

Original Research

Enrichment Process and Efficient Removal of Thallium from Steel Plant Desulfurization Wastewater

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Abstract

Thallium (Tl) is a typical trace metal of extreme high toxicity. As a concomitant element, Tl is widely found in various sulfide minerals and K-containing rock minerals. The outburst of Tl pollution in drinking water sources of the northern branch of the Pearl River in China as reported in 2010 has greatly aroused public concerns about Tl pollution in China. Apart from typical sources of Tl pollution such as Pb and Zn smelting and the mining and utilization of Tl-containing pyrite ores, the steel-making industry was discovered a new significant source that contributed to this Tl pollution incidence. Thallium contents in raw materials, fly ash and wastewater collected from a typical steel-making enterprise were determined by inductively coupled plasma mass spectrometry (ICP-MS). The results showed that Tl contents (0.02-1.03 mg/kg) are generally low in the raw materials, while fly ash samples have generally enriched Tl levels (1.31-6.45 mg/kg). Wastewater obtained from the dedusting process of the sintering furnace also exhibited excessive Tl levels (574-2130 µg/L). All these results suggested a possible release and gasification of Tl compounds from the raw materials under high temperatures (>800°C) during the sintering processes, which were then accumulated in the flue gas and fly ash and washed into the wastewater by wet dedusting. Lime precipitation method is not effective for removing Tl from wastewater, since Tl mostly is present as dissolved Tl⁺ in the water. The study initiated a preliminary design of a fast and effective treatment method for Tl removal from Tl-containing industrial wastewater by using a deep oxidation system.

Keywords: thallium, steel-making, desulfurization wastewater

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Introduction

Thallium (Tl) is a rare metal dispersed in the natural environment, which was discovered in 1861 by William Crookes [1]. Pure Tl is bluish-white in color and it is very soft and malleable. Thallium is considered to be more toxic than Pb, As, Hg, Cd and Cu, with a lethal dose reported to be 10-15 mg/kg in humans [2-3]. It is a cumulative poison, with symptoms of intoxication including alopecia, nausea, persistent weakness, tachycardia, high blood pressure, abdominal pain, vision loss and so on [2]. Since Tl has caused a number of accidental and occupational poisonings, it is included on the list of priority toxic pollutants by the U.S. Environmental Protection Agency (U.S. EPA) and China's Ministry of Environmental Protection (MEP, China). The Maximum Permissible Level of Tl in drinking water is fixed at 2 µg/L by the U.S. EPA [4], 0.8 µg/L by Canada and 0.1 µg/L by China and Russia [2, 4]. The predominant source of Tl released into the environment is industrial activities utilizing Tl-bearing minerals, such as smelting of Pb, Cu, and Zn ores, rather than from facilities producing or using Tl compounds [1-7]. Tough Tl is highly toxic and has often been excluded from the list of metals to be supervised before 2010, when a serious Tl pollution incidence occurred in the northern branch of the Pearl River – the 3rd longest river in China. Since then, Tl-bearing wastewater discharge has been greatly controlled and regulated by the local Environmental Protection Bureau [1]. Worse still, rapid industrial development and general overlook of Tl pollution control in recent decades and outbursts of Tl pollution have been successively reported over several different provinces in China [5]. The threshold limit value of Tl in wastewater has been proposed at 2-5 µg/L by the Environmental Protection Bureau in several provinces (Table 1 [9-12]). In addition, apart from typical sources of Tl pollution such as Pb and Zn smelting and mining and the utilization of Tl-containing pyrite ores previously investigated, the steel-making industry has been discovered quite recently as a new significant source of Tl pollution [1].

According to previous literature, the main methods for Tl removal from wastewater are chemical precipitation using jarosite [13, 14], adsorption by metal oxides (e.g., Al₂O₃ [15-17]), solvent extraction [18, 19], and ionic exchange [20, 21]. All these proposed methods

are effective in Tl removal from synthetic wastewater that only contains Tl and/or simple wastewater systems, such as drinking water systems. However, due to a very complicated matrix arising from condensed levels of salt and complex organic matter present in steel-making desulfurization wastewater, removal efficiency of available methods so far cannot yet reach the Tl emission standard for industrial wastewater regulated by local government [9-12].

The aims of this study were (1) to systematically investigate Tl distribution in raw ore materials of a typical steel-making plant and figure out the main processes responsible for Tl pollution in the desulfurization effluent; and (2) to propose a fast and feasible treatment method to remove Tl from the desulfurization wastewater.

