

Speciation of Mercury Contaminant in Public Gold Mine Tailing and its Stabilization Using Sulfur and Sulfide

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ABSTRACT

The mercury-containing tailing waste from public gold mines in Indonesia is generally deposited on soil without treatment. This research aimed at determining the amount and composition of mercury species in the tailing, and testing the effect of sulfur and sulfide on mercury stabilization. Samples were collected from a tailing pile at different depths in a public gold mine in Kulon Progo, Indonesia. The samples were characterized according to the mercury concentrations and Toxicity Characteristic Leaching Procedure (TCLP) test. Mercury speciation was carried out using nitrogen gas flow into tailing samples, which were placed in three test tubes. The released mercuric species was entrapped in KCl and KMnO₄ solutions. The mercury stabilization was carried out using sulfur and sodium sulfide. TCLP test was performed to the stabilization products. The mercury concentrations were measured using a mercury analyzer. The results showed that the mercury in the tailings were dominated by elemental Hg⁰, the concentrations of which in the tailing piles of 30, 60, and 90 cm depths were 74.7%, 71.6%, and 76.5% respectively. Those of ionic Hg²⁺ form were 25.3%, 28.4%, and 23.5%, respectively. Additions of sulfur powder and sodium sulfide solution produced stable black-colored mercury sulfide. When compared to sulfide, sulfur was more recommended for stabilizing mercury in the tailing waste.

Keywords: mercury; gold mine, speciation, sulfide, sulfur, tailing

INTRODUCTION

Public gold mining activities in Indonesia have been practiced using the amalgamation process, where mercury is used for separating the precious metal from other minerals (Ilyas et al., 2014). The tailing waste generated from the amalgamation process allows mercury to spread around the mining area and can cause an environmental hazard (Herman, 2006). Mercury, which is in liquid form at ambient temperature, has a low vapor pressure but high toxicity. It is generally less toxic and soluble in the elemental form than in several inorganic and organic compounds (Lopez et al., 2008).

A public gold mining area in Kulon Progo, Indonesia, has been operated for decades. The untreated tailing waste is directly discharged at several collection ponds around the mine site (Pamayo

and Trihadiningrum, 2015, Rachman et al., 2017, Rachman et al., 2018). Kalimantan (2016) reported that the mercury concentration in soil around the mining site was 164–384 mg/kg. According to Government Regulation No. 101/2014 concerning Hazardous Waste Management, when mercury concentration in soil or waste is higher than 300 mg/kg and the results of Toxicity Characteristic Leaching Procedure (TCLP) test are higher than 0.3 mg/L, the material is considered as toxic of acute level (or category 1). A material is classified as toxic with chronic level (or category 2), if the mercury concentration is lesser than 300 mg/kg but higher than 75 mg/kg, and TCLP test result of less than 0.3 mg/L but higher than 0.05 mg/L.

Stabilization/solidification (S/S) method has been commonly used for treating hazardous and toxic waste. This method is very useful for

treating the heavy metals in mud and inorganic waste (Chang et al., 1993). However, there is a problem which relates to the cement-based treatment of the mercury-contaminated waste. It is believed that elemental mercury has a strong potential to evaporate from cemented solid mud (Hamilton and Bowers, 1997). This problem is due to the fact that elemental mercury can be easily volatilized at room temperature (López et al., 2008).

Therefore, an effective process is needed to stabilize the mercury element into stable compounds by using additives with affordable cost and/or that can be operated economically on both small and large scales. Sulfur and sulfide are examples of the additives which can be used for this purpose. Mercury sulfide (HgS) is the most stable chemical form among the various mercury compounds (López et al., 2010). It is the preferred chemical compound in long-term storage due to its low leaching properties and its lower vapor pressure than in the case of other compounds (López et al., 2008). The low leaching property is due to the very low mercury sulfide solubility (0.017 mg/L at 18 °C). It was reported that mercury sulfide did not emit mercury vapor (Hamilton and Bowers, 1997).

Mercury has three stable oxidation states, namely Hg^0 , Hg^{1+} , and Hg^{2+} (Richard, 2016). The ionic species Hg^{1+} and Hg^{2+} forms are obviously more soluble than the elemental Hg^0 form (Biester et al., 2002). Therefore, it is necessary to investigate the mercury forms before performing any treatment. Determination of Hg^0 or $\text{Hg}^{1+}/\text{Hg}^{2+}$ forms can be completed by a speciation process. Mercury stabilization can be performed by the amendment of sulfide compounds into the waste. Sulfur powder can also be used for stabilization because it can react with the mercury element to form mercuric sulfide (Blanchard, 1936).

