



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 4
ATLANTA FEDERAL CENTER
61 FORSYTH STREET, SW
ATLANTA, GEORGIA 30303-8909

FEB 12 1998

4APT-ARB

Mr. Claire H. Fancy, P.E.
Chief
Bureau of Air Regulation
Florida Department of Environmental
Protection
Twin Towers Office Building
2600 Blair Stone Road
Tallahassee, FL 32399-2400

SUBJ: Piney Point Phosphates, Inc., Palmetto, Florida (PSD-FL-242)

Dear Mr. Fancy:

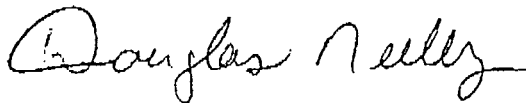
This is to acknowledge receipt of the preliminary determination and draft Prevention of Significant Deterioration (PSD) permit for the above referenced facility submitted by a letter dated January 8, 1998, from your office. The permit is for the repair and restoration of an existing double absorption sulfuric acid plant and associated molten sulfur handling equipment. The permitted capacity of the plant will be equivalent to the previous production rate of 2,000 tons/day of 100 percent sulfuric acid. The sulfuric acid plant is subject to 40 CFR 60, Subpart H (Standards of Performance for Sulfuric Acid Plants).

As indicated in the State's best available control technology (BACT) analysis, SO₂ emissions from the sulfuric acid plant will be controlled by use of the double absorption process, and sulfuric acid mist emissions will be controlled by the use of fiber mist eliminators. Piney Point Phosphates will replace the degraded portion of the vanadium containing (VC) pelletized catalyst in Converter 1 with low pressure VC ring catalyst, and all pelletized VC catalyst in Converter 2 will be replaced with low pressure VC ring catalyst. As indicated in the draft permit, cesium-promoted VC catalyst will be installed in the final converter pass (Converter 2), and it will be used for at least one plant turnaround cycle, or approximately two years, whichever is longer. This will be the first required use of the catalyst to reduce SO₂ emissions. Since cesium-promoted catalyst is more effective than other ringed catalyst at lower temperatures, emissions of SO₂ should be reduced. The proposed BACT SO₂ emission limit is 3.5 lb per ton of 100 percent sulfuric acid produced (48 hour rolling average based on CEMS data). The Subpart H emission limit of 4.0 lb SO₂ per ton of 100 percent sulfuric acid produced (3 hour rolling average based on CEMS data) must also be met, and an annual

EPA Method 8 test will be required. The proposed sulfuric acid mist emission limit is 0.15 lb per ton of 100 percent sulfuric acid produced. We have reviewed the preliminary determination and draft permit and do not have any adverse comments.

Thank you for the opportunity to review and comment on the draft permit and supporting information. If you have any questions regarding our review, please contact Keith Goff of my staff at (404) 562-9137.

Sincerely yours,



R. Douglas Neeley
Chief
Air and Radiation Technology
Branch
Air, Pesticides, and Toxics
Management Division

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A Two-Stage Process Combination for the Production of Sulfuric Acid or Oleum with Next to Zero SO₂ Emissions

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We are introducing a process combination aimed at practically zero SO₂ emissions (< 3 ppm) and able to handle low and variable SO₂ concentrations. The total plant comprises two stages, each stage based on true and tried technology.

Example: 119233 Nm³/h waste gas with 7.3 % SO₂ from a metallurgical plant.

	Production t/d	Off-gas SO ₂ ppm	Energy cons. KWh	Investment million DM
Double-absorption plant	904.5	248	2200	32.4
Jäger-Fattinger plant	907.2	<3	1510	30.0

In the first stage (Jäger contact plant) gas is cooled and cleaned before conversion into sulfuric acid in the contact plant. Acid of 95-98 % and oleum up to 32 % free

SO₂ can be produced. In a converter with only one catalyst bed 65-70 % of the sulphur dioxide is converted into sulphur trioxide. After absorption of the sulphur trioxide, the off-gas of the first stage is piped to the second stage (Fattinger acid process). This is an ungraded version of the old NO_x process (earlier called the chamber process or tower process). Here the sulphur dioxides is converted almost to extinction while producing 76 % strong acid. Since this is hardly a commercial grade, it is returned to the contact plant to supply the necessary reaction water to produce strong acid and/or oleum, thereby closing the loop. The 76 % acid is produced in plastic towers. Instead of returning it to the contact plant the extremely pure acid can also be used for special purposes (e.g. battery acid).

