



Burning pyrites compared to sulphur

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Synopsis

Present day capital costs are analysed for a 2 000 metric tonne per day (MTPD) pyrite burning plant and compared with a sulphur burning plant of the same capacity. Power, raw material and steam production rates are then compared for the two facility types. A sensitivity analysis is conducted to highlight the impact changing sulphur, pyrite, capital and operating costs have on the relative economics of these feeds.

Technological improvement effects on capital cost and energy recovery are also discussed. Besides the steam produced from the burning of pure sulphur or pyrite, plants using an advanced form of heat recovery can produce up to 10 bar steam using heat from acid formation. The quantity depends on the overall water balance which is influenced by such factors as gas strength and product acid concentration. Modern materials and innovative process design also improve the ability to increase the high pressure steam from the roaster boiler in pyrite plants above the traditional 1.25 kg of superheated steam per kg of acid produced.

Introduction

In the recent past, high sulphur prices provided the impetus for a search for substitute sulphur feeds such as pyrite. However, the rapid drop in sulphur prices, from a high of US\$600/tonne to a low of US\$30, has reduced this economic motivation. This has not completely removed consideration of pyrite as a sulphur source as transportation considerations as well as downstream calcine use, gold and uranium leaching recovery improvements for example, still can provide economic justification. Recently, SNC-Lavalin Fenco designed and built a pyrite burning plant complete with an advanced heat recovery system (HRS) and all ancillaries including an effluent treatment plant.

This paper does not address the many complex factors which may influence the overall corporate decision to use sulphur versus pyrite as feedstock. Rather, it focuses on the basic economic and process trade-offs of a new capital investment decision.

Feedstock economics

From a historical perspective, alternate

feedstocks have often been studied when sulphur prices were high or shortages existed.

For most industrial users, the price difference between sulphur and pyrite was usually not enough to justify the additional capital investment and operating risk of a pyrite plant. In general, past analyses favoured the use of commercial sulphur as feedstock for acid plants because capital investment was substantially lower and the process was less complex and more reliable.

In countries such as Turkey and China where large pyrite deposits are available, and where tax structures, duties, government subsidies, mining and shipping costs have favoured the use of pyrites, valuable process experience has evolved. One example of this is Fenco's recent pyrite roaster project at ETI Holding in Turkey where power and calcine sales contributed to project viability.

Feedstock quality

In general, the sulphur content in pyritic ores can range from about 20% to 50%. If different ore grades are to be roasted, the fluid bed design must be based on the ore that limits heat and mass transfer at the maximum design rate. For the most part, ore impurities affect downstream acid plant operation and must be removed from the gas stream.

Impurities

Arsenic can poison and deactivate catalyst. When gas containing arsenic vapour is cooled, submicron particles are formed which may be recovered as arsenic oxide. However, since the producer is left with a product that is difficult to sell, the most common method of treatment is to cool and scrub the gas with water. The weak acid effluent from the scrubber is treated to recover an arsenic cake or, more commonly,

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to fix the arsenic as an insoluble compound. After gas scrubbing usually two-stage high efficiency mist precipitators are required for complete arsenic removal.

Lead behaves similarly to arsenic but generally higher concentrations are tolerable in the product acid. Some plants have experienced fouling in the weak acid coolers due to lead and bismuth, increasing maintenance costs.

Fluorides are not normally found in pyrites. However, specific treatment methods including sodium silicate injection into the wet gas cooling section are available if fluorides are present in amounts greater than about 0.1 g/l in the recirculating liquid.

Sometimes chlorides are present in trace amounts in pyrite ore. If chloride concentration exceeds roughly 0.2 g/l in the gas cleaning section, stainless steel components become susceptible to corrosion.

Occasionally mercury is also present in small quantities. Mercury easily slips through the gas scrubbing equipment as elemental vapour or fine mist particles. Special attention is needed in the construction of mist precipitators to avoid lead amalgam formation. Mercury contaminates product acid, fouls heat exchangers and is very difficult to remove. When mercury is found in detrimental quantities, the calomel process can be used to remove it from the acid plant feed gas.

Increased dust loading associated with pyrite roasting also requires more efficient gas cleaning. Dust causes catalyst plugging and pressure drop build-up, especially in the first converter pass. Dust also plugs the mist eliminators in the contact section and discolours acid.

