PYRITE: THE STRATEGIC MINERAL THAT BECAME AN INDUSTRIAL NUISANCE

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RESUMEN

La pirita, conocida desde la antigüedad, tuvo en un tiempo histórico una gran importancia estratégica porque fue el componente principal para la fabricación de azufre para la fabricación de pólvora y de SO_2 para la producción de ácido sulfúrico. Sin embargo, cuando aparecieron otras fuentes de obtención del azufre más baratas, la pirita no solo perdió su importancia sino que llegó a ser considerada un problema para la industria metalúrgica, debido a los problemas asociados a su eliminación. En el momento actual, solo se trata la pirita aurífera para la recuperación de oro.

PALABRAS CLAVE: Pirita, industria metalúrgica.

ABSTRACT

Pyrite, known since antiquity, had at one time a great strategic importance because it was the main raw material for making elemental sulfur for gun powder manufacture and for making SO_2 for sulfuric acid production. However, when other sources of cheap elemental sulfur became available, pyrite not only lost its importance but became a nuisance for the metallurgical industry because of problems associated with its disposal. At present only pyrite-containing gold is treated by a variety of methods to recover gold.

KEY WORDS: Pyrite, metallurgical industry.

INTRODUCTION

Pyrite has been known to man since antiquity. It was mentioned by the Greek writer Theophrastus (ca. 372-287 BC) in his work *On Stones* and named for the Greek word for fire "Pyr," as it produces sparks when it is struck with another stone. It is often difficult to tell gold from pyrite because they are so similar in appearance. Pyrite has been used for ornamental pieces and in jewelry in the ancient civilizations of the Greeks, Romans. The Incas in South America used slabs of polished pyrite as mirrors. Sometimes chalcopyrite has been called 'copper pyrite', i.e., pyrite containing copper. Pyrite forms attractive crystals, most frequently is simple cubes (Fig. 1) which reflects its cubic atomic structure (Fig. 2). Pyrite also exists in a rhombic phase known as marcasite.
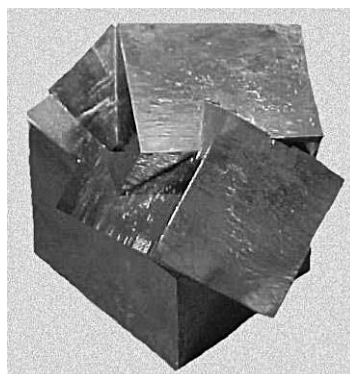

Figure 1. Naturally-occurring pyrite cubes.

Pyrite is the most common sulfide mineral and is widely associated with other metal sulfide deposits. It had at one time a great strategic importance because it contains approximately 53% sulfur and was therefore the main raw material for making elemental sulfur for gun powder (also known as black powder because of its color) and for making SO_2 for sulfuric acid manufacture. In the sixteenth century, heap leaching of copper-containing pyrite was practiced in the Harz mountains area in Germany and in Río Tinto mines in Spain. In these operations, pyrite was piled in the open air and left for months to the action of rain and air whereby oxidation and dissolution of copper took place. A solution containing copper sulfate was drained from the heap and collected in a basin. Metallic copper was then precipitated from this solution by scrap iron, a
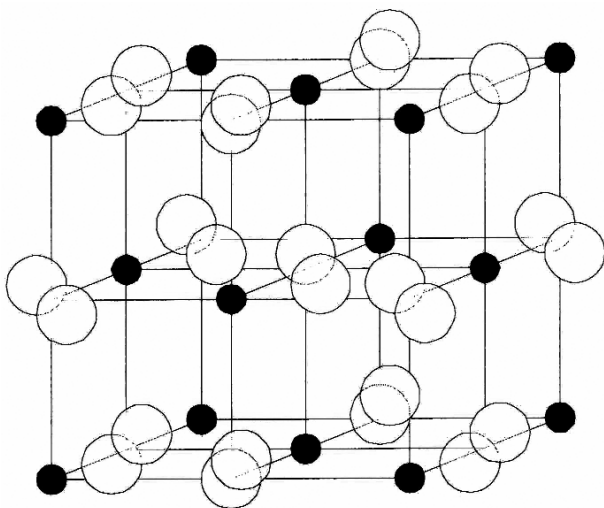
Figure 2. Cubic structure of pyrite.

Figure 3. French translation of Johann Friedrich Henckel's book on the mineralogy of sulfide minerals published in Paris in 1760.

A—LOWER POT. B—UPPER POT. C—LID.
Figure 4. Recovery of sulfur from pyrite [Agricola, 1555].

process that became known as "cementation process", which is apparently derived from the Spanish "cementación" meaning precipitation.

The importance of the mineral can be judged from a book published in 1725 in Leipzig by Johann Friedrich Henckel (1679-1744) on the mineralogy of sulfide minerals entitled *Pyritologia, oder Kiess-Historie*. The book was translated in English in 1757[1] and in French in 1760 (Fig. 3). In 1907 the French chemist P. Turchot published a comprehensive book on pyrite. However, when other sources of cheap elemental sulfur became available, pyrite not only lost its importance but became a nuisance in the metallurgical industry.

PYRITE FOR GUN POWDER MANUFACTURE

Black powder the only explosive available for centuries before the invention of dynamite was approximately composed of 75 % saltpeter (potassium nitrate), 15 % charcoal, and 10 % sulfur. Sulfur for this purpose must be of high quality. Limited amounts of sulfur were mined from a deposit in Sicily consisting of a mixture of sulfur, gypsum, limestone, and clay, containing typically about 25% sulfur. Sulfur was melted from the excavated material then purified by sublimation into a high quality product. Major quantities of sulfur were, however, obtained by heating pyrite in absence of air. Agricola (1494 -1555) in his *De Re Metallica* described the recovery of sulfur from brimstone and from pyrite. Figure 4 shows the recovery of sulfur from pyrite.

Production of sulfur from pyrite was also described by Diderot in his Encyclopedia (1751-1772). Pyrite lumps were stacked on wood logs and on igniting the wood, sulfur vapors were condensed on the roof of the chamber and collected in pots below (Fig. 5). Sulfur was then refined by heating the sulfur in the pots and the sublimed crystals are collected in a special cone constructed in the roof of the furnace (Fig. 6). So Important was this operation that the distinguished French chemist Antoine Lavoisier (1743-1794) was in charge of the black powder factory in Paris and when he was executed during the French Revolution, his student Eleuthére Irénée du Pont de Nemours, emigrated to America and established in 1802 a plant near Wilmington, Delaware to produce black powder based on the French technology.