In a plant based on elemental sulfur, the converter in the contact stage has only one catalyst bed. It operates with a gas inlet of 12 % SO₂. Exit gases of the contact plant with 4.5-5.5 % SO₂ pass to the second stage, the system in which the formation of sulfuric acid is catalysed by the presence of NO and NO₂. Existing plants can be modified to lower the emissions while at the same time increasing the production of sulfuric acid.

EVOLUTION OF THE TWO-STAGE PROCESS

Ever-increasing demands on clean air requirements regarding sulfur dioxide emissions of metallurgical, chemical and power plants have influenced production of sulfuric acid.

The mid 1950s saw a revival of the double absorption process, which could reduce sulfur dioxide emissions by 75 % compared to conventional single absorption plants. However, because of ever increasing plant sizes, the absolute discharged volume of sulfur dioxide is still significant. Furthermore, the lower and varying concentrations of sulfur dioxide generated by metallurgical plants impose a problem for double absorption.

To address this, we are introducing a process combination aimed at practically zero sulfur dioxide emissions (< 3 ppm) and able to handle low and variable sulfur dioxide concentrations. The total plant comprises two stages, each stage based on tried and tested technology (Fig. 1).

Before describing both processes we are presenting a list of compiled data, which will illustrate the seamless fit of both plants with each other.

Based on German costs for equipment, we have calculated the investment required for

- a standard double-absorption plant (SEA)
- a Jäger-Fattinger combination (JFC)

Table I shows the feedstock for a plant producing 98.5 % acid based on

waste gases from a nickel ore smelter. Production will be 907.2 t/d or 1000 s.tons/d. Table II shows a comparison of a standard double absorption (SEA) and a Jäger-Fattinger combination (JFC) for the mentioned plant size.

Table I
Feed Gas Composition and Temperatures

Gas composition	SO ₂	7.3 vol-%
	O ₂	3.0 vol-%
	H ₂ O	25.0 vol-%
	N ₂	balance
Gas temperature		300°C
Cooling water temperature		18°C

Table II
Comparison of A Standard Double Absorption (SDA) and A Jäger-fattinger Combination (JFC)

		SDA	JFC
Production as 100% H ₂ SO ₄	kg/h	37686	37800
	lb/h	83193	83444
Off-gas SO ₂ emission	kg/h	76	0.9
	lb SO ₂ /s.ton acid	4	0.047
	ppm	248 *	<3
Total plant pressure drop	mbar	275	125
	inch WG	10.8	4.9
Chemical additive consumption (HNO ₃ + H ₂ O ₂)	kg/h	-	<6
		-	<13
Energy consumption	kWh/h	2200	1510
Investment	million DM	32.4	30.0
	US \$ million	18.0	16.67

* Lower values are possible but result in higher investment costs

The significantly lower pressure loss within the plant requires much less energy, in this case resulting in savings of DM 1 million/year on electricity alone.

Further advantages:

- The same Sulfur dioxide volume yields 912 t/a more acid
- Since the 76 % acid never sees mild steel, cast iron or lead during production, it can be withdrawn as chemically pure acid, for instance battery acid. Acid produced in conventional contact plants contains 20 - 50 mg Fe/kg. Acid produced in plastic equipment of a Fattinger process has only 0.3 mg Fe/kg. High-purity acid might be of interest in production of semi-conductors.

In the first stage (Jäger contact plant), gas coming from the metallurgical plant is cooled and cleaned before conversion into sulfuric acid in the contact plant. Acid of 95-98.5 % and oleum of up to 32 % free SO₃ can be produced.