In comparison to the above, for sulphur burning plants, commercial sulphur impurities are usually significantly lower with little or no metal contamination. Typical levels range from 0.005% to 0.02% ash and 0.01% to 0.25% hydrocarbons, which is typical for recovered refinery sulphur. If solid sulphur is used, provision must be included for melting and filtration.

Process differences

A pyrite-fed sulphuric acid plant includes roasting, waste heat recovery, gas scrubbing and contact sections. Pyrite roasting using a fluidizing furnace to generate SO₂ gas is the first major process step.

The residual solids from the roasting process, a calcine (iron oxide) cinder, are generally in the form of a fine dust which can be difficult to handle. For those operations requiring calcine leaching, a wetting and slurry system can simplify material handling.

Hot SO₂ gas leaving the roaster is treated to remove excess heat and coarse dust using high pressure waste heat boilers followed by cyclones. In some cases, hot dry electrostatic precipitators are used after the cyclones.

Volatilization of minor impurities from the roaster such as lead and arsenic depends upon whether the roaster operates with a deficiency or excess of air. Roasters operating with excess air tend to evolve less submicron particulate at the cost of greater acid losses in the wet gas cleaning circuit. Wet scrubbing using an open spray tower removes most coarse entrained dust particles having diameters greater than 5 microns. Scrubbing efficiencies are on the order of 70% with SO₃ mist removal in the same range. Other types of scrubbing devices include those of the venturi and tray type.

Gas cooling in larger plants is typically carried out in a packed cooling tower circuit with weak acid coolers. The solids content of the weak acid circulating through the tower is maintained around 1% to 2% to prevent plugging. Gas cooling is designed to remove enough water to achieve control of the overall water balance and to maintain desired product acid strength.

Gas leaving the wet scrubbing and cooling equipment still contains traces of dust along with residual acid mist particles. To remove the mist and dust, the gas is cleaned in wet electrostatic precipitators. The gas is then dried in a packed drying tower using sulphuric acid to remove water vapour. Gas from the drying tower next goes to a centrifugal compressor.

After compression, the gas is heated to the ignition temperature for catalytic oxidation of SO₂ in the first converter pass using a combination of gas to gas heat exchangers. The heat generated in the converter by the exothermic oxidation reaction of SO₂ to SO₃ is transferred by these exchangers. Usually there are four converter passes with interpass and final absorption towers. This double absorption design is required to achieve the low SO₂ emissions required by law in most jurisdictions. Heat exchangers are used to bring the gas leaving the interpass absorbing tower up to ignition temperature before reentering the converter.

Depending upon the initial SO₂ concentration in gas there is often excess heat left over which can produce superheated steam or heat exhaust air for pollution control reasons. Proper arrangement of the gas heat exchangers when steam equipment is integrated in the contact section achieves minimum capital cost and maximum thermal efficiency.

For a sulphur burning plant, the contact section of the acid plant is simpler as two of the four gas to gas exchangers are not required. These, and the major differences listed below, lead to lower capital costs for the sulphur burning alternative.

Major differences:

- ▶ The elimination of roasting and gas cleaning operations, the latter due to the sulphur feedstock being a cleaner raw feed material
- ▶ Absence of calcine residuals or weak acid effluent when using sulphur
- ▶ Higher inlet SO₂ gas strengths with sulphur versus pyrites, e.g. 11.5% versus 9.5%
- ▶ Simplified acid flow scheme for sulphur plants
- ▶ Simplified gas flow scheme since the gases are clean and dry enough to pass directly to the catalytic converter after combustion and cooling.

Equipment design implications with pyrite plants

Roasting section

The pyrite roasting operation represents a large portion of a plant's overall investment costs (perhaps up to 30% to 40% of plant capital). Over the years, roasters have increased in size to achieve better economies of scale. For a 2000 MTPD pyrite plant, however, two parallel roasters lines would still be required.

In terms of the roaster outputs, processes are continually being developed to balance the trade-offs between effluent quantities, cinder by-product, nonferrous metal extraction,

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energy recovery and sustained performance. For example, downstream metal recovery can be greatly influenced by roasting temperature and off-gas oxygen content. The adjustment of these in turn affects heat recovery and gas strength to the acid plant.

Gas cleaning section

The wet electrostatic precipitators in a pyrite facility's gas cleaning section typically represent about 10% of the overall plant investment. Effective mist precipitator operation is required to achieve high plant on-stream times. In order to achieve quality operations with a standard alloy or plastic tube design, a minimum four second residence time is normally used. In large plants there are usually two or more parallel trains of precipitators each with two units in series.

