

LURGI

**Is Gypsum
Decomposition Commercially
Ready Now?**

by

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Introduction

Lurgi, who has been involved in gypsum decomposition for the past three or four decades has from time to time been required to take a step back from our activities and access where the industry is going? (or not going?).

That is to say that just because Lurgi has extensive experience in:

- Gypsum decomposition
- Pyrite roasting
- Sulphur recovery
- H₂SO₄-production
- Sintering
- Calcining
- Cement production
- CFB's
- Kilns
- Traveling grates

does not mean that the economics of a technically feasible plant or concept based upon these operations is attractive.

In fact, that is what we are here to discuss today.

Is Gypsum Decomposition Commercially Ready Now?

Based upon Lurgi's in depth knowledge and experience in the above mentioned fields and unit operations Lurgi seriously doubts the viability of incorporating gypsum decomposition into the fertilizer industry now.

1 Aim of Phosphogypsum Decomposition

As we all know phosphogypsum is the ultimate destination of most of the sulfur consumed in the production of phosphoric acid. Approximately 120 million tons of phosphogypsum are produced annually through out the world. Of this some 30 million tons per year are produced in Florida, alone.

Power plant flue gas desulfurization units also generate considerable quantities of calcium sulfate and calcium sulfide. These are already the subject of serious environmental concerns in some countries.

Obviously, recycling of the sulfur content of the gypsum would offer many advantages:

- a) Some countries like Tunisia, Morocco and South Africa have phosphate deposits but need to import the sulfur required to produce sulfuric acid. They must use hard currency to pay for the sulfur they import.
- b) Reprocessing the phosphogypsum eliminates dumping problems. In Central Europe (where new gypsum piles are infeasible) it is virtually impossible to obtain a construction permit for a new phosphoric acid plant if the resulting gypsum is discharged into rivers or the sea. Additionally restrictions on existing phosphoric acid plants are becoming more and more stringent, involving considerable cost.

A process using phosphogypsum as a raw material and thus reducing the existing gypsum piles would be most welcome as it would also eliminate the liquid effluents and gaseous emissions from such disposal areas.

- c) Thermal decomposition of gypsum is an endothermic reaction. If a low-cost fuel could be successfully used to recover the value of the sulfur from the gypsum we would have an attractive concept. Decomposition may be worth considering utilizing coal tailings, high sulfur coals, petroleum coke or sulfur-laden waste gases whose disposal are costly, thus providing a double benefit.
- d) The decomposition of gypsum should be examined not only from the point of view of recovering the sulfur, (in the form of sulfuric acid), but also the generation of useful byproducts such as quick lime, cement or road aggregate, all of which are of a certain commercial value. Ammoniumsulfate produced from gypsum and ammonia has been commercialised already some 60 years ago (Merseburger Process).
- e) In past years, the phosphate fertilizer industry has not enjoyed great profits. It was widely believed that only the sulfur suppliers benefited from the crisis of the fertilizer industry. Prices of nearly \$ 200 per ton of sulfur supplied, which had to be paid, seemed to prove this. Gypsum decomposition might make the fertilizer industry independent of sulfur suppliers.

These advantages are so obvious (Figure 1) that one wonders why such decomposition plants have not been built everywhere. Are there no suitable processes? Is no capital available for such plants? Has the industry been sleeping?

Unfortunately, the answers to these questions are very complex.

Nothing will be presented in this paper about the direct use of phosphogypsum (1). It is well-known by all of us that natural gypsum can be replaced by phosphogypsum, that phosphogypsum can be used as: Fertilizer, a soil conditioner, a setting retardant for cement, for conversion to ammonium sulfate, a filler for paper, paint and plastics, and in the building industry. Although these applications have been successfully demonstrated in many places around the world, they consume only about 10 - 15 % of the world phosphogypsum production. The exception to this is Japan, where practically all the phosphogypsum produced is put to other uses. In fact phosphogypsum is even imported from other countries (such as Korea) because natural gypsum is scarce.

2 Decomposition Processes

2.1 Müller - Kühne Process

The Müller-Kühne process coproduces sulfuric acid and Portland cement by thermal decomposition of gypsum in a rotary kiln. A semi-commercial plant commenced operation in 1916. Since then an additional 25 units have been built throughout the world (Table 1). The most recent unit was built in China in 1987. Presently the plants in East Germany and hopefully the one in China are in operation.

The basic reactions of the Müller-Kühne process are still the same as 70 years ago (2):

Part of the calcium sulfate is reduced with carbon to yield calcium sulfide



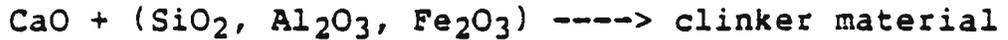
The carbon required for the reduction is added in the form of coke.

In the hotter zone, the calcium sulfide reacts with additional calcium sulfate



Experts believe that the reduction to calcium sulfide is not a solids reaction, but has CO as an intermediary product. The presence of cement clinker additives (SiO₂, Al₂O₃ and Fe₂O₃) decreases the temperature of this reaction to about 900°C.

Finally, the calcium oxide reacts with the oxides (SiO_2 , Al_2O_3 , Fe_2O_3) exothermally in the sintering zone to produce cement clinker.



The necessary sintering temperature is approximately 1350 - 1400°C. The rotary kiln offgas consists of SO_2 , CO_2 , O_2 , N_2 and H_2O . It is purified in a gas treatment plant and processed to sulfuric acid in a contact plant according to the overall reaction



The clinker quality depends heavily upon accurate ratios between the carbon and calcium sulfate quantities. In actual operation, a carbon surplus of approximately 20 % is provided, since a part of the carbon is burned and cannot be used for reduction.

Over years of operation the process was further refined and advanced. Noteable improvements were made in the areas of feed preparation, process control, and energy efficiency.

Initially, only natural gypsum was used as a raw material. Phosphogypsum was first introduced in the thirties. The engineers learned how to handle it over the following several years.

A plant consists of the following unit operations (Figure 2):

1. Drying and calcining of phosphogypsum
2. Grinding of additives
3. Preparation of kiln feed meal
4. Decomposition of gypsum and clinkering
5. Production of sulfuric acid

The phosphogypsum is dried and calcined in order to expel surface moisture and some of the crystal water. Fuel costs can be reduced by using hemihydrate phosphogypsum produced for instance by the Norsk Hydro Hemihydrate Phosphoric Acid Process. The additives (0.2 t clay, 0.1 t sand, 0.1 t coke per tonne of clinker) are dried, ground and mixed in appropriate proportions.