In a converter with only one catalyst bed, 70 % of the sulfur dioxide is converted into sulfur trioxide. After absorption of the sulfur trioxide, off-gas of the first stage is piped to the second stage (Fattinger acid process). This is an up-graded version of the old NO process (earlier called the chamber process, which later evolved into the tower process). Here the remaining sulfur dioxide is converted almost to extinction while producing 76 % strong acid. Since this is hardly a commercial grade and fertilizer production in modern plants demands 95 % acid, it is returned to the contact plant to supply the necessary reaction water to produce strong acid and/or oleum, thereby closing the loop. The following is a description of the two stages.

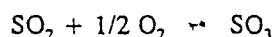
FIRST STAGE (JÄGER CONTACT PLANT)

Figure 2 is a process flow diagram of the Jäger contact plant. Sulfur dioxide gas coming from metallurgical plants is usually generated while roasting sulfur-bearing ores. These hot raw gases are first cooled and cleaned in the gas scrubbing tower [101] with scrubbing liquor under simultaneous water evaporation. During this process most entrained solids are removed and are carried out into the sludge separator [102], thereby clearing the recirculating scrubbing liquor of solids.

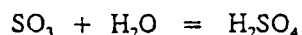
Further cooling to the dewpoint, which is required for acid production, takes place in tubular coolers [103]. The ensuing condensate is returned to the scrubber recirculation. A wet electrostatic precipitator [104] follows the tubular cooler [103] and removes acid mist and the last traces of the finest solids (especially arsenic). The now optically clear gas enters predryer [105]

where it is dried in two stages, first by 65 % acid and then by 76 % acid in the second stage. The heat generated by water absorption is removed in acid cooler [106] and the produced acid of 65 % strength is piped to plant stage 2, while the gas goes to the drying tower [107], where acid of 94 - 96 % strength conditions it to the required degree of dryness. Cooler [108] removes the heat generated by water absorption.

Thereafter the sulfur dioxide gas is heated in countercurrent flow in heat exchanger [109] to ignition temperature by hot sulfur trioxide gas coming from the converter [110] and then the sulfur dioxide gas enters converter [110] for conversion to sulfur trioxide according to the equation:



Here 70 % of the sulfur dioxide is converted to sulfur trioxide. It is then cooled in heat exchanger [109] and enters the absorption tower [111] which is irrigated by 98.5 % acid. Water contained in this acid reacts with sulfur trioxide according to formula



Since the recirculated acid in the absorption tower would continually increase in strength, 76 % acid produced in plant stage 2 is used as diluent in required proportions.

The heat generated by cooling, and the absorption heat are removed in acid cooler [112]. Due to cross flow of 98.5 % acid to pre-dryer and drying tower and cross flow of 95.5 % from drying tower to absorption tower the absorbed water is transported to the absorption tower and the concentration of acid is held constant in both towers.

The off-gases from contact plant I containing approximately 2 % SO₂ are routed to stage 2 (Fattinger process) for final conversion.

SECOND STAGE (FATTINGER ACID PROCESS FOR GASES > 1 % SO₂)

The plant will be designed to achieve an outlet gas containing not more than 3 ppm of sulfur dioxide and 20 ppm NO_x. A flow diagram is given in Fig. 3.

Consumption of additional chemicals is extremely low. Based on 1000 kg H₂SO₄ produced in the first stage, consumption is less than 0.2 kg HNO₃ and 0,3 kg H₂O₂. The process operates by passing gases with more than 1. % Sulfur dioxide through six packed towers [201], [202], [203], [204], [205]

and [206]. The formation of sulphuric acid is catalysed by the presence of NO and NO₂, which act as oxygen carriers. These gases are released into the gas phase in the denitration tower [206]. In the old lead chamber acid process this tower was called the Glover. The tower [201] is used for the complete denitration of the 76 % acid produced in the system. Gases leaving tower [206] pass through the gas cooler [207] and enter the sulfur trioxide absorption tower [202].

The bases for the Fattinger acid process are results of laboratory work as well as from industrial plants. Sulfur dioxide can be fully absorbed using a reaction time of less than 10 seconds. At the same time, NO is being oxidized to an absorbable mix of NO + NO₂ under the following conditions:

- concentration of nitrosylsulfuric acid-containing sulfuric acid of approx. 65 % H₂SO₄
- tower packings with large surface
- temperature of sulfuric acid < 35°C
- NO-concentration in the gas equal or higher than the Sulfur dioxide-concentration

According to M. Bodenstein the time required to oxidize 0.5 vol.-% NO in air (in the gaseous phase) to a mixture NO: NO₂ = 1:1 exceeds 100 seconds.