PYRITE FOR SULFURIC ACID MANUFACTURE

The second important demand for pyrite was for the manufacture of sulfuric acid, the backbone of chemical industry. The major industrial demand for sulfuric acid
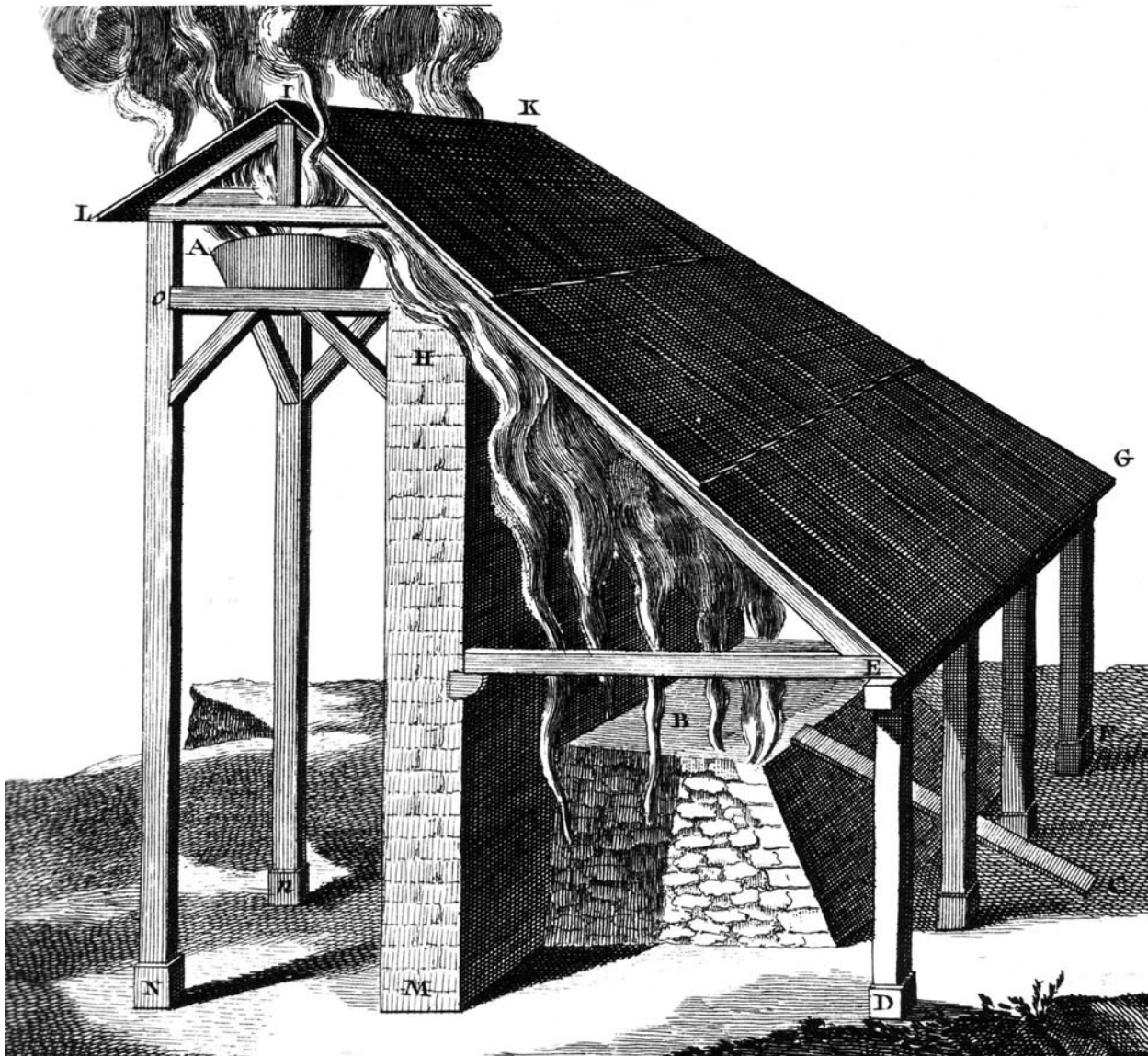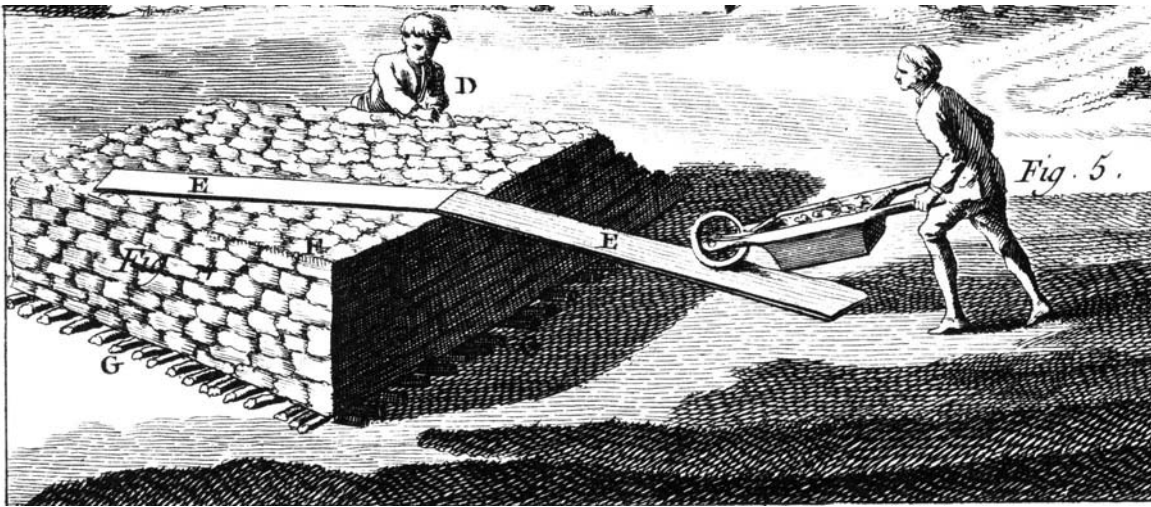
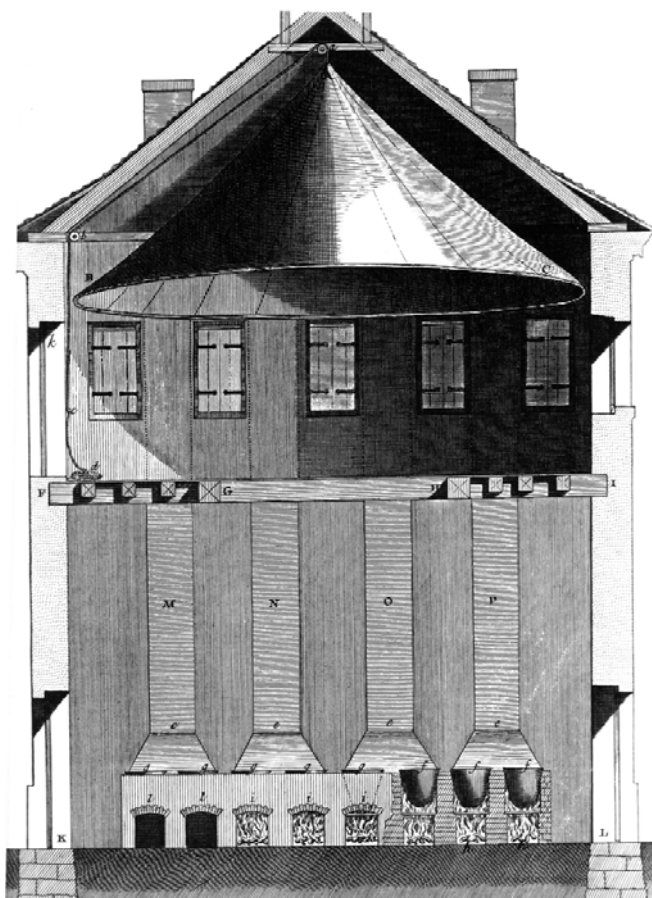Figure 5. Production of sulfur from pyrite as described by Diderot in his Encyclopedia (1751-1772).

Figure 6. Refining of sulfur obtained from pyrite by sublimation [Diderot].
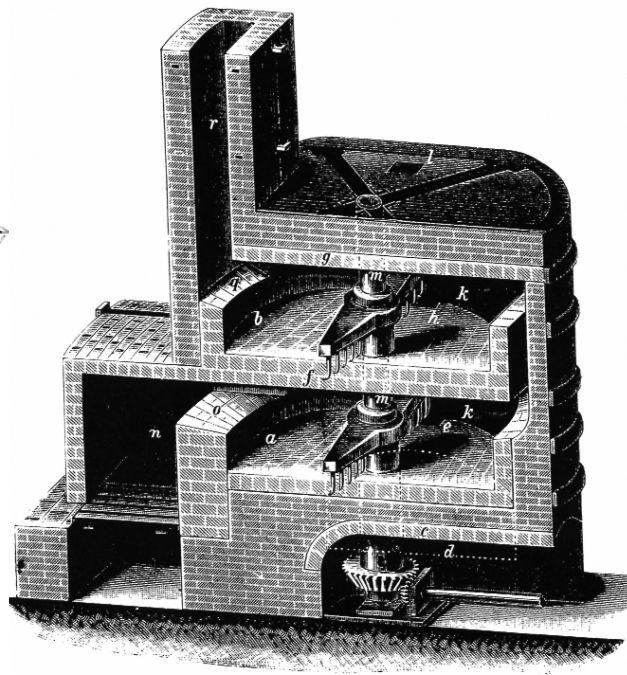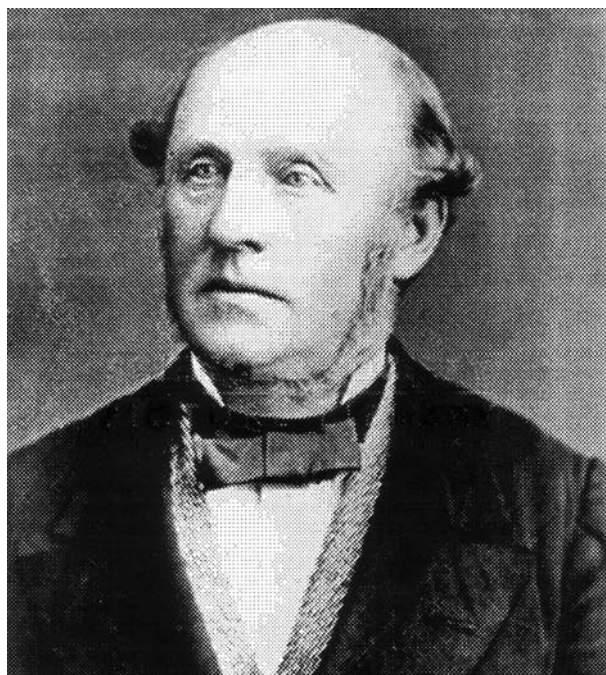

Figure 7. The first multiple-hearth roaster for pyrite.

