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THE CONTINUOUS USE OF DILUTE SULPHURIC ACID
(SCRUBBER ACID) IN THE PRODUCTION OF
HIGH ANALYSIS NPK FERTILISERS

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When sulphuric acid is produced from the gases obtained by roasting of sulphide-containing ores or concentrates, then, besides the pure concentrated acid, a certain amount of weak impure scrubber acid is obtained. This acid is formed from the moisture and the sulphur trioxide contained in the gases when the roasting gases are scrubbed in the washing towers, which are located at the beginning of the sulphuric acid process line. A part of the dust-like impurities of the gases are washed into the scrubber acid. The most important of these are ferrous impurities.

Part of the iron compounds which are mainly oxides are dissolved, forming an almost completely saturated iron sulphate solution, while part of them remain as an insoluble solid substance. The scrubber acid solution has the following typical composition:

H ₂ SO ₄	15 - 30 weight per cent
Soluble iron	10 - 20 gram/litre
Solids	1 - 10 gram/litre
Chlorides	1 - 2 gram/litre.

The main constituent of the solid substance is iron oxide (over 60 per cent); in minor quantities there are elements such as: selenium, zinc, arsenic, copper, nickel, cobalt and calcium.

The concentration and composition of the scrubber acid depend on the water content and composition of the material which is being roasted and also on the roasting process itself. The amount of scrubber acid also varies depending on the roasting and gas washing practices. The amount is of the order of 1 - 5 per cent of the total acid production.

Previously, it has been possible to use the dilute

scrubber acid, e.g., for the manufacture of ordinary superphosphate. Alternatively, it has been disposed of with the plant waste water. Along with the decreasing use of superphosphate and, on the other hand, with increasing sulphuric acid production, the dilute scrubber acid now poses a difficult problem as pollution control simultaneously imposes increasing restrictions on wastes and waste water treatment.

It is possible to use the dilute scrubber acid for various chemical industrial purposes, if it is purified and concentrated. Purification requires crystallization of the iron sulphate by cooling and/or concentrating the acid. Waste acid is purified and concentrated by this method in a number of plants. Dilute sulphuric acid is concentrated, e.g., in pulp and paper mills in Finland in small plastic evaporation units up to 70 per cent acid & on a bigger scale in Japan in chemical plants with evaporation units made from special quality steel up to 80 - 85 per cent acid. However, the acid evaporation is technically inconvenient, firstly owing to the crystallization and crystal-removing procedure and secondly to the powerful corrosion and tendency to clogging of the acid evaporation equipment. Furthermore, this method is very expensive, owing to the many process stages involved and the high cost of machinery required by the use of expensive materials. The cost of acid obtained by this process is, therefore, several times that of common product acid.

For these reasons, other possible means for the disposal and utilization of scrubber acid have been investigated within our company, too. The following is a short account of a new method whereby waste acids can be put to use in a modern fertiliser factory.

Outline of the Principle of the Slurry Evaporation Process

Kemira Oy has developed and carried out in practice a method whereby the scrubber acid can be used in the manufacture of concentrated NPK fertilisers. The dilute acid is first fed into a preammoniating reactor and the slurry thus obtained is then concentrated by evaporation to an appropriate composition before it is fed to the fertiliser process for a final adjustment of composition before granulation.

Figure 1 illustrates the principle of the method.

The scrubber acid coming from the sulphuric acid process is taken into storage tanks, in which the solids in the acid settle to the bottom and are removed from time

to time as a dense slurry to be returned to the roasting ovens either as such or after having been filtered in a filter press. The clarified acid is conducted into the ammoniating reactor, in which the neutralization of the required amounts of both nitric and sulphuric acids with ammonia to about pH 3-4 is effected. The dilute slurry obtained is pumped into multistage evaporator units, in which the required amount of water is removed from the system. The slurry thus produced is then fed to the NPK fertiliser process for further treatment to various fertiliser grades.

Development of the Process

The general principle outlined above was first thoroughly tested in pilot plant experiments in our research laboratory. These experiments included among other things, the following investigations:

- water balances for the evaporation and fertiliser processes to determine the practical water contents at each stage of the whole process.
- behaviour of the slurry on heat-transfer surfaces to determine the best conditions for operation.
- determination of heat-transfer coefficients.
- corrosion tests with heat-transfer materials.
- dissolution of solid raw materials into the slurry.
- granulation of the fertiliser slurry.
- production of high-grade NPK fertilisers such as 15-20-15, 10-25-25 and chlorine-free NPK 7-24-14 + Mg + Mn + B. About 5 - 20 per cent of nitrogen is in the nitrate form.
- caking of the various fertiliser grades.
- salt composition studies of the various fertiliser grades.
- effect of impurities in the scrubber acid on caking.

