



Mercury distribution characteristics in primary manganese smelting plants



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ABSTRACT

The mercury (Hg) distribution characteristics were investigated in three primary manganese smelting plants in Korea for the assessment of anthropogenic Hg released. Input and output materials were sampled from each process, and Hg concentrations in the samples were analyzed. Among the input materials, the most mercury was found in the manganese ore (83.1–99.7%) and mercury was mainly released through fly ash or off gas, depending on the condition of off gas cleaning system. As off gas temperature decreases, proportion and concentration of emitted gaseous elemental mercury (Hg⁰) in off gas decreases. Based on mass balance study from these three plants and national manganese production data, the total amount of mercury released from those Korean plants was estimated to 644 kg/yr. About half of it was emitted into the air while the rest was released to waste as fly ash. With the results of this investigation, national inventory for Hg emission and release could be updated for the response to Minamata Convention on Mercury.

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1. Introduction

Since the outbreak of Minamata disease in 1956, mercury (Hg) has been recognized as a significantly toxic substance, and its usage and production have been carefully managed. However, Hg is used in various industries worldwide, intentionally or unintentionally. From those various industries, matrixes that contain or contaminated by Hg are emitted into the air, soil, water and waste. Hg emitted into the environment remains in the ecosystem and influences both human health and the overall environment. The European Community listed Hg, cadmium (Cd) and lead (Pb) as long-range trans-boundary air pollutants when it signed the Aarhus Heavy Metals Protocol in 1998 (United Nations, 1998). Also, following discussions of Hg and its compounds as global pollutants, the Governing Council of the United Nations Environment Programme (UNEP) undertook a global assessment of Hg (UNEP, 2002, 2008). After that assessment, Hg was deemed an internationally

controlled substance, and in 2013, the Minamata Convention on Hg was signed. Annex D of that convention categorized the major emission sources of Hg and its compounds as coal-fired power plants; coal-fired industrial boilers; smelting and roasting processes used in the production of non-ferrous metals such as lead (Pb), zinc (Zn), copper (Cu) and industrial gold (Ag); waste incineration facilities; and cement clinker production facilities (UNEP, 2013). The UNEP determined those major emission sources using its estimations of global anthropogenic Hg emissions into the air for 2008–2010. According to the result of 2010, artisanal and small-scale gold mining, coal-fired power plants, primary production of non-ferrous metals (Al, Cu, Pb, Zn) and cement production accounted for 37.1%, 16.1%, 9.9% and 8.8%, respectively of total Hg emissions of the world (AMAP and UNEP, 2013). The management of Hg in such plants has focused on preventing emissions into the atmosphere. If the off gas released from an industrial process contains Hg or its compounds that indicates a raw material or additive used in the process must contain Hg, which means that the wastewater or solid waste from that process might also contain Hg or its compounds, thereby creating another route for environmental emission. Hg and Hg compounds are emitted into atmosphere from anthropogenic sources and Hg is deposited to aquatic

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and soil ecosystem (Ahn et al., 2011; Driscoll et al., 2007). It is volatilized and has adverse effect on environment and ecosystem (During et al., 2009; Rinklebe et al., 2009, 2010). Therefore, it is important to understand and control behavior of Hg from anthropogenic sources. Off gas containing Hg or its compounds is controlled by air pollution control devices (APCD), which themselves generate wastewater or solid waste containing Hg or its compounds (Stergaršek et al., 2008). Convention also deals with Hg and its compounds released to land and water and waste. Convention classifies Hg wastes into three categories: wastes consisting of Hg or Hg compounds, wastes containing Hg or Hg compounds and wastes contaminated with Hg or Hg compounds (UNEP, 2013; UNEP and ISWA, 2016). Wastes consisting of Hg or Hg compounds mean mainly released elemental Hg and Hg compounds, with these Hg recovered from wastes containing and contaminated with Hg or Hg compounds. Wastes containing Hg or Hg compounds include discarded Hg-added products (e.g. lamps, batteries, switches, thermometers, etc.). And wastes contaminated with Hg or Hg compounds are residues industrial, mining and waste treatment processes such as sludge, fly ash, slag, etc. Appropriate treatment means have been emphasized according to characteristics of Hg wastes. The distribution of Hg and its compounds in each process of a plant can be investigated by considering the total amount of Hg used and emitted. Measuring the amount of Hg in each input and output material can indicate the main input and release pathways of Hg. In this study, the distribution of Hg was investigated in primary manganese (Mn) smelting plants in Korea. Manganese smelting plants in Korea are classed into the alloy industry and usually produce ferroalloy. The primary smelting plants in Korea use raw ore to produce non-ferrous metals (such as Cu, Pb and Zn) or alloyed metals (such as Fe-Mn, Si-Mn and Fe-Ni). The anthropogenic Hg emitted from the primary smelting plants for Cu, Pb and Zn was assessed previously, and the results were published in a UNEP report (AMAP and UNEP, 2013). The environmental impact of the alloy metal industry is relatively low compared with that of the non-ferrous metal industry. However, plants that produce Fe-Mn and Si-Mn have been reported to have high Hg content in the manganese ore and thus release high levels of Hg, especially plants that produce Si-Mn (European Commission, 2001). Other than these, there were few studies reported regarding mercury release from manganese smelting plants. Therefore, to assess the anthropogenic Hg mass balance in manganese smelting plants, the Hg distribution characteristics was investigated in three primary manganese smelting plants in Korea. To assess the anthropogenic Hg released from a manganese smelting plant, Hg distribution in each input material (manganese ore, supplementary material, reductant and reused by-product of the smelting process) and output material (products, waste slag, fly ash and off gas) were investigated. The national emission and release amount of Hg and the contribution of Hg emitted from manganese smelting plants in Korea, which were estimated in this study. Regarding Hg emission in off gas, the speciation of Hg is important to understand the behavior of Hg such as removal and transformation from one to another species, between elemental Hg, oxidized Hg, and particulate bound Hg. Therefore the speciation measurements were conducted for off gas in this study. These data would provide the implication how APCD type and operating conditions affect to removal efficiencies of Hg as studied by other researchers (Lei et al., 2007; Shah et al., 2008; Wang et al., 2009).