Materials and Methods

Sample Collection and Pretreatment

In June 2014, 19 different types of raw ore materials (RM1-RM19), four kinds of fly ash and three different types of wastewater were collected from a steel-making plant in northern Guangdong Province, China.

Solid samples such as raw ore materials and fly ash were collected by stainless shovel and put into a plastic bag. They were ground in an agate mortar and sieved to less than <100 µm. Subsequently, samples were totally digested based on the following brief procedure: approximately 100 mg of each sample were digested with 10 mL of 65% HNO₃ (v/v) and 5 mL of 48% HF (v/v) in a Teflon vessel. The mixture was heated on a hot plate at 180°C in open air until near dryness. Subsequently, 2 mL of HClO₄ was added into the mixture, which was left again to evaporate close to near dryness. Finally, several mLs of 8 mol/L HNO₃ were used to dissolve the residue, which was then diluted with deionized water (Milli-Q Millipore, 18.25 MΩ cm⁻¹). Certified Reference Material (GBW 07311, Beijing, China) and analytical blanks were digested via the same procedures as those used for the samples for quality control.

Wastewater samples (approximately 10 L each) were collected manually with plastic containers from different sintering furnaces in the steel-making plant. Water pH was measured *in-situ* by a portable pH device. The

Table 1. Maximum permissible level of wastewater for Tl in China

Standard	Maximum Permissible Level
Surface Water Environmental Quality Standards fixed by MEP, China [8]	0.1 µg/L
Thallium Emission Standard for Industrial Wastewater regulated in Hunan Province [9]	5 µg/L
Thallium Emission Standard for Industrial Wastewater in Guangdong Province [10]	5 µg/L
Thallium Emission Standard for Steel Industry Wastewater in Jiangsu Province [11]	2 µg/L
Integrated Wastewater Discharge Standard in Shanghai [12]	5 µg/L

samples were filtered via pre-washed 0.45 μm membrane filters and then acidified to $\text{pH} < 2$ using ultrapure HNO_3 and stored in coolers at -4°C until further analysis.

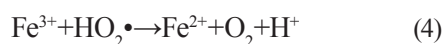
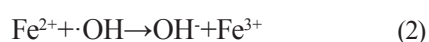
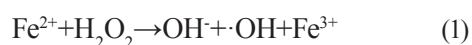
Determining Metal Concentration by ICP-MS

The concentrations of Tl, As, Cd, Cu, Pb, and Zn were measured by inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer-NexION-300, U.S.) under standard operating conditions. Each sample was analyzed five times, and quality control standards were run after each batch of 10 samples. The precision was overall better than 5%. The determination limits for studied elements were 0.01 $\mu\text{g/L}$ for Cd, Cu, Tl and Pb, and 0.5 $\mu\text{g/L}$ for As and Zn.

Preliminary Treatment of Tl-containing Wastewater from a Steel Plant

Basic Mechanism of Designing a Method for Effective Tl Removal from Wastewater

The basic design used in this study consisted of a deep oxidation system mainly using ferrous ions (Fe^{2+}) and hydrogen peroxide (H_2O_2). The key mechanism of this deep oxidation system is to use ferrous ions to react with H_2O_2 , generating hydroxyl radicals ($\cdot\text{OH}$) with powerful oxidizing ability, as shown in Eqs. (1)-(4)



Previous studies showed that the presence of H^+ is required in the decomposition of H_2O_2 , and an acid environment of pH is often used to produce the maximum amount of hydroxyl radicals. This deep oxidation system can oxidize not only various refractory organic pollutants, but also Tl^+ in the wastewater. The deep oxidation was subsequently followed by using excessive lime (CaO) to remove Tl(III) in the wastewater as Tl(OH)_3 ($K_{\text{sp}} = 1.68 \times 10^{-44}$) precipitate.

Experimental Design for Tl Removal from the Wastewater

Firstly, 20 mL of wastewater was mixed with several drops of dilute HNO_3 to adjust pH , which was monitored using a Satorius-PB-10 pH meter. A portion of FeSO_4 and H_2O_2 was then added into the wastewater and shaken by a SHY-2A dual-function digital temperature-controlled oscillator for 20 min. Finally, proper amount of CaO was added to adjust pH above 9.0 and centrifuging for 15 min. The supernatant was taken

and measured for Tl concentration by using ICP-MS as described in Section 2.2.

