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COMBUSTION OF SOLID SULPHUR AND CALCINE IN A FLUIDIZED BED ROASTER FOR THE PRODUCTION OF SULPHURIC ACID[1]

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SUMMARY

The present innovation is a technical breakthrough in burning solid sulphur in a conventional fluidized bed roaster designed for metallurgical pyrite concentrate feed. The process invention was successfully introduced into the existing 1,500 MT/day double contact sulphuric acid plant of Philippine Phosphate Fertilizer Corporation (PHILPHOS).

The process uses a feed of powdered sulphur or pastilles premixed with moist calcine from the previous pyrite roasting operation at a ratio that approaches the analysis of pyrite concentrate.

The process is straight forward and has the following advantages:
a. very little investment
b. roaster rate of not less than 90% capacity to sustain bed temperature
c. sulphur conversion to SO_2 is not less than 99%
d. can be used to upgrade pyrite concentrates with low sulphur content
e. lower roaster operating temperature which prolongs the life of the bricklinings.

RESUME

La présente innovation est une percée technique dans la combustion de soufre solide dans un four à lit fluidisé conçu pour être alimenté en concentré de pyrite métallurgique. L'invention du procédé a été introduite avec succès dans l'unité d'acide sulfurique à double contact de 1500 t/j existante de Philippine Phosphate Fertilizer Corporation (PHILPHOS).

Le procédé utilise une alimentation de soufre pulvérulent ou en pastille prémélangé avec un produit calciné humide résultant de l'opération précédente de grillage de pyrite en un rapport voisin de l'analyse de concentré de pyrite.

Le procédé est simple et offre les avantages suivants:
a. investissement très faible
b. taux de calcination non inférieure à 90 % de capacité pour maintenir la température du lit
c. la conversion du soufre en SO_2 n'est pas inférieure à 99 %
d. peut servir pour enrichir les concentrés de pyrite avec une faible teneur en soufre
e. température de grillage plus basse ce qui prolonge la vie du revêtement de briques

✦ ✦ ✦

Burning solid sulfur in the conventional fluidized bed roasters has been attempted several times in the past but with little success. Attendant problems of sulfur sublimation and subsequent clogging of waste heat boiler tubes and gas coolers have prevented prolonged operation, not to mention the reduction in the burning capacity of the roasters.

TECHNICAL BACKGROUND:

Sulfur burning in a fluidized bed roaster is a process invention aimed at replacing pyrite burning to produce sulfuric acid using existing facilities. The innovation is such that the feed used is sulfur pastilles (up to 5 mm) pre-mixed with calcine from the previous pyrite roasting operation at a ratio of 4:5. The feed mixture is called calsul. Except for the feed, the whole process remains the same.

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[1] *Combustion d'un mélange de soufre solide et de produit calciné dans un four à lit fuidisé pour la production d'acide sulfurique*

The process innovation is a technological breakthrough in burning solid sulfur in a conventional fluidized bed roaster with hardly any additional investment. It was conceived and developed in an effort to fully utilize the idled 10-year old two-train fluidized bed roasters designed for metallurgical pyrite concentrate for sulfur burning.

The process kinetics of the present innovation takes advantage of the property of sulfur to melt and form vapor coupled with the ability of the fluidized bed roaster to disperse the molten sulfur evenly on the chamber bed before vaporization and with adequate air oxygen efficient combustion into SO_2 is effected. This is accomplished by pre-mixing powdered or pastilled sulfur (up to 5 mm) with a low grade pyrite and/or inert material such as furnace grade silica sand or iron cinders at a ratio that results to 40-45% sulfur content. The mixture is preferably moistened up to about 15% H_2O to avoid segregation of the sulfur and the inert material and at the same time to minimize dusting. A simple drum or paddle mixer is adequate in the preparation of the calsul feedstock.

The premixed feedstock is introduced into the hot roaster through a rotary feeder. As soon as the sulfur melts, it is immediately dispersed and suspended with the inert mass by the percolating action of the fluidized bed. This promotes the vaporization of the sulfur at high rate due to the very large surface area created. Complete combustion of the sulfur into SO_2 gas is accomplished within the plenum of the roaster. To ensure complete combustion, adequate fluidizing air is supplied so that the resulting SO_2 gas is at most 11%.

The coarser cinder from the roaster overflow and the primary cyclones are normally recycled to premix the sulfur feedstock.

