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Source Analysis of Thallium-Containing Wastewater Pollution

Penghao Dong, Yaozong Zhang and Derun Zhao

North China University of Science and Technology, Tangshan 063000, China

Abstract

This paper systematically analyzes the pollution sources, environmental impacts, and prevention strategies of thallium-containing wastewater. It focuses on the physicochemical properties and environmental behavior of thallium, analyzes domestic and international pollution control policies and standards, and reviews the migration and emission characteristics of thallium in typical industrial processes such as lead-zinc smelting, iron and steel, and sulfuric acid production. The article also summarizes the principles, effectiveness, and limitations of thallium removal technologies, including chemical precipitation, adsorption, ion exchange, solvent extraction, and biological treatment. It points out that oxidation-precipitation and adsorption methods show good prospects for engineering applications, particularly emphasizing the high removal efficiency of thallium by manganese and iron-based materials. Finally, based on the migration patterns of thallium in the hydrometallurgical zinc process, it proposes strengthening the refined management and treatment process optimization of thallium-containing wastewater to provide a theoretical basis and technical support for achieving green industrial transformation.

Keywords

Thallium pollution; Pollution source analysis; Industrial wastewater; Prevention policy; Treatment technology; Hydrometallurgical zinc.

1. Introduction

The thallium element is located in group IIIA of the sixth period of the periodic table, between mercury (Hg) and lead (Pb). It was first discovered in 1861[1]. Its atomic properties are shown in the table below:

Table 1. Atomic Properties of Thallium[2]

Property	Relevant Data
Atomic Number	81
Relative Atomic Mass	204.4
Natural Isotopes	2
Metallic Radius (pm)	170
Electron Configuration	$[Xe]4f^{14}5d^{10}6s^2p^1$
Ionic Radius (III) (pm)	88.5
First Ionization Energy (kJ/mol)	589.1
Second Ionization Energy (kJ/mol)	1970.5
Third Ionization Energy (kJ/mol)	2877.4

Thallium metal is a silvery-white or bluish-white metal. It is somewhat malleable. In terms of chemical properties, thallium has certain volatility, chalcophilicity (sulfur-loving), and lithophilicity (oxygen-loving). It is unstable at room temperature and therefore needs to be sealed in water or paraffin. Thallium has two chemical valence states, +1 and +3. It more readily forms thallium(I) compounds, contrary to its group neighbors gallium and indium, because the outermost electron configuration of thallium is $6s^2$, which is a stable electron configuration. Therefore, thallium(I) ions and their compounds are more stable than the trivalent ones, similar to alkali metals like K and Na, and are highly soluble in water. Conversely, thallium(III) ions and their compounds are unstable and prone to losing halogens or water (dehalogenation, dehydration). These two valence states can also interconvert under certain conditions.

Thallium, as a typical rare and dispersed element, has a very low Clarke number, generally on the order of 10^{-9} to 10^{-6}. Its average content in the continental crust is 5.81 mg/kg, in the oceanic crust it is 0.15 mg/kg, in unpolluted soil it is 0.01–3 mg/kg, in water it is 0.25 μg/L, and in the ocean it rarely exceeds 20 ng/L. In grains, it is 0.03–0.3 mg/kg[3,4]. Thallium also exhibits dual characteristics: high-temperature dispersion and lithophilia, and low-temperature ore formation and chalcophilicity. It is mainly enriched in lead, mercury, antimony, arsenic sulfosalt minerals, and sulfide mineral resources. Moreover, thallium is closely related to potassium, rubidium, cesium, sodium, and calcium. Most thallium minerals and thallium-bearing minerals found in nature are sulfides and sulfates. Scholars previously believed it could not form independent ores. However, recent research shows that dispersed elements can not only be enriched but also super-enriched, or form independent ores through enrichment in non-independent mineral forms. More than 50 thallium minerals have been discovered so far, with most thallium combining with sulfur and other elements to form various new sulfide minerals, accounting for 45 types or 80.3% of all thallium minerals. With increasing human activities, industrial mining, mineral smelting, etc., lead to thallium exposure and dispersion into the natural environment, causing thallium environmental pollution.