The feed material is preheated counter-currently to the offgas from the rotary kiln before it is fed to that kiln, (which is slightly inclined). The inclination and rotation of the kiln moves the material thru the kiln and into the clinker cooler.

The rotary kiln is fired with pulverized coal, fuel oil or natural gas. As mentioned before, decomposition of the calcium sulfate and clinkering takes place in the kiln. The clinker is cooled with air and, after the addition of gypsum, the material is ground to cement. This cement is delivered to the cement silos for interim storage prior to shipment.

The hot gases leaving the heat exchanger upstream of the kiln are dedusted, demisted, dried, and finally processed to sulfuric acid.

2.2 Lurgi Circulating Fluid Bed Process (CFB)

Thermal decomposition of gypsum is an endothermic process. The more successfully the process parameters can be controlled and the heat losses minimized, the more economic the process will be.

The circulating fluid bed provides the mechanism to meet these requirements (Figure 3).

The sequence of reactions is similar to that of the Müller-Kühne process. The fluid bed furnace is provided with a reducing section promoting the decomposition of the calcium sulfate. In the upstream oxidising section the reaction is completed.

This has the advantage of being able to closely control the system temperatures (within a range of 900 - 1100°C), as required by raw material variations. The same is true for the oxygen content of the gas in order to prevent an inverse reaction. The decomposition products are SO₂-laden gas and CaO. A clinker mix is produced when the appropriate additives such as Al₂O₃, SiO₂, Fe₂O₃ are fed to the CFB chamber together with the gypsum (4). Clinkering cannot be achieved in the same unit because it requires higher temperatures. A conventional rotary kiln is therefore used to clinker the material in a counter-current flow to the heat source at the discharge end.

This circulating fluid bed system has some very specific advantages

- exact control of all process parameters (like temperatures, gas composition)
- minimum heat losses
- no premixing of raw materials required
- no rotating equipment, except air blowers

If the desired products are CaO and sulfuric acid, the plant will consist of the following unit operations (Figures 4):

1. Drying and calcining of phosphogypsum
2. Decomposition of gypsum
3. Production of sulfuric acid

If clinker and/or cement and sulfuric acid are the desired products, the plant will consist of the following unit operations (Figure 5):

1. Drying and calcining of phosphogypsum
2. Grinding of additives
3. Preparation of kiln feed meal
4. Decomposition of gypsum
5. Clinkering
6. Production of sulfuric acid

2.3 DMC/FIPR Process

The basic goal of the development work pursued jointly by Davy McKee Corporation (DMC) and the Florida Institute of Phosphate Research (FIPR) is to apply the commercially proven circular grate sintering machine to the decomposition of phosphogypsum to produce SO₂ gas (which can be processed to sulfuric acid), and aggregate material for road construction. (3)

Carbonaceous materials such as petroleum coke, lignite or coal are used as reductants and, pyrite as a fuel. The phosphogypsum together with a binder are mixed, pelletized, and charged to the sinter machine. Ignition burners are used to fire the raw material mix and initiate the combined decomposing and sintering process. A suitable gas flow arrangement at the sinter machine (similar to that developed for iron ore sintering) ensures that the gases produced in the decomposition and sintering process contain a maximum of SO₂.

At the end of the cycle, the sintered material is crushed, cooled and screened, then part of it is recycled to the sinter machine as a bottom layer, the so-called hearth layer.

According to publications, the use of pyrite has significantly improved the quality of the sintered material. Unfortunately it has also brought another sulfur bearing material to the process. This means that eventually more sulfuric acid is produced than consumed. Thus putting the phosphoric acid and phosphogypsum production out of balance. The last flow sheets for the DMC/FIPR process of which we are aware are based upon using the phosphogypsum and pyrite as they are delivered with their natural moisture content. The coal, on the other hand, is gasified separately and the residual char used as a reductant at the sinter machine while some part of the fuel gas is used to operate the ignition burners.

The process as a whole is reportedly rendered more cost-effective by gasifying additional coal and burning the gaseous components to generate steam and/or electricity. The LP steam is used to concentrate the phosphoric acid. Some of the sulfur which may be introduced with the coal is eliminated separately - again for reasons of cost-effectiveness. But the flow sheet becomes very complex, due to the dependence of the unit operations.

Hence, the DMC/FIPR process comprises the following unit operations (Figure 6):

1. Preparation of raw materials
2. Pelletizing
3. Coal preparation
4. Coal gasification
5. Fuel gas processing
6. Gas turbine system
7. Power generation
8. Circular grate
9. Aggregate processing
10. Sulfuric acid production

3 Comparison of Capital and Operating Cost**3.1 Assumptions****a) Capital Costs**

- T.I.C. for new process plants within battery limits, including cost for commissioning;
- infrastructure in existence;
- cost for land, taxes, dues not included;
- location Unites States, 1987;
- no provision has been made for unit operation to clean phosphogypsum from impurities, like P₂O₅, F or others;
- cogeneration facilities are included if electric power is produced and exported;
- cost data are based on Lurgi in-house estimates and for the DMC/FIPR process from Davy communication, dated March, 21, 1988;
- provisions for capital expenditures during construction period have not been included;
- depreciation 10 years
- interest rate 10 %, 10 years

calculated $\frac{\text{TIC} \times 0.1 \times 0.575}{\text{H}_2\text{SO}_4 \text{ production per annum}}$

b) Operating Cost

- Comparison is based on a feed of 1.000.000 mt phosphogypsum per year (analysis as per Table 2);
- Coal analysis as per Table 3;
- The sulfur content of the coal is converted to sulfuric acid in these examples. This is the reason for slightly different sulfuric acid capacities for the processes.