The process is straight forward and has the following advantages:

1.0 Very little investment.
2.0 Roaster rate of not less than 90% of design capacity to sustain bed temperature.
3.0 Sulfur conversion to SO_2 at the roaster is not less than 99%.
4.0 SO_2 gas concentration is maintained within normal range.

<u>THE PROCESS APPLICATION</u>:

The present innovation was successfully introduced into an existing 1500 MT/day double contact sulfuric acid plant equipped with two (2) trains of pyrite roasters designed to handle 24.1 MTPH each of metallurgical pyrite concentrate. The plant was designed by Mitsubishi-Lurgi and started to operate in 1984 until it became idle in 1993 due to the high cost of pyrite.

Powdered or sulfur pastilles (up to 5 mm) is premixed with moist (up to 15% H_2O) calcine from the previous pyrite roasting operation at a ratio that approaches the analysis of pyrite concentrate. Table I shows comparative analysis of raw materials. The premix is called calsul. A 4:5 ratio of sulfur to calcine (Table II - Calcine's analysis) has proven to be very satisfactory. Coarse sulfur like flakes and slates tend to segregate from the calcine and result to erratic SO_2 concentration from the roaster.

As shown in Table III, the fluidizing air requirement for calsul is about 5% lower than for pyrite since the calcine is already inert. A minimum of 15% excess air also ensures complete combustion within the roaster plenum and avoids sublimation of the sulfur. The calcine being inert and introduced cold, absorbs part of the heat of combustion rendering the roaster bed temperature cooler than the design. This results in lower steam generation from the waste heat boiler.

The calcine generated from the calsul operation shows a reduction of 30% in the sulfur content from the original feed and a minimal reduction in its particle size.

After operating the roasters for three months, the waste heat boiler and the downstream gas cleaning equipment were inspected and found to be relatively free of sulfur deposits except for a thin coating of black material composed of calcine dust and a little sulfur.

On a prolonged operation, it was observed that the calcine carryover into the downstream equipment was heavier with the use of sulfur in flake or slate form of more than 5 mm in size. Prilled or pastilled sulfur of not more than 5 mm in size is ideal.

Except for the normal preventive maintenance and inspection, the roasters were operated with calsul feed for twenty (20) months prior to the annual turnaround without signs of efficiency diminution.

Table I - Average Chemical Analysis (dry basis %)

	Design (pyrite)	Typ. Pyrite	Calsul*
Total S	46-47	45.00	45-46
Cu	0.24	0.30	0.15
Fe	41.70	40.00	31.70
SiO_2	5.80	7.5	5.50
H_2O	9-11	10-12	12-13

*Calsul is a mixture of sulphur pastille and pyrite cinder (calcine) at 4.5 ratio

Table II - Analysis of Calcine (dry basis %)

	Feed	Outlet
Total S	0.30	0.20
+ 35 M	0.69	0.00
+ 60 M	1.34	0.25
+ 100 M	3.77	0.29
+ 150 M	8.18	5.77
+ 200 M	14.67	16.49
+ 325 M	17.50	19.57
- 325 M	53.85	57.83

Table III-Comparative Operating Data at the Roaster Section

	Design (pyrite)	Typ. Pyrite	Calsul*
Fluidizing Airflow (NM3/H)	53,500	53,500	50,400
Feed Rate (MT/H)	24.1	24.1	24.1
Roaster Outlet P (MM H2O)	0-10	0-10	0-10
SO2 Gas at Roaster Outlet (%)	14.0	14.0	14.0
Roaster Gas O2 Content (%)	3.0	3.0	3-6
Calcine Temp. after Cooler(deg.C)	90	90	90
Gas Temp. after Cooler (deg.C)	43	43	39
SO2 Gas after Drying Tower (%)	8.5	8.5	8-9
Roaster Bed Temp. (deg. C)	800-1,000	800-1,000	600-800
Roaster Outlet Temp. (deg. C)	900+/-20	900+/-20	800+/-20
Waste Heat Boiler Outlet T (deg. C)	350	350	350
Elec. Precipitator Outlet T (deg. C)	330+/-20	330+/-20	330+/-20

** Calsul is a mixture of sulfur pastille and pyrite cinder (calcine) at 4:5 ratio.*

CHART AND TABLE EXPLANATION

CHART 1 - Location map of Philphos

Philippine Phosphate Fertilizer Corporation (PHILPHOS)
Leyte Industrial Estate, Isabel, Leyte, Philippines

CHART 2 - Schematic diagram of SAP

PHILPHOS has a double contact sulfuric acid plant employing turbulent layer fluidized bed roasters. Pyrite is roasted with air in a fluidized bed roaster to generate sulfur dioxide (SO_2). Passing through a waste heat boiler, dust cyclone, electrostatic precipitators, venturi scrubber and gas coolers, the hot SO_2 gas is cooled, cleaned of dust and dried. The gas, together with required air, enters a four-bed converter where SO_2 is converted into SO_3. SO_3 gas is absorbed and strengthened in a series of absorption towers from which a draw-out of acid product goes to the acid storage tanks.

