International Fertilizer Industry Association

ISMA* Technical Meetings

Madrid, Spain

23-28 September 1957

**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

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TO ALL MEMBERS.
TECHNICAL MEETINGS 1957.

LE/910
received on 7th August 1957.

CONFIDENTIAL

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SULPHURIC ACID MANUFACTURE - SOME FACTORS AFFECTING CHOICE OF PLANT.

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In selecting plant for sulphuric acid manufacture there are factors which can, from the outset, exert a decisive influence on the choice of process, as for example, where specially pure or specially strong acid is required. For superphosphate manufacture, and for fertiliser manufacture generally, neither strong nor specially pure acid is necessary and the choice of plant is otherwise determined - principally on economic grounds. Although in this paper, different processes are generally and briefly reviewed, it is particularly intended to consider the effect on the relative cost of sulphuric acid production of choice of process. Such a study is bound to be on general lines only since cost factors must be greatly influenced by local conditions. Accordingly, the results may well be taken as indicative only of the circumstances currently prevailing in the United Kingdom.

The process of acid manufacture may conveniently be split into two parts - the production of SO_2 and its subsequent conversion to sulphuric acid.

SO_2 Production.

(a) From Brimstone.

A considerable number of burners is available for burning elemental sulphur falling into three classes; those in which solid sulphur is fed to and burned in a rotary kiln, those in which molten sulphur is burned on a checker brickwork and those in which molten sulphur is atomised either by compressed air, steam or mechanical means and burned in the form of a spray. For contact acid plants, more especially since the use of dark sulphur has been adopted, filtration of molten sulphur to remove dirt has increasingly become accepted practice, thus protecting the catalyst bed and lengthening the time between cleanings of the hot gas filter and removing, to some extent, the bituminous impurity present in the darker grades of sulphur. Filtration is also recommended where spray burning is practised. The cascade type of burner where the molten sulphur is burned on a mass of brickwork is commonly used for SO_2 production for acid making but it may well be that the use of spray type burners will increase as these are probably more suited for automatic control.

(b) From Pyrites.

The multihearth mechanical furnace has been in use for many years and has given reliable service. It is now, however, near to being obsolescent and its place is being taken by Flash Roasting installations and the Fluidised Bed Roasters developed over comparatively recent years. The multihearth burner takes up, for equivalent output, much more room than either of the two latter plants, is rather more expensive to erect and is more expensive to operate, both in labour and maintenance. Furthermore, it is not really suited to waste heat recovery. Both flash roaster systems and fluidised bed systems are well suited to waste heat recovery and both work at higher outputs relative to the size of the plant. For small scale installations where waste heat recovery is not economically attractive it is understood that air or water cooling may be adopted in fluidised bed roasters. The fluidised bed roaster more recently developed, has several advantages over the flash roaster which would seem to lead to its selection for most applications. Its main advantage is that it can use relatively large pyrites - up to 4 mm. at least - and thus the costly and unpleasant operations of drying and grinding pyrites may be dispensed with. The elimination of these processes leads to considerable savings in fuel, power and maintenance as well as a reduction in capital outlay on drying and grinding equipment. Given a supply of lump pyrites at an attractive price lump burners may still, in some circumstances, be of interest. Their relatively high labour requirement can be outbalanced by the fact that elaborate de-dusting and gas cleaning equipment is unnecessary. Their use is limited to small units, however, as they take up more ground space than other types of roaster and they are unsuited to waste heat recovery.

(c) From other Sulphur Bearing Materials.

SO_2 production from by-product materials such as spent oxide or H_2S is largely dependent on the local availability of supplies of the waste material. The economics of by-product processes are, however, too complex for treatment in this paper and it is not proposed to deal with them here.

The anhydrite process for the manufacture of sulphuric acid and cement is also beyond the scope of this paper, since the economics of its operation are largely a function of a readily and cheaply available supply of anhydrite and a nearby market for cement clinker. Even so, the capital costs of an anhydrite acid installation are considerably greater than any other commercially used process and have been quoted at £25 - £30 per ton of monohydrate per annum.

Conversion of SO_2 to Sulphuric Acid.

(a) Tower Processes.

The two main tower processes, Petersen and Kachkaroff, have largely displaced chamber plants for new installations. There are circumstances, namely for small installations and where lead is comparatively cheap, where a small intensive working chamber plant may be attractive but in most cases tower plants would appear to be more attractive. The principles of both processes are well documented and no attempt at lengthy description will be made here. Both processes make extremely intensive use of reaction space as compared with chamber processes and are thus able to offer considerable savings in capital outlay as compared with a chamber type plant.