The fact that in the Fattinger acid process the oxidation needs less than 10 seconds proves that not a gas phase reaction occurs but that the oxidation takes place within the large interface offered by the tower packings.

Gases leaving the sulfur trioxide absorption tower 1 [202] are free of sulfur dioxide, but contain NO_x which is absorbed by sulfuric acid of 76-78 % in two towers: NO_x-absorption tower 1 [203] and NO_x-absorption tower 2 [204]. The circulating sulfuric acid is cooled to 5-8°C to maintain NO_x-absorption efficiency.

Acid from NO-absorption tower 1 [203] with a high nitrosyl level is withdrawn and denitrated in tower [206] (Glover). The acid leaving the Glover has a low nitrosyl level (i.e. low quantity of nitrosylsulfuric acid dissolved in sulfuric acid). Part of this acid is withdrawn as production and completely denitrated in tower [201] and flows to the absorption tower of the contact plant (stage 1).

The bigger part of the denitrated acid returns to NO_x-absorption tower 2 [204].

Exit gases of NO_x-absorption tower 2 [204] contain small amounts of NO and enter the final gas washing [205]. In this final gas washing [205] the gases are scrubbed with approx. 5 % nitric acid containing H₂O₂ in order to reduce the nitrogen oxide concentration to very low levels prior to discharge to the atmosphere.

The humidity of the gases is very low and the contact with 5 % nitric acid results in an appreciable degree of evaporative cooling. As a result the lower section of the final gas washing operates near 0°C, allowing highly efficient NO scrubbing.

Part of the weak nitric acid is fed into the sulfur trioxide absorption circulation [202]. The upper section of the final gas washing tower [205] is used as an evaporation cooler.

The formation of H₂SO₄ in the sulfur trioxide absorption tower [202] is exothermic. Excess heat is transported into the atmosphere by contacting the exit gases with circulating cooling liquid of the heat exchanger [208].

A historical view of the lead chamber process

The technological development of sulfuric acid production started in 1746, when Dr. Roebuck of Birmingham first wheeled an iron cart containing a burning mixture of brimstone and saltpetre into a lead chamber and collected the condensed vapours inside the chamber as sulfuric acid.

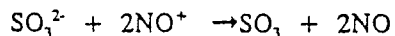
In a paper presented at the International Conference "Sulphur 87" in Houston, Texas (USA) V. Fattinger illustrated the drastic reduction in reaction time of gases in a nitrogen sulfuric acid process (lead chamber and tower process respectively) between 1900 and 1986. The required space demand dropped to less than 0.5 %. In the 1963 listing of sulfuric acid plants, the US only shows 60 chamber plants out of 220 acid facilities.

We see two reasons for the displacement of the NO sulfuric acid process by contact plants:

- a) the low strength of the produced acid.
- b) a general disinterest in the particular process of H₂SO₄ formation from sulfur dioxide, free oxygen and water in an NO_x environment. Maybe even a misconception of the reaction mechanism or economic consideration.

Between 1904 and 1907, two eminent researchers in chemistry and process engineering had many very lively disagreements, aired in publications pro

and con. Fritz Raschig of Ludwigshafen and Georg Lunge of the ETH Zurich were the combatants. In 1953 F. Seel and M. Meier published test results, showing that the lead chamber synthesis is based on Ion exchange between sulfite ions and nitrosyl-ions



Builders of tower plants mainly subscribed to the theories of Lunge and much less to the findings of Raschig as well as Seel and Meier.

V. Fattinger, a co-author of this presentation, published a treatise in 1979 at the 3rd International Conference on Fertilizers in London, pertaining to the NOx sulfuric acid process.