The precipitate was dried to constant weight, ground and then passed through a 200-mesh sieve. The precipitate was characterized by semi-quantitative XRD analysis via a PANalytical-PW3040/60 X-ray powder diffractometer (XRD) and Philips X'Pert High Score software equipped with the JCPDS PDF-2 database for detection of their mineralogical compositions [22, 23]. The scanning electron microscope (SEM; JSM-7001F, JEOL, Japan) equipped with an X-ray energy-dispersive spectrometer (EDS) (Oxford Instruments, UK) was used to study morphological properties and surface compositions of the precipitate.

Results and Discussion

Distribution of Tl Contents in the Waste Materials from the Steel-Making Plant

As shown in Table 2, the contents of Tl in all the studied raw materials (0.02-1.03 mg/kg) from the steel-making were relatively low when compared to the upper crust background value (0.45 mg/kg) [4]. However, enriched Tl contents were observed in fly ash (1.31-6.57 mg/kg). The enrichment of Pb, Zn and Cd was also found in fly ash. As displayed in Fig. 1, significant positive correlation relationships were shown between the contents of Tl and Pb ($r^2 = 0.925$), Tl and Zn ($r^2 = 0.877$), and Tl and Cd ($r^2 = 0.992$) in raw materials and fly ash.

The pH values of wastewater samples obtained from the dedusting process of sintering furnace ranged from 4.98 to 5.91. They were also measured for concentrations of Tl, Pb, Zn, Cd, Cu and As. The results were listed in Table 3. The wastewater had very enriched Tl levels (574 - 2130 $\mu\text{g/L}$), which exceeded the emission standard for industrial wastewater (5 $\mu\text{g/L}$) that was enacted by most provinces in China by more than two magnitudes of order. This suggests that most Tl compounds from the raw materials released and gasified under high temperatures ($>800^\circ\text{C}$) during the processes of sintering ores, which were accumulated in the flue gas and fly ash. Specifically, Tl in the raw iron ores mainly occurs in the form of Tl_2S_3 , Tl_2S , and/or Tl halides [4]. Most of these Tl compounds have low melting and boiling points and they are apt to volatilization during the ore sintering process ($>800^\circ\text{C}$). Moreover, Tl may also form extremely volatile Tl compounds such as TlCl , TlF and Tl_2O [23]. The melting and boiling points of Tl compounds are shown in Table 4 [24]. A reasonable part of Tl originally in the iron ore feedstock was hence enriched in flue gas produced by sintering. Thallium-bearing flue gas was subsequently washed into seriflux effluent by wet dedusting during desulfurization process. For most of steel-making plants, this seriflux effluent was required to be recycled into the system after dehydration of gypsum slurry to reduce desulfurization cost. Therefore,

Table 2. Distribution characteristics of Tl and other heavy metals (mg/kg) in different iron ore raw materials.

		Tl	Pb	Zn	Cd	Cu	As
Iron ore raw materials	RM 1	1.03	384	1070	6.37	162.5	196
	RM 2	0.02	1.40	11.0	BDL ^b	122	56.7
	RM 3	0.76	557	793	4.63	2710	427
	RM 4	0.07	14.4	38.0	0.06	47.6	8.30
	RM 5	0.02	1.30	46.0	BDL	58.3	5.00
	RM 6	0.05	3.70	13.0	0.02	11.0	5.00
	RM 7	0.02	3.20	BDL	0.03	6.90	17.0
	RM 8	0.14	15.6	32.0	0.04	96.9	259
	RM 9	0.06	9.90	28.0	0.06	23.5	13.5
	RM 10	0.04	21.3	222	0.05	567	42.8
	RM 11	0.02	12.5	86.0	0.03	198.5	20.8
	RM 12	0.02	58.5	586	0.56	120	88.8
	RM 13	0.07	29.9	90.0	0.32	112	5.50
	RM 14	0.10	4.60	1110	0.25	46.8	250
	RM 15	0.20	14.9	43.0	0.11	14.4	24.8
	RM 16	0.03	7.20	11.0	0.05	6.80	6.70
	RM 17	0.09	7.60	28.0	0.06	11.6	11.7
	RM 18	0.02	2.60	BDL	BDL	6.70	18.8
	RM 19	0.12	29.0	77.0	0.54	23.4	7.10
Fly ash	FA1	2.46	2700	5910	15.3	60.7	20.7
	FA2	6.57	NA	NA	NA	NA	NA
	FA3	1.62	NA	NA	NA	NA	NA
	FA4	1.31	NA	NA	NA	NA	NA
Upper crust ^a		0.45	15.0	70.0/	0.20	55.0	1.80

