Pyrite roasting, an alternative to sulphur burning

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Synopsis

The roasting of sulphide ores and concentrates is often the first step in the production of metals or chemicals. In many processes, the production of sulphuric acid is viewed as a by-product, whereas in some plants production is an important economic factor. Regardless of the purpose, a pyrite roasting plant consists of mainly three plant sections: roasting, gas cleaning and sulphuric acid. With the addition of air, the pyrite concentrates are transformed into solid oxides and gaseous sulphur dioxide at temperatures of 600–1000°C. After cleaning and cooling, the sulphur dioxide in the roasting gas is further processed to sulphuric acid. Two types of reactors are used depending on the application: stationary or circulating fluid bed.

For over 60 years, Outotec has progressively been developing the principle of fluidized bed technology in several different reactor types for a multitude of process applications. The versatility of the fluidized bed reactor system has manifested itself in the treatment of minerals, including solid fuels, and for metallurgical processes both in the ferrous and non-ferrous fields. Process applications have included roasting, calcining, combustion and charring of coals, as well as off-gas treatment.

This paper provides a summary of the pyrite roasting technology currently used along with a simple cost comparison of pyrite roasting and sulphur burning processes.

Introduction

Pyrite roasting and sulphur burning plants are built for the production of sulphuric acid. Whereas the burning of elemental sulphur is the main source for sulphuric acid, the roasting process is an interesting alternative once pyrite concentrate is available. In addition to these two applications, Figure 1 shows a wider variety of sources for the production of sulphuric acid, as there are also sulphidic ores, tail/flue gases, iron sulphate, to name only a few.

In some countries, pyrites and iron sulphide ores still constitute an important raw material basis for sulphur dioxide production, especially as the primary stage for sulphuric acid manufacture. The most important iron sulphide minerals are pyrite FeS_2 as well as pyrrhotite Fe_7S_8. They occur in varying purity as sedimentary rocks in all formations, and as minor constituents in coal deposits. Apart from gangue materials, which are present in varying proportions in pyritic ores, other constituents include sulphides of non-ferrous metals, especially copper, zinc, and lead and to a lesser extent cobalt, nickel, and gold. In some cases, pyrites may also contain significant amounts of arsenic as well as fluorides and chlorides. The production of pyrites, either as crude pyrites or as beneficiated pyrites, is highly dependent on the fertilizer market, sulphur prices and the amount of produced sulphuric acid. Flotation pyrites are, however, obtained in marketable quantities as a byproduct of non-ferrous metal sulphide beneficiation plants.

The roasting processes as shown in Figure 1 are related to the fluid bed reactor. The largest single line stationary fluid bed roasting plant in operation today has a capacity of 1 130 t/d of pyrite/pyrrhotite concentrate. Further development have now increased this maximum capacity for a single roasting line up to 1 800 t/d of concentrate. From an economic and technical standpoint, this throughput can be achieved for one line only by applying circulating fluid bed technology. In similar applications, the throughput, e.g. in whole ore gold roasting plants, can reach up to 3 800 t/d.

- *Stationary fluid bed furnace* (SFB)—This roaster was developed for dry pyrite feeding and designed to recover the maximum amount of heat for steam production. The temperature of the fluid bed is kept constant by indirect cooling; the surplus heat is removed in the fluid bed by immersed cooling elements, which form part of a waste heat system for the production of high-pressure steam.

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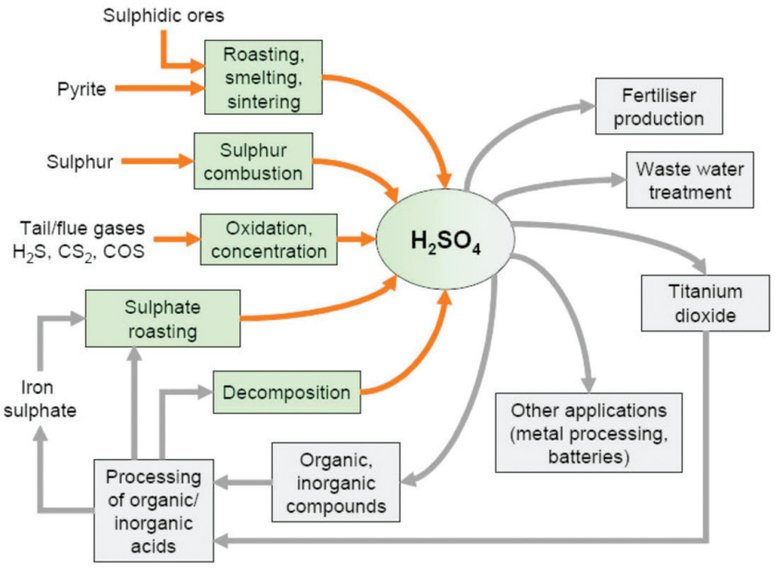