Plant Capacity : 1,500 MT / Day
Designed by : Mitsubishi Lurgi
2 trains pyrite roasting
to handle 44 MT / hr. of metallurgical pyrite concentrate

CHART 3 - 3A Pyrite consumption since 1987 to 1992
3B Cost of pyrite since 1987 to 1992

Commercial operation started in 1984 with production capacity of 1,500 MT / day of sulfuric acid. Supply of pyrite concentrate was then abundant within the locality at reasonable prices. However, in 1992 price rose to US$ 50 due to high mining cost. Imported pyrite was also expensive. SAP operations was suspended due to high cost of pyrite

A capital outlay of US$ 11.0 million was approved to retrofit the acid plant with a sulfur burner. The retrofitting would take about 18 months to complete and with the short supply of acid, the fertilizer granulation plant would have to operate at 50% capacity. In a last ditch effort to salvage the situation, approval was obtained on an experimental basis to use the existing roaster section to burn solid sulfur by blending with calcine. A 3,000 ton lot of sulfur pastilles was brought in for the test. The roaster bed was prepared using pyrite as initial feed followed by the calsul mix. The plant operated normally and continuously at capacity until the sulfur stock was depleted.

<u>CHART 4</u> - Schematic diagram of Sulfur Burner to the system

<u>CHART 5</u> - Technical - process flow sheet

Table I - Average chemical analysis of raw materials
Powdered or sulfur pastilles (up to 5 mm) is premixed with moist (up to 15% H_2O) calcine from the pervious pyrite roasting operation at a ratio that approaches the analysis of pyrite concentrate. We call the premix as calsul. In our case, a ratio of 4:5 of sulfur to calcine has proven to be satisfactory. Coarse sulfur like flakes and slates tend to segregate from the calcine and results to erratic SO_2 concentration from the roaster.

Table II - Calcine analysis, feed & outlet
The premixed feedstock is introduced into the hot roaster through a rotary feeder. As soon as the sulfur melts, it is immediately dispersed and suspended with the inert mass by percolating action of the fluidized bed. This promotes the vaporization of the sulfur at high rate due to the very large surface area created. Complete combustion of the sulfur into SO_2 gas is accomplished within the plenum of the roaster. To ensure complete combustion, adequate fluidizing air is supplied so that the resulting SO_2 is at most 11%.

As shown in **Table III**, the fluidizing air requirement for calsul is about 5% lower than for pyrite since the calcine is already inert. A minimum of 15% excess air also ensures complete combustion within the roaster plenum and avoid sublimation of the sulfur. The calcine being inert and introduced cold, absorbs part of the combustion rendering the roaster bed temperature cooler than the design. This results to lower steam generation.

The calcine generated from the calsul operation shows a reduction of 30% in the sulfur content from the original feed and a minimal reduction in its particle size.

After operating the roasters for three months, inspection of the SAP internals were found normal. No indication of sulfur sublimation was observed. The roasters, waste heat boiler and the downstream gas cleaning equipment were also found to be relatively free of sulfur deposits except for a thin coating of black stuff composed of calcine dust and a little sulfur.

On a prolonged operation, it was observed that the calcine carryover into the downstream equipment was heavier with the use of sulfur in flakes or slate form of more than 5 mm in size. Prilled of pastilled sulfur of not more than 5 mm in size is ideal.

Except for the normal preventive maintenance and inspection, the roasters were operated with calsul for twenty (20) months prior to the annual turnaround without signs of efficiency diminution.

Calsul process advantages:

1. Very little investment
2. Roaster rate of not less than 90% of design capacity to sustain bed temperature.
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4. SO_2 concentration is maintained within normal range.

The process innovation is a technological breakthrough in burning solid sulfur in a conventional fluidized bed roaster with hardly any additional investment. The process which is straight forward was successfully introduced into an existing 1,500 MT/day double contact sulfuric acid plant equipped with two (2) trains of pyrite roasters designed to handle 24 MT/hr each of metallurgical pyrite concentrate. The plant was designed by Mitsubishi-Lurgi and started to operate in 1984 until it became idle in 1993 due to high cost of pyrite.