Note: ^a upper crust background value from the literature [14]; ^bBDL:below detection limit; NA: not analyzed

Tl concentrations in seriflux effluent is further enriched in the recycling system. Meanwhile, for maintaining stability and mass balance of the whole system during industrial production, a portion of seriflux effluent was continuously drained out. All these lead to very high Tl concentrations in desulfurization wastewater. The mechanism of Tl accumulation in sintering flue gas from the desulfurization system is depicted in Fig. 2. Generally excessive levels of Pb, Zn, Cd, Cu and As were also observed in the wastewater when compared to the maximum permissible level regulated in China [25]. It indicates that these elements may also have experienced a similar transfer process as Tl.

Further comparison of distribution patterns of Tl and other studied elements among raw materials, fly ash and desulfurization wastewater indicated that elements like Tl, Pb, Zn and Cd partly distributed in fly ash and partly were washed into wastewater by wet dedusting for desulfurization. Meanwhile, unlike Tl, Pb, Zn and

Cd, elements like Cu and As were mostly washed into the wastewater by the dedusting process. The different enrichment patterns among these studied elements can be mainly explained by their variations of physio-chemical properties and their geochemical speciation originally associated in raw materials.

It is worth noting that elements like Pb, Zn, Cd and As usually present in high valency, which can be easily removed from wastewater by using the conventional method of lime precipitation. However, Tl predominantly occurs as dissolved monovalent state (Tl^+) in wastewater, which prevents it from being precipitated by conventional neutralization method of using only limestone or other alkaline [11].

Treating Thallium-Containing Wastewater

The deep oxidation system here mainly employed ferrous ions (Fe^{2+}) and hydrogen peroxide (H_2O_2)

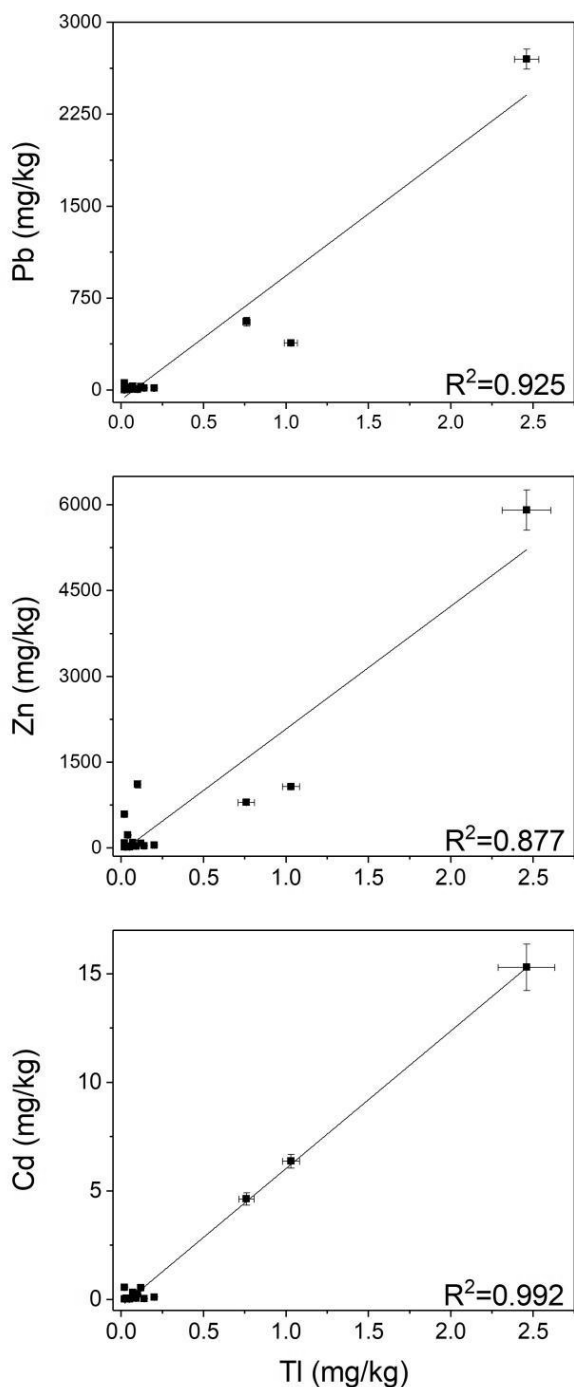


Fig. 1. Linear regression analysis in the samples of raw materials and fly ash.