There have been recent attempts to reduce the cost of mist collection through material of construction changes and through changes in the basic technology—with mixed results. A failure in this area, however, can cause significant losses in plant operating time.

Other gas cleaning equipment including quench/humidification and gas cooling tower circuits are modified as required to address specific impurity levels.

Contact section

Whereas multiple roasters with up to 1000 MTPD maximum acid capacity per train are usually required, and multiple units of mist precipitators are still needed, the contact section can be designed as a single train for all but the very largest of plants (pyrite or sulphur based).

Plant cost comparisons

Estimates of manufacturing costs for 2000 MTPD pyrite and sulphur burning sulphuric acid plants are shown in Table I. The following assumptions were made in the assembly of these costs:

- Interpass sulphuric acid plant with motor drive
- Turbogenerator included with electric power generation based on 400°C and 40 bar (600 psi) steam condensed at 76 mm Hg at 85% efficiency. Electric power credit is \$0.05/kWh
- Delivered pyrite cost is \$20/t with 46% sulphur content. (Note that pyrite credits in the form of

increased metal recovery or calcine sales can substantially reduce this cost.) Delivered sulphur cost is \$50/t with 99.9% sulphur content

- Dry, 10% moisture content or less, pyrite feed to the roaster
- Pyrite plant operates with a 9.5% SO₂ gas strength to the converter. The sulphur burning plant operates with an 11.5% SO₂ gas strength. SO₂ conversion is greater than 99.7%
- Minimum disposal costs are assumed for the pyrite plant. Actual costs may be different. Additional value added processing of by-products can significantly increase capital requirements.

From Table I, the major difference in total manufacturing costs is due to utility, labour, and maintenance costs. With a fuller cost analysis; however, indirect charges will also show to have significant impact (most notably for depreciation). General overhead costs will vary based on site specific factors and financing. Direct costs are offset by credits received for site power (see negative values or credits on Table I).

The total direct production costs from Table I show a substantial spread between the two alternatives. This spread will be considered in corporate decision making along with the projected return on capital, an evaluation of associated risks and other site specific factors. At the feed costs shown, sulphur is the superior choice both from a capital and operating cost perspective. However, in some cases, additional revenue not considered in this analysis may offset these costs. Increased recovery of precious metals from a refractory ore or the sale of calcine are two examples.

As a reference point and using the cost structure from Table I, a pyrite credit of approximately US\$6/tonne is required to push the pyrite option into an economically viable option, defined as an internal rate of return of 10%, compared to its sulphur counterpart. Note that this is an internal comparison Table and is not the overall project expected return.

The sensitivity of this analysis to four major variables is shown in Figure 1. Operating costs are defined as all those shown in Table I save that of feedstock.

Using the economic data from Table I above, the net present value at 10% of the incremental costs, both capital and operating, is -US\$ 90 million. In other words, the sulphur option is strongly favored.

The two most sensitive relationships are pyrite and sulphur price. An approximate doubling of sulphur cost, all other things equal, or a small credit for pyrite would be enough to change the economic preference to a pyrite roaster.

With purchased feedstock, price and supply stability must be addressed. Between 1990 and 2006, sulphur prices varied from \$90 to \$150 per tonne (and trended upwards). In 2007 to mid 2008, sulphur prices sky rocketed to \$900 per tonne although they have since dropped significantly. The price range for pyrites is more difficult to establish as no active market exists. Delivery and storage charges also significantly affect raw material costs with the result that feedstock costs are largely site specific.

The environmental and political consequences of waste disposal from a pyrite plant are more difficult to determine. In roasting processes that use excess air, most of the arsenic from the ore ends up in a liquid waste stream of weak

Table I

Simple production costs for pyrite and sulphur burning acid plants*

	Feed type	
	Pyrites	Sulphur
Capital investment	\$150 000 000	\$90 000 000
Direct production cost (\$/tonne acid)		
Feedstock	\$14.50	\$16.70
Power	-\$10.80	-\$12.90
Utilities	\$7.00	\$3.90
Labour	\$4.50	\$2.70
Maintenance	\$6.40	\$3.90
Total direct production cost	\$21.60	\$14.30