2. Domestic and International Thallium Pollution Prevention Policies and Standards

2.1. Foreign Thallium Pollution Prevention Policies and Standards

Due to its high toxicity, thallium and its compounds were listed as controlled substances in the *Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal* (Basel Convention) as early as 1989. Subsequently, thallium compounds were included in the WHO's list of major restricted hazardous substances. Thallium and its compounds are listed on the US *Clean Water Act*'s toxic pollutant list, and thallium is listed as a priority controlled pollutant in both the US EPA and European management framework guidelines.

The US Environmental Protection Agency (USEPA) set the maximum allowable level for thallium in drinking water at 2 μg/L in 1993, with a health advisory level of 0.5 μg/L. Russia (former Soviet Union) set the standard limit for thallium (Tl) in surface water and drinking water at 0.1 μg/L. Canada's drinking water standard limit is 0.8 μg/L. The US has set an emission limit for thallium pollutants in industrial wastewater at 140 μg/L. Only a very few countries have established concentration limits for thallium pollutants in ambient and indoor air, such as Switzerland and Germany, whose Clean Air Acts stipulate a thallium emission standard of 2 $\mu g/m^3/d$. The International Occupational Safety and Health Administration (OSHA) sets the maximum permissible concentration of thallium in workplace air at 0.1 mg/m^3, while Russia sets it at 0.01 mg/m^3. Currently, no emission limits for thallium pollutants in environmental media like drinking water or surface water have been seen from Japan, Australia, or the EU.

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2.2. Domestic Thallium Pollution Prevention Policies and Standards

Domestically, as early as 1989, thallium and its compounds were included in the *List of Priority Controlled Water Pollutants in China* issued by the former National Environmental Protection Agency. Later, in the 12th Five-Year Plan period (2011), the *Comprehensive Prevention and Control Plan for Heavy Metal Pollution during the 12th Five-Year Plan* listed thallium as a key controlled heavy metal pollutant, proposing to improve local standards for heavy metal pollutant emissions. In 2016, the *Interpretation by the Supreme People's Court and the Supreme People's Procuratorate* stipulated that "discharging, dumping, or disposing of thallium-containing pollutants exceeding three times the national or local pollutant emission standards shall be considered as causing severe environmental pollution." In the same year, the *13th Five-Year Plan for Ecological and Environmental Protection* proposed organizing investigations into thallium pollution emissions from typical industries such as metal mining, beneficiation, smelting, and iron and steel, as well as typical regions like the Qianxinan Buyi and Miao Autonomous Prefecture in Guizhou, and formulating thallium pollution prevention plans.

In recent years, relevant departments have issued multiple notices concerning thallium control, such as the *Notice on Carrying out Investigation and Remediation Work for Thallium-Related Enterprises* (2021), *Opinions on Further Strengthening the Prevention and Control of Heavy Metal Pollution* (2022), and the *Technical Guide for Pollution Hazard Investigation and Management of Thallium Pollution Sources* (2023, trial) to strengthen the supervision and management of thallium pollution treatment and disposal. Local policies have actively responded since 2022, issuing relevant policies for thallium control and improvement (see Table 3). Domestic standards related to thallium are shown in Table 4. This shows that although China started relatively late in thallium prevention and control, due to its high standards and strict requirements, it has become the country with the strictest thallium pollution control in the world.

3. Sources of Thallium Pollution in Typical Industries

Due to thallium's properties, industries involving sulfides can lead to thallium pollution emissions. Thallium's physicochemical properties cause it to be widely distributed throughout various process stages of smelting, which is detrimental to the smelting of valuable metals and increases the difficulty of treating smelting products and waste. Common sources of thallium pollution include non-ferrous metals, ferrous metals, and the sulfuric acid industry.