Table 4. Melting and boiling points of Tl-containing compounds [24].

Chemical formula	Melting point (°C)	Boiling point (°C)
Tl	303.5	1457
TlCl	430	720
TlF	327	655
Tl ₂ O	300	1080
Tl ₂ O ₃	717±5	875
Tl ₂ S	448.5	1367

for generating hydroxyl radicals ($\cdot\text{OH}$). The radicals can initiate quick and strong oxidation of not only all refractory organic pollutants and reducing reagents, but also all Tl into Tl(III) in the wastewater. Tl(III) was then removed from wastewater as precipitate by using excessive lime (CaO) and/or other alkaline (e.g., NaOH). The key factors controlling the efficiency of Tl removal from the desulfurization wastewater were preliminarily studied and discussed as follows.

Effect of Initial pH on Removal rate of Tl in Desulfurization Wastewater

One of the key factors for Tl removal efficiency is initial pH. Previous studies showed that the presence of H^+ is required in the decomposition of H_2O_2 , and acidic pH levels near 3.0 are usually optimum for producing deep oxidation [26]. A few drops of H_2SO_4 were added to adjust the wastewater system to pH 2.9, 3.0, 3.1, 3.2, 3.3 and 3.4. As shown in Fig. 3, the removal rate of Tl ranged from 98% to 99.7%. The removal rate exhibited an increasing trend as pH increased from 2.9 to 3.2, which then decreased sharply as pH changed from 3.2 to 3.4. This suggested that optimal starting pH of deep oxidation was 3.2 for this desulfurization wastewater system.

Effect of Molar Ratio of $[\text{Fe(II)}/\text{H}_2\text{O}_2]$

Another key factor for removal efficiency is the molar ratio of $[\text{Fe(II)}/\text{H}_2\text{O}_2]$ (shown in Fig. 4). The removal rate of Tl varied from 88.5% to 99.7% as

Table 3. Distribution characteristics of Tl and other heavy metals ($\mu\text{g/L}$) in different typical Tl-containing wastewater.

Desulfurization effluent	Tl	Pb	Zn	Cd	Cu	As	pH
1	574	258	7950	2190	617	10680	4.98
2	2130	5980	30300	19790	1154	10810	5.91
3	1372	5880	48200	2750	17280	2160	5.89
Maximum Permissible Level ^a	5	1000	2000	1500	500	500	6-9

Note: ^a The maximum permissible level of Tl was cited from [9-12], and of the other elements and pH was cited from [25].

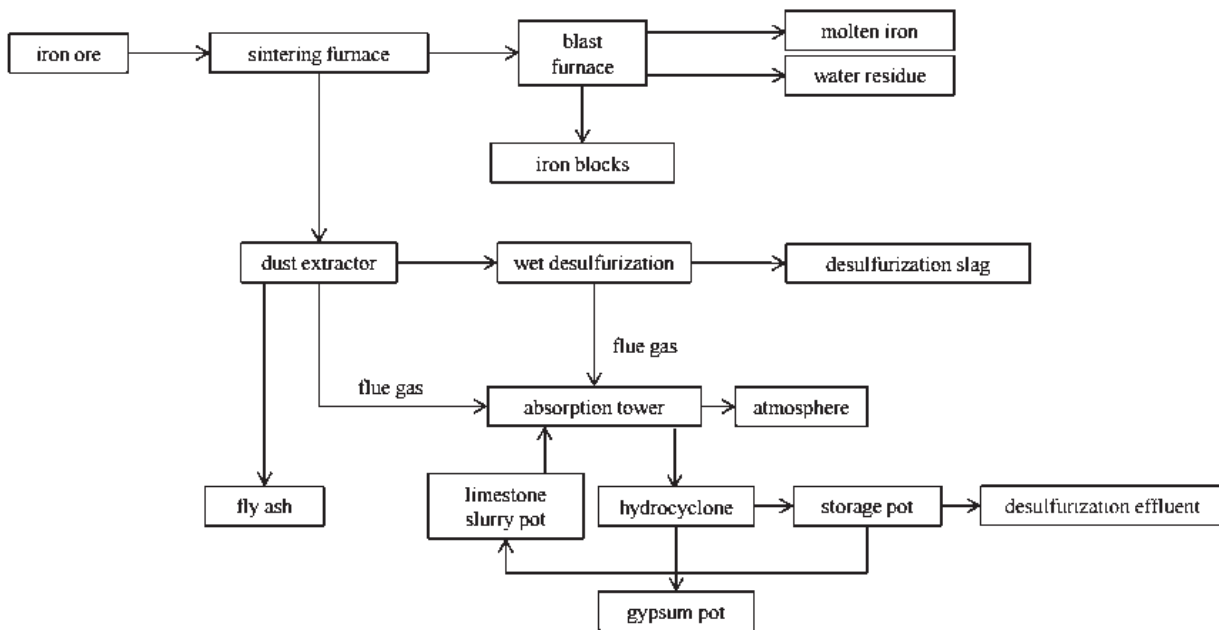


Fig. 2. Path of formation of Tl pollution in desulfurization wastewater during the steel production process.