Figure 8. British engineer Alexander Parkes (1813-1890) inventor of the multi-hearth roaster for pyrite.

was the Leblanc process for making sodium carbonate (developed c.1790)[2], for treating phosphate rock to manufacture superphosphate, and for pickling of steel. Sulfuric acid was usually produced from brimstone found in Sicily. But, when the Neapolitan Government in 1838 gave a French firm the monopoly of trading with its brimstone, the firm increased the price from £ 5 to £ 14 per tonne. As a result, sulfuric acid manufacturers turned to pyrite a source of SO_2:

$$2 \, FeS_2 + {}^{11}/_2 \, O_2 \rightarrow 4 \, SO_2 + Fe_2O_3$$

The discovery of selenium by the Swedish chemist Jöns Jacob Berzelius (1779-1848) took place in 1817 when he observed the formation of a red deposit in the lead chamber acid plant using pyrite from the Falun mine. The lead chambers were also deteriorated when pryrite containing traces of mercury was roasted. Mercury that volatilized attacked the lead lining of the chambers. These elements are also harmful for the contact process which later replaced the chamber process since they poison the catalyst.

The demand for sulfuric acid increased later to be used for manufacturing phosphatic fertilizers, pickling steel, manufacturing of organic dyestuffs, nitro compounds for explosives, refining petroleum products, and many other applications while SO_2 was needed for the pulp and paper industry.
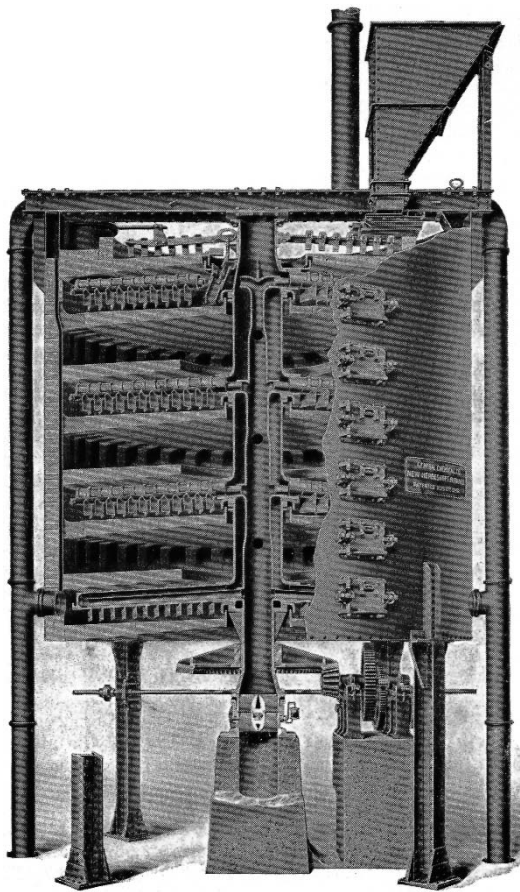
Figure 9. An improved design of a multi-hearth furnace invented by the American engineer John Brown Francis Herreshoff (1851-1932).
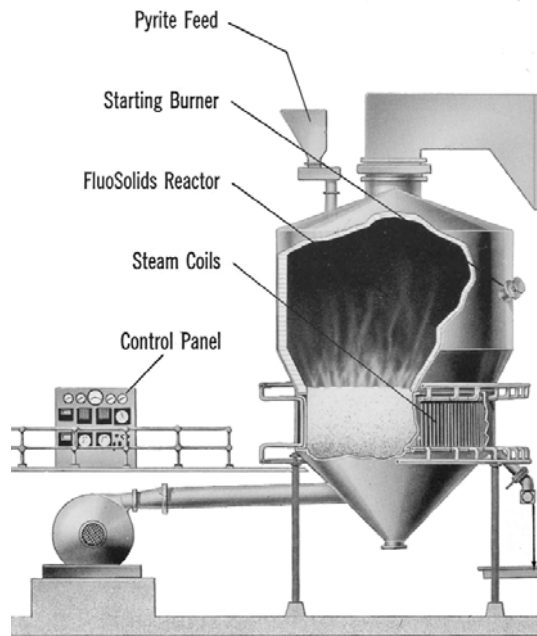

Figure 10. Fluidized bed reactors for roasting pyrite concentrates.

Figure 11. German chemist Fritz Winkler (1888-1950) inventor of the fluidized bed for roasting pyrite concentrates.

	%		ppm
Iron	54-58	Cobalt	300-1500
Gangue	6-10	Nickel	10-1500
Sulfur	2.5-4	Manganese	300-3000
Copper	0.8-1.5	Silver	25-50
Zinc	2.0-3.2	Gold	0.5-1.5
Lead	0.3-0.5	Cadmium	40-100
		Thallium	15-45
		Indium	1-50

Table 1 - Typical analysis of pyrite cinder

Roasters

A variety of roasters were specially developed for roasting pyrite for acid manufacture. Figure 7 shows the first design in 1850 by the British inventor Alexander Parkes (1813-1890) (Fig. 8). A later design by the American engineer John Brown Francis Herreshoff (1851-1932) is shown in Figure 9. Multi-stage roasters were later replaced by the more efficient fluidized bed reactors (Fig. 10) invented in Germany in 1922 by Fritz Winkler (1888-1950) (Fig. 11).

Pyrite cinder

While SO_2 can be readily converted to SO_3 and then to H_2SO_4, iron oxide (called cinder) cannot be used directly for manufacturing iron because of the presence of impurity metals. Table 1 shows typical analysis of cinder. Also, some pyrite contained appreciable amounts of copper and zinc and it was desirable to recover these values. As a result, a method was patented in England in 1844 by W. Longmaid to purify the cinder and at the same time to recover the nonferrous metals present. It was first applied by William Henderson of Scotland in 1859. Lower copper content in the pyrite especially since World War I compelled the firm to extract further products from pyrite. In the process developed, known as Longmaid-Henderson process, the pyrite cinder was roasted with sodium chloride then leached with water to recover the nonferrous metal chlorides. The technology was adapted in Germany for over a century at the Duisburger Kupferhütte in Duisburg from 1876 to 1982 (Fig. 12).

Figure 12. Duisburger Kupferhütte plant in Duisburg, Germany operated from 1876 to 1982 to process pyrite cinder.
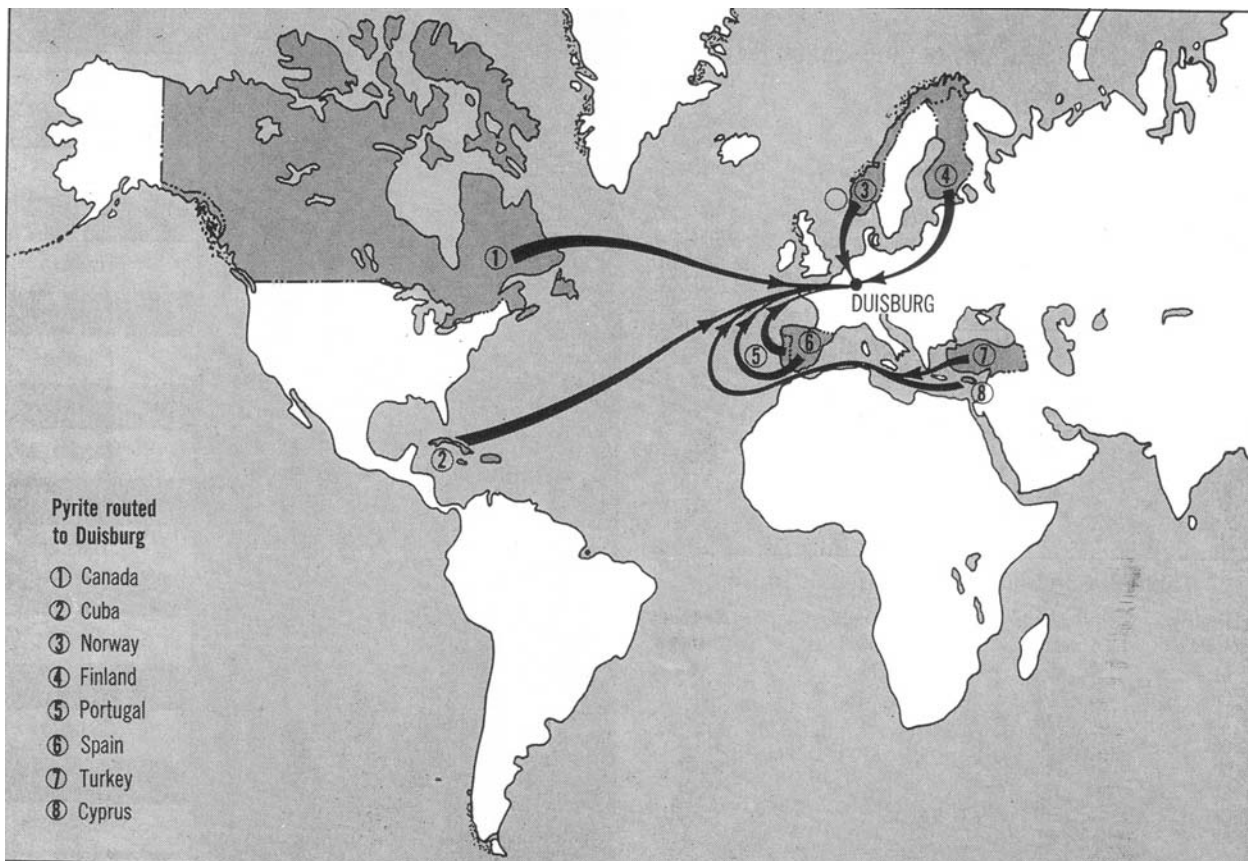

