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Use-Phase Environmental Risk and Sustainability Assessment of Liquid Polyferric Sulfate Produced Through Comprehensive Utilization of Waste Sulfuric Acid

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Abstract

Comprehensive utilization of hazardous industrial waste can recover resources but may also transfer residual hazardous constituents into downstream products. Preparing water treatment agents with low environmental risk is an important path towards sustainable development for the sulfuric acid industry. Following the framework of hazard identification, exposure assessment, hazard characterization, and risk characterization in the forthcoming Chinese national standard "General Principles for Environmental Risk Assessment of Products from Comprehensive Utilization of Hazardous Wastes", this case study evaluated the use-phase human-health and aquatic ecological risks of a liquid polyferric sulfate coagulant produced from waste sulfuric acid. As, Pb, Hg, Cr, Zn, and Ni were reported in the product at 8.6×10^{-4}, 8.6×10^{-5}, 1.5×10^{-7}, 4.78×10^{-3}, 7.96×10^{-3}, and 2.10×10^{-4} mg/L, respectively. Three predefined scenarios were considered: direct worker dermal contact during dosing, indirect dermal contact with receiving water, and aquatic exposure after discharge. Under the case-study parameterization, the total carcinogenic and non-carcinogenic risks were 2.46×10^{-7} and 3.90×10^{-4} for occupational exposure and 8.04×10^{-18} and 5.47×10^{-15} for indirect population exposure, respectively. The available ecological-effect dataset supported only a partial Hg-based screening. Thus, the conclusions are limited to the measured product composition, selected scenarios, assumptions, and benchmarks and do not constitute a comprehensive occupational, life-cycle, or multimedia environmental-safety assessment.

Keywords: resource recovery; sustainability; coagulant; dermal exposure; risk characterization; aquatic toxicity

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1. Introduction

Because of hazardous properties such as toxicity, corrosivity, and reactivity, hazardous waste has long been a major focus of environmental risk prevention and control for solid waste. Previous studies reported that as hazardous-waste generation increased, comprehensive utilization became increasingly important for reducing disposal pressure, improving resource-use efficiency, and promoting recycling [1–4]. Compared with conventional industrial raw materials, hazardous waste was also reported to originate from more complex sources and to exhibit greater compositional

variability, with substantial fluctuations in both the types and concentrations of hazardous constituents in the feedstocks [5–8]. Previous studies further indicated that if the safety of comprehensive utilization was judged solely on whether the resulting products met conventional quality standards, environmental risks associated with the transfer of hazardous constituents into downstream applications might not be adequately identified [9–16]. Therefore, systematic evaluation of hazardous substances, exposure receptors, exposure pathways, and risk levels in relation to the actual use of utilization products is an important technical step toward the safe comprehensive utilization of hazardous waste.

Waste sulfuric acid was reported to be a common hazardous waste generated by industrial processes and to be amenable to comprehensive utilization through cascade use, purification for use as a substitute raw material, or conversion into inorganic salts [17]. According to China's National Catalogue of Hazardous Wastes (2025 Edition) [18], the waste acid considered in this case is classified under HW34, the national category for waste acids, and is generated mainly during metal-surface pickling and rust removal in steel-pipe production and processing and during waste-gas treatment in the chemical industry. The production of sulfate-based water treatment agents from waste sulfuric acid enables recovery of the acid resource while yielding a utilization product with a stable end use.

Polyferric sulfate was widely reported as a water-treatment coagulant whose production requires sulfuric acid and iron salts [19,20]. The substitution of waste sulfuric acid for part of the conventional acid feedstock has resource-recovery value; however, hazardous elements such as arsenic, lead, mercury, chromium, nickel, and zinc may be present in the waste acid. Previous work also applied environmental risk assessment to a water treatment agent prepared from industrial waste acid [21], illustrating the importance of evaluating product-specific exposure pathways in addition to conventional product quality. Potential adverse effects associated with the transfer of hazardous constituents through water-treatment products were previously recognized for occupational populations, the general population, and aquatic organisms [21,22]. Accordingly, the finished liquid polyferric sulfate coagulant was selected as the case-study product. The assessment followed the forthcoming Chinese national standard "General Principles for Environmental Risk Assessment of Products from Comprehensive Utilization of Hazardous Wastes" (hereafter, the "General Principles") and focused on the selected use-phase exposure scenarios described below. Using waste sulfuric acid as the raw material to produce polymeric ferric sulfate water treatment agents with low environmental risk is an important path towards sustainable development for the sulfuric acid industry.

1.1. Comprehensive Utilization of Waste Sulfuric Acid for Polyferric Sulfate Production

Water treatment agents, including polyferric sulfate, are produced by the case-study enterprise for use in industrial water, recirculating water, and various wastewater-treatment applications. The archived case materials identify the waste-acid feedstock as waste sulfuric acid supplied by enterprises in Changzhou and surrounding areas; these sources were reported by the enterprise as relatively stable. The comprehensive-utilization facility was designed with a waste sulfuric acid utilization capacity of 80,000 t/a and a polyferric sulfate production capacity of 200,000 t/a. Before being accepted by the facility, the waste acid is subjected to quality control in accordance with the relevant requirements of Water Treatment Chemicals—Polyferric Sulfate (GB/T 14591-2016) [23]. Waste acid exceeding the specified acceptance limits is rejected.

1.2. Assessment Objective

The subject of this assessment is the finished liquid polyferric sulfate coagulant produced through the comprehensive utilization of waste sulfuric acid. The study evaluates selected direct and indirect risks arising during downstream wastewater-treatment use rather than conducting a comprehensive assessment of the production facility or intermediate materials. Specifically, hazardous substances potentially present in the finished product were identified, three case-study exposure scenarios were established, health risks to occupational and indirectly exposed populations were characterized for dermal contact, and the available aquatic ecological screening information was evaluated for receiving-water exposure.