Figure 1—Source and demand for sulphuric acid plants

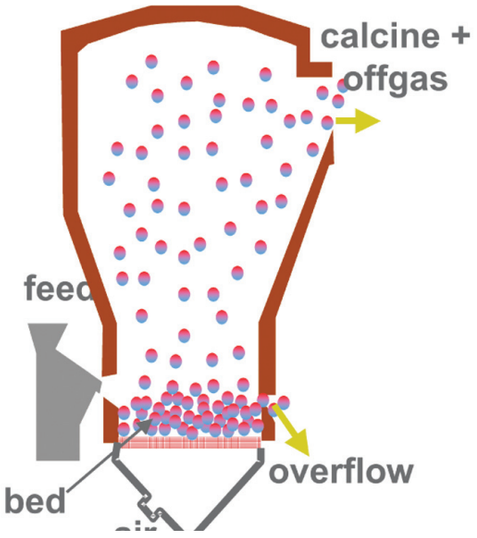

Figure 2—Principle of stationary fluid bed roaster (SFB)

Pyrite grain size is usually up to 6 mm in diameter. The coarser the grain, the higher the gas velocity must be to maintain the bed in a fluidized state. Even flotation pyrites with a grain size less than 70 μm can be processed in the fluid bed roaster. Gas velocity in the fluid bed ranges from 0.4–1.5 m/s at 1 bar and 850°C. (Figure 2.)

➤ *Circulating fluid bed roasting* (CFB)—a further step towards more efficient roasting in terms of higher throughput rates and process controllability is the the CFB process. This technology was originally applied in the calcination of hydrated alumina or clay and combustion of coal, and was later adapted for the roasting gold-bearing minerals. Following extensive pilot-plant tests, the first industrial-scale plant was built by Lurgi—now Outotec—and commissioned in 1991 in Australia. The company has been responsible for introducing the advantages of the technology to the industry throughout its development. Contrary to a 'normal' stationary fluid bed, circulating fluid bed roasters are operated at higher gas velocities in the range of 3–6 m/s. Due to the velocity, the fine solids are entrained with the gas and partly recycled to the roaster via a cyclone. (Figure 3, Table I.)

Pyrite dead roasting

The major objective of the roasting process is to eliminate the sulphur contained in the concentrate and to provide a calcine