Pyrite routed to Duisburg

① Canada
② Cuba
③ Norway
④ Finland
⑤ Portugal
⑥ Spain
⑦ Turkey
⑧ Cyprus

Figure 13. Importing pyrite from world wide suppliers to Duisburger Kupferhütte plant.
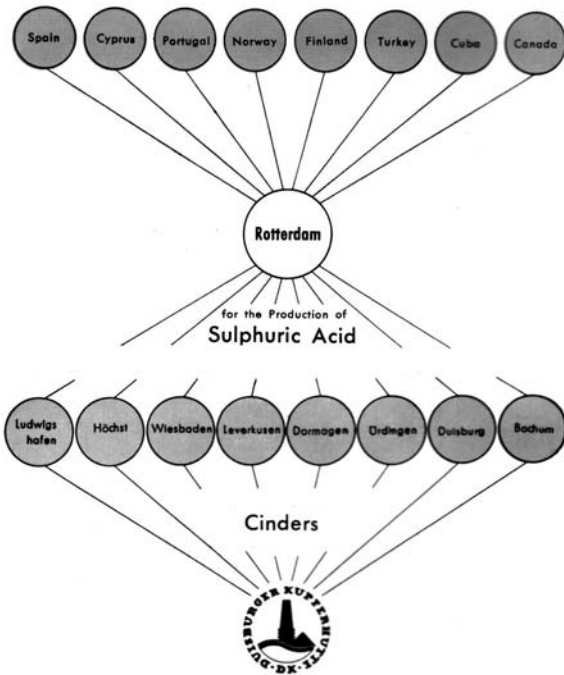
Figure 14. Distribution of pyrite to German sulfuric acid manufactures.

Figure 15. General flow sheet for processing pyrite cinder.

In this plant, pyrite was imported from all over the world by the company, sold to acid manufacturers in Germany on the agreement that the iron oxide resulting from roasting, called cinder, is shipped back to Duisburg for further treatment to recover nonferrous metals, precious metals, and metallic iron (Fig.13-15). The pyrite cinder was mixed with NaCl and heated continuously in a multiple hearth furnace at 800 °C to transform nonferrous metals into water-soluble chlorides (Fig. 16). Each batch requires about 2 days for leaching in vats (Fig. 17). Copper was precipitated from solution in two steps:

$$Cu + CuCl_2 \rightarrow Cu_2Cl_{2(ppt)}$$

$$Cu^{2+} + Fe \rightarrow Cu + Fe^{2+}$$

Copper for the first step was obtained from the second step (Fig. 18). It is interesting to note that the blue $CuCl_2$ solution turns pink after reduction and precipitation of Cu_2Cl_2 due to the presence of Co^{2+} in the remaining solution. Also the residual Cu^+ is colorless. Cuprous chloride recovered is then treated with calcium hydroxide to precipitate copper (I) oxide which was reduced with coal in a furnace to black copper:
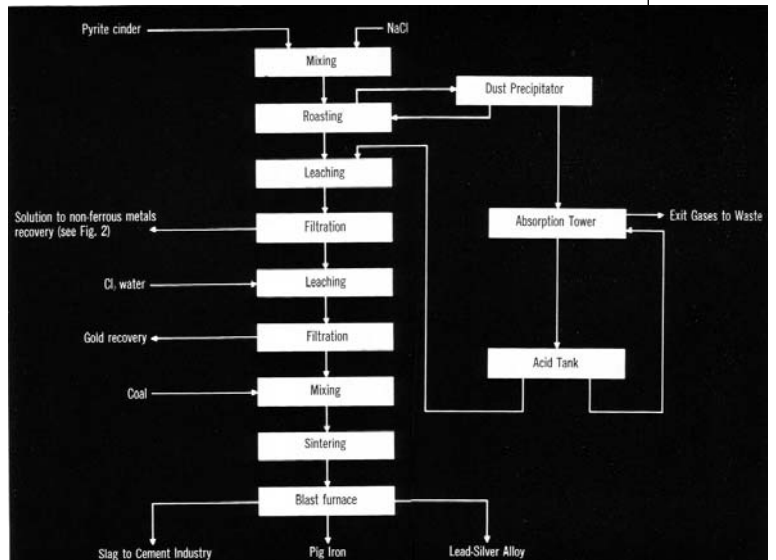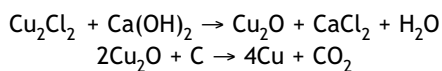
$$Cu_2Cl_2 + Ca(OH)_2 \rightarrow Cu_2O + CaCl_2 + H_2O$$
$$2Cu_2O + C \rightarrow 4Cu + CO_2$$

Figure 16. Salt roasting of pyrite cinder.

The black copper was cast into anodes and refined electrolytically; the precious metals were collected in the anodic slimes. The solution obtained after cementation is evaporated under vacuum to recover $Na_2SO_4.10H_2O$ (Fig. 19). In 1975, the production of black copper was abandoned in favor of a hydro-electowinning process: cuprous oxide was leached in recycle acid and the $CuSO_4$ solution obtained was electrolyzed to produce copper cathodes.

Figure 17. Leaching plant for purple ore.

Figure 19. Sodium sufate plant.

Figure 18. Cementation plant.