1.3. Assessment Method

In accordance with the methodological requirements of the "General Principles", hazard identification was first conducted on the basis of the raw and auxiliary materials, production process, and relevant hazardous-substance lists. Sampling and analysis were then used to identify hazardous substances reported in the finished product. Based on product use and the contact routes specified for the case study, assessment receptors and exposure pathways were defined, and the corresponding health-exposure and ecological-exposure quantities were characterized. Hazard characterization was subsequently conducted using the toxicological and ecological-effect parameters available in the archived case dataset. Finally, carcinogenic risk, non-carcinogenic risk, and ecological risk characterization values were compared with the adopted screening benchmarks. This study is therefore a case-specific screening assessment of selected product-use pathways and does not constitute a complete occupational-hygiene, life-cycle, or multimedia exposure assessment.

2. Experimental and Case-Study Data

2.1. Basic Information and Data

2.1.1. Hazardous Waste Information

The waste acid evaluated in this case was generated mainly during metal-surface pickling and rust removal in steel-pipe production and processing enterprises and from waste-gas treatment in the chemical industry, and it was classified as HW34 waste acid. Table 1 presents five archived case-study samples collected from waste-acid sources in Changzhou and surrounding areas. The samples demonstrate that sulfuric acid content and metal impurities varied among the available source records; however, the five samples were not collected as a statistically designed regional survey. Sampling dates, replicate measurements, and complete batch-level metadata were not retained in the archived case materials and are therefore not reconstructed here. The table is used to illustrate the observed case-study composition range rather than to claim statistical representativeness of all regional waste acid.

To limit the transfer of feedstock variability to the resulting comprehensive-utilization product, the enterprise applied operational acceptance criteria for incoming waste acid on the basis of the quality control requirements for polyferric sulfate products. These criteria were operational control limits and were not derived in this study from a metal-by-metal quantitative transfer model. The controlled parameters include sulfuric acid, Fe(II), As, Pb, Cd, Hg, Cr, and Zn, as shown in Table 2. Ni was not included in the legacy incoming-waste control list, although it was later detected in the product; this inconsistency is identified as a monitoring gap, and inclusion of Ni in future incoming-waste control is recommended.

Table 1. Analytical results for waste acid samples (unit: %).

Hazardous Waste Category	Analyte	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Waste sulfuric acid	Sulfuric acid	20.28	4.14	70.21	43.65	97.6
	Ferrous iron	2.64	7.71	—	—	—
	Lead	1×10^{-4}	1×10^{-4}	—	2.7×10^{-6}	—
	Arsenic	4×10^{-5}	1.6×10^{-4}	—	1.2×10^{-6}	—
	Mercury	2.8×10^{-7}	—	—	5×10^{-6}	2.6×10^{-6}
	Chromium	5.8×10^{-3}	5.4×10^{-3}	—	1.5×10^{-3}	—
	Nickel	2.8×10^{-4}	2.1×10^{-4}	—	—	7×10^{-5}
	Zinc	0.014	4.5×10^{-3}	1×10^{-4}	6.5×10^{-4}	—
	Cadmium	—	—	—	—	4.8×10^{-6}

Note: "—" indicates below the detection limit.

Table 2. Quality control requirements for incoming waste acid.

Hazardous Waste Category	Requirement	
Waste sulfuric acid	Sulfuric acid	≥10%
	Fe(II)	≥3%
	Arsenic (As)	≤0.0005%
	Lead (Pb)	≤0.004%
	Cadmium (Cd)	≤0.0005%
	Mercury (Hg)	≤0.00005%
	Chromium (Cr)	≤0.01%
	Zinc (Zn)	≤0.15%

2.1.2. Process for Producing Polyferric Sulfate from Waste Sulfuric Acid

Waste acid streams of different concentrations that meet the acceptance criteria are first combined in a storage tank. Based on the operating experience of the case-study facility, sulfuric acid accounts for approximately 29% of the total solution mass after mixing; accordingly, 29% waste sulfuric acid is used as the basis for the reported material-flow summary. After the waste acid is analyzed, a formulation sheet is prepared, and the required amount is pumped into the batching tank. Ferrous sulfate is added concurrently to adjust the iron concentration, and water is added for dilution. After dilution, the acid content of the feed solution is approximately 9% of the total solution mass. The mixture is then transferred to a closed reactor, where ferrous ions are oxidized to ferric ions at temperatures not exceeding 75 °C; pure oxygen is used as the principal oxidant, while sodium nitrite is added as an oxidation-promoting auxiliary reagent and participates in the nitrogen-containing side-reaction cycle. Polyferric sulfate is subsequently formed through hydrolysis and polymerization. After completion of the reaction, the product is cooled to room temperature and pumped into the finished-product tank for sale. The storage, batching, reaction, and finished-product storage stages correspond to off-gas points G1-1, G1-2, G1-3, and G1-4, respectively (Figure 1). The archived case materials do not provide complete information on batch/continuous operation, residence-time profile,

instantaneous oxygen dosage, detailed pH trajectory, or Fe(II)-to-Fe(III) conversion; these parameters are therefore not reconstructed.

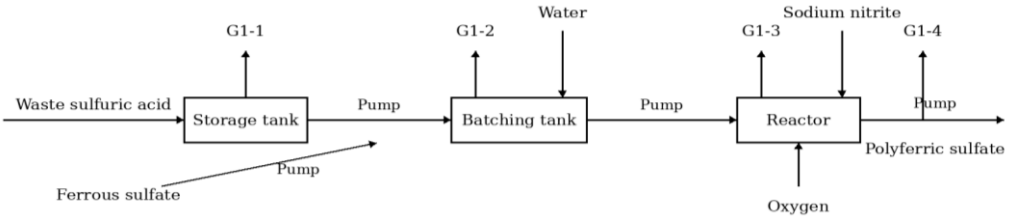


Figure 1. Process flow diagram for polyferric sulfate production.