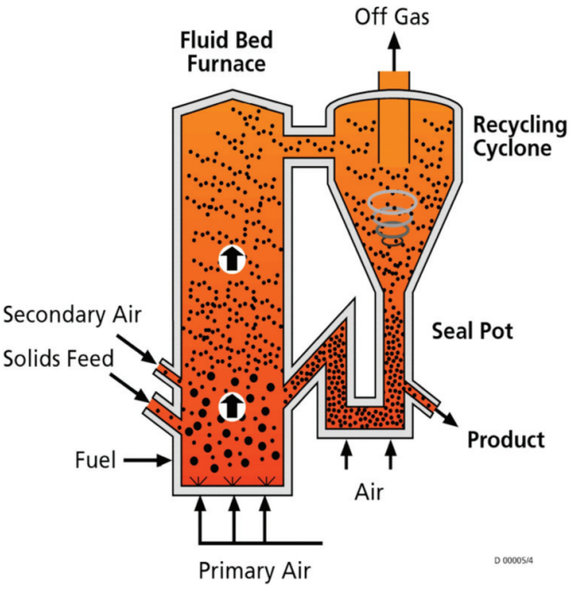

Figure 3—Principle of circulating fluid bed

Table I

Outotec roasting technology for pyrite concentrate, latest plants installed

Year	Location	Number and plant type	Concentrate
2009	Syama, Mali	1 x 590 t/d CFB	Pyrite (gold)
2007	Tongling, China	1 x 1130 t/d SFB	Pyrite/pyrrohtite
2004	ETI, Turkey	1 x 630 t/d SFB	Pyrite
1996	Wengfu, China	2 x 600 t/d SFB	Coarse pyrite
1991	KCGM/Gidji W.A.	2 x 575 t/d CFB	Pyrite (gold)
1984	Almagrera, Spain	1 x 725 t/d SFB	Pyrite
1983	Siilinjärvi, Finland	1 x 420 t/d SFB	Pyrite

product and SO_2 containing gases. A roasting temperature of 600–1000°C is generally the most suitable range, depending on the process and mineralogical requirements. As the sulphur content of the sulphide concentrate is primarily pyrite (FeS_2), the following simplified main equations may apply, whereas the predominants of the reactions depend on partial pressure of oxygen and the temperature range:

$$2FeS_2 + 11/2\ O_2 \longrightarrow Fe_2O_3 + 4\ SO_2 \qquad \Delta H = -1666\ \text{kJ/mol} \qquad [1]$$

$$3FeS_2 + 8\ O_2 \longrightarrow Fe_3O_4 + 6\ SO_2 \qquad \Delta H = -2381\ \text{kJ/mol} \qquad [2]$$

$$FeS_2 + 3\ O_2 \longrightarrow FeSO_4 + SO_2 \qquad \Delta H = -1054\ \text{kJ/mol} \qquad [3]$$

Since all three equations represent strictly exothermic reactions, a considerable amount of excess heat is developed during the roasting process in the fluid bed system and is recovered in the waste heat boiler system.

The oxygen necessary for the roasting reactions is supplied to the fluid bed system as atmospheric air.

The products gained from the roasting process are calcine and roasting gas. The calcine consists of Fe_2O_3, Fe_3O_4, $FeSO_4$ and gangue material, while the roasting gas has SO_2, SO_3, O_2, N_2 and H_2O as steam. Depending on the chlorine content in the roaster feed, HCl may also exist in the roasting gas in corresponding concentrations.

The design of a roasting plant depends on the type of concentrate. Some of the main process relevant figures are the sulphur content and the particle grain size. Additional important process figures are the reaction temperature and the concentrate throughput.

The pyrite concentrates can be classified as shown in Table II.

In the case of a high arsenic content in the pyrite, a special treatment is required using a two-stage roasting process. Arsenic occurs in pyrites as arsenical pyrite (FeAsS; $FeAs_2{*}FeS_2$). Under the usual roasting conditions, with a slight excess of oxygen in relation to the stoichiometric requirement for converting the iron content of the pyrite to haematite, the majority of the arsenic is oxidized to As(V) and will react with the haematite to form stable iron arsenate ($FeAsO_4$). In this way, about 70–80% of the arsenic content in the pyrite feed becomes bound to the cinder. This conversion can be optimized in a CFB reactor according to special process conditions. The remaining arsenic, which is oxidized to As(III) as shown in Equation [4], is volatilized and entrained by the roaster gas and must be separated in the wet gas cleaning system:

$$2FeAsS + 5\ O_2 \longrightarrow Fe_2O_3 + 2SO_2 + As_2O_3 \qquad \Delta H = -1987\ \text{kJ/mol} \qquad [4]$$

In instances where the cinder is to be used in steelmaking, high arsenic pyrites must be processed in a two-stage fluid bed roasting system. In the first stage, operating under oxygen-deficient conditions, no haematite, nor iron arsenate will form. The arsenic is thus almost completely volatized and discharged with the roaster gases. In the second fluid bed stage, the separated cinder is oxidized to haematite. This principle is applied on an industrial scale using the Boliden roasting process.