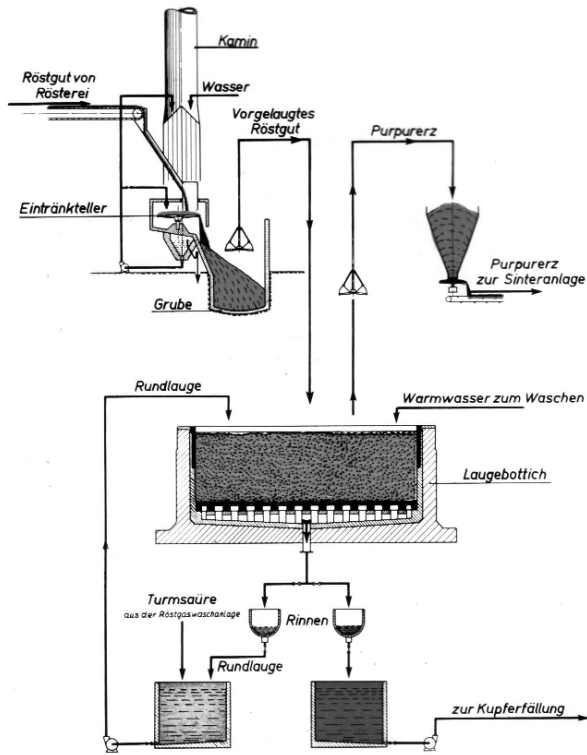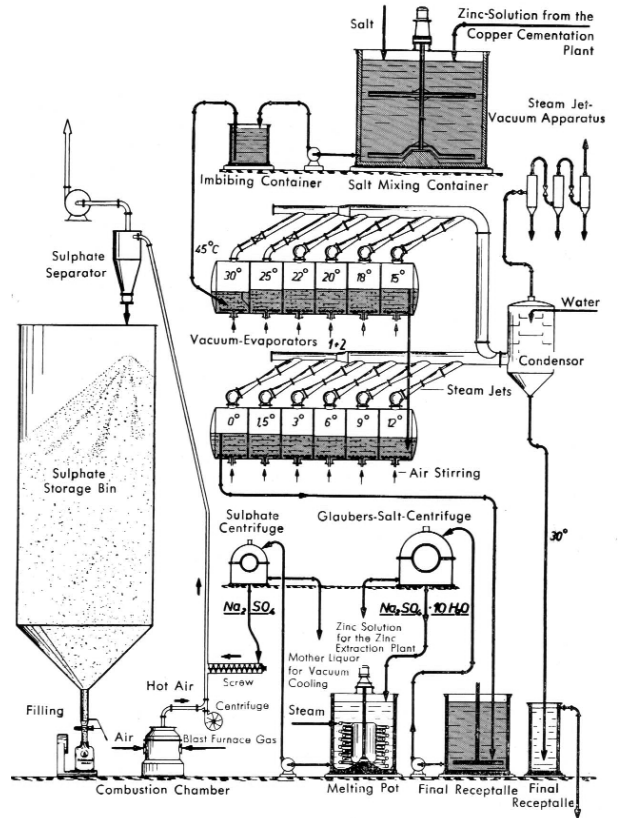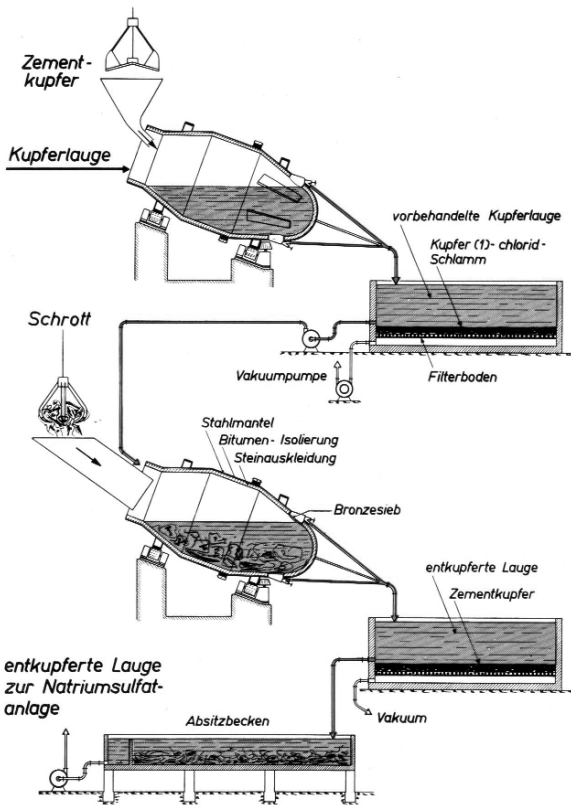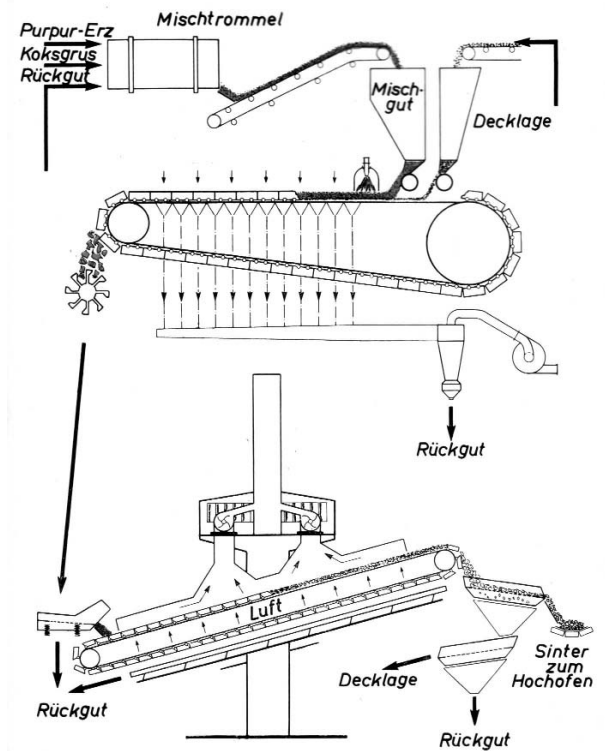Figure 20. Sintering plant.
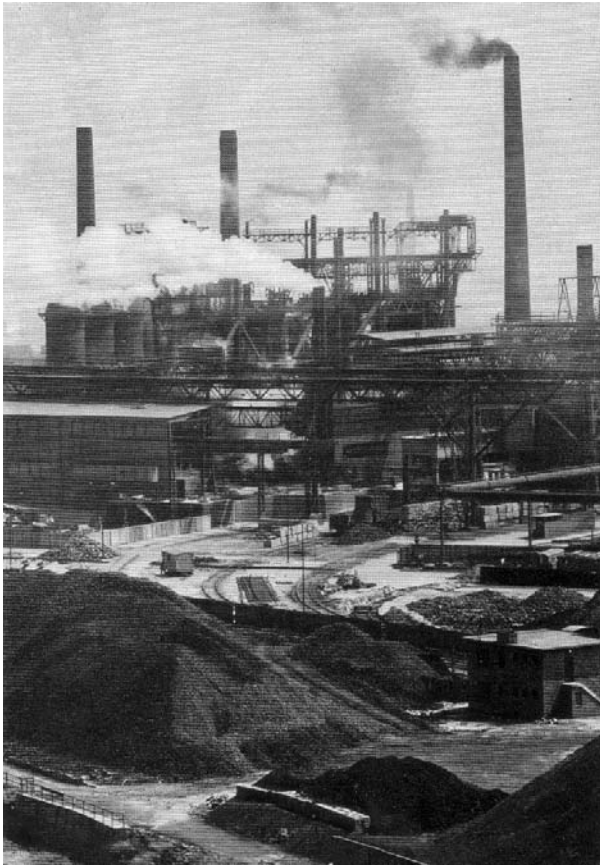
Figure 21. Blast furnace plant producing pig iron and lead-silver alloy.

Figure 22. Chemical Research Laboratory at Duisburger Kupferhütte.

Figure 23. Location map of Orkla plant.

The residue, called "purple ore", now a high-grade iron ore (61–63 % Fe), is sintered (Fig. 20) and delivered to the blast furnace (Fig. 21). Since lead and silver form chlorides during roasting which are insoluble in the leaching step, they remained in the purple ore. When the sintered purple ore was charged in the blast furnace, lead - silver alloy is formed. Being insoluble in iron and has a higher density it settles at the bottom of the hearth. The furnace was provided with an opening

- Imported 3 million tonnes of pyrite annually
- Processed 2 million tonnes of cinder
- Employed 4100 people
- Produced annually:
    - 1.2 million tonnes pig iron
    - 6 000 tonnes Pb
    - 24 000 tonnes Cu
    - 60 000 tonnes Zn
    - 50 tonnes Ag
    - 70 tonnes Cd
    - 10 tonnes Tl
    - Minor amounts of Co, Au, In, Pt
    - 170 000 tonnes sodium sulfate
- Consumed 200 000 tonnes NaCl

Table 2. Data on Duisburger Kupferhütte plant
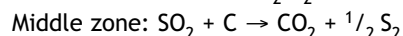
below the iron notch to tap the lead - silver alloy once a week.

Some plant production data are given in Table 2. Evidently, the firm had an excellent research laboratory staffed by a large number of highly skilled chemists and engineers who were capable to devise successfully such a complex process (Fig. 22).

SMELTING OF PYRITE CONCENTRATES

Pyrite smelting was developed to melt massive sulfide ore to form matte, and at the same time to recover the excess sulfur in the elemental form. It was first successfully operated in 1928 by Orkla Grube in Norway (Fig. 23). Similar operations were in Sweden, Portugal, Spain, and Russia. Pyrite containing about 2% Cu is mixed with coke, quartz, and limestone and heated in a blast furnace (Fig. 24). In the upper part of the furnace, one atom of sulfur in pyrite is distilled as elemental sulfur. In the oxidizing zone, FeS formed is oxidized to ferrous oxide and SO_2. In the middle part of the furnace, the reduction zone, SO_2 is reduced by coke to elemental sulfur which is volatilized as vapor. The reactions taking place can be represented by the following equations:

Upper zone: $FeS_2 \rightarrow FeS + {}^1/_2 S_2$
Oxidation zone: $FeS + {}^3/_2 O_2 \rightarrow FeO + SO_2$
Middle zone: $SO_2 + C \rightarrow CO_2 + {}^1/_2 S_2$
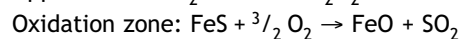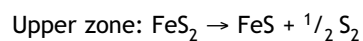
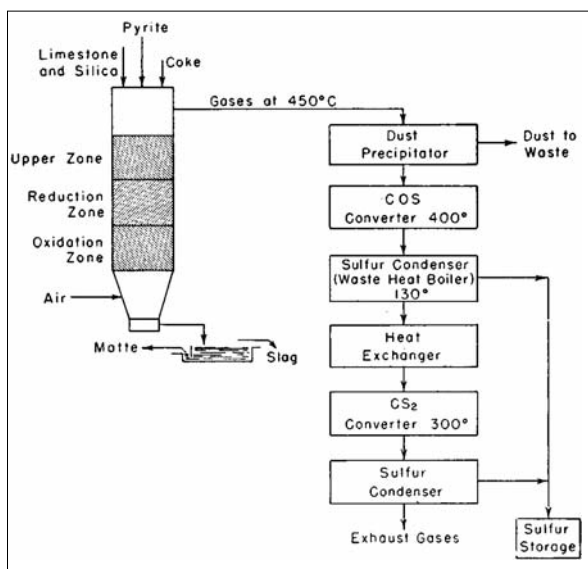| Analysis of ore		Analysis of slag		Analysis of matte		Analysis of furnace exit gases		
	%		%		%		% vol	g/m^3
S	41.0	Cu	0.3	Cu	38.50	S	—	300
Cu	1.8-2.5	Fe	42.0	Fe	32.46	CO	13.2	
Fe	38.0	S	2.3	S	25.55	CO_2	0.2	
Zn	1.9	SiO_2	33.5	SiO_2	0.14	O_2	0.5	
Co	0.1	Zn	1.6	Zn	—	SO_2		75.0
SiO_2	12-16	CaO	4.5	CaO	—	H_2S		12.3
Al_2O_3	0.3	Al_2O_3	1.4	Al_2O_3	—	CS_2		28.8
CaO	0.8	MgO	0.13	MgO	—	COS		22.3
MgO	0.3	Co	—	Co	0.11			
As	0.05							
Se	0.005							
Ag	20 g/ton							
Au	0.2 g/ton							

Table 3. Data for the Orkla process

Figure 24. Orkla process for treating pyrite concentrates to recover copper and elemental sulphur.