Only after this did he fully recognized that the theories of Raschig, along with the additional findings of Seel and Meier are valid and not the reaction schematics of Lunge. Only sufficiently low temperatures yield high concentrations of the prominent reaction partners (sulfite ions and nitrosyl-ions). Formation and degradation of the nitrosylsulfuric acid is important for the transport of NOx from end to beginning of the system, but the nitrosylsulfuric acid is not an intermediate product during oxidation of sulfur dioxide into H₂SO₄, as assumed by Lunge.

An important development of the last four decades was a process-step introduced by Gerd Petersen. In the tower process developed by his father, Hugo Petersen, circulating acid was always above 76 % (Glover acid).

In the German Patent Brief 1031292 Gerd Petersen described a so called "Cooling Tower" in a plant irrigated mostly with acid over 76 %. This Petersen tower plant included the following towers: a denitration tower (Glover), two production towers and two Gay-Lussac towers for NOx-absorption. In the range of the highest NOx concentration in the gas before the first Gay-Lussac tower, a tower irrigated with 62 % acid and a void tower were installed. The conditions allowed formation of nitrosyl-ions thereby rapidly oxidizing sulfur dioxide (i.e. sulfite-ions). Gerd Petersen proposed the void tower for reoxidation of the NO behind the cooling tower.

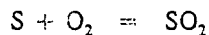
V. Fattinger recognized that with sufficiently low temperatures and a large reaction surface NO oxidation -besides sulfur dioxide oxidation- takes place more rapidly. This quickly establishes an optimal relation of NO : NO₂. In contrast to the proposals of Gerd Petersen, V. Fattinger avoids any void spaces within the sulfur dioxide absorption section or behind it. He recognized that void spaces are of negative influence on the process. Only the very large wetted surfaces in the tower packings are important. This was the

starting point of the Fattinger Acid process, in which the arrangements for controlling the NO : NO₂ ratio are distinctly different to the Petersen Tower process.

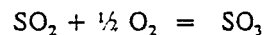
SULFURIC ACID PLANT BASED ON ELEMENTAL SULFUR

First stage (Jäger Contact Plant, Fig. 4)

Liquid sulfur is atomized in a sulfur combustion furnace [301] and burned with dried, preheated air to form sulfur dioxide according to the equation

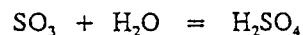


This hot gas goes to the waste heat boiler [302] and is cooled down before entering the converter [303]. Here the conversion from sulfur dioxide to sulfur trioxide takes place according to the equation



takes place with 60 % conversion. From the converter the gas goes now to the heat exchanger [304] and cools off before entering the feed water preheater [305]. The heat extracted by heat exchanger [304] is used to preheat the combustion air for the sulfur combustion furnace.

The gas leaves the feedwater preheater [305] where it is cooled. At this lowered temperature the gas now enters the absorption tower [306]. Here the SO₃ is contacted by irrigation acid whereby the SO₃ reacts with the water content in the acid according to



Since now the acid would constantly increase in strength, a diluent (water or weak acid) is added to the recirculating acid. Here is where the loop is closed, by using weak acid from the second plant stage. Heat from absorption and gas cooling is removed by the acid coolers [307] in the recirculation lines. The combustion air is first dried to a certain degree in an acid irrigated predryer (308). The heat generated by the water absorption is transferred to the acid cooler [309] in the acid recirculation. The acid is kept at 65 % by adding 76 % acid from stage 2. To transport the water from the combustion air to stage 2, a defined amount of 65 % acid is fed to stage 2.

The air is dried further in the acid irrigated drying tower [310]. The absorption heat is removed in the acid cooler (311). By means of a cross exchange of 98.5 % and 96 % acid between absorption and drying tower, absorbed water is consumed and the acid concentration of both towers is correctly balanced.

High pressure steam generated in waste heat boiler [302] goes to the steam turbine driven generator (312). At a branch point LP steam is tapped off and used for melting sulfur, heating sulfur lines and tank, as well as feeding the degasifier [313]. The remaining steam is further letdown in the turbine and is then condensed in the condenser [314]. Condensate goes to the degasifier and feedwater collector [313] and returned to the feed water preheater [305] via feed water pump to the waste heat boiler [302].

The second stage (Fattinger Acid Process) is the same as before (Fig. 3).