Sulphuric acid plant based on roasting of pyrite concentrate

The technology for the roasting of fine flotation pyrite concentrates is a stationary fluid bed for small throughputs or a circulating fluid bed for high throuphputs up to approx. 1800 t/d. . With a heat recovery system, this roasting plant layout can be considered classic consisting of a fluid bed roaster, waste heat boiler, gas cleaning and calcine handling equipment. The SO_2 off-gas produced is then recovered in the sulphuric acid plants. The dry feed throughput can reach up to 370,000 tpa in an SFB and 590 000 tpa in a CFB plant. (Figure 4.)

The cinder product consists of 58 per cent iron and is about 80 per cent by weight smaller than 50 microns. This cinder product is a competitive source material for the cement industry as the iron containing additive. However, the extreme fineness of the cinder and its dusting tendency are undesirable and an agglomerating technique is needed. In order to keep the price of agglomerated pyrite cinders at a competitive level, the agglomerating method must be chosen so that the capital and operating costs (maintenance, power and water consumption) are low.

Table II

Types of pyrite concentrate

Type	Composition	Grain size
Pyrite concentrate (flotation)	S 47–48 wt%; Fe 42–43 wt%	Fine particles 55% < 45 μm
Coarse pyrite	S 47–48 wt%; Fe 42–43 wt%	Coarse particles 0–6 mm
Pyrrhotite concentrate (flot.)	S 34–38 wt%; Fe 50–54 wt%	Fine particles 55% < 45 μm
Coarse pyrrhotite	S 28–29 wt%; Fe 47–50 wt%	Coarse particles 0–4 mm

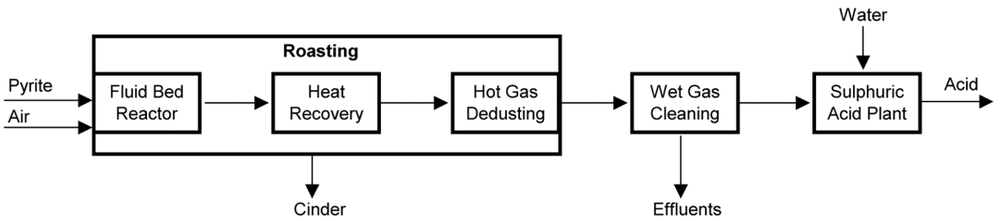

Figure 4—Block diagram pyrite roasting plant

Table III

Example of pyrite roasting plants

	Gidji (gold)	ETI (pyrite)	Tongling (pyrite/pyrrhotite)
Location	Kalgoorlie/Australia	Bandirma/Turkey	Tongling/China
Roaster type	CFB	SFB	SFB
Roaster grate area m²	8.5	100	138
Raw material	flot. pyrite	flot. pyrite	flot. pyrite/pyrrothite
Feed	slurry	dry (9% H_2O)	dry (6% H_2O)
S content in feed wt%	33	48	37
Capacity t/d	575	650	1130
Roast temperature °C	640	850	900
Steam production t/h	no steam	43	82
Steam parameters MPa/°C	no steam	4.2/400	3.82/450
Cinder t/h	20	20	41
Off-gas roaster Nm³/h	58 000	60,000	100,000
Acid production t/d	no acid	750	1200
Power consumption roasting kW	1000	1250	1400

Roasting

The roasting of sulphide concentrates is often the first process step in the production of metals or chemicals. With the addition of air, iron sulphides are transformed into solid oxides and gaseous sulphur dioxide at temperatures of 600–1000°C. After cooling in a waste heat boiler to 320–400°C, the waste gases, loaded with 50–150 g/Nm³ of dust, pass through a cyclone for preliminary separation of the coarse particles. The majority of the dust remaining in the hot gas is then removed in a hot-gas electrostatic precipitator. After cleaning and cooling, the sulphur dioxide in the roasting gas is further processed in the wet gas cleaning section. (Table III.)

Gas cleaning

The gas cleaning section can be divided into the hot area, which usually consists of the roasting section, and the wet gas cleaning area, which starts at the quench throat of the Venturi scrubber. The gas is cooled to approx. 65°C by water evaporation in the circulating week acid.