The principal reactions reported for the case study include catalytic oxidation, nitrogen-containing side reactions, hydrolysis, and polymerization. The hydrolysis and polymerization expressions are schematic representations of polymeric ferric hydroxo-sulfate formation rather than unique molecular stoichiometric reactions. Sodium nitrite is described separately as an oxidation-promoting auxiliary reagent, while the side-reaction sequence demonstrates that it participates in the nitrogen-containing reaction cycle rather than acting as an inert catalyst. The equations are numbered consistently below.

Main oxidation reaction:

$$4FeSO_4 + 2H_2SO_4 + O_2 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O \quad (1)$$

Representative side reactions:

$$2NaNO_2 + H_2SO_4 \rightarrow Na_2SO_4 + 2HNO_2 \quad (2a)$$

$$2FeSO_4 + H_2SO_4 + 2HNO_2 \rightarrow Fe_2(SO_4)_3 + 2NO + 2H_2O \quad (3b)$$

$$2NO + O_2 \rightleftharpoons 2NO_2 \quad (4c)$$

$$2FeSO_4 + H_2SO_4 + NO_2 \rightarrow Fe_2(SO_4)_3 + H_2O + NO \quad (5d)$$

The NO produced is further oxidized to NO_2, and the resulting NO_2 is used to oxidize ferrous salts, thereby sustaining a cyclic oxidation process.

Hydrolysis (schematic):

$$Fe_2(SO_4)_3 + nH_2O \rightarrow Fe_2(OH)_n(SO_4)_{(6-n)/2} + (n/2)H_2SO_4 \quad (6)$$

Polymerization (schematic):

$$m\left[Fe_2(OH)_n(SO_4)_{(6-n)/2}\right] \rightarrow \left[Fe_2(OH)_n(SO_4)_{(6-n)/2}\right]_m \quad (7)$$

2.2. Raw and Auxiliary Materials

The main raw and auxiliary materials used for polyferric sulfate production are 29% waste sulfuric acid, 90% ferrous sulfate, oxygen, 99% sodium nitrite, and water. Their annual consumption and procurement categories are listed in Table 3, and their principal physicochemical properties and toxicity information are presented in Table 4. Supplier names and countries of origin were not retained in the archived case materials; therefore, no unverified supplier information is added.

Table 3. Consumption of main raw and auxiliary materials.

Product	Name	Specification	Annual Consumption (t/a)	Source and Transport
Polyferric sulfate (200,000 t/a)	Waste sulfuric acid	29%	67,200	External transport
	Ferrous sulfate	90%	101,300	Purchased externally
	Oxygen	—	2800	Purchased externally
	Sodium nitrite	99%	200	Purchased externally
	Water	—	22,129.51	Pipeline

Table 4. Physicochemical properties of the main raw and auxiliary materials.

No.	Name	Characteristics	Toxicity
1	Sulfuric acid H_2SO_4	Transparent, colorless oily liquid; Density: 1.841 g/cm^3; Melting point: 10.46 °C; Boiling point: 210–338 °C; non-flammable (flash point not applicable).	LD_{50}: 2140 mg/kg (rat, oral).
2	Ferrous sulfate $FeSO_4 \cdot 7H_2O$	Appearance: blue-green monoclinic crystals or granules, odorless; Molecular weight: 278.01; Vapor pressure: 19.418 kPa at 25 °C; Melting point: 64 °C; Solubility: soluble in water, slightly soluble in alcohol, and soluble in anhydrous methanol; Relative density: 1.897 (water = 1).	Acute toxicity: LD_{50}: 1520 mg/kg (mouse, oral).
3	Oxygen O_2	Appearance: colorless, odorless gas; Molecular weight: 32; Vapor pressure: 506.62 kPa at −164 °C; Melting point: −218.8 °C; Boiling point: −183.1 °C; Solubility: sparingly soluble in water; Relative density: 1.14 (water = 1, −183 °C); 1.43 (air = 1, −252 °C).	/
4	Sodium nitrite $NaNO_2$	Appearance: white or pale-yellow fine crystals, odorless, with a slightly salty taste; Molecular weight: 68.995; Vapor pressure: /; Melting point: 271 °C; Boiling point: 320 °C; Solubility: readily soluble in water and liquid ammonia; aqueous solutions are alkaline; slightly soluble in absolute ethanol, methanol, and ether; Relative density: 2.17 (water = 1).	Acute toxicity: highly toxic. LD_{50}: 85 mg/kg (rat, oral); 65 mg/kg (rat, intravenous).

According to the archived case-study records, annual inputs of 67,200 t of waste sulfuric acid, 101,300 t of ferrous sulfate, 2800 t of oxygen, 200 t of sodium nitrite, 22,129.51 t of water, and 6674.25 t of recycled water were reported. Table 5 is presented as the reported overall material-flow summary. Because the archived source does not provide species-resolved closure for every oxygen-, nitrogen-, trace-metal-, wastewater-, and solid-residue stream, the table is not interpreted as a complete elemental mass balance.

Table 5. Reported material-flow summary for production through comprehensive utilization of waste sulfuric acid (unit: t).

Input	Output			
	Product	Waste Gas	Wastewater	Solid Waste
Waste sulfuric acid 67,200 Ferrous sulfate 101,300 Oxygen 2800 Sodium nitrite 200 Water 22,129.51 Recycled water 6674.25	Liquid polyferric sulfate 200,000	G1-1: sulfuric acid mist 1.9488; G1-2: sulfuric acid mist 1.949; G1-3: sulfuric acid mist 3.361; nitrogen oxides (archived source value ambiguous); water vapor 290.12; G1-4: sulfuric acid mist 1.51	/	/
Total: 200,303.76	200,000	303.76	/	/
	Total: 200,303.76			

Note: The original case table contains an ambiguous nitrogen-oxides numerical entry. Because the archived source value cannot be unambiguously reconstructed, no corrected NOx mass is inferred here. Table 5 is therefore treated as a reported process-flow summary rather than a species-resolved elemental mass balance.

