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Mercury speciation and mobility in mine wastes from mercury mines in China

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Abstract. Mine wastes calcines were formed through retorting of cinnabar ores at high temperature, which are considered as significant sources of mercury (Hg) contamination to the local environment. To better understand the role of mine waste in Hg geochemical cycle in Hg mining areas, Hg speciation and mobility were evaluated in mine waste calcines and waste rocks from 9 Hg mines in China. The total mercury (THg) concentrations in the mine wastes ranged from 0.369 to 2620 mg·kg^{-1} and varied widely in different Hg mines. Cinnabar and Hg^0 are dominant forms in the mine wastes. The calcines had significant higher Hg^{2+} and Hg^0 concentrations than the waste rocks, which indicated the retorting process can produce large amounts of secondary by-product Hg compounds. The leaching experiment confirmed mine wastes were important Hg pollution sources to local aquatic system. The mine wastes are also significant Hg sources to the atmosphere.

Keywords: mercury; speciation; mobility; mine waste; calcines

Introduction

Mercury mines are considered as hot spots of Hg pollution. During the processing of Hg ores, secondary Hg phases form and accumulate in mine waste calcines, which are more soluble than cinnabar and can cause a greater extent of Hg contamination to the surrounding environment. Mine wastes are considered as significant sources of Hg contamination to the surrounding aquatic ecosystems. China is rich in Hg mineral resources and most Hg mines are distributed in southwestern China. Guizhou province is the most important Hg production center, with approximately 80000 tons of Hg reserves. The long history of mining activities have produced large amount of mine wastes in the Hg mining area, which have not been properly treated. This study was designed to: (1) evaluate Hg speciation in the mine waste from different Hg mines in China; and (2) simulate the mobilization of Hg by runoff under the environmental conditions.

Materials and Methods

A total of 9 Hg mines in China were selected in this study. Wanshan, Danzhai, Xiushan and Xunyang are ranked as super-large Hg mines. Wanshan is located in eastern Guizhou Province and is known as the "capital of Hg" because it was the largest Hg mine in China. Its total Hg production was estimated to be 30,000 tons from the 1950s to 2003. Xunyang Hg mine is located in southern Shaanxi province and is the only large scale Hg mine in operation in China. Three large (Tongren, Chatian and Xinhuang) and two medium (Sandu and Yulan) Hg mines were also selected in this study. A total of 132 mine waste samples were collected from these 9 Hg mines, which included 91 calcines and 41 waste rocks. The mine waste samples were determined for total mercury (THg), elemental Hg (Hg^0) and Hg^{2+} and for leaching experiment.

Results and Discussion

The THg concentrations in the mine waste samples from different Hg mines varied widely from 0.369 to 2620 mg·kg^{-1} (Fig. 1) and followed a log-normal distribution with a geo-mean of 18.8 mg·kg^{-1}. The geo-means of THg concentrations in the calcines and waste rocks were 18.2 and 20.1 mg·kg^{-1}, respectively, which were significantly higher than the baseline of 0.35 mg·kg^{-1} in rocks reported in Wanshan area. The waste rocks had significant higher THg concentrations than the calcines ($p<0.01$), which indicated probable existence of cinnabar in the waste

rocks.

The Hg^{2+} concentrations in the calcines and waste rocks varied from 0.002 to 3.81 mg·kg^{-1} (with a mean of 0.52 mg·kg^{-1}) and from 0.003 to 8.33 mg·kg^{-1} (with a mean of 0.65 mg·kg^{-1}), respectively. The calcines had significant higher percentages of Hg as Hg^{2+} (with a mean of 1.8%) than the waste rocks (with a mean of 0.4%). Three relative high values of Hg^{2+} ratio (6.88%, 9.30% and 10.6%) were all found in the calcines, which indicated the retorting process can produce large amounts of secondary by-product water soluble Hg compounds in the calcines. A significant correlation ($r=0.60$, $p<0.001$) was found between the Hg^{2+} and THg concentrations in the mine waste, which indicated the presence of significant ionic Hg^{2+} in the mine waste.

The Hg^0 concentrations in the calcines and waste rocks ranged from 0.22 to 79 mg·kg^{-1} and from 0.14 to 15 mg·kg^{-1}, respectively. The calcines had significant higher Hg^0 concentrations (with a mean of 16 mg·kg^{-1}) than the waste rocks (with a mean of 6.2 mg·kg^{-1}). During Hg ore retorting process, most Hg compounds are converted to Hg^0 at high temperatures. Some Hg^0 in the gas phase is re-adsorbed to matrix components when the material cooled down. A significant correlation ($r=0.43$, $p<0.05$) was found between Hg^0 and THg concentrations in the mine waste samples.

The percentages of Hg as Hg^{2+} and Hg^0 in the calcines were higher than those in the waste rocks (Fig. 2). The major form of Hg in the mine waste is cinnabar, which is very insoluble and much less volatile and leachable than other forms of Hg.

During leaching experiment, highly variable TSHg concentrations were found in the leachates. The mean of TS-Hg concentration in the leachates was 0.45 μg·L^{-1} with a range of 0.012-2.8 μg·L^{-1}. It only accounted small portion of THg in the mine waste (with a mean of 0.051% and a range of 0.0020-0.61%). There are no significant differences of TS-Hg concentration in the leachates from calcines and waste rock. A significant correlation ($r=0.72$, $p<0.001$) between leachate TSHg concentrations and THg concentrations in the corresponding mine waste leached was observed.