A study on the stabilization of mercury-containing wastes was conducted by Piao and Bishop (2006) by using sulfide in various pH and sulfide/mercury molar ratios. These researchers found that most effective mercury stabilization occurred at pH 6 with sulfide/mercury molar ratio of 1, in which the waste stabilization efficiency reached 98%. This study aimed at determining the elemental and ionic compositions of the mercury waste from a public gold mine tailing in Kulon Progo, Indonesia, and determining the efficiency of the mercury waste stabilization using sulfur and sulfide amendment.

MATERIALS AND METHODS

Preparation and Characterization of Mercury Waste Samples

The tailing samples were collected from a tailing pile at 30, 60, and 90 cm depths in a public gold mine site in Kokap District, Kulon Progo, Indonesia. The tailing samples were tested for mercury concentrations and Toxicity Characteristics Leaching Procedure (TCLP) test. The TCLP test was conducted according to US EPA (1992) method. The mercury concentrations were measured using Lab Analyzer 254 Mercury Instrument Type VM-3000 Mercury Vapor Monitor, Serial number 0408/609.

Mercury Speciation

Mercury speciation in the tailing was conducted with chemical method using the equipment comprising 3 glass tubes of 70 mL (Richard, 2016). The glass tubes were connected to a nitrogen gas tank (Figure 1). Tubes 1, 2, and 3 contained ± 1 g of tailing, 25 mL KCl solution of 10 mmol/L, and 25 mL KMnO_4 of 5%, respectively. The KMnO_4 solution was centrifuged for 16 minutes at 1000 rpm before used. The nitrogen gas was applied at 100 mL/min for 20 minutes at room temperature. The mercury speciation process was performed in duplicates. After speciation, the mercury concentrations in Tubes 1, 2, and 3 were measured using the mercury analyzer.

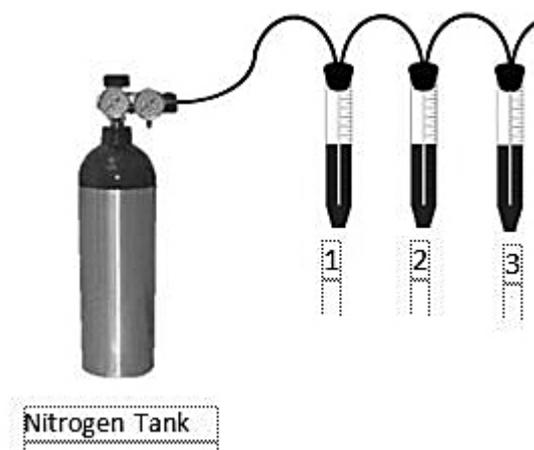


Figure 1. Apparatus for Mercury Speciation (Richard, 2016)

Mercury Stabilization with Sulfur and Sulfide

Sulfur addition. About 0.5 g sulfur powder was added into 50 g (dry weight) tailing in a test tube. The precipitation process was conducted at room temperature. The test tube was closed and shaken for 5 minutes. Upon accomplishment of the reaction, TCLP tests (USEPA, 1992) were performed to the samples in order to measure the leaching potential of the mercury sulfide precipitate.

Sulfide addition. Precipitation was done by adding 75 mL of 0.67% sodium sulfide (w/v) solution into 50 g (dry weight) tailing in a test tube at room temperature. The test tube was closed tightly and shaken thoroughly. The mixture was left for 1 day (Piao and Bishop, 2001). Upon the accomplishment of reactions, the TCLP tests were performed.



Figure 2. Tailing waste flows from the amalgam mixing drum near the sample collection point

RESULTS AND DISCUSSIONS

Mercury content in tailing

The mercury concentrations in the tailing pile samples varied from 277.47 to 352.32 mg/kg (Table 1). The T1 and T2 tailing samples were classified as toxic of acute level (category 1), whereas T3 sample was toxic of chronic level (category 2).

The mercury from the tailing pile has contaminated soil in the public gold mine area. Rachman et al. (2017) investigated that the mercury concentrations in 15 soil samples varied from 0.30 to 22.51 mg/kg, much higher than those of the control soil of 0.000 to 0.300 mg/kg. The mercury concentrations in soil exceed the quality standards for contaminated soils of 0.3 mg/kg, as regulated in the State. Figure 2 shows limited care of mercury containing tailing discharge from amalgam mixing drum. The tailing flowed to a collection pond, which is located near the mixing drum (Figure 3).