*Basis: 2000 t/d H₂SO₄, USA site

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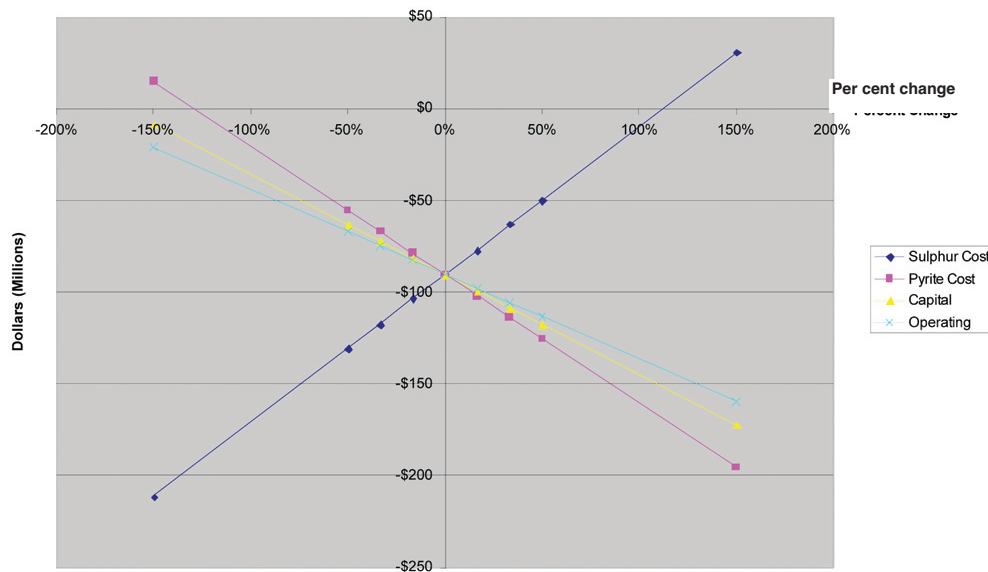


Figure 1—Sensitivity analysis—NPV (10%)

Table II

Steam and power summary

Steam produced (Kg/h)	Pyrites	Sulphur
High pressure (40 Barg 400°C)	112 500	116 600
Power generated, MW (non HRS)	27.5	28.5
Site power used, MW	9.5	7
Total net power	18	21.5

sulphuric acid. This is easily removed in an effluent treatment plant as was done for Fenco's recent roaster facility, but the solid effluent must still be segregated from the environment. The volume of cinder ash is also substantial. Disposal must be based on the most cost-effective methods amenable to safe containment which fully comply with in-place regulations. Disposal problems can significantly affect project viability.

Site turbogeneration

Site turbogeneration can significantly increase the revenue stream of sulphur and pyrite plants as shown in Table II. Energy credits shown in Table I are derived from the following steam flows with a power credit of \$0.05/kWh applied.

If there is surplus site power, negotiations would be pursued by the plant operator with the local utility authority in order to obtain the highest grid credit and maximum value.

Recent technological developments

Heat recovery system (HRS)

Applicable to both pyrite and sulphur burning plants, this advanced recovery technology can provide significant benefits for new and existing plant operators. The heat recovery system (HRS) operates in a low corrosion window allowing the use of common commercial stainless steels for

high temperature SO₃ absorption and energy recovery.

Energy recovered from the HRS is used to heat boiler feedwater and generate steam at pressures up to 10 barg. With HRS, about 0.5 kg steam per kg acid can be produced depending mainly upon gas strength and product acid concentration.

The HRS is integrated in the sulphuric acid circuit with a heat recovery tower replacing the conventional interpass absorbing tower. The heat recovery tower operates at acid temperatures of about 200°C to provide the necessary driving force for generating steam. Further, and instead of using acid coolers, stainless heat exchangers are put in place to recover acid circuit heat.

The use of an HRS adds an additional 6 MW of power to the generating and, hence, the revenue stream (\$3.60 / tonne of acid produced).

Conclusions

The modern pyrite plant can be nearly double the cost of an equivalent size sulphur burning sulphuric acid plant. This coupled with higher operating costs makes it difficult to justify pyrite burning plants on acid generation alone. Additional revenue streams such as increased gold recovery or calcine sales are necessary to justify the additional CAPEX and OPEX costs. Site specific factors such as shipping, storage and by-product handling can also significantly influence corporate decision making when evaluating the pyrite plant alternative.

As gas cleaning and contact sections continue to improve resulting in more efficient and reliable operations, manufacturing costs are being reduced for both pyrite and sulphur burning plants especially when integrating site turbogeneration. The heat recovery system developed by MECS can significantly increase power production in this respect. Return is maximized by satisfying process heating needs, offsetting purchased site power and establishing a fair credit for surplus energy. ♦