2.3. Products

The comprehensive-utilization product evaluated in this case is a liquid polyferric sulfate coagulant with an annual output of 200,000 t/a. It is used mainly in industrial wastewater-treatment plants in Changzhou, Jiangsu Province. Product quality is controlled in accordance with Water Treatment Chemicals—Polyferric Sulfate (GB/T 14591-2016), with specified parameters including total iron, reducing substances, basicity, pH, density, insoluble matter, As, Pb, Cd, Hg, Cr, Zn, and Ni, as shown in Table 6. Symbols w_1–w_{11} denote the mass fractions of the corresponding quality-control items.

Table 6. Quality control requirements for liquid polyferric sulfate products.

Item	Requirement
Mass fraction of total iron, w_1/%	11.0
Mass fraction of reducing substances (as Fe^{2+}), w_2/%	0.10
Basicity, w_3/%	5.0~20.0
pH (10 g/L aqueous solution)	1.5~3.0
Density (20 °C) (g/cm^3)	1.45
Mass fraction of insoluble matter, w_4/%	0.3
Mass fraction of arsenic (As), w_5/%	5×10^{-4}
Mass fraction of lead (Pb), w_6/%	1×10^{-3}
Mass fraction of cadmium (Cd), w_7/%	2.5×10^{-4}
Mass fraction of mercury (Hg), w_8/%	5×10^{-5}
Mass fraction of chromium (Cr), w_9/%	2.5×10^{-3}
Mass fraction of zinc (Zn), w_{10}/%	5×10^{-3}
Mass fraction of nickel (Ni), w_{11}/%	5×10^{-3}

3. Assessment Methodology

3.1. Hazard Identification

Identification of Hazardous Substances

Hazard identification was initiated by examining the raw and auxiliary materials and the production process. Waste sulfuric acid, ferrous sulfate, oxygen, and sodium nitrite were identified as the raw and auxiliary materials used in production. Enterprise testing showed that, in addition to sulfuric acid and ferrous iron, Pb, As, Hg, Cr, Ni, and Zn were present in the waste sulfuric acid, whereas Cd was below the detection limit. Detailed results are presented in Table 7.

Table 7. Analytical results for the main components of waste sulfuric acid.

Analyte	Unit	Result
Sulfuric acid	%	29
Ferrous iron	%	3.4
Lead	%	6.7×10^{-5}
Arsenic	%	6.7×10^{-5}
Mercury	%	1×10^{-7}
Chromium	%	3.73×10^{-3}
Nickel	%	1.63×10^{-4}
Zinc	%	6.2×10^{-3}
Cadmium	%	—

Note: "—" indicates below the detection limit.

Compositional specifications for the ferrous sulfate and sodium nitrite raw materials were provided in the case study on the basis of GB/T 664-2011 [24] and GB/T 2367-2016 [25], respectively, as shown in Tables 8 and 9. Table 8 documents the purity requirement and impurity limits for ferrous sulfate heptahydrate, while Table 9 documents the sodium nitrite specification and possible nitrate/chloride impurities considered during subsequent hazard identification.

Table 8. Composition of ferrous sulfate heptahydrate.

Name	Chemical Purity
Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), w/%	98.0~101.0
Water-insoluble matter, w/%	≤0.02
Chloride (Cl), w/%	≤0.005
Total nitrogen (N), w/%	—
Phosphate (PO_3), w/%	≤0.002
Arsenic (As), w/%	≤0.0002
Manganese (Mn), w/%	—
Ferric iron (Fe), w/%	≤0.10
Copper (Cu), w/%	≤0.01

Zinc (Zn), w/%	≤0.02
Lead (Pb), w/%	≤0.005
Ammonia-nonprecipitable matter (as sulfate), w/%	≤0.2

Note: Table 8 reports a main-component purity specification together with maximum impurity limits from the cited reagent standard; the listed values are specification limits and are not additive components expected to sum to 100%.

Table 9. Composition of sodium nitrite.

Name	Requirement		
	Superior Grade	**First Grade**	**Qualified Grade**
Sodium nitrite ($NaNO_2$, dry basis), w/%	≥99.0	≥98.5	≥98.0
Sodium nitrate (dry basis), w/%	≤0.8	≤1.3	—
Chloride (as NaCl, dry basis), w/%	≤0.10	≤0.17	—
Water-insoluble matter (dry basis), w/%	≤0.05	≤0.06	≤0.10
Moisture, w/%	≤1.4	≤2.0	≤2.5
Looseness (non-caking fraction), w/%		≥85	

Based on the raw and auxiliary materials and the reported reaction/impurity pathways, a broad screening inventory of substances potentially relevant to the polyferric sulfate coagulant was established. The purpose of this inventory is hazard identification only; inclusion in the list does not indicate that a substance is formed or present at an environmentally significant concentration. Actual product testing was subsequently used to narrow the substances of concern, as described in Section 3.2. Chemical identifiers in the screening inventory were rechecked during revision; corrected CAS entries are highlighted in red.

3.2. Sampling and Analysis

The potential substances listed in Table 10 were further screened using the relevant documents listed in the appendix to the "General Principles". The hazardous substances identified for the case study included nitrate, chloride, arsenic and its compounds, arsenic trichloride, lead and its compounds, lead phosphate, cadmium and its compounds, cadmium sulfate, cadmium chloride, mercury and its compounds, mercuric chloride, chromium and its compounds, zinc compounds, copper compounds, and nickel compounds, as shown in Table 11.

Table 10. Screening list of potential substances considered during hazard identification.