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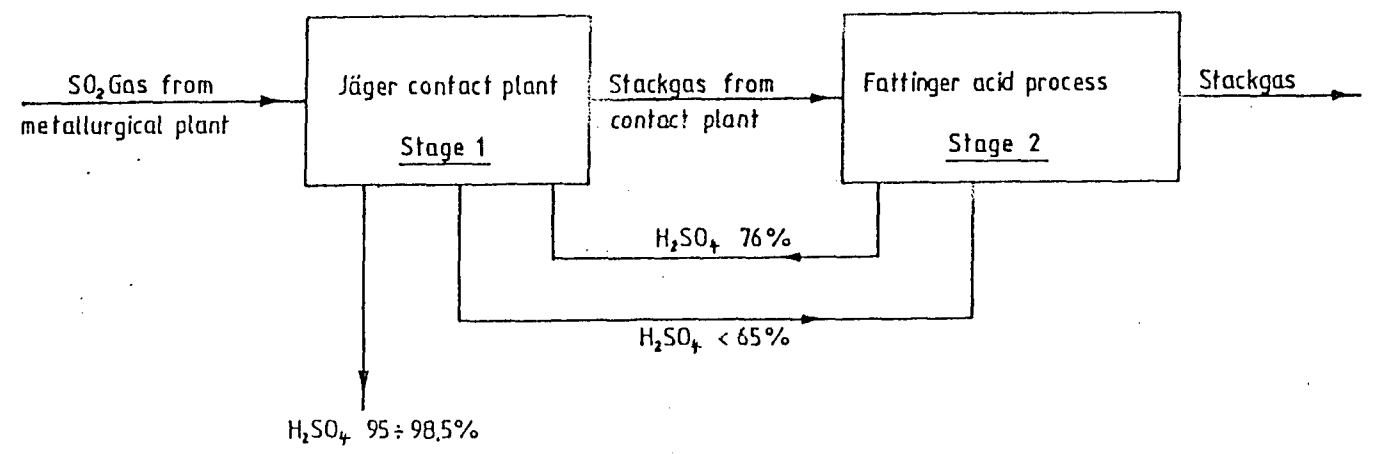