1) Sources of Thallium Pollutants in the Lead Industry

Lead smelting is divided into three types: pyrometallurgy, hydrometallurgy, and electrometallurgy. Lead smelting primarily uses pyrometallurgy[5]. During the high-temperature sintering of lead concentrate, high-thallium flue gas is produced, accounting for 70–80% of the thallium content in the lead concentrate. During blast furnace smelting, thallium mainly enters the dust and crude lead. During crude lead refining, thallium mainly enters the refining dross[6,7].

2) Sources of Thallium Pollutants in the Zinc Smelting Industry

In zinc smelting, thallium originates from zinc concentrate. The smelting process has multiple points of generation and discharge for thallium-containing wastewater/slags and dust, with highly dispersed pollution. It involves processes such as roasting, leaching, purification, electrolysis, dust collection, and washing. To verify the output paths of thallium in the hydrometallurgical zinc process, this project conducted measurements of thallium pollution content throughout the entire hydrometallurgical zinc process, studying the average thallium content in zinc concentrate from a spatial perspective. The results show that in the hydrometallurgical zinc smelting process, thallium is mainly output through kiln slag, high fluorine-chlorine dust, waste acid, and acidic wastewater, accounting for approximately 44%,

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23%, 12%, and 15% respectively. These four items together account for about 94% of the thallium content. Among them, high fluorine-chlorine dust has high thallium content but low material quantity, with a thallium content of about 5000 mg/kg. The other three items have low content but high material quantity, roughly in the range of 5–400 mg/kg. Research on thallium removal from these high-thallium portions and optimization of existing thallium removal processes could play a key role in thallium pollution prevention.

3) Sources of Thallium Pollutants in the Ferrous Metal Industry

Thallium pollutants in the iron and steel industry are mainly generated in the sintering (pelletizing) and ironmaking processes (Figure 3). The thallium content in the iron ore mix of Chinese steel enterprises generally ranges from 0.6 to 2.3 mg/kg. During the sintering (pelletizing) production process, thallium in the iron ore volatilizes at high temperatures and enters the flue gas. Most of the thallium in the flue gas becomes enriched in the dust removal ash. The thallium content indust removal ash from steel enterprises ranges from 1.8 to 5.4 mg/kg (Source: *Explanation for the Draft Modification of the "Iron and Steel Industry Water Pollutant Discharge Standard" (GB13456-2012)*, 2020). Steel enterprises, based on the quantity and composition of variousdust removal ash and combined with other sintering raw material conditions, mix and blend the dust removal ash, pelletize the mixeddust removal ash under certain moisture conditions, and feed it to the secondary mixer of the sintering machine. The reuse of dust removal ash is also one of the sources of thallium in flue gas. If wet desulfurization is used for sintering flue gas, the vast majority of thallium will enter the spray liquid and ultimately become enriched in the desulfurization wastewater[8].

4) Sources of Thallium Pollutants in the Sulfuric Acid Industry

The sulfuric acid production process is relatively simple. The main processes include: combustion of sulfur-containing raw materials to produce sulfur dioxide process gas, purification and washing of the sulfur dioxide process gas, conversion of sulfur dioxide to sulfur trioxide, absorption of sulfur trioxide by concentrated sulfuric acid to produce sulfuric acid product, and washing of sulfuric acid tail gas to meet emission standards. Due to thallium's chalcophilic sulfur-loving nature, and since the sulfuric acid production process does not require additional auxiliary materials, thallium pollution in the sulfuric acid industry mainly comes from raw materials like pyrite. In the pyrite-based sulfuric acid process (Figure 8), pyrite is burned in a fluidized bed roaster. The vast majority of thallium attaches to the surface of particles and enters the purification system with the flue gas. Heavy metals like thallium are carried to the waste acidic water through the gas purification process; another portion becomes enriched in the cinder .