No.	Class	Hazardous Substance	CAS Number
1	Acids	Sulfuric acid	7664-93-9
		Nitric acid	7697-37-2
		Nitrous acid	7782-77-6
		Phosphoric acid	7664-38-2
		Hydrochloric acid	7647-01-0

2	Iron Compounds	Ferric sulfate	10028-22-5
		Ferric nitrate	10421-48-4
		Ferric phosphate	10045-86-0
		Ferric chloride	7705-08-0
3	Arsenic and Its Compounds	Arsenic	7440-38-2
		Arsenic trichloride	7784-34-1
		Arsenic trifluoride	7784-35-2
4	Lead and Its Compounds	Lead	7439-92-1
		Lead sulfate	7446-14-2
		Lead nitrate	10099-74-8
		Lead phosphate	7446-27-7
		Lead tetrachloride	13463-30-4
5	Cadmium and Its Compounds	Cadmium	7440-43-9
		Cadmium sulfate	10124-36-4
		Cadmium nitrate	10325-94-7
		Cadmium phosphate	13847-17-1
		Cadmium chloride	10108-64-2
6	Mercury and Its Compounds	Mercury	7439-97-6
		Mercuric sulfate	7783-35-9
		Mercury nitrate	10045-94-0
		Mercury phosphate	7782-66-3
		Mercuric chloride	7487-94-7
7	Chromium and Its Compounds	Chromium	7440-47-3
		Chromium sulfate	10101-53-8
		Chromium nitrate	13548-38-4
		Chromium phosphate	7789-04-0
		Chromium trichloride	10025-73-7
8	Zinc Compounds	Zinc sulfate	7733-02-0
		Zinc nitrate	7779-88-6
		Zinc phosphate	7779-90-0
		Zinc chloride	7646-85-7
9	Copper and Its Compounds	Copper	7440-50-8
		Copper sulfate	7758-98-7
		Copper nitrate	3251-23-8
		Copper phosphate	7798-23-4
		Copper chloride	7447-39-4

10	Nickel Compounds	Nickel sulfate	7786-81-4
		Nickel nitrate	13138-45-9
		Nickel phosphate	10381-36-9
		Nickel chloride	7718-54-9
11	Manganese Compounds	Manganese sulfate	7785-87-7
		Manganese nitrate	10377-66-9
		Manganese phosphate	39041-31-1
		Manganese chloride	7773-01-5
12	Sodium Compounds	Sodium sulfate	7757-82-6
		Sodium nitrate	7631-99-4
		Sodium nitrite	7632-00-0
		Sodium phosphate	7601-54-9
		Sodium chloride	7647-14-5

In accordance with the sampling and analytical requirements adopted in the case study, the identified hazardous substances were analyzed to determine whether they were reported in the finished product and, if so, at what concentrations. The results are presented in Table 12. Nitrate, chloride, cadmium and related compounds, and copper and its compounds were reported below the detection limits, whereas As, Pb, Hg, Cr, Zn, and Ni were reported as detected. Table 12 is based on archived case-study product-analysis records rather than a statistically replicated batch-characterization campaign. The archived summary did not retain sampling dates, replicate-level standard deviations, recoveries, blanks, or complete method-specific quantification-limit documentation; these limitations are therefore stated explicitly, and the reported concentrations are interpreted as case-specific analytical values rather than population-representative statistics.

Table 11. Hazardous substances identified in the polyferric sulfate product.

No.	Hazardous Substance	CAS Number
1	Nitrate	14797-55-8
2	Chloride	16887-00-6
3	Arsenic and Its Compounds	7440-38-2
4	Arsenic Trichloride	7784-34-1
5	Lead and Its Compounds	7439-92-1
6	Lead Phosphate	7446-27-7
7	Cadmium and Its Compounds	7440-43-9
8	Cadmium Sulfate	10124-36-4
9	Cadmium Chloride	10108-64-2
10	Mercury and Its Compounds	7439-97-6
11	Mercuric Chloride	7487-94-7
12	Chromium and Its Compounds	7440-47-3

13	Zinc Compounds	7440-66-6
14	Copper Compounds	7440-50-8
15	Nickel Compounds	7440-02-0

Table 12. Measured concentrations of hazardous substances in polyferric sulfate.

No.	Hazardous Substance	Concentration/(mg·L^{-1})	Analytical Method
1	Nitrate	/	GB/T 35496-2017 [26]
2	Chloride	/	GB/T 3050-2000 [27]
3	Arsenic (As)	8.6×10^{-4}	GB/T 14591-2016 [23]
4			
5	Lead (Pb)	8.6×10^{-5}	GB/T 14591-2016 [23]
6			
7	Cadmium and Its Compounds	/	GB/T 14591-2016 [23]
8	Cadmium Sulfate	/	GB/T 14591-2016 [23]
9	Cadmium Chloride	/	GB/T 14591-2016 [23]
10	Mercury (Hg)	1.5×10^{-7}	GB/T 14591-2016 [23]
11			
12	Chromium (Cr)	4.78×10^{-3}	GB/T 14591-2016 [23]
13	Zinc (Zn)	7.96×10^{-3}	GB/T 14591-2016 [23]
14	Copper and Its Compounds	/	GB/T 43098.2-2023 [28]
15	Nickel (Ni)	2.10×10^{-4}	GB/T 14591-2016 [23]

Note: "/" indicates below the detection limit. Values are archived case-study results; complete batch-level QA/QC and quantification-limit metadata were not retained in the summary record.

3.3. Exposure Assessment

3.3.1. Exposure Pathways and Assessment Receptors

Liquid polyferric sulfate is used mainly as a coagulant for wastewater treatment. Based on the common exposure scenarios specified in the "General Principles" for products from the comprehensive utilization of hazardous waste and on the actual downstream use considered in the case study, three use-phase scenarios were selected. Scenario 1 represents direct occupational dermal contact that may occur because of splashing or leakage during coagulant dosing. Scenario 2 represents indirect dermal contact of the general population with receiving water during swimming after wastewater-treatment effluent enters a river. Scenario 3 represents aquatic exposure after discharge to the receiving water. These scenarios were selected as predefined screening pathways for the finished product; production-related inhalation of sulfuric acid mist or NOx, accidental ingestion, eye contact, maintenance activities, sludge handling, drinking-water ingestion, fish consumption, sediment contact, and irrigation are outside the present scope and require separate exposure data and models.