Chart 1

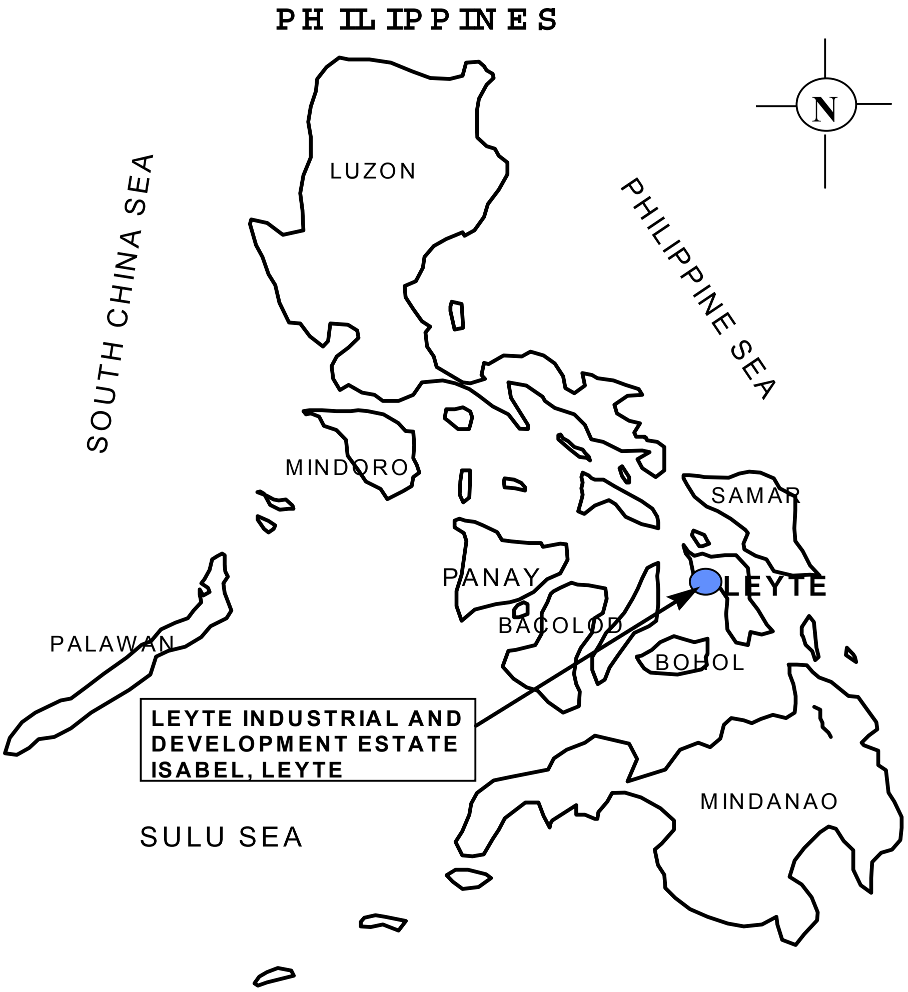

Chart 2

SULFURIC ACID PLANT

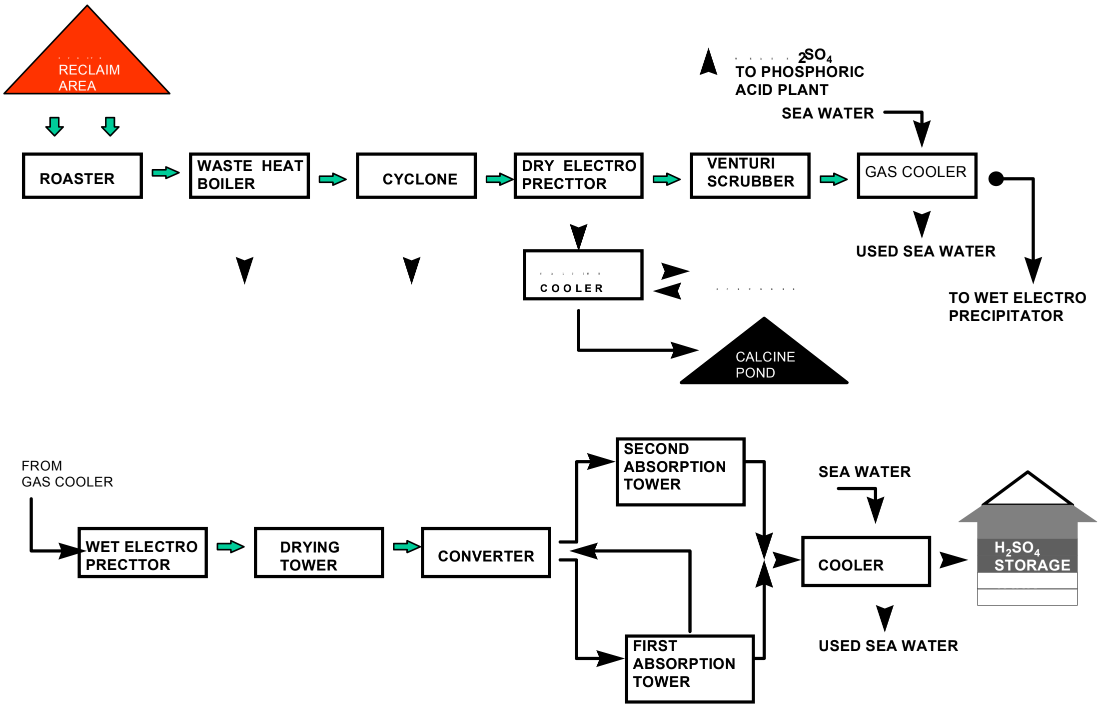

Chart 3A