The pilot plant results were successfully verified with full scale test runs in one of our old fertiliser plants.

Practical Realization of the Process

In view of the successful test results it was decided

that this new method would be used in connection with the construction of a new fertiliser factory at our Kokkola works which is our biggest acid producing centre. Within the works premises the total production of sulphuric acid is 1800-1900 tons per day. This is the output of several production lines all operating with smelter gases. About 40 - 50 tons of scrubber acid per day, calculated as 100 per cent H_2SO_4 , is formed. This is about 3 per cent of the total acid production and the disposal of it had become increasingly difficult during the last years.

The capacity of the new fertiliser plant at Kokkola is about 700 tons per day. Its principal product is NPK fertiliser with composition of 15-20-15.

The clarified scrubber acid, of about 25 - 30 per cent H_2SO_4 strength, is fed at the rate of 8-10 m^3 /hour into the pre-reactor along with ordinary fertiliser process solutions. It is estimated that 6 - 10 tons of water per hour have to be evaporated. This includes both the extra water introduced by the dilute scrubber acid, and also the circulation water amounting to 1-3 m^3 /hour from the scrubbing of the exhaust gases of the fertiliser plant. A three-stage evaporation unit has been built to evaporate this water. The heating of the slurry is performed by steam in tubular heat exchangers and the actual evaporation takes place in a series of vacuum chambers. The first stage operates at normal pressure and at 110 - 120°C and the last stage at a pressure of 200 - 300 torr and at 80 - 90°C. The dry solids content of the slurry fed into the evaporators is about 40 - 50 per cent and the corresponding value after evaporation is 70 - 75 per cent. In some fertiliser grades, it is as high as 80 per cent or more. In the preparation of grades such as 10-25-25 and 7-24-14, it is unnecessary to use the evaporator at all.

Operating Experience

The most important special feature of the evaporation plant to us is its large heat-transfer surfaces of the order 250 m^2 /each stage and, correspondingly, their low thermal loading per surface area 5,000 - 10,000 kcal/ m^2 h. This prevents the depositing of scale on the heat-transfer surfaces and overheating of the solution. No clogging of the heat-transfer surfaces, nor of any other points, has occurred. The normal acid resistant steel of the type SIS 2340 has proved to be fully adequate and there has been no sign of corrosion in the apparatus. It is in fact unlikely that corrosion will occur in the solution in question owing to the good nitrate inhibition.

The evaporation plant has been designed so that one stage, and part of the pipelines, may be washed at fixed intervals while evaporation is in progress. During shut-down of the fertiliser plant the whole evaporator plant can be placed in closed circulation for the avoidance of clogging.

Control of the concentrating process is exceedingly simple: the acidity of the input solution is monitored by its free acid content and the amount of evaporation by the density of the output slurry.

The filtration or separation of solid iron compounds from the slurry has not been necessary so far and the iron content of the fertiliser product has never exceeded the agronomically permissible levels. The iron content in the product has increased by using scrubber acid from 0.3 to 0.6 per cent. This has decreased to some extent the amount of water soluble phosphate from 93 per cent.

Hitherto the use of the waste acid method has not caused any trouble in the fertiliser process itself. Granulation of the products has been quite normal and their quality fully comparable to other high-quality NPK fertilisers. The iron content in the scrubber acid has been found to be beneficial to the caking properties of the fertilisers due to the water-binding effect of the finely-deposited iron phosphates.

The method described above of preparing from the scrubber acid a fertiliser slurry with the right chemical and physical properties has been in operation for almost two years now. So far, the experience gained in practice is very promising. The operation of the plant has been easy and no difficulties have occurred.

Economic considerations

A comparison of the economy of the slurry concentration method and of the sulphuric acid concentration method is presented in the following table. The evaporator capacity is assumed to be 10 tons of water per hour.

	Slurry concentra- tion method (values from practice)	Sulphuric acid concentration method (obtained from tenders)
Investments in the concentration plant	1 500 000 mk	> 3 500 000 mk
Annual capital costs	247 500 "	> 577 500 "
Difference in annual capital costs		330 000 "
Operating costs per ton	27 mk/ton H ₂ SO ₄	> 45 mk/ton H ₂ SO ₄
Operating costs per year	405 000 mk	> 675 000 mk
Total costs per year	652 500 mk	> 1 252 500 mk
Difference in total costs, per year		> 600 000 mk > 60 000 £

From the values given in the table it can be seen that the investment cost as also the operating costs in the slurry concentration method are much lower than the cost of the acid concentration method. Also technically the slurry method is easier than the acid concentration method.