3.2 Capital Cost

3.2.1 Müller-Kühne Process

| | MM \$ |
|--|-----------------|
| 1. Drying of phosphogypsum 3 lines (3030 tpd) <i>SHOULD BE 5 LINES</i> | 50 |
| 2. Preparation of kiln feed meal (3400 tpd) | 6 |
| 3. Decomposition and clinkering 3 lines | 104 |
| 4. Sulfuric acid production 1 line (1500 tpd) | 40 |
| TIC | <hr/> MM/\$ 200 |

3.2.2 Lurgi CFB Process (CaO)

| | MM \$ |
|---|------------------|
| 1. Drying and calcining (3030 tpd) | 16 |
| 2. Decomposition | 30 |
| 3. Sulfuric acid production (1500 tpd) | 37,5 |
| TIC | <hr/> MM/\$ 83,5 |

3.2.3 Lurgi CFB Process (Clinker)

| | MM \$ |
|--|------------------|
| 1. Drying and calcining of phosphogypsum (3030 tpd dry) | 16 |
| 2. Preparation of kiln feed meal (4080 tpd) | 2,5 |
| 3. Decomposition and clinkering | 40 |
| 4. Sulfuric acid production (1500 tpd) | 38,7 |
| TIC | <hr/> MM/\$ 96,2 |

3.2.4 DMC/FIPR Process

| | MM \$ |
|--|-----------------|
| 1. Preparation of raw materials) (receiving, storage, reclaim)) gypsum, pyrite, binder) (4100 tpd dry)) | 11 |
| 2. Preparation of coal (570 tpd)) | |
| 3. Coal Processing) | 37,5 |
| 4. Gas turbine system, power generation) | |
| 5. Circular grate) | 26,5 |
| 6. Aggregate processing (1940 tpd)) | |
| 7. Sulfuric acid production (2300 tpd) | 53 |
| TIC | <hr/> MM/\$ 128 |

3.3 Production Cost per Ton of Sulfuric Acid

3.3.1 Müller-Kühne Process

Capacity: 478 500 tpy sulfuric acid
 On-stream factor 330 d/a
 TIC 200 million \$

| Cost item | Unit consumption t/t H ₂ SO ₄ | Unit cost \$ | Cost per t of H ₂ SO ₄ |
|---|--|-----------------|---|
| <u>Raw materials</u> | | | |
| Phosphogypsum | 2,1 | 1,0 | 2,1 |
| Coal | 0,1 | 35,0 | 3,5 |
| Clay | 0,07 | 10,0 | 0,7 |
| Sand | 0,07 | 10,0 | 0,7 |
| <u>Utilities</u> | | | |
| Fuel oil | 0,25 | 120,0 | 30,0 |
| Cooling water, m ³ | 70,0 | 0,005 | 0,35 |
| Electric power, kWh | 250,0 | 0,05 | 12,5 |
| <u>Products (Credit)</u> | | | |
| Clinker | (1,0) | (33,0) | (33,0) |
| <u>Labour</u> | | | |
| Production 15 per shift x 4,5 x 20.000 \$ | | | 2,82 |
| Overhead 100 % of production labour | | | 2,82 |
| <u>Capital related cost</u> | | | |
| Maintenance material 4 % of TIC | | | 16,72 |
| insurance and taxes | | | |
| Depreciation and interest | | | 65,83 |

3.3.2 Lurgi-CFB Process

Capacity: 495 000 tpy sulfuric acid
 On-stream factor 330 d/a
 TIC 83,5 million \$

| Cost item | Unit consumption t/t H ₂ SO ₄ | Unit cost \$ | Cost per t of H ₂ SO ₄ |
|-----------|--|-----------------|---|
|-----------|--|-----------------|---|

Raw materials

| | | | |
|---------------|-----|------|-----|
| Phosphogypsum | 2,0 | 1,0 | 2,0 |
| Coal | 0,1 | 35,0 | 3,5 |

Utilities

| | | | |
|-------------------------------|-------|-------|------|
| Cooling water, m ³ | 70,0 | 0,005 | 0,35 |
| Electric power, kWh | 110,0 | 0,05 | 5,5 |
| Coal | 0,2 | 35,0 | 7,0 |

Products

| | | | |
|-----|------|------|------|
| CaO | 0,45 | -, - | -, - |
|-----|------|------|------|

Labour

| | | | |
|--|--|--|------|
| Production 7 per shift x 4,5 x 20.000 \$ | | | 1,27 |
| Overhead 100 % of production labour | | | 1,27 |

Capital related cost

| | | | |
|--|--|--|------|
| Maintenance material 4 % of TIC insurance and taxes | | | 6,75 |
|--|--|--|------|

| | | | |
|---------------------------|--|--|-------|
| Depreciation and interest | | | 26,57 |
|---------------------------|--|--|-------|

| | | | |
|--|--|--|----------|
| | | | \$ 54,21 |
|--|--|--|----------|

3.3.3 Lurgi-CFB Process (Clinker)

Capacity: 511 500 tpy sulfuric acid
 On-stream factor 330 d/a
 TIC 97 million \$

| Cost item | Unit consumption t/t H ₂ SO ₄ | Unit cost \$ | Cost per t of H ₂ SO ₄ |
|-----------|--|-----------------|---|
|-----------|--|-----------------|---|

Raw materials

| | | | |
|---------------|-----|------|-----|
| Phosphogypsum | 2,0 | 1,0 | 2,0 |
| Coal | 0,1 | 35,0 | 3,5 |
| Fly ash | 0,2 | 7,0 | 1,4 |

Utilities

| | | | |
|-------------------------------|-------|-------|------|
| Coal | 0,3 | 35,0 | 10,5 |
| Cooling water, m ³ | 70,0 | 0,005 | 0,35 |
| Electric power, kWh | 130,0 | 0,05 | 6,5 |

Products (Credit)

| | | | |
|---------|-------|--------|--------|
| Clinker | (0,9) | (33,0) | (29,7) |
|---------|-------|--------|--------|

Labour

| | | | |
|--|--|--|------|
| Production 9 per shift x 4,5 x 20.000 \$ | | | 1,58 |
| Overhead 100 % of production labour | | | 1,58 |

Capital related cost

| | | | |
|---------------------------------|--|--|------|
| Maintenance material 4 % of TIC | | | 7,58 |
| insurance and taxes | | | |

| | | | |
|---------------------------|--|--|-------|
| Depreciation and interest | | | 29,86 |
|---------------------------|--|--|-------|

| | | | |
|--|--|--|----------|
| | | | \$ 35,15 |
|--|--|--|----------|

3.3.4 DMC/FIPR Process

Capacity: 759 000 tpy sulfuric acid
 On-stream factor 330 d/a
 TIC 128 million \$

| Cost item | Unit consumption t/t H ₂ SO ₄ | Unit cost \$ | Cost per t of H ₂ SO ₄ |
|-----------|--|-----------------|---|
|-----------|--|-----------------|---|

Raw materials

| | | | |
|----------------------------------|------|------|-------|
| Phosphogypsum | 1,33 | 1,0 | 1,33 |
| Coal to char | 0,11 | 35,0 | 3,85 |
| Pyrites (90 % FeS ₂) | 0,36 | 28,0 | 10,08 |
| Binder | 0,1 | 10,0 | 1,0 |