The weak acid bleed is discharged from the scrubber to the effluent treatment plant. The amount of weak acid bleed can vary in a wide range and depends on the process conditions and impurities in the concentrate/off-gas (an average value is ~3 m³/h, max. 10% H_2SO_4). To allow for a convenient treatment of the weak acid, the contaminating, dissolved SO_2 gas is removed in an SO_2 stripping column.

The gas cooling to an outlet temperature of approx. 40°C takes place in a packed gas cooling tower. For the removal of fine particles and acid aerosols, normally two wet electrostatic precipitators (ESP) arranged in a series are used. The wet ESPs are of proven design and are constructed from acid-resistant material.

Sulphuric acid section

The de-dusted, demisted, and cooled but humid gas from the gas cooling and cleaning section is conveyed to the drying tower by the SO_2 blower. The gas might be diluted with atmospheric air to ensure the right operation parameters. The dried gas is then compressed by means of one SO_2 gas blower arranged downstream the drying tower. The vertical converter comprises four catalyst beds of vanadium pentoxide type catalyst facilitating the exothermic oxidation of SO_2 to SO_3. The final conversion efficiency will be approx. 99.8 per cent. To allow for a plant's improved energy recovery, a boiler feed water economizer is placed at the inlet of the final absorber.

In the intermediate absorption tower the SO_3 formed in catalyst beds 1–3 is absorbed by circulating acid (98.5%). The gas leaving the tower contains practically no SO_3, thus shifting the equilibrium to the SO_3 area of the reaction in the fourth catalyst bed.

In the final absorption tower, the SO_3 formed in the fourth catalyst bed is absorbed by sulphuric acid (98.5%, 80°C), which is collected in the pump tank, cooled and recirculated to the tower.

The gas leaving the tower passes a high efficiency candle type mist eliminator before it is released to the atmosphere via a stack. The product acid is cooled in a separate heat exchanger to 40°C and is discharged from the pump tank by a product acid pump to the product acid tank.

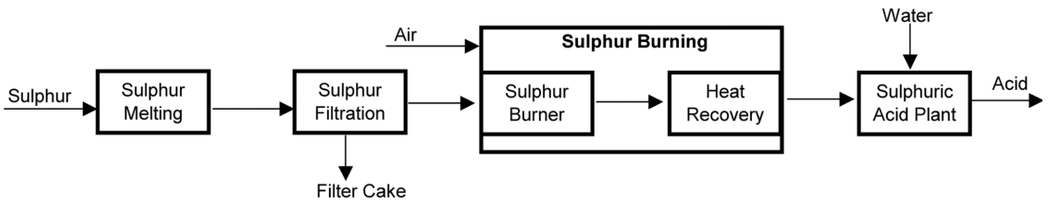

Figure 5—Block diagram sulphur combustion plant

Table IV

Example and comparison of process parameters of recently designed acid plants

	Pyrite roasting		Sulphur burning	
	SFB	CFB		
Capacity sulphuric acid tpd	1200	1500	1500	5000
Feed rate tpd	1130	1800	490	1630
Furnace off-gas volume Nm^3/h	105000	130000	120000	260000
SO_2 content in process gas vol%	~ 11		11.5	18
High pressure steam t/mt Mh	1.35–1.6		1.25–1.4	
Power consumption kWh/mt Mh	~ 70		~ 50	
By-product	Cinder		No by-product	
Effluents/waste	Weak acid		Filter cake	

Sulphuric acid plant based on sulphur combustion

The layout of a sulphur burning plant consists of the sulphur melting section, the sulphur burning section, including the heat recovery, and the sulphuric acid itself. (Figure 5.)

Solid sulphur is supplied to the melting tank with a conveyor belt. Steam heating coils are provided in the melting tank, which automatically controls the liquid sulphur temperature by adjusting the steam flow. The integrated pre-coating section is used to precoat the leaf filter prior to the sulphur filtration cycle. Filter aid (diatomaceous earth) and lime are added to liquid sulphur and homogeneously mixed by the agitator. Precoating will be necessary at the beginning of each sulphur filtration cycle. Leaving the sulphur filter, the sulphur will be treated in an additional cartridge filter, which has only a guard function.

