

Product Description

Ferrous sulfate (FeSO₄), an iron salt, is widely used in food, agriculture and chemical production. In water treatment it is a commonly used coagulant. Ferrous sulfate is primarily produced as a byproduct of steel pickling, a process that relies on iron oxides and sulfuric acid.

Use in Water Treatment

Ferrous sulfate is used as a coagulant in both wastewater and drinking water treatment (AWWA, 2018).

Use as a Precursor to Other Water Treatment Chemicals

Ferrous sulfate is used to manufacture ferric sulfate.

Other Applications

Ferrous sulfate is used as a component of fertilizer, an additive in animal feed, pharmaceuticals, iron fortification of foods, and as a pigment (NCBI, 2021).

Primary Industrial Consumers

Historically, use in fertilizer and as an animal feed additive have been the primary domestic uses of ferrous sulfate. Water treatment is a significant use of ferrous sulfate, historically accounting for up to 30% of domestic consumption (NCBI, 2021).

Manufacturing, Transport, & Storage

Manufacturing Process

Ferrous sulfate can be produced with a number of starting materials. Iron, ferrous oxide, and sulfuric acid are the primary materials used to produce ferrous sulfate. Ilmenite, the raw material used to produce titanium dioxide, can also be used but is a less common source of iron oxides in North America.

The method most commonly used in North America utilizes a reaction of spent steel pickling liquors or scrap iron with sulfuric acid. Pickling of steel removes the surface iron oxide from steel by immersion in a bath containing either a sulfuric or hydrochloric acid solution. When sulfuric acid is used, mixed oxides in the oxidation layer of the steel as well as the underlying iron react with the sulfuric acid to form ferrous sulfate as shown in Figure 1. Ferrous sulfate is then filtered and crystallized to complete the production (Barben Analytical, 2015; de Buzin et al., 2014; EPA, 2001).

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Reaction of Mixed Iron Oxides (Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, and FeO) and Steel with Sulfuric Acid
Iron Oxide + Steel + Sulfuric Acid \rightarrow Ferrous Sulfate + Water
  Fe_2O_3
            + Fe +
                                     3H_2SO_4
                                                  \rightarrow
                                                              3FeSO<sub>4</sub>
                                                                             + 3H<sub>2</sub>O
Iron Oxide + Steel + Sulfuric Acid \rightarrow Ferrous Sulfate + Water
            + Fe +
                                     4H_2SO_4 \rightarrow
   Fe<sub>3</sub>O<sub>4</sub>
                                                              4FeSO₄
                                                                              + 4H_2O
Iron Oxide + Sulfuric Acid \rightarrow Ferrous Sulfate + Water
  FeO
               +
                      H<sub>2</sub>SO₄
                                      \rightarrow
                                                FeSO₄
                                                                 + H<sub>2</sub>O
Iron + Sulfuric Acid \rightarrow Ferrous Sulfate + Hydrogen
   Fe
          +
                H_2SO_4
                                \rightarrow
                                          FeSO<sub>4</sub>
                                                                  H<sub>2</sub>
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Figure 1. Chemical Equation for the Reaction to Manufacture Ferrous Sulfate

Production as a byproduct of the manufacture of titanium dioxide results from the process to remove the iron oxide impurities present in low-grade ilmenite. Acid leaching processes include hydrochloric acid or sulfuric acid leaching. Prior to leaching, pretreatment includes reduction or sequential oxidation and reduction. In the sulfate process, the ilmenite is then digested with sulfuric acid, yielding a titanium sulfate solution which is hydrolyzed and precipitated to form titanium dioxide and a waste stream of ferrous sulfate (EPA, 2001).

Product Transport

Ferrous sulfate is transported by many means including truck, rail, barge, and ship.

Storage and Shelf Life

Ferrous sulfate is stable under recommended storage conditions, but degrades when exposed to direct sun and heat. When stored properly, ferrous sulfate can have a shelf life greater than twelve months, though stability may depend upon many factors (Affinity Chemical, 2019).