Fan Zhenzhen et al. collected samples of raw material pyrite and waste acidic water discharge points from typical pyrite-based sulfuric acid enterprises in China and measured the heavy metal thallium content in the corresponding samples. The thallium content in pyrite from some enterprises in Guangdong and Anhui was 2.57–30 mg/kg. The thallium mass concentration in waste acid from some enterprises in Anhui, Inner Mongolia, Hunan, and Hubei was 6.01–400 μg/L, indicating relatively high thallium content in waste acidic water, which requires treatment to meet standards before discharge.

4. Current Status of Thallium Treatment Methods

Currently, reported methods for thallium pollution control can be roughly divided into chemical precipitation, ion exchange, adsorption, solvent extraction, biological treatment, and phytoremediation.

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4.1. Chemical Precipitation Method

The principle of chemical precipitation is to convert dissolved thallium in the solution into an insoluble state through chemical reactions, achieving removal through filtration and separation. Common chemical precipitation methods mainly include oxidation-precipitation (alkaline precipitation) and sulfide precipitation.

1) Sulfide Precipitation Principle

Sulfide precipitation is a widely used method in industrial wastewater treatment. The principle is to add lime to industrial wastewater to make it alkaline, then add sulfide substances to generate sulfide precipitates, reducing the concentration of heavy metals in the water. The process flow is shown in Figure 1. This method has low processing costs and is widely used. The disadvantages are that it requires adding large amounts of sulfide, generating harmful gases like H_2S, and since Tl_2S is more stable under alkaline conditions, sulfide precipitation requires adjusting the pH above 10, involving large alkali dosages, which increases the salinity of the effluent, causing secondary environmental harm. The chemical equation for sulfide precipitation is:

$$2Tl^{+}+Na_2S=Tl_2S\downarrow+2Na^{+}$$

Thallium(I) chemical precipitation refers to adding an excess of saturated NaCl solution to thallium-containing wastewater to precipitate thallium(I) as TlCl $\downarrow$. In nature, under certain reducing conditions with low temperature and high sulfur, thallium(III) can be reduced to thallium(I) by sulfides, forming Tl_2S $\downarrow$ precipitate. However, this method does not achieve ideal treatment depth and increases effluent salinity. Thallium(III) chemical oxidation-reduction methods involve using oxidants such as hydrogen peroxide, potassium permanganate, sodium (calcium) hypochlorite, ferric sulfate/ferric chloride, the ferrite process, or combined technologies. Using chemical precipitation to treat heavy metal thallium-polluted wastewater has high application value, low cost, and wide availability of raw materials, and it is effective for other heavy metals like chromium, arsenic, lead, zinc, cadmium, and mercury. However, it also has drawbacks such as insufficient treatment depth and potential secondary pollution.

2) Oxidation-Precipitation Principle

The principle of oxidation-precipitation for thallium pollution control is as follows:

$$Tl+ + 3e \rightarrow Tl3+$$

$$Tl3+ + 3OH- \rightarrow Tl(OH)3\downarrow$$

Tl^{3+} begins to hydrolyze and form $Tl(OH)_3$ precipitate when the pH value is greater than 2.5. Therefore, in thallium-containing wastewater treatment, oxidants can be added to oxidize Tl^{+} to Tl^{3+}, which then hydrolyzes and precipitates (e.g., onto zinc leaching residue). Conventional oxidants typically include manganese powder, hydrogen peroxide, oxygen (oxygen-enriched air), potassium permanganate, and ozone. Among these, manganese powder and oxygen are particularly common, but neither can oxidize Tl^{+} to Tl^{3+} because Tl^{3+} is a stronger oxidant than manganese powder or oxygen. *(Note: The original text's redox equation was incorrect; oxidation involves loss of electrons. The corrected version is shown above.)