Conclusion

We have described above how it is possible, by using the slurry evaporating method, to utilize the scrubber acid from sulphuric acid manufacture and the washing waters from the fertilizer plant in a fertilizer process. The various reaction stages before granulation have been developed and designed by Kemira Oy. Since it should be possible to apply the same slurry evaporation method to other fertilizer processes, too, we thought it unnecessary to describe our fertilizer process in detail here. A well-known feature in nearly all compound-fertilizer processes is the neutralization of acids with ammonia in different reaction stages. The conditions within these can be changed by reactor design and operating variables. By evaporating the slurry in the most favourable conditions, we have evolved a new and effective method of disposing of various dilute,

impure solutions in modern fertiliser technology. Increasing demands of industrial pollution control are likely to produce ever-growing amounts of such wastes.

DISCUSSION

MR. E. UUSITALO (Kemira Oy, Finland): As its title indicates, our paper describes one possible way of avoiding the re-lease of diluted, impure waste sulphuric acid in fertiliser manufacture.

The Raw material for most sulphuric acid production today consists of the gases obtained by roasting sulphide-containing ores or concentrates. In these processes, in addition to pure concentrated acid, a certain amount of weak impure scrubber acid is obtained, usually from 1 to 5% of total acid production. For example, one of our sulphuric acid plants produces nearly 20,000 tons of impure diluted scrubber acid per year calculated as 100% H_2SO_4 or more than 100,000 tons/year as 15% H_2SO_4 . The typical composition of this scrubber acid is:-

H_2SO_4	15 - 30 w %
soluble iron	10 - 20 g/l
solids	1 - 10 g/l
chlorides	1 - 2 g/l

In the past, it has been possible to use dilute scrubber acid for the manufacture of ordinary superphosphate or alternatively it has been disposed of with the plant waste water. Nowadays its use and disposal have become more and more difficult for the following reasons:-

- 1) with increasing sulphuric acid production the amount of scrubber acid has increased and is still increasing,
- 2) superphosphate production is diminishing rapidly and the usefulness of scrubber acid is more and more limited,
- 3) dilute scrubber acid now poses a difficult problem because of pollution control on wastes and waste water treatment,
- 4) if mercury is washed out from roasting gases, as must be done in many cases, the amount of waste acid is even greater.

For these reasons, all possible new ways of disposing of or using scrubber acid have been investigated in our company.

We have developed and carried out in practice a method whereby scrubber acid can be used in the manufacture of concentrated NPK fertilisers. The diluted acid is first fed into a pre-ammoniating reactor and the slurry thus obtained is then concentrated by evaporation to an appropriate composition before being fed into the fertiliser process for a final adjustment of its composition before granulation.

A diagram of the principle involved is given in the paper.

From the very simple flow sheet you can see that the crude sulphuric acid is fed in from the left through a clarifier. The clarifying takes place in big storage tanks, from which settled solids are removed from below once or twice a year. When it is necessary to remove mercury with sulphide precipitation, the acid is filtered in a filter press. The clear acid is fed continuously under control into a pre-reactor for the neutralization of acids with ammonia and ammonium nitrate solution. The slurry from the pre-reactor is then concentrated in three phases in big evaporation units. Evaporation presents no difficulties as long as the heat surfaces are not too heavily loaded and can be washed periodically. This involves extra arrangements so that the washing can be carried out in one phase simultaneously with the other processes, in other words evaporating continuously. Development of this type of equipment has taken a great deal of planning and practical experience. The concentrated slurry is then used in fertiliser processes of various kinds.

This slurry evaporation process has been conducted in one of our plants, where total sulphuric acid production is nearly 2000 tons per day calculated as 100 per cent H_2SO_4 and fertiliser production is about 700 tons per day. The principal fertiliser product is NPK 15-20-15. Both production lines have been combined so that the whole of the waste acid production is used in fertiliser manufacture.

In the actual case mentioned above, the clarified scrubber acid, of about 15% H_2SO_4 strength, is fed at the rate of 8-10m³/hour into the pre-reactor along with ordinary fertiliser process solutions. Approximately 6-10 tons of water per hour have to be evaporated. Evaporation itself takes place in a series of vacuum chambers at pressures of 760-200 torrs. The dry solid content of the slurry fed into the evaporators is about 40-50 per cent and the corresponding value after evaporation is 70-75 per cent.

