

Mercury sulfide formation process under mechanochemical reaction using a planetary ball mill

The Minamata Convention on Mercury is a legally binding multilateral environmental agreement that was adopted by governments in 2013. When the Convention is enacted in the near future, Japan will prohibit the export of elemental mercury, except for mercury for essential use, following the lead of the EU and USA [1,2]. Once the export of elemental mercury is prohibited, approximately 70–80 tons of excess mercury, having no commodity value, will accumulate in Japan each year as hazardous waste [3]. It is thus important to prepare for the safe and long-term storage or permanent disposal of such mercury waste. Metal mercury is liquid at room temperature and has high volatility, allowing it to move easily in the environment. It is preferable that elemental mercury be recovered by a distillation method that converts it to mercury sulfide (HgS), which is the most stable chemical form of mercury, for long-term storage or permanent disposal. In this study, we used a planetary ball mill (Pulverisette-6; Fritsch Co., Ltd.) for the stabilization of metal mercury (99.5% purity; Wako Pure Chemical Industries, Ltd.) by mixing it with powdered sulfur (98% purity; Nacalai Tesque, Inc.) under a variety of conditions to gain a better understanding of the stabilization process. The planetary ball mill can produce high-energy conditions and enable samples to react within a short period of time by providing mill pot rotation and revolution movement simultaneously. We were able to observe the process of mercury sulfide formation within a reaction time of 5 to 90 min [4]. This process is shown in Fig. 1. From 5 to 15 min, the first

stage of the reaction, a silver-gray and labile material adhered to the periphery of the mill pot bottom. This material was sufficiently soft to be scraped away with a medicine spoon, and was similar to a dental amalgam. It appears that physical contact between metal mercury and sulfur powder is facilitated, and they then form a solid solution (hereinafter called an intermediate). During the second stage, after 15 min, this labile material gradually hardened and became pulverized by the balls, which resulted in the production of cinnabar ($\alpha\text{-HgS}$) and metacinnabar powder ($\beta\text{-HgS}$). This process was completed at 50°C after 90 min. Oji *et al.* developed a high-shear blending technique for converting elemental mercury into mercury sulfide. Cinnabar is formed when the temperature of the inner vessel is over 270°C [5]; however, cinnabar could be formed at a lower temperature in our method. This suggests that the mechanochemical effect influences the formation of mercury sulfide, which enables the sulfurization of metal mercury without the use of a heating process.

In order to determine the chemical form of the products, we measured the Hg L_{III} -edge XANES spectra at beamline BL01B1. The change in the pattern with the reaction time from 5 to 90 min can be easily seen in the differential XANES spectra shown in Fig. 2(a). The differential XANES spectra of metal mercury, metacinnabar, and cinnabar as standard substances are shown for comparison. At the first stage of the reaction, between 5 and 15 min, during the intermediate remained, the differential XANES spectra were very similar to that of metal mercury. Second, an inflection point appeared at photon energy of around 12,300 eV and the pattern became similar to that of metacinnabar after a reaction time of 20 min when all of the intermediate had been pulverized to powder. Third, another peak appeared at 12,288 eV after 30 min, and the spectrum gradually became that of cinnabar. We conducted pattern fitting of these spectra using the spectra for two standard materials, metacinnabar and cinnabar, to quantitatively determine their ratio. The results are shown in Fig. 2(b). The fitting value after reaction times of 5 to 15 min is not shown because the R value was too large and the spectrum could not be fitted. It appears that the spectrum of the intermediate cannot be represented by a linear combination of those for standard materials. After 20 min, the proportion of cinnabar increased with the reaction time and reached approximately 80 mol% at 90 min. This indicates a continuous change from metacinnabar to cinnabar.

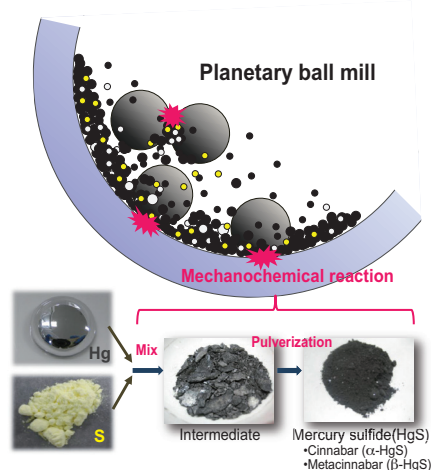


Fig. 1. Stabilization process by which elemental mercury and powder sulfur are converted to mercury sulfide by a planetary ball mill.