2. Materials and methods

2.1. Plants tested

The three primary manganese smelting plants use manganese

ore containing 30–40% manganese as raw feed material, along with silicon as a supplementary material, coke as a reductant and slag as reused by-product. The main reactors used to produce Fe-Mn or Si-Mn were electric furnaces and the main APCD was a bag filter. Plant A produced Fe-Mn and Si-Mn about 290,091 and 98,925 ton/yr, respectively. Plant B produced Si-Mn about 71,955 ton/yr, and Plant C produced Si-Mn about 77,000 ton/yr. The manganese content in Fe-Mn and Si-Mn are 75–85% and 50–70%, respectively. Temperature of electric furnace was in the range of 1300–1400 °C. The plants emitted the waste slag from the furnace, the fly ash from the bag filter and the off gas from the stack to the environment. There is no lime injection to remove acid gases at bag filter. Fig. 1 shows the main process and the input and output materials from Plants A, B and C. The off gas temperature in stacks in Plant A, B and C were 120 °C, 76 °C and 180 °C, respectively.

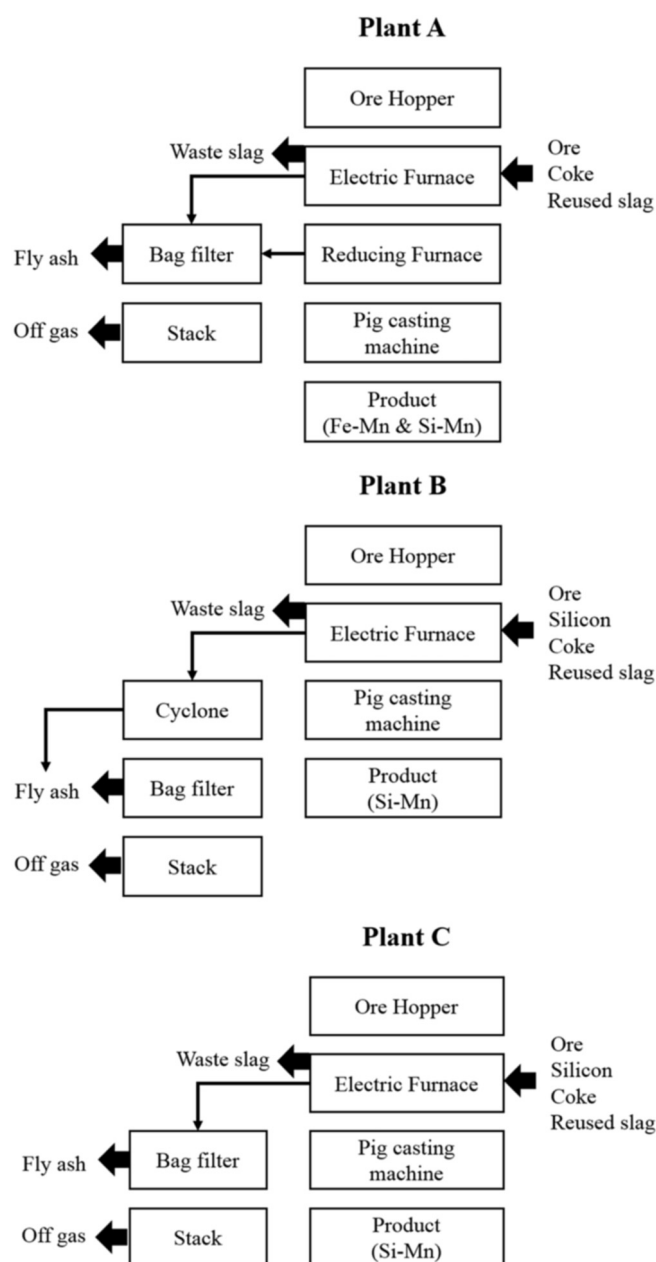


Fig. 1. Processes and input-output materials at plants A, B, and C.

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