Thallium can form precipitates as Tl(III) (hydr)oxides in an oxidizing environment, meaning Tl can be removed from water/wastewater by adopting oxidation or reduction precipitation processes. Compared to Tl(I), Tl(III) can be more easily removed from water by forming Tl(III) (hydr)oxide precipitates followed by filtration.

Davies et al. used $KMnO_4$ for the oxidative precipitation of Tl(I), achieving a 99.8% removal rate with residual T1 concentration less than 2μg/L, but the dissolved Mn concentration (1 mg/L) exceeded the USEPA standard. Besides $KMnO_4$ oxidants, hydrogen peroxide (H_2O_2), ozone (O_3), sodium persulfate ($Na_2S_2O_8$), and sodium hypochlorite (NaClO) are also frequently applied in

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thallium-containing wastewater. High Tl removal rates (96-99%) were achieved via Fenton ($FeSO_4 \cdot 7H_2O + H_2O_2$) or Fenton-like ($Fe^0 + H_2O_2$) technology. The (hydr)oxide precipitation process is simple and widely applicable, but it inevitably has some disadvantages. The large amount of low-density sludge produced by (hydr)oxide precipitation leads to complicated dewatering and subsequent handling issues. It is generally only suitable for treating industrial wastewater containing high concentrations and simple compositions of heavy metals.

Tl(I) is the predominant species in solution over a wide pH range (0-14), making it very difficult to remove Tl by (hydr)oxide precipitation under alkaline conditions. However, under alkaline reducing (anaerobic) conditions, $Tl_2S(s)$ precipitate can form. Li et al. combined the Fenton process with sulfide precipitation to remove trace thallium (<1.0 μg/L) from wastewater, also achieving effective removal of other heavy metals. Compared to hydroxide precipitation processes, metal sulfide precipitates achieve high levels of heavy metal removal over a wide pH range. Furthermore, metal sulfide sludge is easier to handle due to its thickening properties. On the other hand, sulfide precipitation also faces some potential hazards. First, acidic conditions will lead to the production of toxic H_2S fumes, so precipitation needs to be carried out in a neutral or alkaline medium. Second, the separation of sulfide precipitates from wastewater by traditional separation processes (such as sedimentation or filtration) is not very effective . Overall, oxidation-reduction precipitation methods are promising, but relying solely on this technology may not be sufficient to meet China's wastewater discharge standard (<2 μg/L).

4.2. Adsorption Method

Adsorption is an effective method for treating heavy metal pollution. Its core principle is that adsorbents interact with heavy metal ions through Coulombic forces, van der Waals forces, or chemical bonds to achieve adsorption. Currently reported adsorbent materials mainly include activated carbon, (nano)metal oxides, and biological materials. Among them, metal oxides are considered the most effective materials for adsorbing Tl(I) in wastewater, such as hydrous ferric oxide, nano-alumina, magnetic Fe_3O_4 [xxiv], hydrous manganese oxide, titanium oxide [xxx], titanium nanotubes, etc., with hydrous manganese oxide and hydrous ferric oxide being particularly effective [xxx].

In the study by Brewster et al., electrolytically synthesized hydrous ferric oxide reduced the thallium concentration in wastewater from 0.032 ppm to below 0.005 ppm. Chemically precipitated manganese oxide, manganese oxide residue generated during the zinc electrolysis process, nano-manganese oxide, and nano-manganese oxide loaded within D001 resin all showed good effects on the removal of Tl(I) from wastewater. Liu Chenbu et al. directly oxidized manganese nitrate to generate manganese oxides, achieving a Tl^+ removal rate of 98.5% under alkaline conditions, but coexisting ions like Ca^{2+} and Mg^{2+} in the water interfered with thallium adsorption. Bidoglio et al. found that pH value affects the adsorption performance of Tl(I) on hydrous manganese oxide (HMO) particles. The adsorption capacity for thallium first decreased and then increased with increasing solution pH, being weakest at pH 4. This is due to the oxidation of Tl(I) to Tl(III) by MnO_2 under acidic conditions. The reaction formula is: *(See section 4.2 below)*