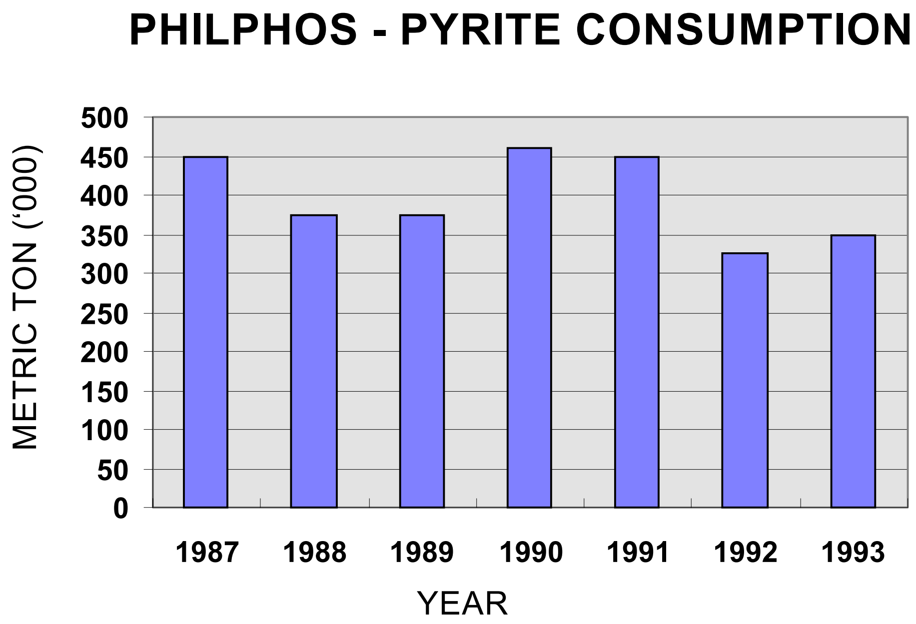

Chart 3B

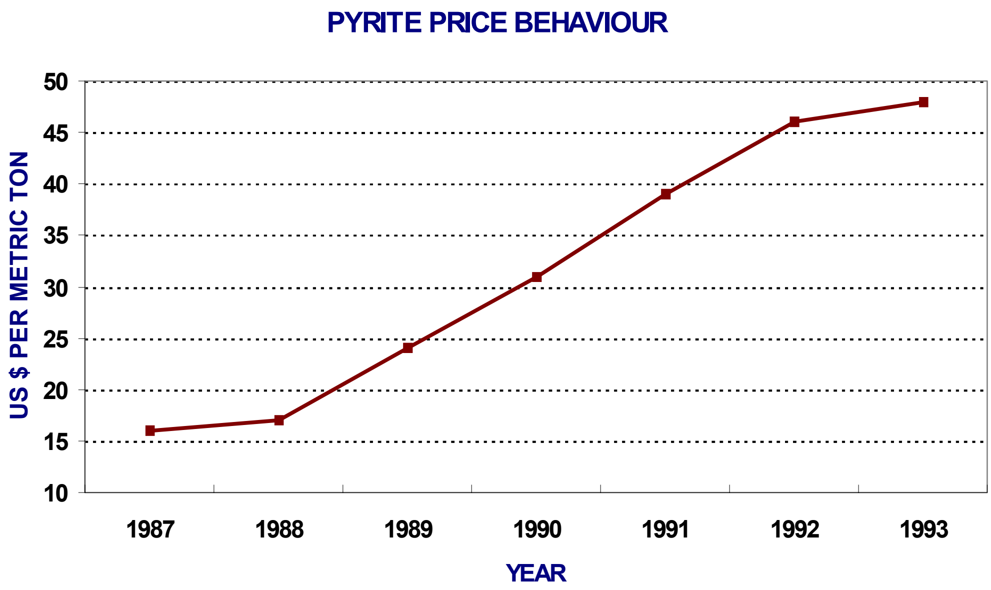

Chart 4

SULPHURIC ACID PLANT