Domestic Production & Consumption

Domestic Production

Production data was collected from the 2016 EPA Toxic Substances Control Act (TSCA) Chemical Data Reporting (CDR) for the year 2015¹, while trade data was collected from the U.S. International Trade Commission (USITC) Dataweb, as shown in Table 1. While production data is specific to ferrous sulfate, trade data includes ferrous sulfate as part of a broader trade category of metal sulfates. For imports, the trade category is specific to iron sulfates, while the export trade category includes ferrous sulfate among metal sulfates, 'not elsewhere specified' (NES).

Production and Trade Data					
Category	Data Source	Identifier	Description		
Domestic Production	2016 EPA CDR	CAS No.: 7720-78-7	Ferrous Sulfate		
Imports and Exports	U.S. International Trade Commission	HTS Code (Imports): 2833.29.2000 HS Code (Exports): 2833.29	Iron Sulfates Metal Sulfates, NES		

Table 1. Ferrous Sulfate Production and Trade Data Sources

Total U.S. domestic manufacturing of ferrous sulfate reported under the CDR was approximately 18 million kilograms (M kg) in 2015; however, several manufacturers claimed confidential business information and did not report production volumes to EPA. Domestic commercial manufacture of ferrous sulfate takes place at a limited number of facilities throughout the contiguous U.S. Primary producers include *USALCO* (formerly *Altivia Chemicals), Kemira Water Solutions*, and *Keystone Steel and Charter Steel* (steel manufacturer). Most ferrous sulfate production facilities are associated with the steel industry. The number of domestic manufacturing locations shown in Figure 2 represents operating facilities as of 2015 (EPA, 2016). Supply of NSF/ANSI Standard 60 certified ferrous sulfate for use in drinking water treatment is limited to a few locations throughout the U.S. (NSF International, 2021). For a more current listing of manufacturing locations and supplier locations, visit the U.S. Environmental Protection Agency's (EPA's) <u>Chemical Locator Tool</u> (EPA, 2022a).

¹ Although 2019 CDR data is available, reporting is less complete when compared to 2015 data due to an increase in the number of companies claiming confidential business information (CBI). In both instances, CBI may account for a significant volume of ferrous sulfate produced that is not reflected in CDR reporting.



Figure 2. Domestic Supply and Manufacturing of Ferrous Sulfate

Domestic Consumption

Due to differences in reporting for production and trade data, as well as the significant number of producers that did not report production data under the CDR, U.S. consumption of ferrous sulfate could not be estimated. Domestic production of ferrous sulfate may represent a small quantity when compared to the import and export volume for the category of sulfates including ferrous sulfate.

Trade & Tariffs

Worldwide Trade

Worldwide import and export data for ferrous sulfate are reported through the World Bank's World Integrated Trade Solutions (WITS), as a category representing metal sulfates, NES. In 2021, the U.S. ranked 18th worldwide in total exports and second in total imports of metal sulfates, NES. In 2021, Germany ranked first worldwide in total exports and imports (WITS, 2022), as shown in Table 2. Import and export data specific to ferrous sulfate is unavailable from the referenced sources.

2021 Worldwide Trade Metal Sulfates, NES (HS Code 2833.29)						
Top 5 Worldwide Exporters		Top 5 Worldwide Importers				
Germany	836 M kg	Germany	348 M kg			
China	636 M kg	United States	267 M kg			
Poland	257 M kg	Austria	144 M kg			
Spain	129 M kg	United Kingdom	99 M kg			
Slovenia	119 M kg	Sweden	93 M kg			

Table 2. WITS Worldwide Export and Import of Metal Sulfates, NES, Including Ferrous Sulfate in 2021

Domestic Imports and Exports

Domestic imports and export data are reported by USITC in categories for metal sulfates. For imports, the trade category is specific to iron sulfates, while the export trade category includes metal sulfates, NES. Figure 3 summarizes imports for consumption² and domestic exports³ between 2015 and 2020. During this period, the overall quantity of imports varied between 62 and 94 M kg. The quantity of exports was consistently much smaller than the quantity of imports. Over this five-year period, Canada was the primary recipient of domestic exports while China replaced Canada and Spain as the primary source of imports (USITC, 2021).



Figure 3. USITC Domestic Import and Export of Iron Sulfates, including Ferrous Sulfate between 2015 and 2020

² Imports for consumption are a subset of general imports, representing the total amount cleared through customs and entering consumption channels, not anticipated to be reshipped to foreign points, but may include some reexports.