FIG. 1: TWO-STAGE SULPHURIC ACID PLANT – BLOCK FLOW DIAGRAM

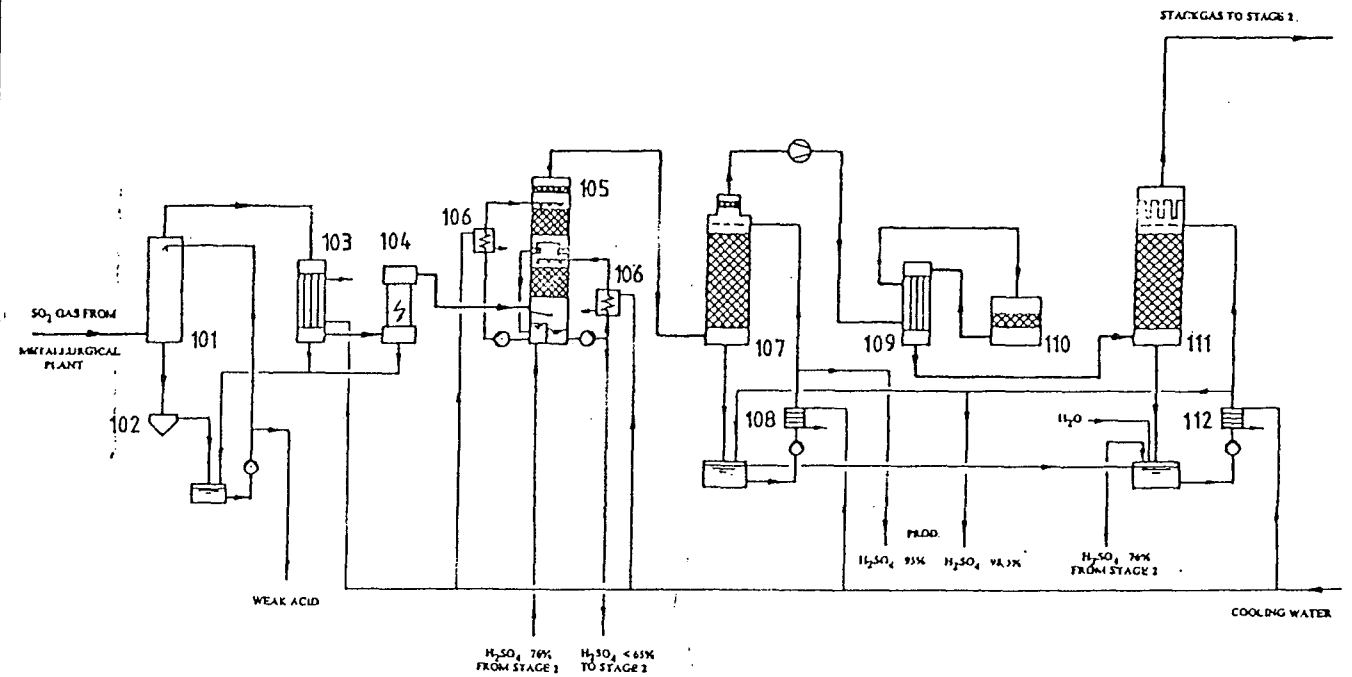


FIG. 2: STAGE I: CONTACT SULPHURIC ACID PLANT

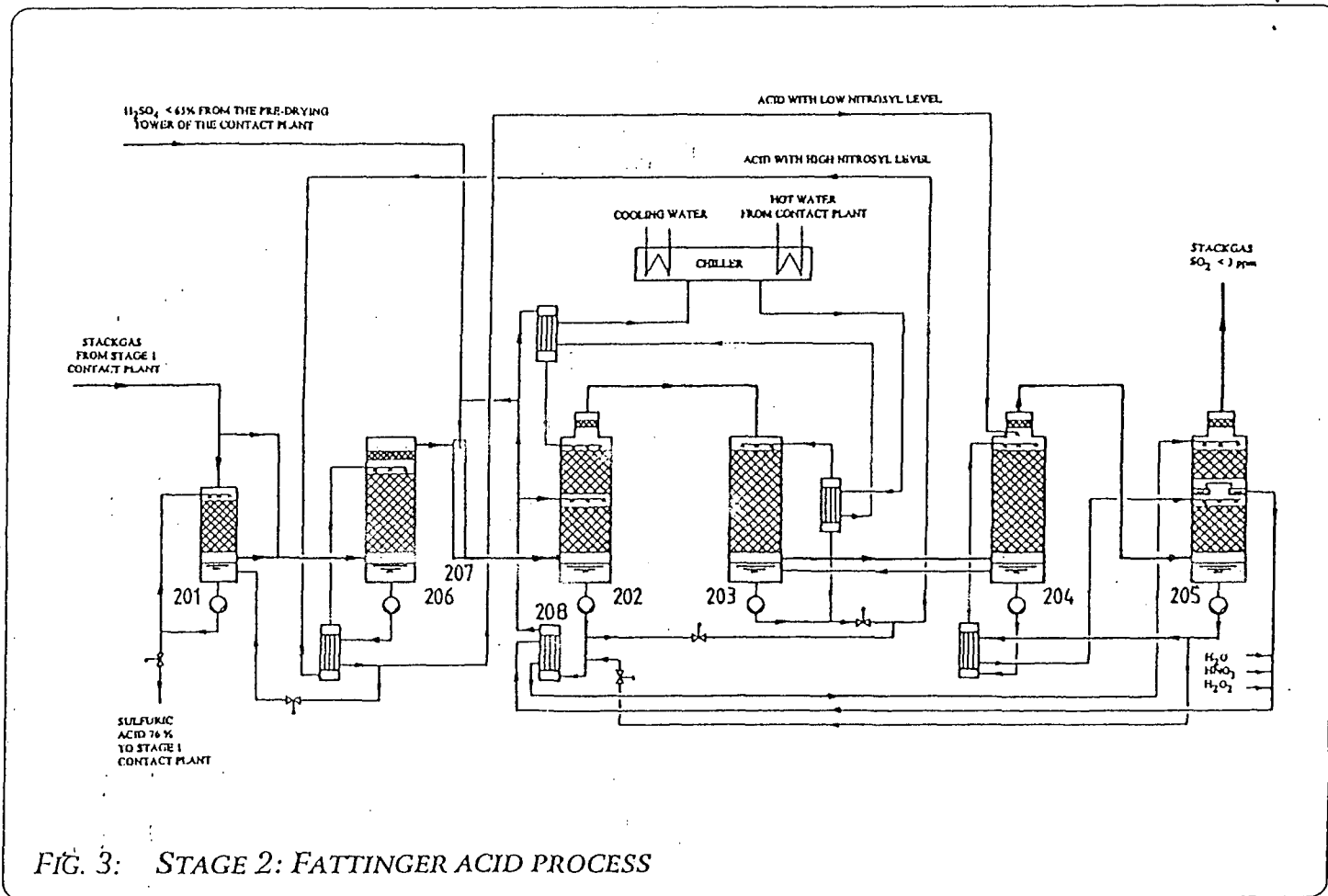