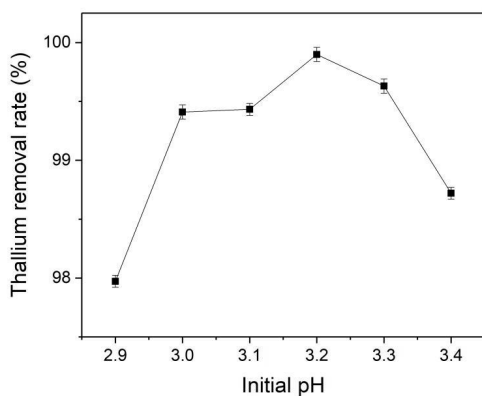


Fig. 3. Removal rate (%) of Tl from desulfurization wastewater of steel production dependant on initial pH of the wastewater system.

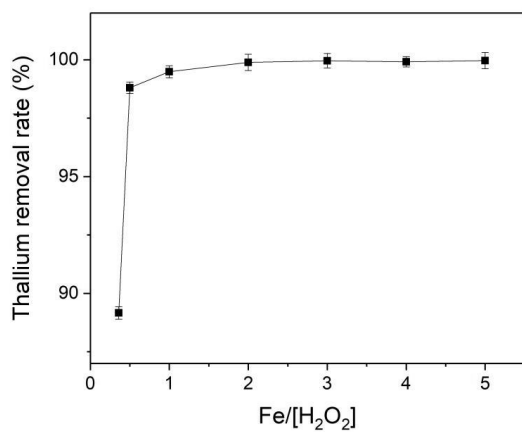


Fig. 4. Removal rate (%) of Tl from desulfurization wastewater of steel production as a function of [Fe/H₂O₂] ratio.

molar ratio of [Fe(II)/H₂O₂] changed from 0.36 to 5.0. It is worth noting that removal rate sharply increased from 88.5% to 98.5% when molar ratio of [Fe(II)/H₂O₂] changed from 0.36 to 0.5. The concentration of Tl was reduced to only 2.95 μg/L at molar ratio of [Fe(II)/H₂O₂] of 1.0. Such removal efficiency is sufficient to meet the Tl Emission Standard of Wastewater regulated by the local government. Taking into consideration wastewater treatment cost, a molar ratio of [Fe(II)/H₂O₂] of 1.0 was chosen as the optimum value.

XRD Characterization of Precipitate after Deep Oxidation Technology

Precipitate from Tl-containing desulfurization wastewater subjected to deep oxidation treatment was detected by XRD for mineralogical characterization (shown in Fig. 5). Thallium in the precipitate predominantly exists in the form of Tl oxidation state (Tl₂O₃), since Tl(OH)₃ is easily dehydrated to Tl₂O₃.

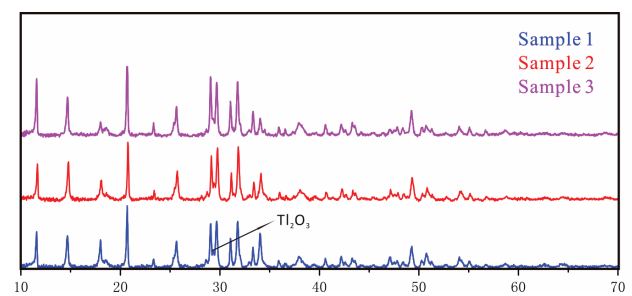


Fig. 5. XRD characterization of the precipitate after deep oxidation of desulfurization wastewater from steel production.