Utilities

| | | | |
|-------------------------------|------|-------|------|
| Coal to energy | 0,14 | 35,0 | 4,9 |
| Cooling water, m ³ | 42,0 | 0,005 | 0,21 |
| Pond water | 83,0 | 0,003 | 0,25 |
| Boiler feed water | 1,13 | 0,1 | 0,11 |

Products (Credits)

| | | | |
|---------------------|-------|------|--------|
| Aggregate | 0,85 | 5,0 | (4,25) |
| Steam | 0,52 | 10,0 | (5,2) |
| Electric power, kWh | 140,0 | 0,05 | (7,0) |

Labour

| | |
|---|------|
| Production 16 per shift x 4,5 x 20.000 \$ | 1,89 |
| Overhead 100 % of production labour | 1,89 |

Capital related cost

| | |
|--|------|
| Maintenance material 4 % of TIC insurance and taxes | 6,74 |
|--|------|

Depreciation and interest

26,56

\$ 12,36

3.4 Results

Assuming a price of sulfuric acid of 30 - 40 US \$ per ton for all processes the cost of raw materials, utilities, maintenance, and labour absorb the selling price.

| | |
|------------------------|-----------|
| 1. Müller-Kühne | 105,04 \$ |
| 2. Lurgi CFB (CaO) | 54,21 \$ |
| 3. Lurgi CFB (Clinker) | 35,15 \$ |
| 4. DMC/FIPR | 42,36 \$ |

Credits for byproducts like clinker, aggregate, quick lime will improve the picture but the financial charges (interest, depreciation) again neutralize the result.

All cases do not provide a return on investment at present conditions.

4 Technical & Economic Assessment

Apart from the economics of phosphogypsum decomposition, which can to a certain extent be described and evaluated by looking at the operating costs, there are a number of other aspects which are all mutually interrelated and therefore cannot be assessed separately:

- a) Technical reliability of the processes
- b) Product quality
- c) Market potential
- d) Environmental aspects

a) **Technical Reliability**

1. **Müller-Kühne-Process**

As previously mentioned, a number of industrial-scale plants based on the Müller-Kühne process are still operating. The largest single-train unit of this type was designed for a phosphogypsum throughput of approximately 175 000 tpy. Future development must aim at larger capacity in order to reduce the capital investment per ton. However in a large rotary kiln it is difficult to accurately control the temperature, gas concentration and rate of deposits.

2. Circulating Fluid Bed (CFB)

CFB reactors are commercially used for a variety of raw materials throughout the world. Lurgi ran pilot tests at their Frankfurt laboratories to verify that such units are suitable for phosphogypsum decomposition. The pilot test runs were on a continuous basis. The resulting SO₂ gas was converted to sulfuric acid in a Peroxidox wash unit. No industrial-scale phosphogypsum decomposition plant based on a circulating fluid bed process has been commissioned to date.

3. DMC/FIPR Process

The circular grate sintering machine has for many years proven its merits as a unit operation in the iron industry. Lab scale, batch tests were made to study its applicability to phosphogypsum decomposition. An order has been placed for a continuous pilot plant.

Commercial coal gasification plants are already operating. However, the design of such plants has to allow for the various specific properties of the coals used. A continuous pilot plant for combined decomposition/gasification can certainly be constructed, but we are not aware of any current plans to do so.

b) Product Quality

The main decomposition product, at least for the purposes of this paper, is sulfuric acid. The market offers technologies by which highly concentrated and sufficiently pure sulfuric acid can be produced under the given conditions. An appropriate gas treatment unit can be designed to remove such impurities like dust, fluorine, and P_2O_5 from the gases. This gas treatment plant - for all three processes alike - constitutes a major critical section of the complex.

A second product can be clinker and/or cement. For obvious reasons, quality requirements are stringent. The cement quality depends on the process arrangement, (which will not be discussed in detail here), but even more on the raw material quality. The maximum P_2O_5 content and the fluorine content of the phosphogypsum are limited. Amounts of less than 1.0 % P_2O_5 , or better even 0.6 % P_2O_5 , can be reached by two-stage phosphoric acid processes such as the Norsk Hydro Hemidihydrate process. However, the specified fluorine contents of less than 0.4 % F in the phosphogypsum requires particular purification processes or specific raw phosphate mixes.

A third product, i.e. aggregate for road construction, also needs to meet stringent quality requirements: Mechanical strength, chemical stability, degradation resistance are important characteristics. We understand the first samples tested in the lab produced satisfactory results. Whether the radioactivity of the has any adverse effect in this application has to be checked with authorities.

A fourth possible product - quick lime - contains all the impurities from the phosphogypsum. Moreover, the quick lime is essentially dead burnt and is very fine. We have not yet made any detailed investigations as to its marketability.

c) Market Potential

Sulfuric acid will certainly be welcome in those geographic areas where phosphogypsum is available and which are dependent upon elemental sulfur. If sulfuric acid produced by gypsum decomposition is economic and the price is independent of the fluctuations of world market prices of sulfur, the fertilizer industry would be pleased. However, the energy situation of most existing plants would have to be studied in detail since steam from sulfur burning would no longer be available for phosphoric acid concentration. Modern phosphoric acid processes can, however, produce highly concentrated phosphoric acid directly from the filter and can virtually operate without steam. A modification of existing plants to use these processes is neither complicated technically nor costly.

The Müller-Kühne process produces a ton of clinker/cement along with each ton of sulfuric acid. Clearly, cement transportation costs from the producer to the consumer are an important factor. Cement market equilibrium, for instance in Florida, may be notably disturbed by one or two new cement plants.

Such a plant however would, be most welcome in Algeria where cement production is insufficient. Although in this case too, the location is important in view of transportation costs.

Obviously present cement producers are not enthused at the prospect of every fertilizer complex becoming cement producer. Therefor we should endeavor to include cement manufacturers as part of the team that develops a gypsum decomposition plant. Or, at least look to them as a good market for the quick lime (which is a good feed material to the cement kiln).

The market potential for aggregate material may be assumed to be even more dependent upon local conditions. Florida is an ideal market, because there are virtually no local materials which could be used as road aggregate. In Algeria, on the other hand, artificial aggregate has virtually no market.

d) Environmental Aspects

It was only a few years ago in the USSR that a gypsum decomposition project (based upon the Müller-Kühne process) was not realized because it did not ensure that the fluorine content in the effluents would be within statutory limits. Throughout the world, regulations are becoming more prohibitive.

Phosphogypsum impurities such as heavy metals (Table 4 + 5) and fluorine, which cannot be tolerated in the products, must be eliminated. This means that a disposal area is required and that one is left with an additional problem.

Some countries are seriously considering placing statutory limits on levels of radioactivity, whether it comes from natural or from artificial sources.