The principle of mercury speciation is separation of elemental Hg^0 from ionic Hg^{2+} by volatilization. A pressurized N_2 gas that was flown into



Figure 3. Tailing collection pond in Kokap District, Kulon Progo

the tailing-containing tube 1 would vaporize Hg^0 . The evaporated Hg^0 was trapped in the $KMnO_4$ solution in Tube 3 and oxidized to form Hg^{2+} . The ionic mercury from Tube 1 might be blown by nitrogen gas, and caught in the KCl solution in Tube 2, or remained in the sample. After the mercury speciation process, the mercury concentrations from the samples varied from 77.46 to 86.93 mg/kg at different depths. In Tube 2, the mercury concentrations ranged from 0.95 to 2.32 mg/kg, whereas, in Tube 3, the concentrations were 189.62–256.84 mg/kg (Table 2).

The mass balance in the mercury speciation process was calculated from the total of mercury concentrations in the tube 1 which contained tailing sample, tube 2 contained a KCl solution, and tube 3 contained the $KMnO_4$ solution. Tubes 1 and 2 contained Hg^{2+} . Tube 3 contained Hg^0 vapor, which was oxidized by $KMnO_4$ to form ionic Hg^{2+} . According to Richard et al. (2016), the mass

Table 1. Mercury Concentrations in Tailing Samples

Sample code	Depth (cm)	Mercury concentration (mg/kg)
T1	30	352.32
T2	60	277.47
T3	90	343.48

Table 2. Mercury Concentrations in Each Tube

Tailing depth (cm)	Mercury concentration (mg/kg) in		
	Tailing sample (Tube 1)	KCl solution (Tube 2)	KMnO ₄ solution (Tube 3)
30	86.93	2.32	256.84
60	77.46	1.31	189.62
90	79.70	0.95	253.00

balance of mercury speciation is shown in equation (1).

$$\text{Hg}_{\text{total}} = \text{Hg}^0 + \text{Hg}_{\text{inorganic}} \quad (1)$$

where: Hg_{tot} = total dissolved Hg,
 Hg_{inorg} = inorganic Hg^{2+} , and
 Hg^0 = total inorganic Hg.

According to Robles et al. (2014), the partial pressure of Hg^0 reached 1 Pa at 42°C and increases exponentially to boiling point ($T_b = 356.5^\circ\text{C}$). At 20°C the vapor pressure of Hg^0 is 0.18 Pa with the mercury concentration in mercury-saturated air is $7.64 \times 10^{-8} \text{ mol/L}$ or $15.3 \mu\text{g/m}^3$. According to Zhang et al. (2012), the reaction which occurred in mercury trapping in tube 3 is as follows:



The evaporated Hg^{2+} was assumed to be dominated by HgCl_2 . This is due to at 20°C HgCl_2 has a low vapor pressure of 0.01 Pa. Trapping of HgCl_2 in Tube 2 occurred by common-ion effect, which decreased the solubility of the compound. Mass balance calculation of mercury species in tailings A, B, and C resulted in some small amounts of mercury loss. These mercury losses, or unaccounted mercury, in tailings A, B, and C were 1.80%, 3.38%, and 2.95% respectively (Table 3).

The unaccounted Hg in this study was considered as Hg^0 , because of the high evaporation

possibility during the nitrogen gas application. The mercury forms in the tailing can be estimated based on the mass balance data (Table 4). The ionic form was the total mercury concentrations in Tubes 1 and 2, whereas that of the elemental form was the total mercury concentrations in Tube 3 and the unaccounted (Table 4). As shown in Table 4, the main species of mercury in the tailing pile in different depths was elemental Hg^0 , with the concentration range of 198.70–263.07 mg/kg, or 71.6–76.5%. Other mercury species was in ionic Hg^{2+} , the concentrations of which were 78.77–89.25 mg/kg, or 23.5–28.4% in 30 to 90 cm depths.

Sulfur and Sulfide Applications

The TCLP test results of tailing samples of 30, 60, and 90 cm depths were 4.30 mg/L, 4.21 mg/L, and 4.11 mg/L respectively (Table 5). These results exceeded the quality standards for hazardous waste, according to Government regulation No. 104/20014 of 0.05 mg/L, and placed the tailing as hazardous waste of Category 1. After sulfide amendment, the TCLP test results in the corresponding depths were $1.7 \times 10^{-4} \text{ mg/L}$, $2.5 \times 10^{-4} \text{ mg/L}$, $1.1 \times 10^{-3} \text{ mg/L}$ respectively. Addition of sulfur powder into tailing pile samples contributed to the TCLP test result values which