Operation of the two processes differs considerably in respect of the strength and nitrosity of the acid circulation systems and the Kachkaroff process offers also the prospect of simultaneous manufacture of nitric acid with sulphuric acid manufacture. Where nitric acid is used in the subsequent manufacture of fertiliser, this may be sufficient advantage to influence the choice in favour of this process. For production of sulphuric acid only, it is, however, considered that the capital cost and operating cost of the two tower systems will be, by and large, comparable. There may well be slight differences both in capital and operating costs but for comparable plants the difference will be marginal as compared with the differences between the cost of the tower plant and the contact plant.

(b) Contact Plant.

Here again the principles of operation are sufficiently well known to obviate the need for description. Different types of contact plant are offered by different manufacturers, each having particular advantages. For the purpose of comparison, however, the division between plant using the products of combustion of brimstone and cold process plant where the gases from the pyrites roasting or from other metallurgical purposes are de-dusted and purified before passing to the convertor. The former process is recognised to be the cheapest method of producing sulphuric acid in capital cost. Its operating cost also compares favourably with other processes and it is extremely simple to control, probably lending itself more readily to automation than any other type of sulphuric acid process.

The cold gas process involving purification of gases from pyrites roasting is a much more expensive type of plant. Extra capital cost is involved for the cleansing of the gas from dust and impurities and for removing the SO_3 mist formed with the traces of water in the pyrites. Further, in the purification process the temperature of the gas is reduced to around 25°C. and the gases must be reheated to around 400°C. for satisfactory initiation of the conversion reaction - the exact temperature depending on the catalyst mass used. This cooling and reheating makes the process less efficient thermally so that, although the heat of combustion of pyrites is considerably greater than that of sulphur, the waste heat recovery, expressed as tons steam per ton of monohydrate, from the cold gas process is commonly little better than that from the brimstone burning process.

Both processes are flexible in output, the tower plant particularly so, both in respect of gas strength and quantity. It has been claimed that throughputs as low as 20% capacity can be operated on the Kachkaroff process. Pyrites roasting equipment is, however, less flexible and for a pyrites burning plant the roasters will prove a limiting factor. Contact plants will normally function quite well at rates down to around 50% of normal loading, the exact minimum depending, to some extent, on the thermal characteristics of the plant, particularly when steam from waste heat recovery is used as part of the process.

Effluent from acid plants can give rise to complaint in populous areas and in this connection it is possible that the rather lower exit acidities of the gas from tower type plants may confer some advantage, although tail gas treatment may be installed on contact plant.

Capital costs estimates for different types of installations were prepared for a plant to produce 61,000 tons per annum of monohydrate. A comparison of these costs is given in Table I. It should be noted that the costs are comparable in as much as they are all for erection on a similar site of a plant to produce 61,000 tons per annum of monohydrate as 78% acid, allowance being made in the case of contact plant for dilution and cooling equipment. Included in the estimates are raw material storage and, in the case of pyrites burning plant, cinder handling equipment. Waste heat recovery has been allowed for also in each case. Nothing has been included, however, for the cost of the land on which the plant is to be sited and in the case of areas where land costs are high this could have some appreciable differential effect on the costs.

The nature of the subsoil would also affect the relative costs by its effect on the foundations required. Other local effects could be the existence of a cheap source of suitable lump packing for use in a tower plant. In general, although lump packings require larger towers they result in the cheaper construction.

The costs are expressed as pounds sterling per ton of monohydrate per annum and also compared with the cost of the sulphur burning contact plant as unity. Operating costs were also estimated for these plants and are shown in Table II. Here also the figures are given in pounds sterling per ton of monohydrate. The total figures quoted include process labour, supervision, maintenance, power fuel, water and nitre where required. A depreciation allowance to allow of obsolescence is shown separately. The amount of this allowance must vary with individual circumstances but in this calculation the figure of 4%, equivalent to a 25 year life, has been used. The costs so far estimated do not allow for any return on the original capital outlay. The precise return expected will, of course, be dependent on a number of factors and estimates showing the cost of acid production allowing for a capital return of both 10% and 15% are also shown in Table II.