As it is inevitable that when one uses such complex raw materials as phosphogypsum and low-cost carbon fuels, particular attention will have to be given to the potential environmental impact.

Conclusions

As you are probably aware Lurgi as a company is uniquely qualified (by way of our worldwide experience in providing plants and units which cover all aspects of each of the presented technologies and in fact all of the processes currently and historically applied to gypsum decomposition and/or processing) to answer the question presented by this paper:

Is gypsum decomposition commercially ready now?

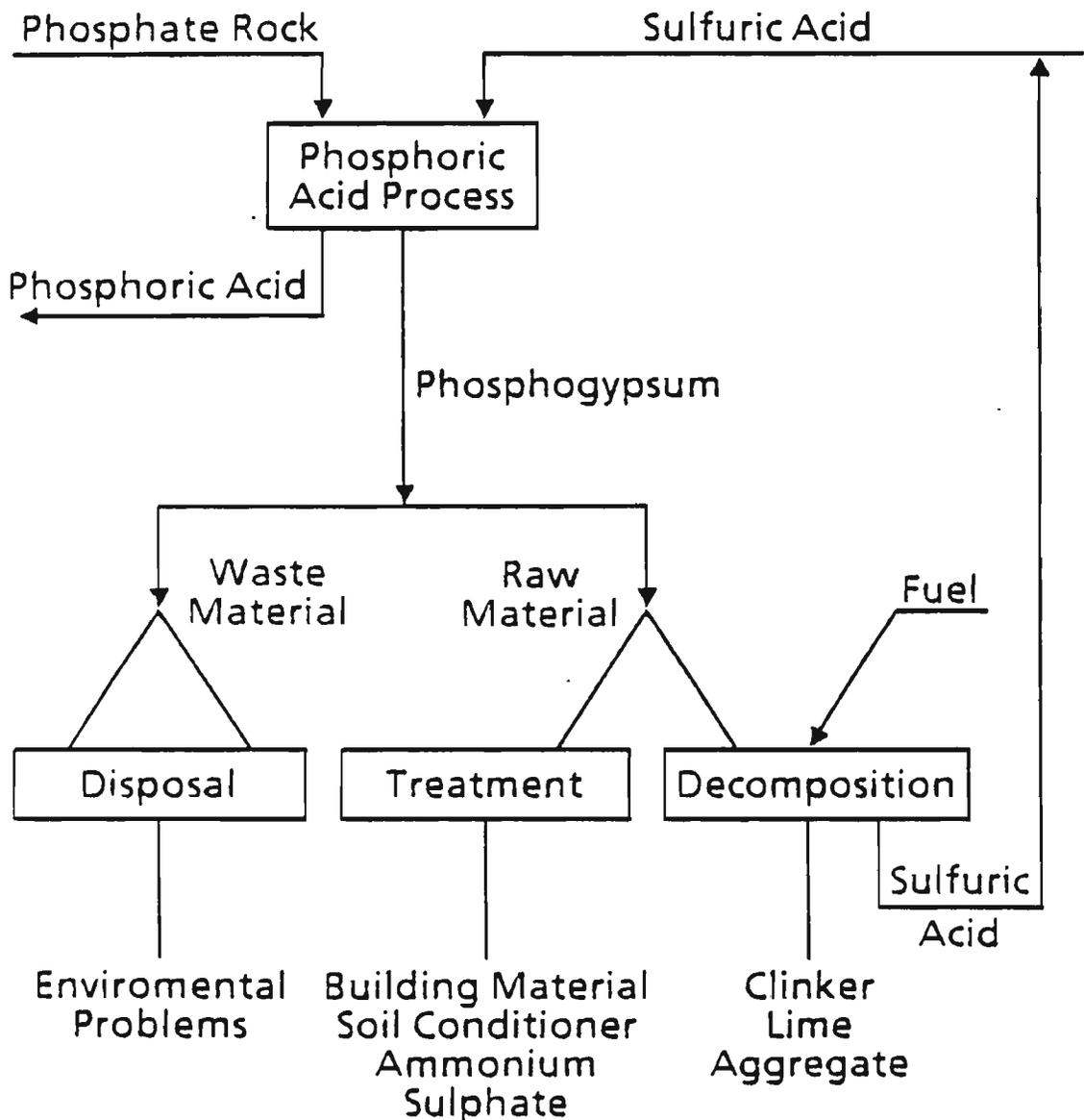
We know that phosphogypsum decomposition is possible by a commercial process - the Müller-Kühne process. The fact that this process has not dominated the field throughout the world is essentially because of economic factors. The technical problems inherent in this process have been mastered.

The other processes have not yet been demonstrated at commercial scale. There may well still be a few technical problems ahead. However, economic obstacles may be even greater. Unless very favorable conditions prevail, these processes are currently unsuitable to provide an acceptable R.O.I. based upon Western standards. This may be different in the future if there is a decisive change in the general situation. There will certainly be special cases where phosphogypsum decomposition may be viable.

All we ask is ... when you think of gypsum decomposition, think of Lurgi!