Conclusion

The THg, Hg^{2+} and Hg^0 concentrations in mine waste varied widely in different Hg mines. Cinnabar and Hg^0 are dominant forms in the mine waste. The calcines had significant higher Hg^{2+} and Hg^0 concentrations than the waste rock, which indicated Hg in the calcines is more active. High TSHg, Hg^{2+} and Hg^0 concentrations in the mine wastes indicated that mine wastes are significant Hg sources to the local aquatic system and the atmosphere. Remedial techniques are required to fix the Hg in the mine waste calcines and to reduce Hg release to the local environment

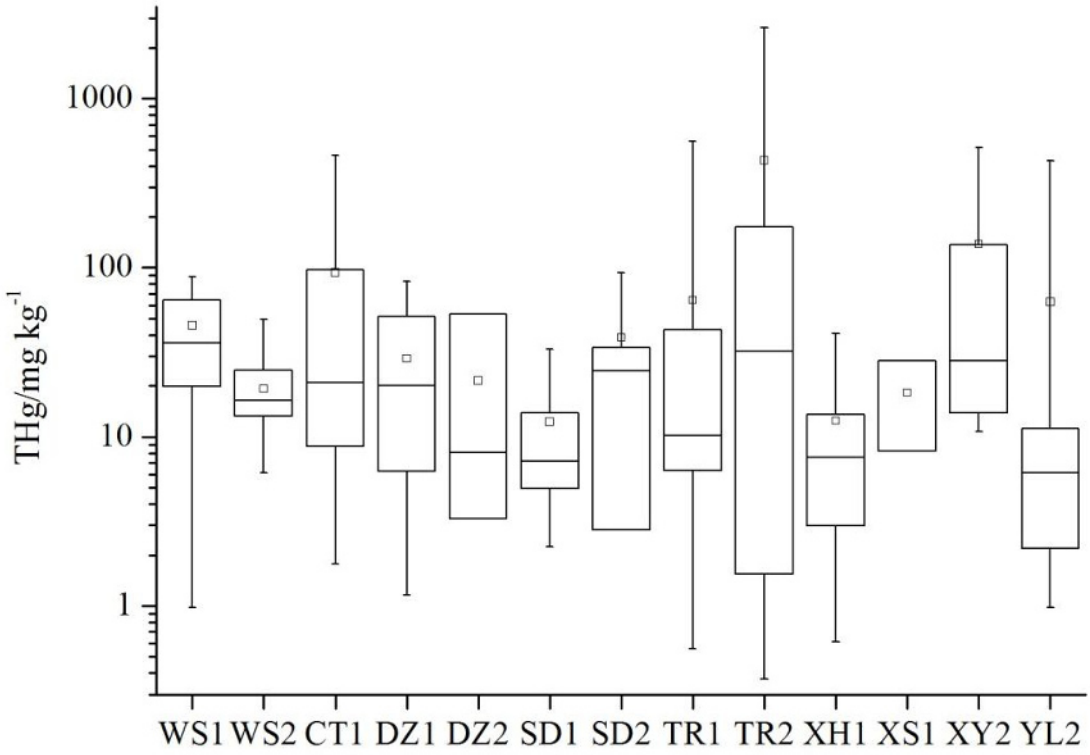

Fig.1 THg concentrations in the calcines and waste rocks from different Hg mines in China. 1, calicines; 2, waste rock; each box represents interquartile range (25th and 75th percentile), the band near the middle of the box is the 50th percentile (the median), and the whisker represents 5th and 95th percentile

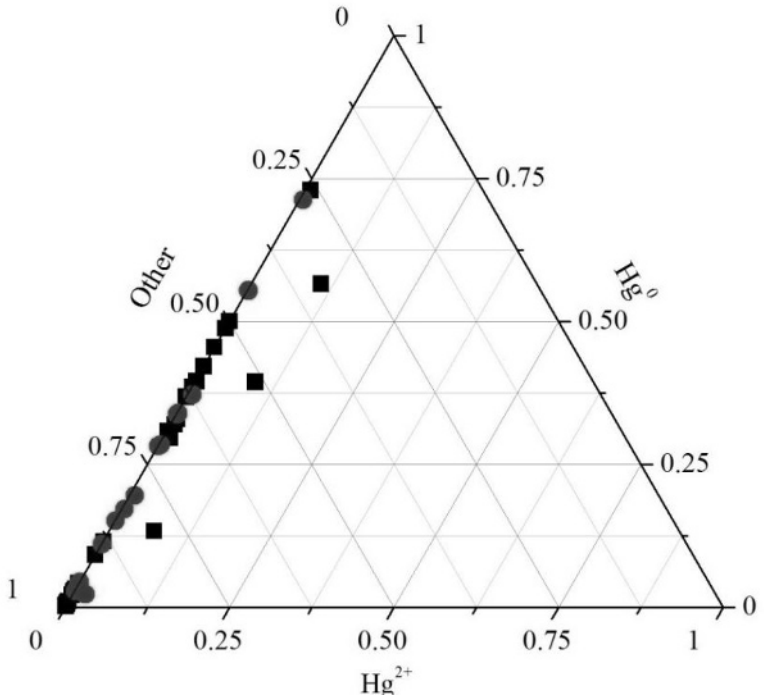

Fig.2 Triangle diagram showing Hg speciation distributions in mine wastes from Hg mines in China

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