14.21	100	2033.44	59.45
	Al	62.59	-	-	-

Note: There were 46 leaching toxicity substances in the directory of national hazardous wastes, not including Al

Table-3 summarizes that the Cu and Zn in copper catalyst waste residue was not overproof if leaching procedure of China and Japan was applied, but if TCLP of the USA was adopted, Cu and Zn obviously exceeded standard, pertaining to hazardous wastes. Reasons for why leaching concentration of TCLP higher than that of other methods were that ethylic acid had buffer action on basicity as well as acetate ions had complexing capacity to metal[5]. Results of other two leaching methods drew near with a little difference, which attributed to different oscillation time and resting time.

Effect of pH on toxic leaching in heavy metal: pH was recognized as the foremost influencing factor for metal leaching. Experiment was carried in deionized water of diverse pH compounded by hydrogen nitrate and sodium hydroxide respectively to investigate effect of pH on toxic leaching of heavy metals in copper catalyst residue (Fig. 1).

Fig. 1 shows that the mass concentration of Cu and Zn was higher when pH was small and when pH was 8-9, mass concentration was lower. As pH rose to above 10, there was no Cu detected while concentration of Zn increased instead.



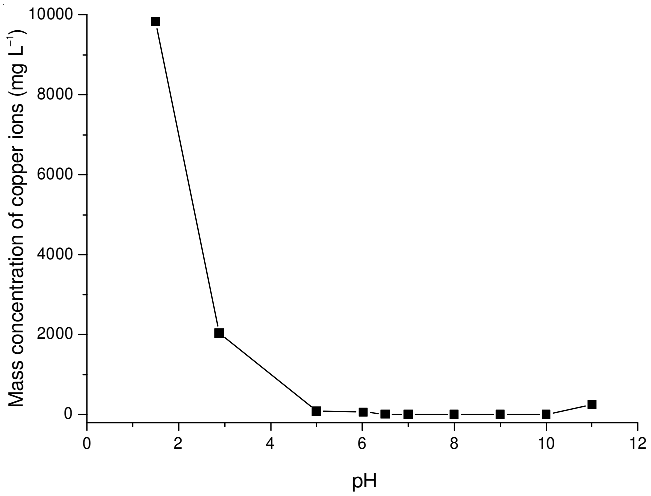


Fig. 1. Metals leaching mass concentration of copper catalyst as a function of pH of deion water solution

Tendency of metal leaching in solid waste depended on the formation rate of metal to soluble oxide, in accordance with the solubility rate of metal in solution[8]. As it was known that Zn could generate soluble hydroxy-metal compounds under alkaline condition, concentration of Zn rose again when pH was high.

Conclusion

According to identification standard for hazardous wastes-extraction procedure toxicity of China and Japan, Cu and Zn in copper catalyst waste residue had not exceeded standard, not belonging to hazardous wastes, while if in accordance with TCLP of the USA, conclusion was exactly right contrary. Then copper was recorded in National Solid Waste List as HW22, using threshold in TCLP for reference, which could protect our ecological environment better. HW22 should also contain copper catalyst in nitrogenous fertilizer industry.

pH was the main controlling factors of leaching toxicity in heavy metals. When pH was low, mass concentration of Cu and Zn was higher, while pH was about 8-9, mass concentration was lower. That's to say, metals exhibited a marked increase in leachability at low, while relatively low leachability of these metals were observed at neutral conditions, but increasing leachability again at high pH.

In the process of toxic leaching in copper catalyst residue, mass concentration of heavy metal leaching had significant change as pH of leaching agent altered slightly when deionized water was prepared by inorganic acid-base, which declared that inorganic leaching system had poor buffering capacity, not suitable for wide range of pH.

REFERENCES

1. L. Wang, *J. Chem. Fertilizer Design*, **3**, 18 (2007) (in Chinese).
2. G.B. Li and M.P. Yang, *J. Environ. Protect. Chem. Ind.*, **23**, 103 (2003). (in chinese)
3. V. Karius and K. Hamer, *J. Sci. Total Environ.*, **278**, 73 (2001),
4. F. Liu, Q. Wang and Q.F. Huang, *J. Res. Environ. Sci.*, **21**, 9 (2008).
5. T. Townsend, J.Y. Chul and T. Tolaymat, Leaching Tests for Evaluating Risk in Solidwaste Management Decision Making, Florida: Florida Department of Environmental Protection, p. 29 (2003).
6. A.J. Yang, J. Li and Y.G. Wu, *Acta Scient. Circumstant.*, **28**, 2336 (2008).
7. L. Zhang, Y.R. Yang and P. Wu, *Anal. Chem. A,* **1**, 268 (2009).
8. H.A. Vander Sloot, A. van Zomeren, R.P.J.J. Rietra and R. Blijerveld, Integration of Lab Scale Testing and Pilot Scale Monitoring of a Stabilized Waste Landfill to Reach Sustainable Landfill Conditions, Eighth International Waste Management and Landfill Symposium, 1-5 October, Sardinia, Italy, pp. 255-264 (2001).