Carbon disulfide and carbon oxysulfide are formed in the furnace; they are converted to elemental sulfur on catalytic beds. The matte produced contains 6–8% Cu and is usually re-smelted with coke, silica, and limestone to 40% Cu. Table 3 gives the average analysis of the ore treated in Norway, and the composition of slag, matte, and the exit gases from the furnace. Ores containing arsenic are difficult to treat by this method because sulfur vapor containing a large percentage of arsenic starts to condense at 350 °C, but arsenic-free vapor condenses at a much lower temperature. Further, liquid sulfur containing arsenic is viscous and difficult to handle. Owing to these facts, passing the gases over catalyst beds for converting CS_2 and COS to S is not successful.

THE RECOVERY OF ELEMENTAL SULFUR FROM PYRITE

It was realized long ago that a method to get elemental sulfur from pyrite would be ideal for acid manufacturers since there will be a great savings in transportation costs. The introduction of flotation technology to concentrate pyrite between the two world wars contributed to the necessity to devise a method for solving this problem.

– Elemental sulfur can be obtained from pyrite by heating in a controlled amount of oxygen such that the heat required by the endothermic reaction:

$$FeS_2 \rightarrow FeS + S$$
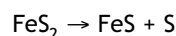
is compensated by the heat generated from the reaction:

$$3\ FeS + 5\ O_2 \rightarrow\ Fe_3O_4 + 3\ SO_2$$
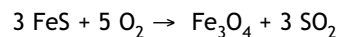
Ferrous sulfide was obtained as a molten phase. A plant based on this idea was designed by Noranda in 1954 and another operated in Finland for some years.

– Heating in SO_2 atmosphere leads to elemental sulfur formation:

$$3\ FeS_2 + 2\ SO_2 \rightarrow Fe_3O_4 + 8\ S$$
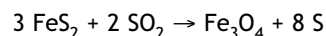
The reaction is ideal since SO_2 required can be generated from part of the sulfur recovered. The reaction was studied extensively by Duisburger Kupferhütte in Germany; the reaction kinetics were very slow.

– Heating in chlorine-oxygen atmosphere leads also to the formation of elemental sulfur:

$$2\ FeS_2 + 2\ Cl_2 \rightarrow 2\ FeCl_2 + 4\ S$$
$$2\ FeCl_2 + 3/2\ O_2 \rightarrow Fe_2O_3 + 2\ Cl_2$$
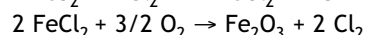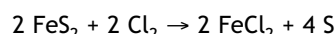
A plant was operated in Niagara Falls in Canada in 1936 using two rotary kilns as shown in Figure 25. The process was known by the name of its inventors Comstock- Wescott.
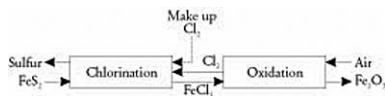
Figure 25. Chlorination plant in Niagara Falls, Canada using two rotary kilns for the recovery of sulfur from pyrite in 1936.

PYRITE AND THE STEEL INDUSTRY

Noting the success of Duisburger Kupferhütte, producers of sulfuric acid from pyrite as a source of SO_2 in Europe, Japan, and USA became interested to market their iron oxide produced to the steel industry. But, the steel industry could not use this source because it contained small amounts of sulfur and some nonferrous metals. Although iron oxide pelletization was invented in Sweden in 1912, it was not introduced in the iron ore industry until thirty years later. This took place when the electric arc furnace was introduced in the steel industry and the need arose for a palletized feed. This gave an incentive to the sulfuric acid manufacturers to upgrade their pyrite cinder for the steel industry. As a result, more processes were developed to deal with this problem.

- *Kowa-Seiko Process*. This is a Japanese process developed at Kitakyushu in which the cinder is mixed with calcium chloride, pelletized, then heated in a rotary kiln at 1100 °C to volatilize nonferrous metal chlorides. These are scrubbed in water from the exit gases and the solution treated for metal recovery. The process was also used in Portugal and in other countries.
- *Bethlehem Steel process*. At the plant at Sparrows Point in Maryland, cobalt from the cinder was recovered by a process based on a careful temperature control during the roasting of pyrite. If the temperature is kept at 550 °C, cobalt in the pyrite will be converted to sulfate and therefore can be leached directly from the cinder with water. The hot pyrite cinder was quenched with water to give a slurry containing 6–8 % solids. When the solids are filtered off, the solution contains 20–25 g/L Co; it is processed further for metal recovery. In the cinder, the Fe:Co ratio is 50:1; in solution it is 1:1. This plant supplied the only domestic source of cobalt in USA.
- *Outokumpu process*. In Finland at the Outokumpu plant in Pori a similar process is in operation in 1979; the sulfated pyrite cinder contains 0.8–0.9 % Co and other nonferrous metals. It is leached with water to get a solution at pH 1.5 analyzing 20 g/L Co, 6–8 Ni, 7–8 Cu, 10–12 Zn, and trace amounts of iron, which is treated for metal recovery.

THE DECLINE IN THE PYRITE INDUSTRY

During the Napoleonic wars, Spanish pyrite entered into competition with Sicilian sulfur in many markets. The production of pyrite, however, declined gradually towards the end of the nineteenth century after the discovery of an economic method for the recovery of sulfur from the sulfur domes in the Gulf of Mexico. There was also a great rise in petroleum refining activities after World War II that resulted in large amounts of sulfur-containing refinery gases and the need to recover this sulfur to avoid polluting the environment with SO_2. Also the availability of large volumes of natural gas containing hydrogen sulfide at Lacq in southern France in 1950s and in Alberta, Canada in 1970s contributed to the decline in pyrite demand.

Elemental sulfur replaced pyrite as a source for SO_2 for sulfuric acid manufacture because of the purity of the gas generated and the elimination of dust recovery equipment in the plant. Sulfur became available by the following processes:

- Sulfur deposits discovered in the Gulf of Mexico were exploited economically since 1895 by Herman Frasch (1851-1914) (Fig. 26) using superheated water to melt the sulfur and float it to the surface by compressed air (Fig. 27). Figure 28 shows a stock pile of sulfur produced by this process. The process applies only when sulfur is stratified between

Figure 26. Herman Frasch (1851-1914) succeeded in producing sulfur economically from the brimstone domes in the Gulf of Mexico, a process that was responsible for ruining the Sicilian sulfur industry and the start of the decline in the pyrite industry.
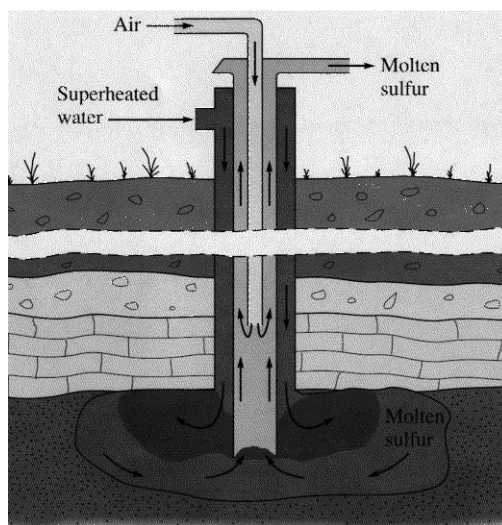