It will be seen that the lowest cost of acid production is shown by the brimstone burning contact plant. From the figures shown it will be clear that the net cost of the sulphur unit from pyrites must be substantially lower than that from brimstone if production of acid from pyrites is to be an economic proposition. It is clear that both brimstone burning tower plants and pyrites burning contact plants are uneconomic as compared with brimstone burning contact plants and pyrites burning tower plants respectively - always provided that the strength and quality of tower plant acid is acceptable.

From the information so far obtained it is relatively simple to calculate the price at which the sulphur in pyrites must be available in order to render a tower plant competitive with sulphur and this is shown in Table III. For the purposes of this calculation it has been assumed that the overall sulphur efficiency of the sulphur burning contact plant is 96% and of the pyrites burning tower plant 95% and that of the pyrites burning contact plant 92%. On this basis it would appear that the net price of the sulphur unit derived from pyrites must be at a level of only 65% of the price of the sulphur unit derived from brimstone (taking as a reference point the value of 3/- for a unit of sulphur from brimstone.)

This value applies only to the net value of the sulphur in pyrites and no allowance has been made at this stage for credit either from the steam produced or for the burnt residues. It is thought better to omit these credits here as their value will be so dependent on local circumstances as to render the substitution of any nominal value quite misleading. Cinders credit will, for example, depend on the type of ore, the degreee of desulphurisation effected, the cost of transportation to the using iron works. Of these factors desulphurisation is the only one affected by the choice of plant. A flash roaster will undoubtedly give best desulphurisation, taking the residual sulphur content to below 1% in most cases while fluidised bed roasting will produce a cinder with a rather higher sulphur content. The difference in sulphur content is not such as to affect significantly the value of the residues.

Steam credit has not been allowed in the costs of any of the plants shown although the cost of equipment for steam raising has been included in the capital expenditure. This is simply because of the value of steam can vary by as much as 300% or more depending on whether process steam is required, or whether the steam raised is to be used only for power generation and on the local costs of fuel and local availability of electric power. In this event, although steam production can have a considerable effect on the economics of the process, the relative effect as between say sulphur burning contact plant, pyrites burning contact plant and pyrites burning tower plant is relatively slight. Steam recovery from a sulphur burning contact plant is at the rate of 0.9 to 1.0 tons steam/ton acid and is generally slightly more than 1 ton steam per ton of acid from the other two processes.

Calculation has been made of the value of the net sulphur unit from pyrites at which it would be economically possible to convert a sulphur burning contact plant to pyrites burning - assuming that the plant had been originally designed so as to make such conversion practicable.

This was done by summating operating costs and capital charges over the life of the plant (assumed at 25 years) on the basis of conversion to pyrites burning occurring after 5, 10, 15 and 20 years and calculating the unit value of pyrites which would make total outlay on operation, capital charges and raw materials the same as if brimstone had been used throughout. The results of this calculation are shown graphically in Figure I, again showing the net value of the sulphur unit from pyrites expressed as a percentage of the cost of a unit of brimstone sulphur at 3/-.

It will be seen that the values are so low that, should it not be considered economic to erect pyrites burning plant at the outset, it is unlikely that it would ever prove to be so at a later date and conversion would probably be justified only in the case of unavailability of sulphur.

Conclusions.

The results of the calculations would seem to be reasonably clear. Under the circumstances covered by the estimate it is clear that the brimstone burning contact plant is the cheapest process as regards both capital outlay and operating costs. Brimstone burning tower plant is considerably more expensive and offers no advantage whatsoever except more ready convertability to pyrites burning. Pyrites burning tower plant is second in order of preference and can compete with sulphur burning contact plant in economic attractions

(1) If the relatively impure and weaker acid is acceptable.
(2) If the net cost of the sulphur unit derived for pyrites is below 65% of the cost of the sulphur unit from brimstone.

When pyrites is available either at an attractive price or as a by-product which must be disposed of the tower process is economically preferable to the contact process from conversion to sulphuric acid for fertiliser manufacture. Only when strong acid or oleum is required is the contact plant attractive.

Once having erected a brimstone contact plant it would appear unlikely that the relative sulphur unit price ratio would change sufficiently to make it economic to convert to pyrites. Little short of a world shortage and physical unavailability of sulphur would justify such a conversion.

Acknowledgements.

In conclusion I wish to express my thanks to the Directors of Scottish Agricultural Industries for permission to present this paper and to those of my colleagues who have assisted in its preparation.