³ Domestic exports are a subset of total exports, representing export of domestic merchandise which are produced or manufactured in the U.S. and commodities of foreign origin which have been changed in the U.S.

Tariffs

There is no general duty for import of ferrous sulfate, however there is an additional 25% duty for imports from China (USITC, 2022), as summarized in Table 3.

 Table 3. 2021 Domestic Tariff Schedule for Iron Sulfates, including Ferrous Sulfate

HTS Number	General Duty	Additional Duty - China (Section 301 Tariff List)	Special Duty
2833.29.2000	None	25%	None

Market History & Risk Evaluation

History of Shortages

The production of ferrous sulfate in North America is heavily reliant on the steel industry and availability of sulfuric acid. Economic slowdowns and a drop in domestic steel manufacturing along with greater recycling of steel pickling liquor and fluctuating prices for sulfuric acid have been known to impact the availability of ferrous sulfate.

Risk Evaluation

The complete risk assessment methodology is described in *Understanding Water Treatment Chemical Supply Chains and the Risk of Disruptions* (EPA, 2022b). The risk rating is calculated as the product of the following three risk parameters:

Risk = Criticality x Likelihood x Vulnerability		
Criticality	Measure of the importance of a chemical to the water sector	
Likelihood	Measure of the probability that the chemical will experience a supply disruption in the future, which is estimated based on past occurrence of supply disruptions	
Vulnerability	Measure of the market dynamics that make a chemical market more or less resilient to supply disruptions	

The individual parameter rating is based on evaluation of one or more attributes of the chemical or its supply chain. The ratings and drivers for these three risk parameters are shown below in Table 4.

Table 4. Supply Chain Risk Evaluation for Ferrous Sulfate



References

- Affinity Chemical, 2019. *Safety Data Sheet for Ferrous Sulfate Solution*, retrieved from https://www.affinitychemical.com/content/uploads/2019/05/AffinityChemical-FerrousSDSV1.pdf
- American Water Works Association (AWWA), 2018. *B402 Ferrous Sulfate*. Denver, CO: American Water Works Association.
- Barben Analytical, 2015. Application Note, Titanium Dioxide Sulfate Process, retrieved from https://www.barbenanalytical.com/applications/application-notes
- de Buzin, P.J.W.K., Vigânico, E.M., Silva, R.D.A., Heck, N.Z., Schneider, I.A.H. and Menezes, J.C.S.S., 2014. Production of Ferrous Sulfate From Steelmaking Mill Scale. *International Journal of Scientific & Engineering Research*, 5(4):353-359.
- EPA, 2001. Final Titanium Dioxide Listing Background Document for the Inorganic Chemical Listing Determination, retrieved from https://archive.epa.gov/epawaste/hazard/web/pdf/tio2-bd.pdf
- EPA, 2016. 2016 TSCA Chemical Data Reporting, retrieved from <u>https://www.epa.gov/chemical-data-reporting/access-cdr-data#2016</u>
- EPA, 2022a. Chemical Suppliers and Manufacturers Locator Tool, retrieved from https://www.epa.gov/waterutilityresponse/chemical-suppliers-and-manufacturers-locator-tool
- EPA, 2022b. Understanding Water Treatment Chemical Supply Chains and the Risk of Disruptions, retrieved from https://www.epa.gov/waterutilityresponse/risk-disruptions-supply-water-treatment-chemicals
- National Center for Biotechnology Information (NCBI), 2021. PubChem Compound Summary for CID 24393, Ferrous Sulfate, retrieved from <u>https://pubchem.ncbi.nlm.nih.gov/compound/24393</u>
- NSF International, 2021. Search for NSF Certified Drinking Water Treatment Chemicals, retrieved from https://info.nsf.org/Certified/PwsChemicals/

- U.S. International Trade Commission, 2021. USITC DataWeb, retrieved from https://dataweb.usitc.gov/
- U.S. International Trade Commission (USITC), 2022. Harmonized Tariff Schedule (HTS) search, retrieved from https://hts.usitc.gov/

World Integrated Trade Solutions, 2022. Trade Statistics by Product (HS 6-digit), retrieved from https://wits.worldbank.org/trade/country-byhs6product.aspx?lang=en#void