Figure 1

Phosphogypsum Destiny



10-15%
EXCEPT
JAPAN

Figure 2

Müller - Kühne Process

900°C
1400°C

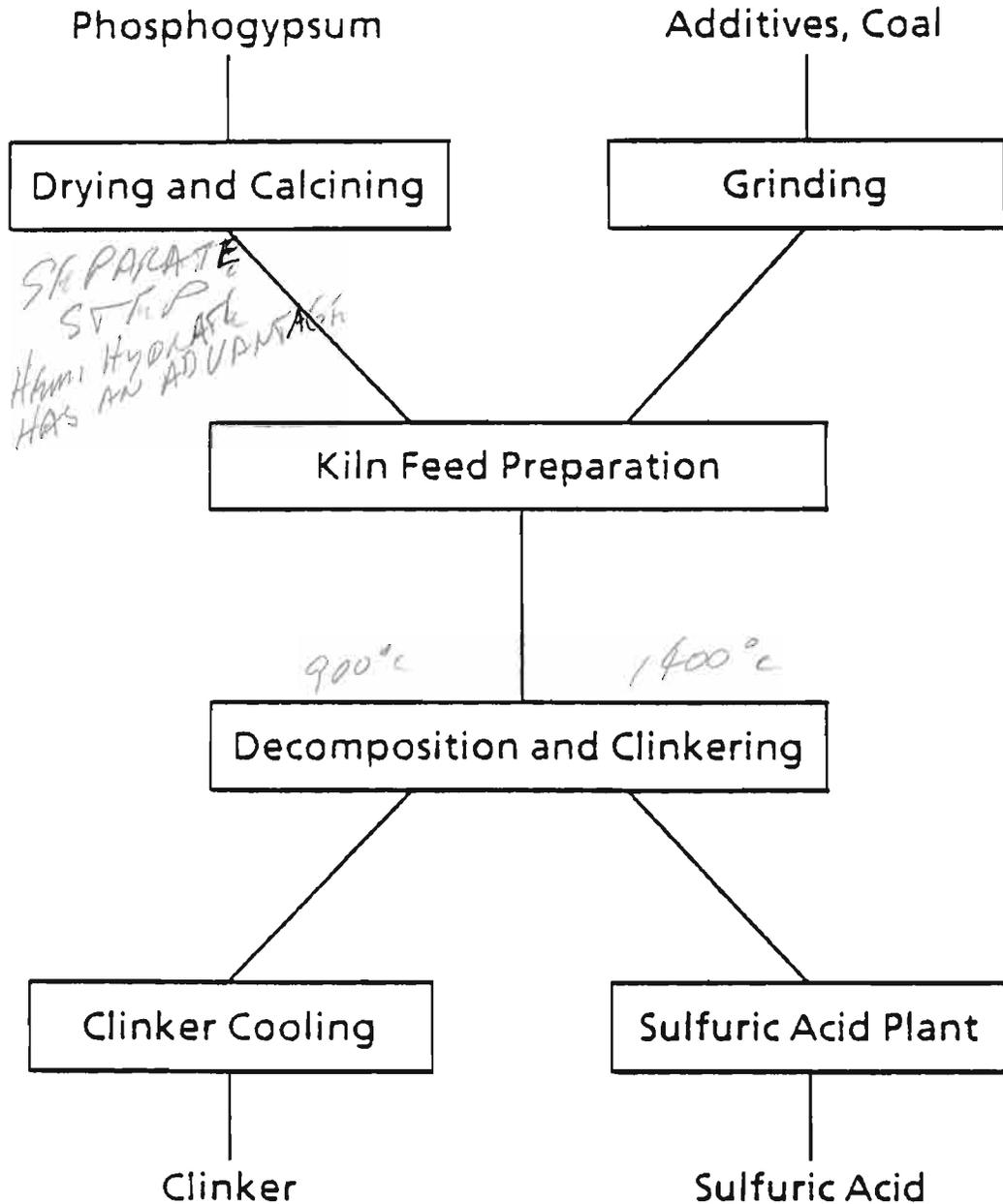


Figure 3

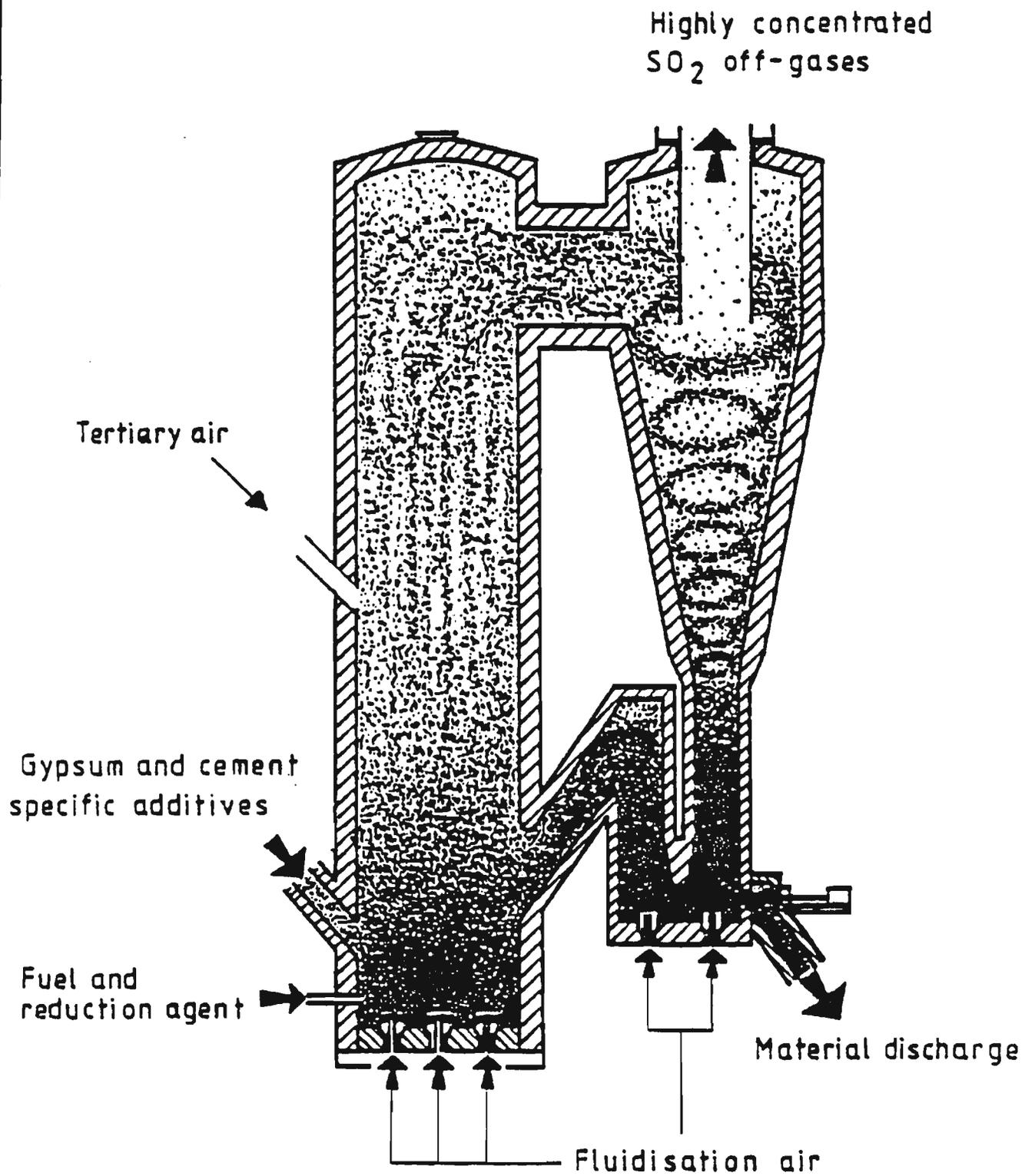


Figure 4

Lurgi Circulating Fluid Bed Process (Lime)