TABLE I

Capital Cost of Different Types of Sulphuric Acid Plant (based on cost of a unit to produce 61,000 tons monohydrate per annum)				
	Brimstone Contact Plant.	Pyrites Contact Plant.	Brimstone Tower Plant.	Pyrites Tower Plant.
Cost in pounds sterling per ton monohydrate per annum	£6.3	£14.7	£10.3	£12.3
Cost ratio with cost of brimstone contact plant as unity.	1	2.33	1.64	1.95

TABLE II

Operating Costs of Different Types of Sulphuric Acid Plant as shown in Table I.				
	Brimstone Contact Plant	Pyrites Contact Plant	Brimstone Tower Plant	Pyrites Tower Plant
1. Operating cost per ton of monohydrate. (a) pounds sterling	£0.61	£1.26	£0.98	£1.28
(b) ratio based on sulphur burning contact plant as unity.	1	2.07	1.61	2.10
2. Depreciation on capital cost at 4%	0.25	0.59	0.41	0.49
3. 1 plus 2.	0.86	1.85	1.39	1.77
4. Capital charge at 10%	0.63	1.47	1.03	1.23
5. Capital charge at 15%	0.94	2.20	1.55	1.84
Total 3 plus 4.	£1.49	£3.32	£2.42	£3.00
Total 3 plus 5.	£1.80	£4.05	£2.94	£3.61

TABLE III

Net value of sulphur unit from pyrites as compared with sulphur unit from brimstone (taken for reference at £0.15) necessary to render other types of plant competitive with brimstone contact plant.				
	Brimstone Contact Plant	Pyrites Contact Plant	Brimstone Tower Plant	Pyrites Tower Plant.
A. at 10% capital charges cost/unit, pounds sterling	£0.15	£0.097	-	£0.106
cost/unit as percentage of cost of brimstone unit	100%	65%	-	71%
B. at 15% capital charges cost/unit, pounds sterling	£0.15	£0.084	-	£0.096
cost/unit as percentage of cost of brimstone unit	100%	56%	-	65%

SUMMARY

In selecting plant for sulphuric acid manufacture there are factors which can, from the outset, exert a decisive influence on the choice of process, as for example, where specially pure or specially strong acid is required. For superphosphate manufacture, and for fertiliser manufacture generally, neither strong nor specially pure acid is necessary and the choice of plant is otherwise determined - principally on economic grounds. Although in this paper, different processes are generally and briefly reviewed, it is particularly intended to consider the effect on the relative cost of sulphuric acid production of choice of process. Such a study is bound to be on general lines only since cost factors must be greatly influenced by local conditions. Accordingly, the results may well be taken as indicative only of the circumstances currently prevailing in the United Kingdom.

The various methods for the production of SO_2 from brimstone and from pyrites are briefly discussed as are also methods of conversion available. Capital and operating costs for units to produce 61,000 tons mono-hydrate per annum by different methods are shown, and from these data are calculated relative values of the sulphur units derived from brimstone and from pyrites, giving acid of equal cost from different raw material.

Brimstone burning contact plant is the cheapest process as regards both capital outlay and operating costs. Brimstone burning tower plant is considerably more expensive and offers no advantage whatsoever except more ready convertability to pyrites burning. Pyrites burning tower plant is second in order of preference and can compete with sulphur burning contact plant in economic attractions