Table 3. Mass balance data of mercury speciation results

Sample	Depth (cm)	Mercury concentration (mg/kg)							
		Tube 1 (Hg^{2+})	(%)	Tube 2 (Hg^{2+})	(%)	Tube 3 (Hg^0)	(%)	Unaccounted Hg	(%)
Tailing A	30	86.93	24.67	2.32	0.66	256.84	72.90	6.23	1.80
Tailing B	60	77.46	27.92	1.31	0.47	189.62	68.34	9.08	3.38
Tailing C	90	79.70	23.20	0.95	0.28	253.00	73.66	9.83	2.95

Table 4. Distribution of Mercury Species

Depth (cm)	Concentration of			
	Hg^{2+} in Tubes 1+2 (mg/kg)	Hg^{2+} (%)	Hg^0 in Tube 3 and unaccounted Hg (mg/kg)	Hg^0 (%)
30	89.25	25.3	263.07	74.7
60	78.77	28.4	198.70	71.6
90	80.65	23.5	262.83	76.5

varied from 1.8×10^{-4} to 6.1×10^{-4} mg Hg/L. Both of TCLP results test values met the above mentioned quality standards.

These results showed that sulfur and sodium sulfide were effective reagents for decreasing the mobility of mercury into aqueous phase. Therefore, the mercury stabilization process with sulfur or sodium sulfide additions is essential before the S/S process of tailings. This argument was supported by a study which states that there was some mercury oxide (HgO) precipitate in the Portland cement in the S/S process (McWhinney et al., 1990). This precipitation was formed by the reaction:



However, there is a problem associated with the Hg treatment with the S/S method. The mercury bound in Portland cement was mainly in Hg^{2+} form. On the other hand, the main mercury species in tailing is the metallic form, Hg^0 . Hamilton and Bowers (1997) stated that Hg^0 had a strong potential to evaporate from solid cement mud. Thus, before the S/S method is applied for tailing treatment, the elemental mercury should be stabilized in order to prevent evaporation. Elemental mercury stabilization can be done by sulfur or sulfide addition. The reactions between mercury and sodium sulfide and sulfur are shown below:



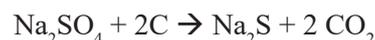
HgS has a low solubility because of the very low constant solubility product (Ksp) of $10^{-51.8}$.

Applicability of sulfur and sulfide for stabilization of mercury contaminated soil

Selection of sulfur or sulfide as stabilization agent for a mercury contaminated tailing or soil should consider some factors. From safety aspect, sulfur is more advantageous than sulfide. According to Material Safety Data Sheet (MSDS) of the US Hazardous Materials Identification System

(HMIS), sulfur is categorized with health hazard of 1 (slight), and reactivity of 0 (minimal). In contrast, sodium sulfide has higher health hazard of 3 (serious) and fire hazard of 3. Sodium sulfide will release toxic H_2S gas when exposed to moisture.

As a mine product, sulfur can be obtained in various forms (granular or powder) more easily than sodium sulfide. Sodium sulfide is a manufacture product, made from sodium sulfate and carbon.



The use of sulfur will be more economical than in the case of sodium sulfide. For example, In Indonesia, a ton of sulfur powder of 100 mesh costs IDR 3,900,000 (US 260), compared to the price of 1 ton of Na_2S of Rp. 5.130.000 (USD 342).

On the basis of the comparison above, sulfur is more suitable as a stabilizing agent for mercury contaminated soil than sulfide compounds for its lower hazard risks, availability, and low cost.

CONCLUSION

The elemental Hg^0 was the prevailing form of mercury in the tailing samples. The elemental Hg^0 concentrations in the tailings at 30, 60, and 90 cm depths were 74.7%, 71.6%, and 76.5% respectively, whereas those of ionic Hg^{2+} were 25.3%, 28.4%, and 23.5%, respectively. Additions of both sulfur powder and sodium sulfide solution formed stable black-colored mercury sulfide compound. The TCLP tests conducted on treated tailing pile samples from 30, 60, and 90 cm depths showed the results which met quality standards. Sulfur is more recommended for use as mercury stabilizing agent than sulfide for the safety, availability, and economical reasons.

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REFERENCES

1. Biester H., Müller G., and Schöler H. 2002. Binding and mobility of mercury in soils contaminated by emissions from chlor-alkali plants. *Journal of Science of the Total Environment* 2002, 284(1–3): 191–203.