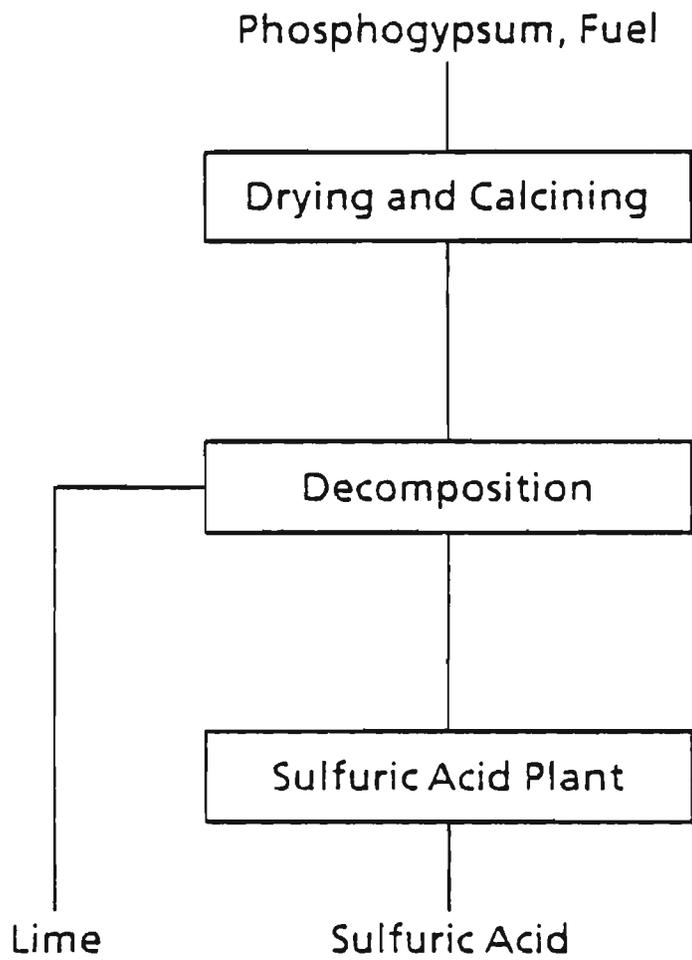


Figure 5

Lurgi Circulating Fluid Bed Process (Clinker)