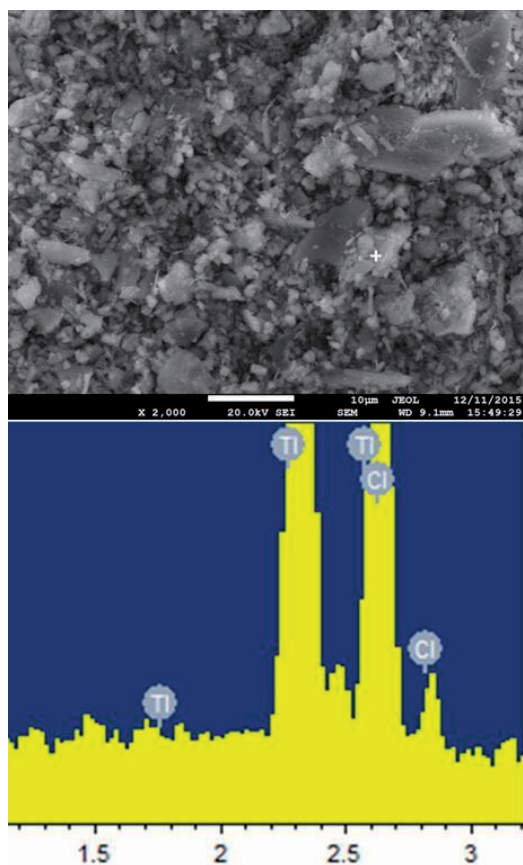


Fig. 6. SEM-EDS characterization of the precipitate after deep oxidation of desulfurization wastewater from steel production.

[27]. This further confirms that deep oxidation technique has successfully oxidized Tl in wastewater and removed it from wastewater.

SEM-EDS Characterization of Precipitate after Deep Oxidation Technology

Precipitate of Tl-containing desulfurization wastewater was also characterized by SEM-EDS for morphological properties and surface compositions (Fig. 6). The result showed that there was an enriched content of Tl in the precipitate, and the surface is relatively loose with a larger specific surface area. The surface can provide sufficient adsorption sites for Tl_2O_3 obtained after oxidation and co-precipitation of lime and Tl_2O_3 .

Conclusions

Thallium is a very toxic metal dispersed in the natural environment, which is concurrent with sulfide minerals such as Pb, Zn and Fe. Though its concentration is very low in raw materials due to the high temperature of the sintering ore process during steel-making production, a major part of Tl is enriched in flue gas. The Tl-bearing flue gas was then washed into seriflux

effluent by wet dedusting during the desulfurization process. The seriflux effluent was recycled into the system after dehydration of gypsum slurry to reduce desulfurization cost. These main causes leading to very high levels of Tl in desulfurization wastewater observed here can also be encountered in the other steel-making plants in China. Therefore, it is high time to take effective measures to control Tl pollution for preventing Tl pollution incidents nationwide in the near future. The deep oxidation technology initiated in this study highlights a potential way that needs to be further investigated.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

References

- LIU J., LUO X.W., WANG J., XIAO T., CHEN D., SHENG G., YIN M.L., LIPPOLD H., WANG C.L., CHEN Y.H. Thallium contamination in arable soils and vegetables around a steel plant: A newly-found significant source of Tl pollution in South China. *Environmental Pollution*, **224**, 445, **2017**.
- KARBOWSKA B. Presence of thallium in the environment: sources of contaminations, distribution and monitoring methods. *Environmental Monitoring and Assessment*, **188** (11), 640, **2016**.
- LONG J.Y., CHEN D.Y., XIA J.R. Equilibrium and Kinetics Studies on Biosorption of Thallium (I) by Dead Biomass of *Pseudomonas fluorescens*. *Polish Journal of Environmental Studies*, **26** (4), 1591, **2017**.
- XIAO T.F., YANG F., LI S.H. Thallium pollution in China: A geo-environmental perspective. *The Science of the Total Environment*, **421**, 51, **2012**.
- CHEN Y.H., WANG C.L., LIU J., WANG J., QI J.Y., WU Y.J. Environmental exposure and flux of thallium by industrial activities utilizing thallium-bearing pyrite. *Science China Earth Sciences*, **56** (9), 502, **2013**.
- ÁLVAREZ-AYUSO E., OTONES V., MURCIEGO A., GARCÍA-SÁNCHEZ A., REGIN I.S. Zinc, cadmium