Table 5. Results of TCLP Test

Depth (cm)	Results of TCLP test (mg Hg/L)		
	Tailing	Tailing + Na_2S	Tailing + Sulfur
30	4.30	1.7×10^{-4}	6.1×10^{-4}
60	4.21	2.5×10^{-4}	1.8×10^{-4}
90	4.11	1.1×10^{-3}	4.0×10^{-4}

2. Blanchard A.A. 1936. Synthetic inorganic chemistry. 151–152, New York.
3. Chang C.Y., Hsu C.P., Jann J.S., Chen Y.W., Shih Y.C., Mao C.F., Lin W.Y., Lin KL, Wu Y.M. 1993. Stabilization of mercury containing sludge by a combined process of two-stage pretreatment and solidification. *Journal of Hazardous Materials*, 35(1): 73–88.
4. Hamilton WP, Bowers A.R. 1997. Determination of acute Hg emissions from solidified/stabilized cement waste forms. *Journal of Waste Management*, 1: 25–32.
5. Herman D.Z. 2006. Evaluation on tailing containing arsenic (As), mercury (Hg), lead (Pb), and cadmium (Cd) from residual ore. *Jurnal Geologi Indonesia*, 1: 31–36. (in Indonesian)
6. Ilyas T.Y., Rahayu W., and Arifin D.S. 2008. Study on strength behavior of peat soil in Kalimantan after stabilization with Portland cement. *Jurnal Teknologi* 1: 1–8. (In Indonesian)
7. Lee S.J., Seo Y.C., Jung J., Hong J.H., Park J.W., Hyun J.E., and Lee T.G., 2004. Mercury emissions from selected stationary combustion sources in Korea. *Journal of Science of Total Environment*. 325: 155–161.
8. Kalimantoro T.T., Trihadiningrum Y. 2016. Stabilization/Solidification of tailing from public gold mining in Kulon Progo using Portland cement and trass soil. *Jurnal Teknik ITS*, 5 (2): 2337–3539. (In Indonesian).
9. López F.A., Alguacil F.J., Roman C.P., Tayibi H., and López-Delgado A. 2008. Disposal of Elemental Mercury Via Sulphur Reaction by Milling. First International Conference on Hazardous Waste Management, 1–3 October, Chania, Greece
10. López F.A., López-Delgado A., Padilla I., Tayibi H., Alguacil F.J., 2010. Formation of Metacinnabar by Milling of Liquid Mercury and Elemental Sulphur for Long Term Mercury Storage. *Journal of Science of the Total Environment* 2010, 408(20): 4341–4345
11. McWhinney H.G., Coker D.L., Balke K., Ortego J.D. 1990. An Investigation of Mercury Solidification and Stabilization in Portland Cement Using X-Ray Photoelectron Spectroscopy and Energy Dispersive Spectroscopy. *Cement and Concrete Research*, 20 (1): 79–91.
12. Pamayo A.I. and Trihadiningrum, Y. 2015. Stabilization/solidification of tailing pile from public gold mining in Kulon Progo using Portland cement. *Jurnal Teknik ITS*, 5 (2): 242–247.
13. Piao H. and Bishop P.L. 2001. Sulfide-induced mercury stabilization. In: Proceedings, American Chemical Society, 221st Annual Meeting & Exhibition, San Diego, California.
14. Piao H. and Bishop P.L. 2006. Stabilization of mercury containing wastes using sulfide. *Journal of Environmental Pollution*, 139(3): 498–506.
15. Rachman R.M., Kharismawati E., and Trihadiningrum Y. 2017. Stabilization/solidification of mercury contaminated soil of traditional gold mining in Kulon Progo Yogyakarta, Indonesia using a mixture of Portland cement and tras soil. *ARPN Journal of Engineering and Applied Sciences*, 22 (12): 6380–6387
16. Rachman, R.M., Bahri, A.S., Trihadiningrum, Y. 2018. Stabilization/solidification of tailing on traditional gold mining in Kulon Progo using fly ash. *Journal of Ecological Engineering* 19 (3), 178–184
17. Richard J.H. 2016. Mercury contaminated groundwater: Speciation Analysis, Modeling, and Remediation. TU Braunschweig. Institut für Geoökologie, Umweltgeochemie, Germany.
18. Robles I., Lakatos J., Scharek P., Planck Z., Hernández G., Solís S., Bustos E. 2014. Characterization and Remediation of Soils and Sediments Polluted with Mercury: Occurrence, Transformations, Environmental Considerations and San Joaquin's Sierra Gorda Case. *Environmental Risk Assessment of Soil Contamination*, Chapter 29: 827–850.
19. USEPA, 1992. EPA Test Method 1311 – TCLP, Toxicity Characteristic Leaching Procedure.
20. Zhang H., Chen J., Liang P., Wang L., 2012. Mercury Oxidation and Adsorption Characteristics of Potassium Permanganate Modified Lignite Semi-Coke. *Journal of Environmental Science*, 24 (12): 2083–2090.