FIG. 3: STAGE 2: FATTINGER ACID PROCESS

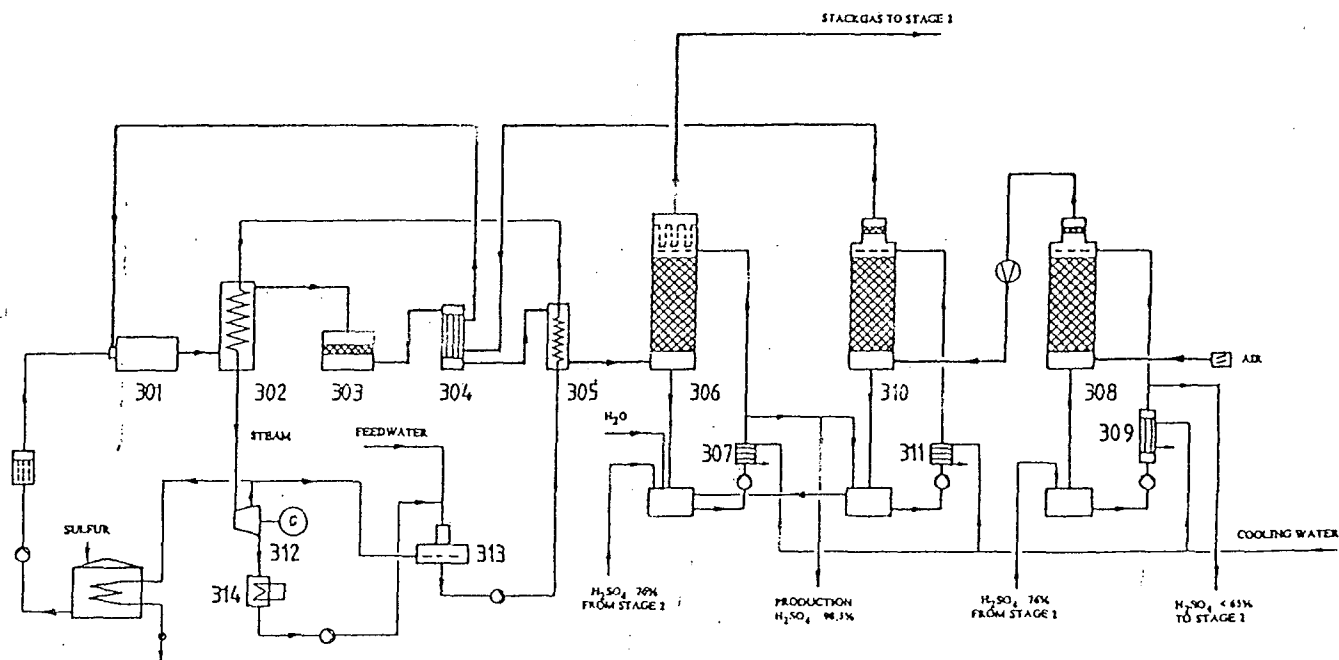


FIG. 4: STAGE I (CONTACT SECTION) OF SULFUR-BURNING COMBINED SULPHURIC ACID PLANT