Because the hazardous substances listed in the Integrated Wastewater Discharge Standard (GB 8978) [29] do not fully encompass those identified in this case, quantitative health and ecological risk assessments were still required.

3.3.2. Health Exposure Assessment

To maintain a conservative screening basis within the selected scenarios, the concentrations of hazardous substances in the liquid polyferric sulfate product were directly used in Scenario 1 as worker dermal-contact concentrations. A polyferric sulfate dosage of 7.00×10^{-5} t/t wastewater was reported in the case investigation. In Scenario 2, it was assumed that no coagulant was lost during wastewater treatment and that the entire dose entered the river with the effluent; no additional dilution by river water was considered. Scenario 3 likewise used the wastewater-treatment effluent concentration before river dilution as the ecological exposure concentration. These assumptions intentionally represent simplified screening conditions and should not be interpreted as a complete multimedia fate-and-exposure model.

Average daily dermal exposure for the human-health assessment was represented using the water-contact dermal equation in WS/T 777-2021 [30]. The equation documented in the previous manuscript incorrectly mixed the soil-contact terms AF and ABS with the water-contact parameter table. It has therefore been corrected to the water-contact formulation and is numbered sequentially as Equation (5).

$$\mathrm{ADD_{der}} = \frac{\mathrm{C} \times \mathrm{CF} \times \mathrm{SA} \times \mathrm{PC} \times \mathrm{EF} \times \mathrm{ED} \times \mathrm{ET}}{\mathrm{BW} \times \mathrm{AT}} \quad (8)$$

where ADD_{der} is the average daily dermal exposure to a hazardous substance, mg/(kg·d); C is the concentration of the hazardous substance in water, mg/L; CF is the conversion factor, L/cm^3; SA is the skin contact area, cm^2; PC is the skin permeability coefficient, cm/h; EF is the exposure frequency, d/a; ED is the exposure duration, a; ET is the exposure time, h/d; BW is body weight, kg; and AT is the averaging time, d. For non-carcinogenic effects, AT corresponds to the exposure duration in days; for carcinogenic effects, AT is fixed at 25,550 d (70 years).

The exposure parameters used in the archived case study were selected with reference to the Chinese Exposure Factors Handbook, WS/T 777-2021 [30], GBZ 2.1-2019 [31], and other case-study sources. Table 13 reports the parameter values available in the archived summary. The source table identifies PC as a chemical-specific lookup parameter but does not retain the individual lookup values or the complete source worksheet; therefore, the summary table alone does not allow an independent reconstruction of every value in Table 14. This limitation is explicitly acknowledged rather than resolved by inventing missing parameters.

Using the exposure-parameter framework in Table 13 and the exposure concentrations in Table 14, the archived case-study calculation outputs for carcinogenic and non-carcinogenic average daily exposure are reported in Table 15. Because the chemical-specific PC lookup values were not retained in the archived summary, these outputs are presented as case-study results rather than as a newly and independently reproduced calculation. Within the reported case-study parameterization, occupational exposure values were substantially higher than the indirect population values because of the markedly different exposure concentrations and scenario assumptions.

Table 13. Recommended exposure parameter values.

Parameter	Definition	Unit	Reference Value		Parameter Source
			Occupational Population	Consumer/Indirectly Exposed Population	
C	Chemical concentration in liquid	$mg \cdot L^{-1}$	Measured	Measured	Measured
CF	Conversion factor	$L \cdot cm^{-3}$	1×10^{-3}	1×10^{-3}	WS/T 777—2021 [30]
SA	Skin contact area	cm^2	1200	16,000	Chinese Exposure Factors Handbook: recommended hand/head skin area for the Chinese population
PC	Dermal permeability coefficient	$cm \cdot h^{-1}$	Chemical-specific lookup value	Chemical-specific lookup value	WS/T 777-2021 [30]; individual lookup values not retained in archived summary
EF	Exposure frequency	$d \cdot a^{-1}$	225	9.8×10^{-6}	Archived case-study parameter; complete source worksheet not retained
ED	Exposure duration	a	30	70	
ET	Exposure time	$h \cdot d^{-1}$	0.25	0.086	GBZ 2.1—2019 [31]
BW	Average body weight	kg	61.9	61.9	Chinese Exposure Factors Handbook: recommended body weight for the Chinese population
AT carcinogenic	Average lifetime exposure time	d	25,550	25,550	WS/T 777—2021 [30]
AT non-carcinogenic	Average exposure time	d	10,950	25,550	WS/T 777—2021 [30]

Table 14. Exposure concentrations of hazardous substances under the three exposure scenarios.

No.	Hazardous Substance	Exposure Concentration/$(mg \cdot L^{-1})$		
		Exposure Scenario 1	Exposure Scenario 2	Exposure Scenario 3
1	Arsenic (As)	8.6×10^{-4}	6.02×10^{-8}	6.02×10^{-8}
2	Lead (Pb)	8.6×10^{-5}	6.02×10^{-9}	6.02×10^{-9}
3	Mercury (Hg)	1.5×10^{-7}	1.05×10^{-11}	1.05×10^{-11}
4	Chromium (Cr)	4.78×10^{-3}	3.35×10^{-7}	3.35×10^{-7}
5	Zinc (Zn)	7.96×10^{-3}	5.57×10^{-7}	5.57×10^{-7}
6	Nickel (Ni)	2.10×10^{-4}	1.47×10^{-8}	1.47×10^{-8}

Table 15. Calculated exposure doses.