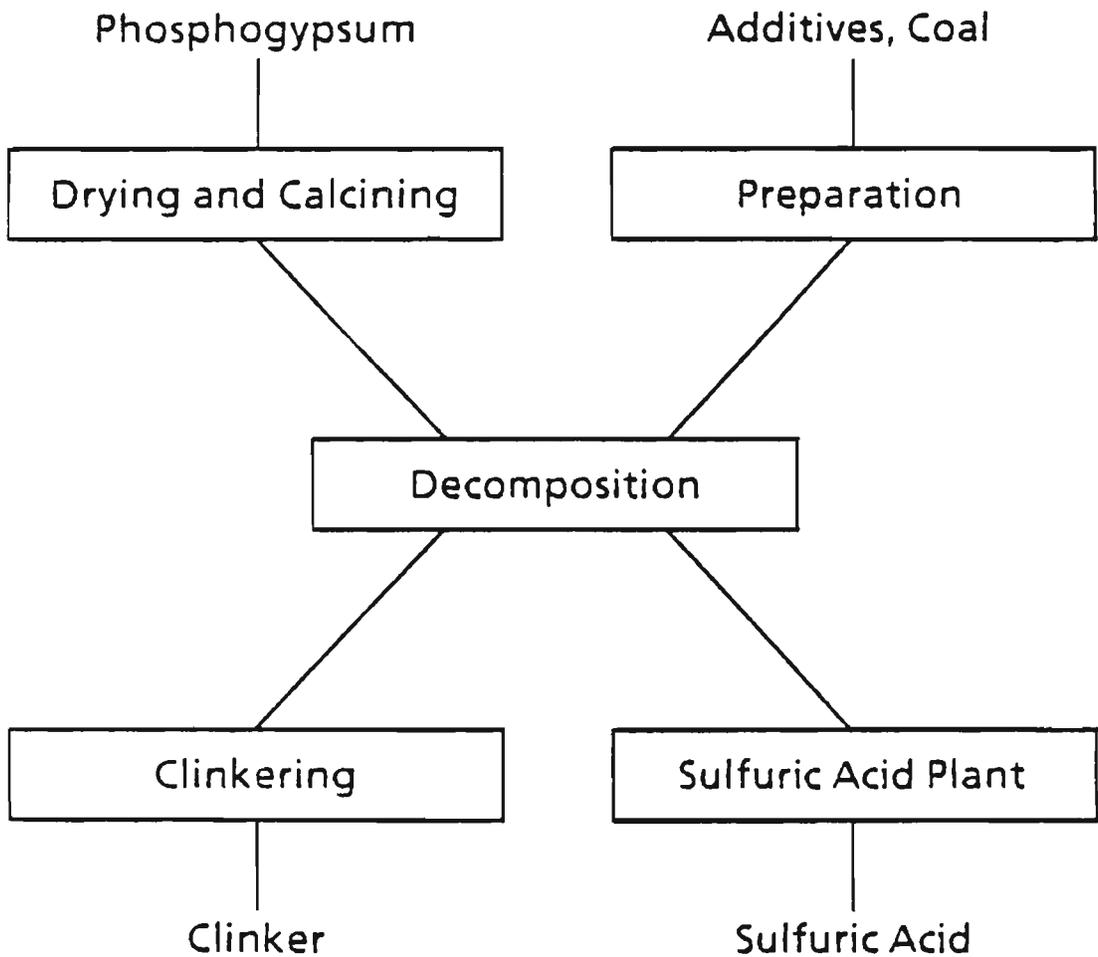


Figure 6

DMC / FIPR Process

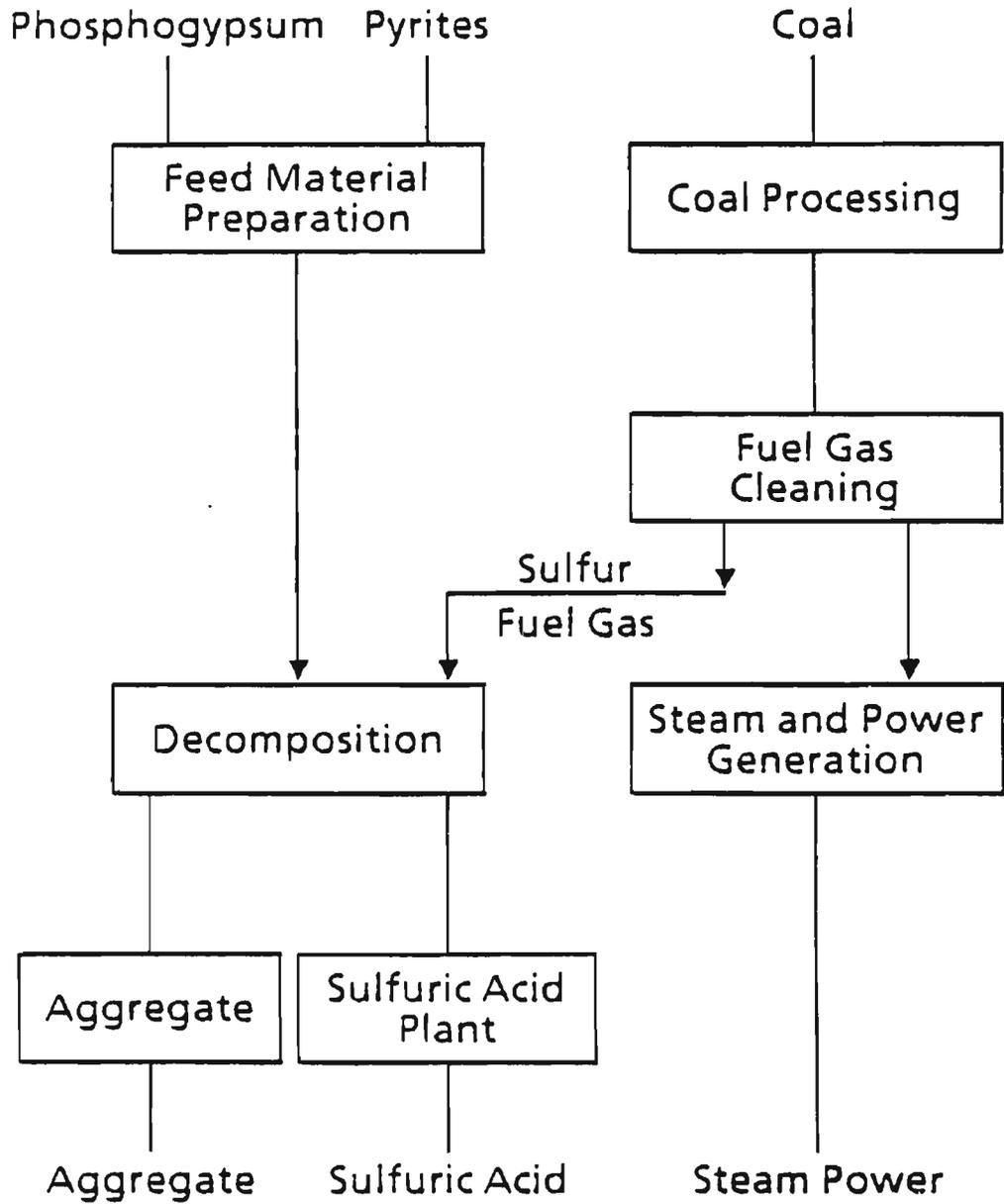


Table 1

Müller-Kühne Process
Reference List

| Location | Year | No. of kilns | No. of S.A.-Plants | Capacity H ₂ SO ₄ tpd | Remarks |
|------------------------|------|--------------|--------------------|---|-------------|
| Leverkusen, Germany | 1918 | 1 | | 40 | Pilot Plant |
| Wolfen, Germany | 1936 | 1 | 2 | 2 x 50 | |
| | 1938 | 1 | 2 | 2 x 50 | |
| | 1954 | 2 | 4 | 4 x 50 | |
| Billingham, U.K. | 1931 | 1 | 1 | 130 | |
| | 1935 | 1 | 1 | 200 | |
| | 1955 | 1 | 1 | 280 | |
| Miramas, France | 1938 | 1 | | 70 | Pilot Plant |
| Widnes, U.K. | 1955 | 1 | 1 | 210 | |
| | 1966 | 1 | 1 | 210 | |
| Whitehaven | 1955 | 2 | 2 | 2 x 180 | |
| | 1962 | 1 | 1 | 240 | |
| | 1966 | 2 | 2 | 300 | |
| Linz, Austria | 1954 | 1 | 1 | 150 (230) | |
| Coswig, Germany | 1960 | 2 | 2 | 2 x 250 | |
| | 1962 | 2 | 2 | 2 x 250 | |
| Wizow, Poland | 1955 | 2 | 2 | 520 | |
| Palabora, South Africa | 1972 | 1 | 1 | 350 | |
| China | 1987 | 1 | 1 | | |

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Table 2

Typical Phosphogypsum Analysis

(% by weight, dry basis)

| | | | |
|--------------------------------|-------------|---|-----------|
| CaO | 30,0 - 32,0 | % | (30) ** |
| SO ₃ | 42,0 - 44,0 | % | (42,4) ** |
| P ₂ O ₅ | 0,65 | % | |
| F | 1,0 | % | |
| Al ₂ O ₃ | 0,2 | % | |
| SiO ₂ | 2,0 | % | |
| Fe ₂ O ₃ | 0,1 | % | |
| K ₂ O | 0,02 | % | |
| MgO | 0,1 | % | |
| H ₂ O * | 19,0 | % | |
| free moisture | 12,0 | % | |

* water of crystallization

** for calculation of capacities

Table 3

Typical Coal Analysis
Low-grade bituminous coal

(% by weight, dry basis)

| | | |
|------------------|------|---|
| C | 57,5 | % |
| H | 4,0 | % |
| O | 7,5 | % |
| N | 1,1 | % |
| H ₂ O | 5,0 | % |
| S | 8,0 | % |
| Ash | 16,9 | % |

Table 4

Heavy Metals in Phosphogypsum (1)

from Maritime and Magmatic Phosphates

(typical average in ppm)

| | Maritime | Magmatic |
|----|-----------------|-----------------|
| Zn | 15 | 1 |
| Cu | 6 | 4 |
| Pb | 4 | 6 |
| As | 5 | 3 |
| Ni | 9 | < 1 |
| Hg | 0,1 | - |
| Cd | 8 | < 1 |

Table 5

Cadmium in Phosphate Rock (5)

(typical average in ppm)

| | |
|---------|----|
| Algeria | 23 |
| Israel | 26 |
| Jordan | 1 |
| Marocco | 17 |
| Nauru | 90 |
| Senegal | 84 |
| Togo | 54 |
| Tunesia | 56 |
| Florida | 8 |

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