13. SECONDARY AND MICRONUTRIENT FRTILIZERS-Manufacturing of Zinc sulphate and Ferrous sulphate

Zinc

Zinc is the fourth most common metal in use, trailing only iron, aluminium, and copper with an annual production of about 12 million tonnes.[14] The world's largest zinc producer is Nyrstar, a merger of the Australian OZ Minerals and the Belgian Umicore.[74] About 70% of the world's zinc originates from mining, while the remaining 30% comes from recycling secondary zinc.[] Commercially pure zinc is known as Special High Grade, often abbreviated *SHG*, and is 99.995% pure.

Worldwide, 95% of the zinc is mined from sulfidic ore deposits, in which sphalerite ZnS is nearly always mixed with the sulfides of copper, lead and iron.[77] There are zinc mines throughout the world, with the main mining areas being China, Australia and Peru. China produced 29% of the global zinc output in 2010.

Zinc metal is produced using extractive metallurgy.[78] After grinding the ore, froth flotation, which selectively separates minerals from gangue by taking advantage of differences in their hydrophobicity, is used to get an ore concentrate.[78] A final concentration of zinc of about 50% is reached by this process with the remainder of the concentrate being sulfur (32%), iron (13%), and SiO₂ (5%).[78]

Roasting converts the zinc sulfide concentrate produced during processing to zinc oxide:[77]

 $2 \text{ ZnS} + 3 \text{ O}_2 \rightarrow 2 \text{ ZnO} + 2 \text{ SO}_2$

The sulfur dioxide is used for the production of sulfuric acid, which is necessary for the leaching process. If deposits of zinc carbonate, zinc silicate or zinc spinel, like the Skorpion Deposit in Namibia are used for zinc production the roasting can be omitted. For further processing two basic methods are used: pyrometallurgy or electrowinning. Pyrometallurgy processing reduces zinc oxide with carbon or carbon monoxide at 950 °C (1,740 °F) into the metal, which is distilled as zinc vapor.[80] The zinc vapor is collected in a condenser.[77] The below set of equations demonstrate this process

 $2 ZnO + C \rightarrow 2 Zn + CO_2$

 $ZnO + CO \rightarrow Zn + CO_2$

Electrowinning processing leaches zinc from the ore concentrate by sulfuric acid

 $ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$

After this step electrolysis is used to produce zinc metal.[77]

 $2 \text{ ZnSO}_4 + 2 \text{ H}_2\text{O} \rightarrow 2 \text{ Zn} + 2 \text{ H}_2\text{SO}_4 + \text{O}_2$

The sulfuric acid regenerated is recycled to the leaching step.

Ferrous Sulfate

In the finishing of steel prior to plating or coating, the steel sheet or rod is passed through pickling baths of sulfuric acid. This treatment produces large quantities of iron(II) sulfate as a by-product.[2]

 $Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$

Another source of large amounts results from the production of titanium dioxide from ilmenite via the sulfate process.

Ferrous sulfate is also prepared commercially by oxidation of pyrite:

$$2 \text{ FeS}_2 + 7 \text{ O}_2 + 2 \text{ H}_2\text{O} \rightarrow 2 \text{ FeSO}_4 + 2 \text{ H}_2\text{SO}_4$$

[edit]

Reactions

On heating, iron(II) sulfate first loses its water of crystallization and the original green crystals are converted into a dirty-yellow anhydrous solid. When further heated, the anhydrous material releases sulfur dioxide and white fumes of sulfur trioxide, leaving a reddish-brown iron(III) oxide. Decomposition of iron(II) sulfate begins at about 480 °C.

 $2 \text{ FeSO}_4 \rightarrow \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$

Like all iron(II) salts, iron(II) sulfate is a reducing agent. For example, it reduces nitric acid to nitrogen oxide and chlorine to chloride:

 $6 \text{ FeSO}_4 + 3 \text{ H}_2\text{SO}_4 + 2 \text{ HNO}_3 \rightarrow 3 \text{ Fe}_2(\text{SO}_4)_3 + 4 \text{ H}_2\text{O} + 2 \text{ NO}$

 $6 \text{ FeSO}_4 + 3 \text{ Cl}_2 \rightarrow 2 \text{ Fe}_2(\text{SO}_4)_3 + 2 \text{ FeCl}_3$

Ferrous sulfate outside titanium dioxide factory in Kaanaa, Pori.

Upon exposure to air, it oxidizes to form a corrosive brown-yellow coating of basic ferric sulfate, which is an adduct of ferric oxide and ferric sulfate:

12 FeSO₄ + 3 O₂ \rightarrow 4 Fe₂(SO₄)₃ + 2 Fe₂O₃