No.	Hazardous Substance	Occupational Population Average Daily Exposure, ADD/(mg/(kg·d))		Consumer or Indirectly Exposed Population Average Daily Exposure, ADD/(mg/(kg·d))	
		Carcinogenic	Non-Carcinogenic	Carcinogenic	Non-Carcinogenic
1	Arsenic (As)	1.10×10^{-9}	2.57×10^{-9}	3.59×10^{-20}	3.59×10^{-20}
2	Lead (Pb)	1.10×10^{-10}	2.57×10^{-10}	3.59×10^{-21}	3.59×10^{-21}
3	Mercury (Hg)	1.92×10^{-13}	4.48×10^{-13}	6.27×10^{-24}	6.27×10^{-24}
4	Chromium (Cr)	1.22×10^{-8}	2.86×10^{-8}	3.99×10^{-19}	3.99×10^{-19}
5	Zinc (Zn)	1.02×10^{-8}	2.38×10^{-8}	6.65×10^{-19}	6.65×10^{-19}
6	Nickel (Ni)	2.69×10^{-10}	6.27×10^{-10}	1.75×10^{-20}	1.75×10^{-20}

3.3.3. Ecological Exposure Assessment

A survey of aquatic organisms in waters near the river outfall was included in the case study. Economically important aquatic species in the area included eels, obscure pufferfish, tapertail anchovy, and Chinese mitten crab, whereas rare and endangered species included the Yangtze finless porpoise and Chinese sturgeon. Considering common aquatic biota in the Yangtze River Delta water system, common carp, crabs, algae, and rotifers were selected as representative sensitive organisms. Ecological exposure concentrations were taken from Exposure Scenario 3 in Table 13.

3.4. Hazard Characterization

3.4.1. Human-Health Toxicity Assessment

For the human-health toxicity assessment, the archived case-study framework used toxicity parameters attributed to dose–response information from the U.S. Integrated Risk Information System (IRIS) and related screening sources. The corrected chemical identifiers are shown in Table 16. However, the archived case file does not preserve a parameter-by-parameter IRIS retrieval date/version or a complete oral-to-dermal conversion worksheet; therefore, the values are retained and interpreted only as case-study screening parameters, and no unverified provenance or route-conversion factors are reconstructed. In addition, only total Cr and total As concentrations were measured; species-resolved Cr(III)/Cr(VI) and arsenic data were not available. Accordingly, the Cr- and As-related risk values are screening-level case-study estimates and should not be interpreted as species-confirmed risk estimates. The absence of an RfD for Pb in the adopted table means that a Pb HQ was not calculated; it does not mean that Pb has zero non-carcinogenic risk.

Table 16. Toxicological parameters for hazardous substances.

No.	Hazardous Substance	CAS Number	Carcinogenic SF/((kg·d)·mg^{-1})	Non-Carcinogenic RfD/(mg·kg^{-1}·d^{-1})
1	Arsenic (As)	7440-38-2	1.50×10^{0}	3.00×10^{-4}
2	Lead (Pb)	7439-92-1	8.50×10^{-3}	/
3	Mercury (Hg)	7439-97-6	/	2.10×10^{-6}
4	Chromium (Cr)	7440-47-3	2.00×10^{1}	7.50×10^{-5}

5	Zinc (Zn)	7440-66-6	/	3.00×10^{-1}
6	Nickel (Ni)	7440-02-0	/	8.00×10^{-4}

Note: "/" indicates that the corresponding parameter was not used in the adopted case-study framework; it does not indicate zero risk. Toxicity values are retained as case-study screening parameters because parameter-specific database version and route-conversion metadata were not preserved in the archived record.

3.4.2. Ecological-Effect Characterization

Ecological-effect information in the archived case dataset was available only for Hg for common carp and rotifers, as shown in Table 17. Compatible effect endpoints for As, Pb, Cr, Zn, and Ni were not contained in the case record. To avoid combining heterogeneous endpoints solely to fill missing cells, the present study retains the available data but explicitly treats the ecological analysis as a partial Hg-based screening rather than a comprehensive ecological assessment of all detected metals.

Table 17. Available ecological-effect parameters for partial screening.

No.	Hazardous Substance	Ecological-Effect Parameter/(mg/L)			
		Common Carp	Crab	Algae	Rotifer
1	Arsenic (As)	/	/	/	/
2	Lead (Pb)	/	/	/	/
3	Mercury (Hg)	0.053	/	/	1.3
4	Chromium (Cr)	/	/	/	/
5	Zinc (Zn)	/	/	/	/
6	Nickel (Ni)	/	/	/	/

3.5. Risk Characterization

3.5.1. Human Health Risk

Carcinogenic and non-carcinogenic risks were characterized using Equations (6) and (7), respectively. These equations correspond to the screening formulation adopted in the case-study framework.

$$CR = ADD_{der} \cdot SF \quad (9)$$

where *CR* denotes the carcinogenic risk characterization value, ADD_{der} is the average daily dermal exposure to a hazardous substance, and SF is the carcinogenic slope factor.

$$HQ = \frac{ADD_{der}}{RfD} \quad (10)$$

where *HQ* denotes the non-carcinogenic risk characterization value and *RfD* is the reference dose for the hazardous substance; ADD_{der} is as defined for Equation (6).

Risk-characterization results for occupational populations and indirectly exposed populations are presented in Table 18. Within the adopted case-study parameterization, the total carcinogenic and non-carcinogenic risks for occupational populations were 2.46×10^{-7} and 3.90×10^{-4}, respectively, whereas the corresponding values for indirectly exposed populations were 8.04×10^{-18} and 5.47×10^{-15}. The occupational values were therefore approximately 3.06×10^{10} and 7.13×10^{10} times higher, respectively. These ratios reflect the different exposure concentrations and scenario assumptions rather than intrinsic differences in population susceptibility. Cr made the largest numerical

contribution within the adopted screening parameterization; accordingly, verification of Cr speciation and strengthened Cr source/incoming-material control are identified as the highest-priority risk-management actions for this case. The lower calculated contributions of the other assessed metals under these scenarios should not be interpreted as zero risk.

Table 18. Carcinogenic and non-carcinogenic risk characterization values for hazardous substances.