PROCESS FLOW DIAGRAM FOR PYRITE ROASTING AND DUST REMOVING

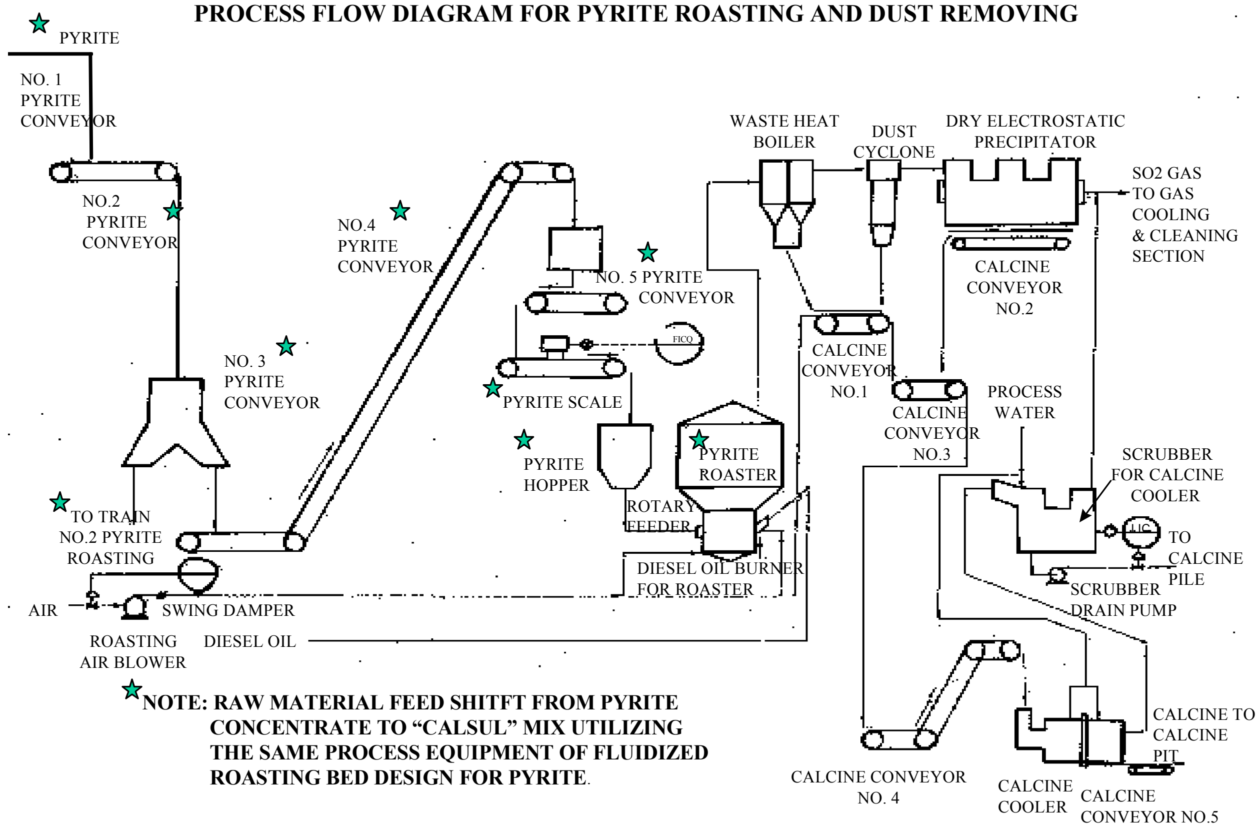

Chart 5

RETROFITTING OF 1,500 TPD PYRITE BURNING PLANT