- and thallium distribution in soils and plants of an area impacted by sphalerite-bearing mine wastes. *Geoderma* 207-208, 25-34, **2013**.
7. ANTIĆ-MLADENOVIĆ S., FROHNE T. KRESOVIĆ M., STÄRK H J., SAVIĆ D., LIČINA V., RINKLEBE J. Redox-controlled release dynamics of thallium in periodically flooded arable soil. *Chemosphere*, **178**, 268, **2017**.
 8. Environmental Quality Standards for Surface Water. State Environmental Protection Administration. GB/3838-2002, **2002**.
 9. Thallium Discharge Standard for Industrial Wastewater. Hunan Provincial Environmental Protection Bureau, Hunan Provincial Bureau of Quality and Technical Supervision. DB43 / 968-2014, **2014**.
 10. Emission Standard of Thallium for Industry Wastewater. Guangdong Provincial Environmental Protection Agency, Guangdong Bureau of Quality and Technical Supervision. DB44 / 1989-2017, **2017**.
 11. Discharge Standard of Thallium Pollutants in Wastewater for Iron and Steel Industry. Available online: http://hbt.jiangsu.gov.cn/art/2018/2/11/art_2470_7485867.html (accessed on 1st January **2018**).
 12. Integrated Wastewater Discharge Standards. Available online: <http://www.sepb.gov.cn/fa/cms/upload/uploadFiles/2017-08-07/file2772.pdf> (accessed on 1st January **2018**).
 13. DUTRIZAC J.E. The behavior of thallium during jarosite precipitation. *Metall Mater Trans B Process Metall Mater Process Science*, **28** (5), 765, **1997**.
 14. DUTRIZAC J.E., CHEN T.T., BEAUCHEMIN S. The behaviour of thallium (III) during jarosite precipitation. *Hydrometall*, **79** (3), 138, **2005**.
 15. HUANGFU X.L., MA C.X., MA J., HE Q., YANG C., ZHOU J., JIANG J., WANG Y.A. Effective removal of trace thallium from surface water by nanosized manganese dioxide enhanced quartz sand filtration. *Chemosphere*, **189**, 1, **2017**.
 16. ZHANG G.S., FAN F., LI X.P. Superior adsorption of thallium(I) on titanium peroxide: Performance and mechanism. *Chemical Engineering Journal*, **331**, 471, **2018**.
 17. CHEN M.Q., WU P.X., YU L.F. FeOOH-loaded MnO₂ nano-composite: An efficient emergency material for thallium pollution incident. *Journal of Environmental Management*, **192**, 31, **2017**.
 18. NAZARI S., MEHRI A., HASSANNIA A.S. Fe₃O₄-modified graphene oxide as a sorbent for sequential magnetic solid phase extraction and dispersive liquid phase microextraction of thallium. *Microchimica Acta*, **184** (9), 3239, **2017**.
 19. SHIRAZIAN S., FADAEI F., ASHRAFIZADEH S.N. Modeling of thallium extraction in a hollow-fiber membrane contactor. *Solvent Extraction and Ion Exchange*, **30** (5), 490, **2012**.
 20. TERESHATOV E.E., BOLTOEVA M.Y., MAZAN V. Thallium Transfer from Hydrochloric Acid Media into Pure Ionic Liquids. *Journal of Physical Chemistry*, **120** (9), 2311, **2016**.
 21. TERESHATOV E.E., BOLTOEVA M.Y., FOLDEN C.M. Resin ion exchange and liquid-liquid extraction of indium and thallium from chloride media. *Solvent Extraction and Ion Exchange*, **33** (6), 607, **2015**.
 22. LIU J., WANG J., XIAO T.F., BAO Z.A., LIPPOLD H., LUO X.W., YIN M.L., REN J.M., CHEN Y.H., LINGHU W.S. Geochemical dispersal of thallium and accompanying metals in sediment profiles from a smelter-impacted area in South China. *Applied Geochemistry*, **88**, 239, **2018**.
 23. LIU J., WANG J., CHEN Y.H., XIE X.F., QI J.Y., LIPPOLD H., LUO D.G., WANG C.L., SU L.X., HE L.C., WU Q.W. Thallium transformation and partitioning during Pb-Zn smelting and environmental implications. *Environmental Pollution*, **212**, 77, **2016**.
 24. IPCS (International Program on Chemical Safety). 1996. WHO Report. Environmental Health Criteria 182. Thallium (available at: <http://www.inchem.org>).
 25. Discharge Standard of Water Pollutants for Iron and Steel Industry. Ministry of Environmental Protection, General Administration of Quality Supervision, Inspection and Quarantine. GB 13456-2012, **2012**.
 26. NEYENS E., BAEYENS J. A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials*, **98**, 33, **2003**.
 27. WICK S., BAEYENS B., FERNANDES M.M., VOEGELIN A. Thallium adsorption onto illite. *Environmental Science & Technology*, **52**, 571, **2018**.