No.	Hazardous Substance	Occupational Population Risk Characterization Value		Consumer or Indirectly Exposed Population Risk Characterization Value	
		Carcinogenic Risk CR	Non-Carcinogenic HQ	Carcinogenic Risk CR	Non-Carcinogenic Risk HQ
1	Arsenic (As)	1.65×10^{-9}	8.56×10^{-6}	5.39×10^{-20}	1.20×10^{-16}
2	Lead (Pb)	9.36×10^{-13}	/	3.05×10^{-23}	/
3	Mercury (Hg)	/	2.13×10^{-7}	/	2.98×10^{-18}
4	Chromium (Cr)	2.45×10^{-7}	3.81×10^{-4}	7.99×10^{-18}	5.33×10^{-15}
5	Zinc (Zn)	/	7.93×10^{-8}	/	2.22×10^{-18}
6	Nickel (Ni)	/	7.93×10^{-8}	/	2.19×10^{-17}
Total		2.46×10^{-7}	3.90×10^{-4}	8.04×10^{-18}	5.47×10^{-15}

Under the screening benchmarks adopted in the case study, the acceptable total carcinogenic risk for occupational populations is 10^{-4} and the non-carcinogenic benchmark is 1. For indirectly exposed populations, the corresponding carcinogenic benchmark is 10^{-6} and the non-carcinogenic benchmark is 1. The reported case-study totals were below these benchmarks for the selected dermal scenarios. No Pb HQ was calculated because no RfD was specified in the adopted parameter set; the blank entry therefore indicates "not calculated", not "zero risk". These findings are limited to the selected pathways and adopted parameterization.

3.5.2. Ecological Risk

Ecological risk was represented using the risk-quotient approach in the "General Principles". For an assessed substance–receptor pair, the ecological risk characterization value is the ratio of the predicted environmental concentration (PEC) to the predicted no-effect concentration (PNEC), as shown in Equation (8). A general aggregation expression is provided in Equation (9); however, aggregation is only meaningful when compatible effect data are available for the substances and receptors being combined.

$$RCRe = \frac{PEC}{PNEC} \quad (11)$$

where *RCRe* denotes the ecological risk characterization value for an assessed substance–receptor pair, *PEC* is the predicted environmental concentration, and *PNEC* is the predicted no-effect concentration.

$$\mathrm{RCR_{te}} = \sum \mathrm{R\,CR_{e1}} + \sum \mathrm{R\,CR_{e2}} + \sum \mathrm{R\,CR_{e3}} + \sum \mathrm{R\,CR_{e4}} + \sum \mathrm{R\,CR_{e5}} + \sum \mathrm{R\,CR} \quad (12)$$

The partial ecological screening results for Scenario 3 are presented in Table 19. Based on the available Hg effect parameters, the RCR values for common carp and rotifers were 2×10^{-10} and 8.1×10^{-10}, respectively. The sum of these two available Hg endpoints is 1.01×10^{-9}; this value is not interpreted as a comprehensive "combined ecological risk" for all

detected metals because effect data for As, Pb, Cr, Zn, and Ni were unavailable in the archived case dataset.

Table 19. Partial ecological risk characterization based on available effect data.

No.	Hazardous Substance	Ecological Risk Characterization Value			
		Common Carp	Crab	Algae	Rotifer
1	Arsenic (As)	/	/	/	/
2	Lead (Pb)	/	/	/	/
3	Mercury (Hg)	2×10^{-10}	/	/	8.1×10^{-10}
4	Chromium (Cr)	/	/	/	/
5	Zinc (Zn)	/	/	/	/
6	Nickel (Ni)	/	/	/	/
Sum of available Hg endpoints		2×10^{-10}	/	/	8.1×10^{-10}

A risk quotient of 1 is the decision threshold adopted in the case-study framework; it is not a calculated value assigned to missing entries. Both available Hg RCR values were far below 1. However, because most detected metals lacked compatible ecological-effect data in the archived case record, no generalized ecological-safety conclusion is drawn for As, Pb, Cr, Zn, or Ni. Additional species- and endpoint-consistent effect data would be required for a comprehensive ecological assessment.

4. Conclusions

Using industrial waste sulfuric acid as the raw material to produce liquid polymeric ferric sulfate is an important path for waste resource utilization, pollution prevention and sustainability. This study evaluated the use-phase risks of the finished liquid polyferric sulfate coagulant produced from waste sulfuric acid under three predefined case-study scenarios. The assessment did not evaluate the production facility as a complete occupational-hygiene system and did not constitute a life-cycle or multimedia exposure assessment. The analytical dataset was also limited by the metadata retained in the archived case materials; therefore, the results should be interpreted as case-specific screening results rather than as a statistically representative characterization of all waste-acid-derived polyferric sulfate products.

As, Pb, Hg, Cr, Zn, and Ni were reported in the finished product. Within the adopted dermal-exposure parameterization, the reported total carcinogenic and non-carcinogenic risks were 2.46×10^{-7} and 3.90×10^{-4} for occupational exposure and 8.04×10^{-18} and 5.47×10^{-15} for indirect population exposure, respectively; Cr made the largest numerical contribution in the adopted screening calculation. These values were below the corresponding case-study screening benchmarks, but the conclusion applies only to the measured product composition, selected dermal scenarios, assumptions, and toxicity parameters used here.

For aquatic exposure, the archived ecological-effect dataset supported only a partial Hg-based screening. The available Hg RCR values for common carp and rotifers were far below the threshold of 1, but the absence of compatible effect data for As, Pb, Cr, Zn, and Ni precluded a comprehensive ecological-risk conclusion for all detected metals. Overall, the study demonstrates a case-based approach for linking hazardous-waste feedstocks, finished-product composition, downstream exposure scenarios, and risk characterization, while also showing that transparent treatment of missing sampling, toxicity, speciation,

and ecological-effect information is essential when defining the scope of environmental-safety conclusions.

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