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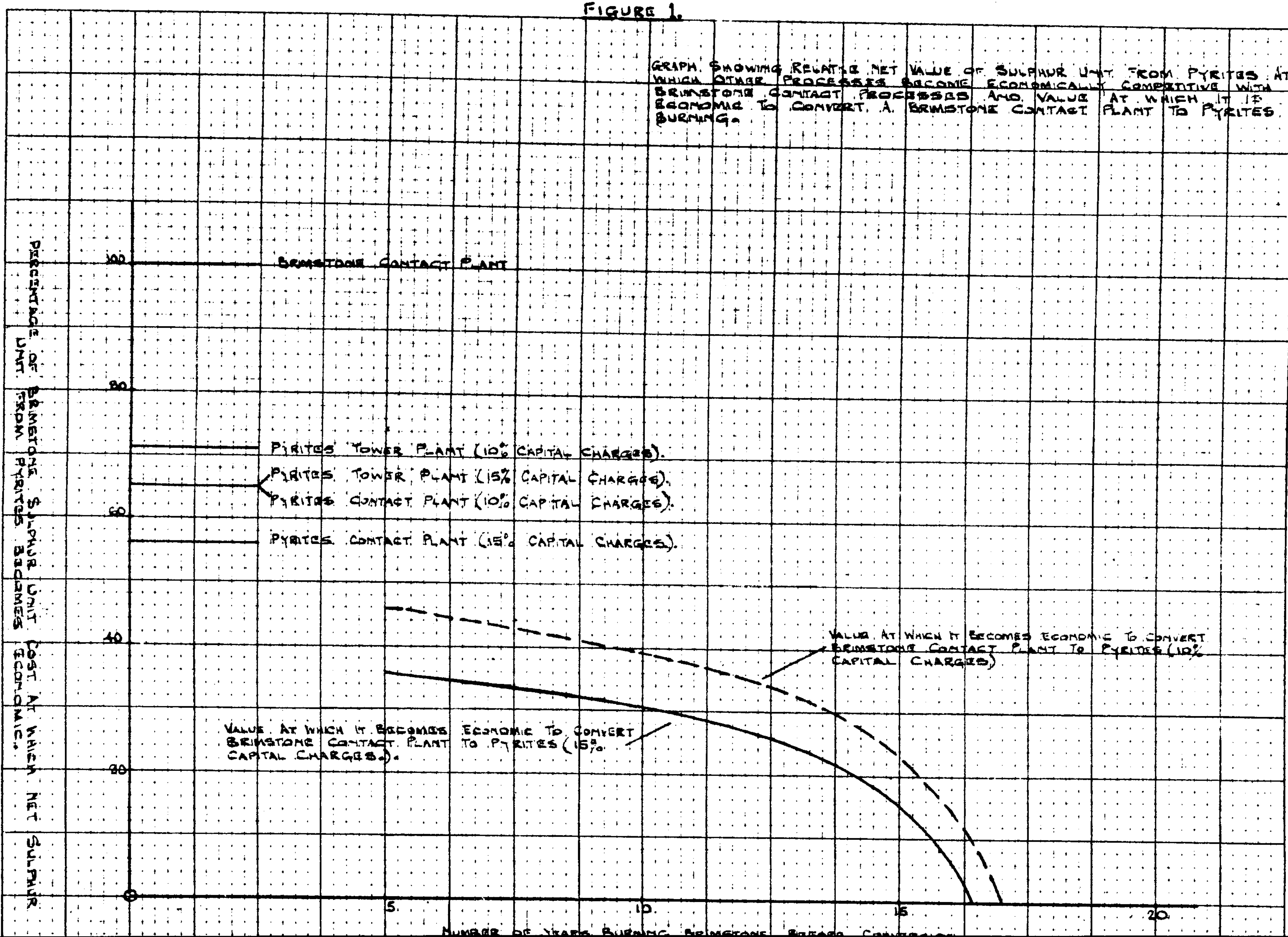
Once having erected a brimstone contact plant it would appear unlikely that the relative sulphur unit price ratio would change sufficiently to make it economic to convert to pyrites. Little short of a world shortage and physical unavailability of sulphur would justify such a conversion.

FIGURE 1.


GRAPH SHOWING RELATIVE NET VALUE OF SULPHUR UNIT FROM PYRITES AT WHICH OTHER PROCESSES BECOME ECONOMICALLY COMPETITIVE WITH BRIMSTONE CONTACT PROCESSES AND VALUE AT WHICH IT IS ECONOMIC TO CONVERT A BRIMSTONE CONTACT PLANT TO PYRITES BURNING.
PERCENTAGE OF BRIMSTONE SULPHUR UNIT COST AT WHICH NET SULPHUR UNIT FROM PYRITES BECOMES ECONOMIC.
100
80
60
40
20
0
5.
10.
15.
20.
BRIMSTONE CONTACT PLANT
PYRITES TOWER PLANT (10% CAPITAL CHARGES).
PYRITES TOWER PLANT (15% CAPITAL CHARGES).
PYRITES CONTACT PLANT (10% CAPITAL CHARGES).
PYRITES CONTACT PLANT (15% CAPITAL CHARGES).
VALUE AT WHICH IT BECOMES ECONOMIC TO CONVERT BRIMSTONE CONTACT PLANT TO PYRITES (10% CAPITAL CHARGES)
VALUE AT WHICH IT BECOMES ECONOMIC TO CONVERT BRIMSTONE CONTACT PLANT TO PYRITES (15% CAPITAL CHARGES).