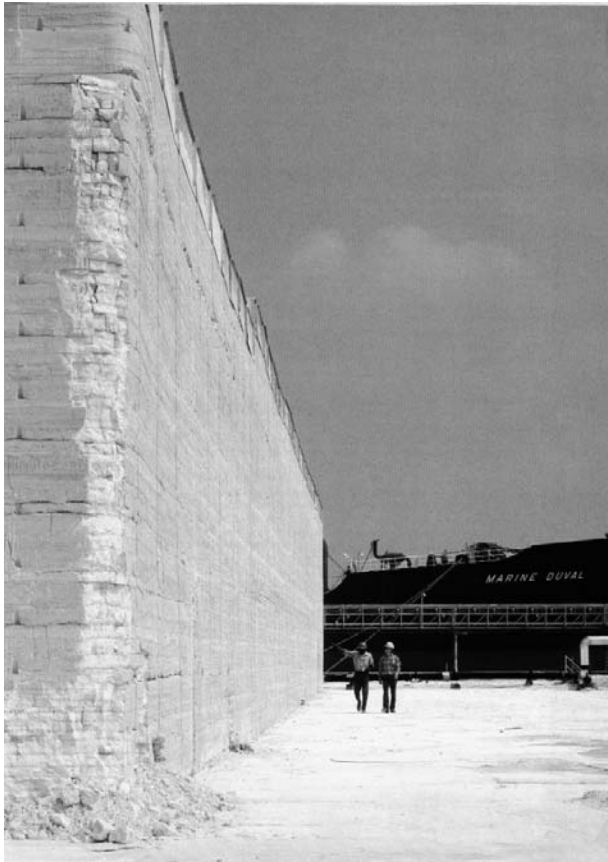Figure 27. Principle of the Frasch process.

Figure 28. Stockpile of elemental sulphur produced by the Frasch process.
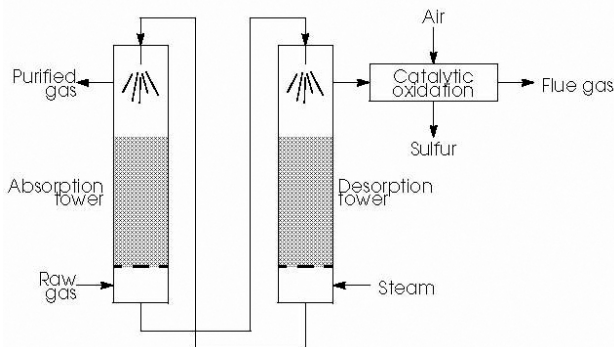
Figure 29. Absorption–desorption process for recovery of H_2S from natural gas or petroleum refinery gases.

impervious rock formation which was not the case for Sicily. The success of Frasch process ruined the Sicilian sulfur industry.

– H_2S-containing natural gas or petroleum refining gases not only became a source of elemental sulfur but recovering this sulfur solved an environmental problem since the gases were burned generating large amounts of SO_2. Hydrogen sulfide must first be separated from the gases by an absorption – desorption process (Fig. 29), then oxidized by a

controlled amount of oxygen at 400ºC on aluminum oxide or bauxite bed using Claus reaction discovered in 1883 by the German chemist Carl Friedrich Claus:

$$H_2S + \frac{1}{2} O_2 \rightarrow S + H_2O$$
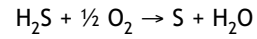
Figure 30 shows a Claus plant and Figure 31 shows a stock pile of sulfur produced by this process. Liquid sulfur produced by this process contains some dissolved H_2S which presents odor problems and potential toxic and/or explosive hazards during storage and transportation. Degasification is carried out in a pressurized vertical vessel that counter-

Figure 30. Claus plant for transforming H_2S to elemental sulphur.

Figure 31. Stockpile of elemental sulfur obtained from H_2S.

currently contacts liquid sulfur with pressurized air at a controlled temperature to accelerate the oxidation of the residual H_2S and polysulfides (H_2S_x) to sulfur (Fig. 32).

As soon as these new sources of elemental sulfur became available, pyrite roasters for sulfuric acid manufacture were dismantled and replaced by sulfur burners and the decline in pyrite production started to decline rapidly. Acid plants based on pyrite roasting were expensive because it included bulky equipment for dust separation.

PYRITE AND THE GOLD INDUSTRY

A problem in gold metallurgy was the treatment of gold locked up in pyrite or arsenopyrite crystals and therefore unresponsive to cyanidation. Roasting fol-

Figure 32. Degasification reactor to accelerate the oxidation of the residual H_2S and polysulfides (H_2S_x) to sulphur.
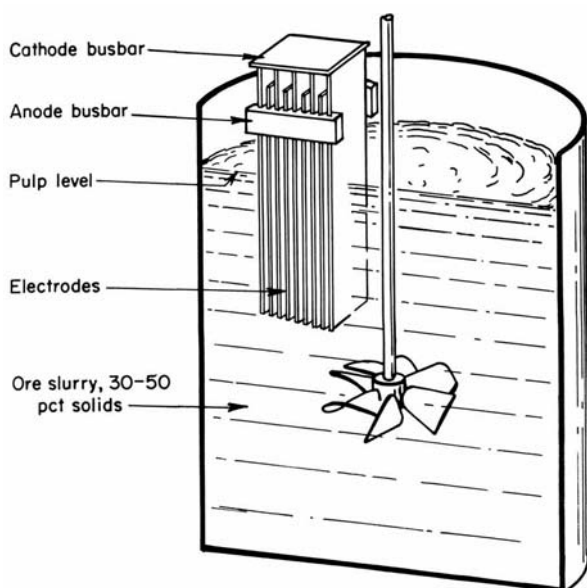
Figure 33. US Bureau of Mines oxidation process developed in 1971 in which NaOCl generated electrochemically oxidizes the pyrite (as well as organic matter) to sulfate.

lowed by leaching is an expensive and polluting proposition but is used under certain circumstances. Researchers at the former US Bureau of Mines have developed in 1971 an aqueous chlorination process in which the oxidizing conditions in situ can be achieved by passing electric current in a pulp prepared from a finely ground ore and NaCl solution: NaOCl generated oxidizes the pyrite (as well as organic matter) to sulfate. The reactor used is shown in Figure 33 and the pilot plant in Figure 34.

Pressure leaching

A hydrometallurgical approach was developed in 1985 and proved to be a successful solution for this type of ores. Barrick Goldstrike (Fig. 35) now treats a pyrite ore-water slurry in autoclaves at high temperature and oxygen pressure. Horizontal autoclaves are used, each being 30 m long and 5 m in diameter, operating at 160-180 °C and 2000 kPa, with a retention time of 20 minutes. The autoclaves are made of carbon steel 8 cm thick, lined with as 6 mm lead membrane and two layers of acid-resisting brick 22.5 cm total thickness. After this treatment, the ore is then suitable for cyanidation. Table 4 gives data on some aqueous oxidation operations for refractory gold ores.

Figure 34. Pilot plant of the Bureau of Mines process.

Figure 35. Barrick Goldstrike plant at Elko, Nevada.

Start up	Plant Location	Owner	Feed	Medium	Capacity t/d
1985	McLaughlin USA	Homestake USA	ore	acid	2700
1986	San Bento Brazil	Genmin S. Africa	concentrate	acid	240
1988	Mercur, Utah USA	American Barrick Canada	ore	alkaline	680
1989	Getchell USA	First Miss Gold	ore	acid	2730
1990	Goldstrike Nevada, USA	American Barrick Canada	ore	acid	1360
1991	Goldstrike Nevada, USA	American Barrick Canada	ore	acid	5450
1991	Porgera Papua, New Guinea	Placer Dome Canada	concentrate	acid	1350
1991	Campbell Canada	Placer Dome Canada	concentrate	acid	70
1992	Con Lihir	Nerco Minerals	concentrate	---	90
1993	Goldstrike USA	American Barrick Canada	ore	acid	11580
1994	Porgera, Papua New Guinea	Placer Dome Canada	concentrate	acid	2700
1997	Lihir, Papua New Guinea	Rio Tinto	---	---	---

Table 4. Status of Treatment of Refractory Gold Ores by Pressure Hydrometallurgy.