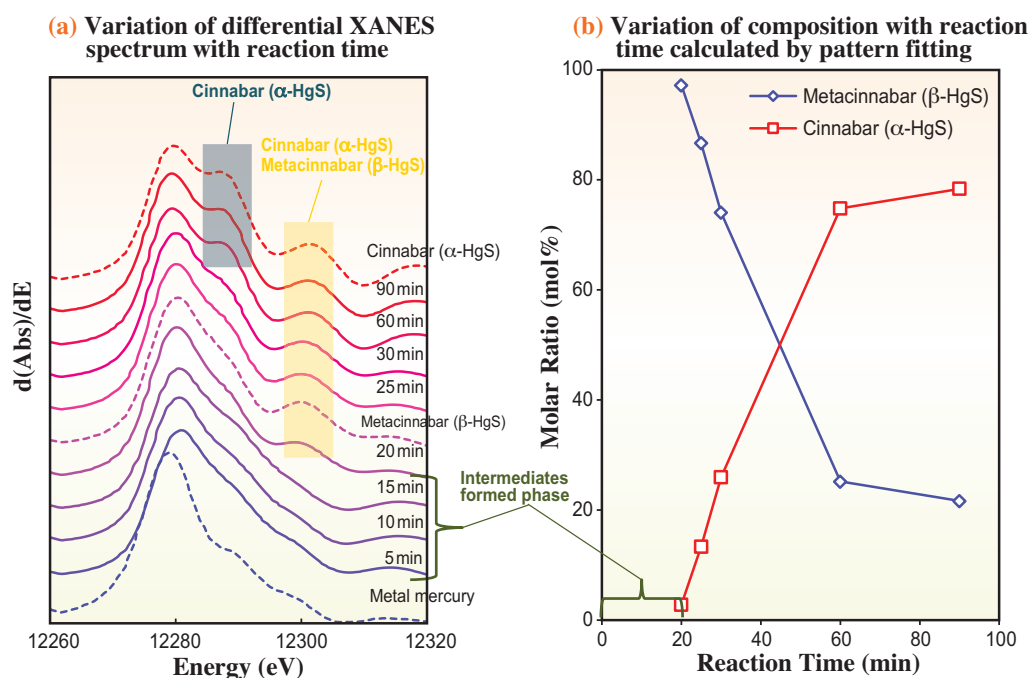


Fig. 2. Variation of (a) differential Hg L_{III} -edge XANES spectrum and (b) composition, calculated by pattern fitting, of metacinnabar (β -HgS) and cinnabar (α -HgS) measured at BL01B1.

We measured the mercury leaching concentration by the Japanese leaching test (JLT-46) at each reaction time to evaluate the stability of the products. The results are shown in Fig. 3. The total mercury leaching concentration is regulated in Japan to be below 0.5 $\mu\text{g/L}$. The intermediate has a high mercury leaching concentration between reaction time of 5 and 15 min, indicating the incomplete formation of mercury sulfide. The mercury leaching concentration decreases rapidly from 15 to 20 min with the complete formation of metacinnabar. After that, it gradually decreases with the transformation from metacinnabar to cinnabar. The environmental criterion is satisfied after 30 min.

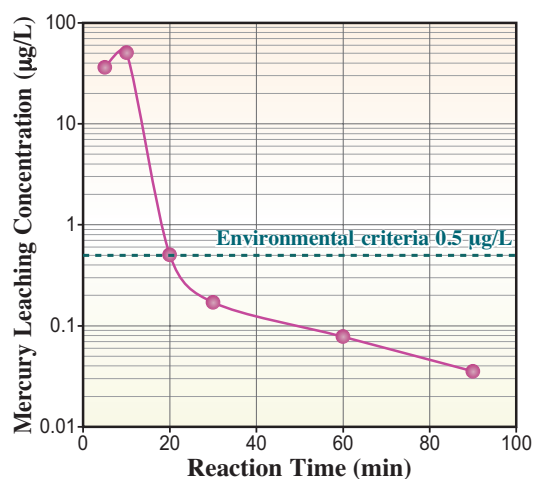


Fig. 3. Variation in mercury leaching concentration of products with reaction time obtained by Japanese leaching test (JLT-46).

In conclusion, we succeeded in mercury stabilization that satisfied the environmental criterion for the mercury leaching concentration without heating using a planetary ball mill. In this process, labile intermediate mercury sulfide was observed in the early stages of milling, and then the intermediate was pulverized into stable metacinnabar. After that, the crystal structure gradually changed from metacinnabar to cinnabar.

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