Outotec's LURO burner will be provided for atomization of the liquid sulphur. The sulphur combustion furnace is of a horizontal design, with a multi-layer refractory lining. After the furnace, the gas is cooled down in a waste heat boiler for the production of high pressure steam. The gases from the combustion section are fed to the converter system. In addition, the excess heat from the SO_2 oxidation is recovered and used to produce high-pressure super-heated steam. Various vessels are used as an integrated part of the sulphuric acid plant.

Comparing the two processes

The comparison of pyrite roasting and sulphur burning can be done only on a general basis with some specific assumptions. Depending on the location of each project and actual market prices for the feed material, the cost analysis might look completely different. Transportation costs for sulphur have not been considered for this comparison, as well as any extra costs for cinder deposits or revenue for iron/haematite content or the recovery of valuable metals in the concentrate/cinder such as nickel, copper, zinc, gold, uranium, etc. Table IV shows a parameter comparison of the two types of sulphuric acid plants. The pyrite roasting process has a maximum capacity of 1200 t/d using an SFB and 1500 t/d with a CFB. Sulphur burning can reach a capacity of 5,000 t/d.

If pyrite is available—and the cinder can be further processed for recovery of valuable metals or even be used in other industry sectors—roasting is definitely more beneficial than sulphur burning. In order to be even more flexible and independent from the world market there is also the possibility of a combination between pyrite roasting and sulphur burning.

The investment costs on a lump sum turnkey basis for both plants with the scope as indicated in the block diagrams shown in Figures 4 and 5 would result in €40 m for a sulphur burning plant and €80 m for a pyrite roasting plant with a capacity of 1000 t/d sulphuric acid. In this case, the pyrite roasting plant has been estimated with a one line stationary fluid bed reactor.

To present a clearer view of the comparison, a break-even analysis was conducted for both processes and the results are shown in Figure 6. It is interesting to note that at a capacity of 1000 t/d the consumption figures for factors such as fuel, water and even labour are not significantly different. In fact, the only element that has a significant effect on the operating cost is the feed rate and consequently the feed price. Even

though almost three times as much pyrite is needed per hour to produce 1,000 t/d of sulphuric acid, the operating cost for a pyrite roasting plant is still lower than that of a sulphur burning plant because the price of sulphur is much more expensive than pyrite.

At the time the analysis was conducted, the cost of pyrite was estimated at US$ 35/ton while the cost of sulphur was estimated at US$150/ton. Based on these prices, the operating cost for pyrite roasting was estimated at US$ 41/ton of acid produced whilet the operating cost for sulphur burning was estimated at US$ 74/ton of acid produced.

The analysis reveals that because the capital cost for the sulphur burning plant is comparatively lower than pyrite roasting, it naturally breaks even earlier than the pyrite roasting plant at three years. However, because the operating cost for pyrite roasting is so low, not only does pyrite roasting break even a mere 12 months after the sulphur burning plant, but it also gains equal returns by the fifth year and exceeds the returns of sulphur burning by the sixth.

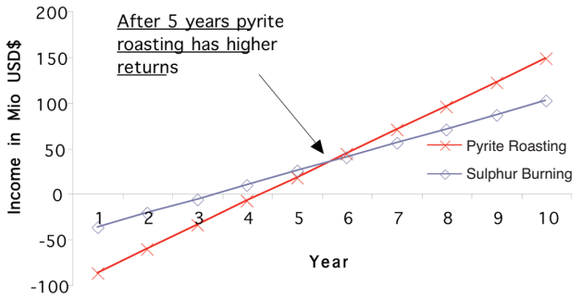

Figure 6—Pyrite versus sulphur breakeven (example 1000 t/d H_2SO_4)

Conclusion

With broad experience in the fluid bed technology, especially in the area of roasting, Outotec has optimized and developed roasting plants with increased throughput capacities. This development now reaches throughputs in a single roasting line for stationary fluid beds of up to 1130 t/d and circulating fluid beds of up to 1800 t/d based on pyrite concentrate and depending on chemical composition. At the capacity range described, the pyrite roasting process is the favourite process route especially when looking at long-term revenues. The economic benefit of a roasting plant as an alternative to the sulphur burning will be significant after an operation of approximately five years.

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