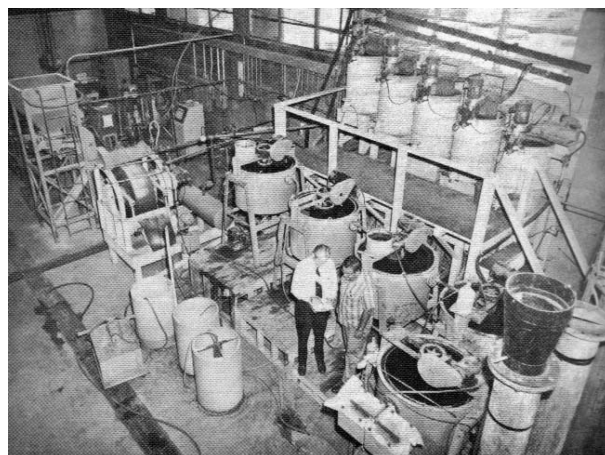- *Ashanti Goldfields Company, Ghana.* Designed with an initial capacity of treating 720 tonnes of concentrate per day, the Sansu plant has since been expanded and currently has four modules processing 960 tonnes per day in all. It is by far the largest biooxidation plant in the world. The capital cost of the plant totalled US $ 25 million (1994 terms) and the operating cost is currently US $ 17/tonne milled.
- *Fairview, South Africa.* The plant at the Fairview mine in Barberton, which was the initial pilot plant, has been fully operational since 1986. It was originally designed to treat of concentrate 10 tonnes/day but with the success of the project this has been increased to 55 tonnes per day. With the purchase of Fairview by Avgold's Eastern Transvaal Consolidated, Avgold concluded a licensing agreement with Gold Fields, formerly known as Gencor entitling it to use the BIOX technology to treat its concentrate.
- *Saõ Bento, Brazil.* A BIOX plant is in operation in Brazil at the Sao Bento Mine where a pressure oxidation circuit is used to treat the refractory flotation concentrate. This plant has confirmed the viability of combining bio-oxidation with pressure oxidation as a cost-effective method of increasing capacity at an existing oxidation plant.
- *Wiluna, Australia.* The plant at Wiluna Gold Mine, Western Australia, was commissioned in 1993. Although originally designed to treat 115 tonnes per day of concentrate this has subsequently been increased to 158.
- Other plants at Tamboraque in Peru, Harbour Lights and at Youanami in Australia have been commissioned recently.

Table 5. BIOX plants currently in operation

- The Greek writer Theophrastus (ca. 372-287 BC) mentions the mineral pyrite in his work *On Stones*
- In the sixteenth century, heap leaching of copper-containing pyrite was practiced in the Harz mountains area in Germany and in Río Tinto mines in Spain
- Agricola (1494 -1555) in his *De Re Metallica* described the recovery of sulfur from brimstone and from pyrite
- 1725 Johann Friedrich Henckel publishes in Leipzig a book on the mineralogy of sulfide minerals entitled *Pyritologia, oder Kiess-Historie*
- Diderot in his Encyclopedia (1751-1772) described the recovery and purification of elemental sulfur from pyrite for gun powder manufacture
- c.1790 all sulfuric acid manufactured at that time was from SO_2 produced by roasting of pyrite
- 1817 The Swedish chemist Jöns Jacob Berzelius (1779-1848) discovers selenium when he observed the formation of a red deposit in the lead chamber acid plant using pyrite from the Falun mine
- 1850 The British inventor Alexander Parkes (1813-1890) builds the first multi-hearth furnace for roasting pyrite
- The American engineer John Brown Francis Herreshoff (1851-1932) builds an improved design of a multi-hearth furnace for roasting pyrite
- 1844 Longmaid in England patents a process to purify pyrite cinder and at the same time to recover the nonferrous metals present
- 1850 British inventor Alexander Parkes (1813-1890) build the first multi-hearth roaster for pyrite
- 1859 William Henderson of Scotland applies the patent for the recovery of copper from pyrite cinder
- 1876 The Duisburger Kupferhütte company in Duisburg in Germany establishes a plant for the recovery of pig iron and non-ferrous metals from pyrite cinder
- 1883 The German chemist Carl Friedrich Claus discovers a process for obtaining elemental sulfur from hydrogen sulphide separated from coke oven gas
- 1895 American chemist Herman Frasch (1851-1914) discovers a method for the recovery of brimstone from sulfur domes in the Gulf of Mexico area
- 1907 French chemist P. Turchot publishes a comprehensive book entitled *Les Pyrites*
- 1922 German chemist Fritz Winkler (1888-1950) invents the fluidized bed
- 1928 by Orkla Grube in Norway develops a method for recovery of elemental sulfur and copper from pyrite concentrates by smelting. Similar operations were in Sweden, Portugal, Spain, and Russia
- 1954 Noranda company in Quebec builds a plant for the recovery of elemental sulphur from pyrite
- 1950s The availability of large volumes of natural gas containing hydrogen sulfide at Lacq in southern France. Claus process applied to convert H_2S to sulfur
- 1968 Kowa Seika process developed in Japan for treating pyrite cinder
- 1970s Recovery of large amounts of elemental sulfur from refinery gases in Alberta, Canada using Claus process
- 1971 Researchers at US Bureau of Mines developed an aqueous chlorination process for treating pyrite concentrate containing gold by passing electric current in the ore slurry containing sodium chloride
- 1975 Canada Center for Mineral Technology in Ottawa created a research group to study the problem of acid mine drainage and suggest solutions to industry
- 1982 The Duisburger Kupferhütte plant is shut down because of the shift of the German sulfuric acid industry from pyrite to elemental sulfur
- 1983 Outokumpu process developed for the recovery of cobalt from pyrite cinder
- 1985 Homestake Company in USA installed the first pressure leaching operation for pyrite to recover its gold content at McLaughlin mine. This was followed later by other plants in Brazil, USA, Canada, and Papua New Guinea
- 1986 Fairview mine in Barberton, South Africa operates the first bacterial leaching operation for the recovery of gold from pyrite concentrates

Table 6. Milestones in the history of pyrite.

Bacterial leaching

Bacterial leaching has been successfully applied for heap leaching of copper ores. It was extended in 1986 to treat auriferous pyrite concentrates to liberate gold and render it amenable to cyanidation by a process known as BIOX (Table 5).

PYRITE AND THE COAL INDUSTRY

One of the problems of using coal as a fuel is the presence of small amounts of pyrite in the coal, which on combustion results in SO_2 in the stack gases. One way to solve this problem is by scrubbing the gases to remove SO_2 in a variety of forms, e.g., as gypsum, $CaSO_4.2H_2O$, which may be marketed to the construction industry. Another option is upgrade the coal by removing the pyrite prior sending it to the market. Standard mineral beneficiation methods were applied with some success. Bacterial leaching of pyrite was also tried by many researchers but it is a slow process and due to the need to supply air to the bacteria, an appreciable amount of coal loses its calorific value.

Two more technologies are available to solve the coal problem as a fuel: gasification and liquefaction. In coal gasification pyrite forms sulfur-containing gases which can be scrubbed to yield a clean gaseous fuel. In coal liquefaction using hydrogen under pressure, coal is transformed into a liquid fuel while pyrite forms H_2S

which can be separated and recovered in form of elemental sulfur.

PRESENT PROBLEMS OF PYRITE

Tailings from beneficiation processes represent a large disposal problem because of the presence of pyrite which undergoes aqueous oxidation when exposed to weathering conditions generating sulfuric acid:

$$FeS_2 + H_2O + {^7/_2}\,O_2 \rightarrow FeSO_4 + H_2SO_4$$
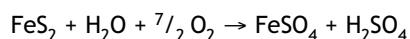
The formation of acid is accelerated by the presence of microorganisms such as Thiobacillus ferrooxidans. The acid generated will solubilize other minerals thus releasing metal ions in solution. As a result, terrains hundreds of hectares, must be prepared to stock-pile the tailings either dry or under water. Precautions must be taken to avoid breakage of the dams, leaks, seepage to underground water, etc. Thus, a large expenditure must be spent to monitor, maintain, and re-vegetate the ponds. A research group known as "Mine Drainage" was founded in 1975 at Canada Center for Mineral Technology in Ottawa to study this problem and suggest solutions to the industry.

In most cases, pyrite is associated with arsenopyrite, FeAsS. In roasting process volatile arsenic oxide is formed and is collected in the dust-collecting chambers. Disposal of this material must be found. When pyrite is treated by hydrometallurgical process, arsenic is precipitated as ferric arsenate for disposal.

SUMMARY

Pyrite was known since antiquity and was mentioned by Greek writers. It is the most common sulfide mineral and is widely associated with most other sulfide minerals. It had at one time a great strategic importance because it was the main raw material for making elemental sulfur for gun powder manufacture and for making SO_2 for sulfuric acid production. However, when other sources of cheap elemental sulfur became available, pyrite not only lost its importance but became a nuisance for the metallurgical industry because of problems associated with its disposal. At present only pyrite-containing gold is treated by a variety of methods to recover gold. Table 6 gives the milestones in the history of pyrite. ⚙

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NOTES

[1] Full title: *Pyritologia, oder Kiess-Historie* (Leipzig 1725) Engl. Transl: *Pyritologia or a History of the Pyrites, the principal body in the Mineral Kingdom. In which are considered its names, species beds, and origin; its iron, copper, unmetallic earth, sulphur, arsenic, silver, gold, original particles, vitriol, and use in smelting.*

[2] Sodium chloride treated with concentrated sulfuric acid to form sodium sulfate which is the reduced with carbon to form sodium sulfide. This in tern is reacted with limestone to form sodium carbonate and calcium sulfide. The process was later replaced by Solvay process in 1863.