Rivera-Utrilla et al. first studied the adsorption capacity of activated carbon for thallium(I). The results showed that the removal rate of thallium(I) by activated carbon was higher than [likely a comparison term is missing], but there was an issue of insufficient treatment depth. (Nano)metal oxides, especially those containing iron-manganese oxides, have significant adsorption efficacy for thallium. The adsorption performance of thallium(I) on hydrous manganese oxide particles is affected by pH value. The adsorption capacity of thallium(I) first weakens and then strengthens with increasing pH. When the pH is 4, the adsorption capacity of hydrous manganese oxide for thallium(I) is the weakest [47]. Research on its adsorption

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mechanism indicates that MnO_2 oxidizes thallium(I) to thallium(III). The reaction equation is shown as formula :

$$MnO_2(s)+Tl^{+}+H^{+}+H_2O=Mn^{2+}+Tl(OH)_3$$

his shows that hydrogen ions promote the adsorption capacity of thallium(I) on the HMO surface under certain conditions, oxidizing thallium(I) to thallium(III), which then forms $Tl(OH)_3$ precipitate. The disadvantage of this method is that metal oxide particles are small,prone to causing secondary pollution, and are difficult to apply industrially.

4.3. Ion Exchange Method

The ion exchange method not only has good treatment capacity for heavy metal ions but can also purify organic matter in wastewater. The types of ion exchangers currently used are mainly ion exchange resins, zeolites, molecular sieves, etc. Research on thallium treatment primarily focuses on ion exchange resins. For example, Lin et al. used Chelex-100 to analyze the valence state distribution of thallium in lake water[10]. Ulrika K et al. used cation exchange column CG12A to quantitatively recover thallium(I) and thallium(III) in field water samples [49]. Xie Xiaoyan et al. used D401 ion exchange resin for adsorption separation and determination of thallium in manganese ore [50]. Wu Wenqi et al. used 001*7 (732) strong acid cation exchange resin to separate and determine trace thallium in high-purity indium [51]. The ion exchange method has advantages such as simple operation, good selectivity, and not prone to causing secondary pollution, making it one of the most promising treatment methods for water purification research. However, due to disadvantages such as ion exchangers easily reaching saturated adsorption capacity and cumbersome regeneration operations, it is not conducive to practical application under real conditions.

4.4. Solvent Extraction Method

Solvent extraction mainly refers to the use of organic solvents, based on the principle of "like dissolves like," to separate the solute and solvent from the original sample using a specific solvent, thereby extracting the solute. Generally, thallium can react with many organic polymers and has a certain selectivity, obeying a certain distribution coefficient, used for purification and separation of heavy metal thallium. However, since organic solvents are toxic, they can only be used to extract and separate specific, small amounts of thallium, mostly for qualitative research.

4.5. Biological Treatment Method

Biological treatment mainly relies on the action of enzymes, using the metabolic activities of microorganisms, such as bacteria and fungi, to decompose and transform pollutants, thereby achieving remediation. Biological treatment methods have advantages such as wide sources, low cost, good treatment effectiveness, and biological sustainability. However, since the use of biological treatment for heavy metal-polluted wastewater is mostly for experimental exploration, whether large-scale cultivation of biological strains under actual conditions would cause secondary damage remains undetermined.

5. Conclusion

This study, targeting the water-related nodes involved in the hydrometallurgical zinc wastewater process, investigates the migration forms of the thallium element, identifies the content and speciation patterns of thallium, supports the refined management and treatment of thallium-containing wastewater in hydrometallurgical zinc production, and provides a basis for optimizing thallium-containing wastewater treatment processes. It holds significant theoretical and practical importance for the transformation, upgrading, and green development of the hydrometallurgical zinc industry.

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