We have made a comparison of the economics of our slurry concentration method and the sulphuric acid concentration method where the acid is concentrated in high quality stainless steel evaporators. Assuming an evaporation capacity of 10 tons of waste per hour, the operating costs of our slurry concentration method are about 27 mk/ton H_2SO_4 while those of the sulphuric acid concentration method are about 45 mk/ton H_2SO_4 . The yearly difference in total cost is over 600,000 mk (£ 60,000) in favour of slurry concentration. The latter is also simpler than acid concentration from the technical point of view.

We now have two years' experience of the slurry concentration system of dealing with waste acid produced in fertiliser manufacture. The effect of the use of scrubber acid on the fertiliser manufacturing process itself and on the

properties of the finished product has been negligible, water solubility has decreased a little and caking has been less than before. The system has been successful and we are satisfied with the results both from the economic and from the technical points of view.

MR. MARTIN CAZORLA: (Union Explosivos Rio Tinto, Spain): When scrubber acid from a sulphuric acid plant is at the stage when it can be regarded as a waste product, its acid concentration is normally very low. What factors affect the concentration of scrubber acid and how - in the case mentioned in the paper - has it been possible to get the concentration of scrubber acid as high as the 15 - 30% H₂SO₄ indicated?

MR. UUSITALO: The amount of scrubber acid is dependent, as the paper explains, on the SO₃ content of the SO₂ gas produced on roasting and its concentration on the water content of the roasting gases in proportion to their SO₃ content as well as on the temperature of the gases leaving the scrubber system.

In the case described in the paper, conditions are such that they allow very effective circulation of scrubber acid if acid with a concentration of up to 40 - 50% H₂SO₄ is used in the scrubber towers. When the gas cools after scrubbing and passing through the electro filters, a condensate forms and is carried to the scrubber acid. In addition, water must be added in a quantity sufficient to lower the halogen content of SO₂ gases to the required level in the scrubber towers.

All these factors taken together determine the concentration of the scrubber acid which we attempt to keep as high as possible; we have managed to keep its concentration generally between 20 and 30%. On roasting certain slicks we have reached 40%.

MR. MARTIN CAZORLA: What is the SO₂ content of the scrubber acid and how has it affected the production of fertilisers when scrubber acid has been used?

MR. UUSITALO: The SO₂ content of the scrubber acid has not been the subject of much analysis because no effect has been noticed on fertiliser production. At its highest it may be 1% in newly-produced acid but it drops rapidly on conditioning and storing. After several days of storage we find an average SO₂ content of the order of 0,05% when conveying it to the fertiliser plant.

MR. MARTIN CAZORLA: How much has the iron content of scrubber acid used in the process reduced the water solubility of the fertilisers produced?

MR. UUSITALO: The water solubility of the fertilisers produced previously was about 92-93%. When scrubber acid was used, it dropped to 89%. This has not had any effect worth mentioning on fertiliser use. Even a slightly lower water solubility is quite acceptable in our conditions. The effect of the iron can be minimised by allowing the scrubber acid to settle and become fully clarified. In this case, almost all the iron remains at the bottom of the tanks. Up to the present, we have not used clarifiers.

MR. W. BOOS (Gewerkschaft Victor, Germany): The use of scrubber acid adds to the ammonsulphate content of the fertiliser. Has this not reached too high a level?

MR. UUSITALO: There is a need for sulphur in fertilisers in Finland and plants which do not use scrubber acid add sulphuric acid. The ammonsulphate content of fertilisers fluctuates between 10 and 20% and has remained within acceptable limits.

MR. BOOS: Does too high an SO₂ content cause secondary reactions, e.g., a lowering of nitrate content in the fertilisers?

MR. UUSITALO: We have not noticed this nor have we investigated it because, as has been explained, the waste acid has always been kept in big storage tanks, in which the SO₂ content has dropped to 0,05% which has had no noticeable effect.

MR. BOOS: How have your economic calculations held true and are there factors in the process which have brought about changes in the original calculations?

MR. UUSITALO: In making our economic calculations, we compared only two methods: straight concentration and slurry evaporation. For sulphuric acid recovery, the method is of course expensive, but, taking into account that scrubber acid must be used in some way, we think that our method is the more economical and our calculations have held true in the sense that they have been proved accurate.

Solid fertilizer raw materials

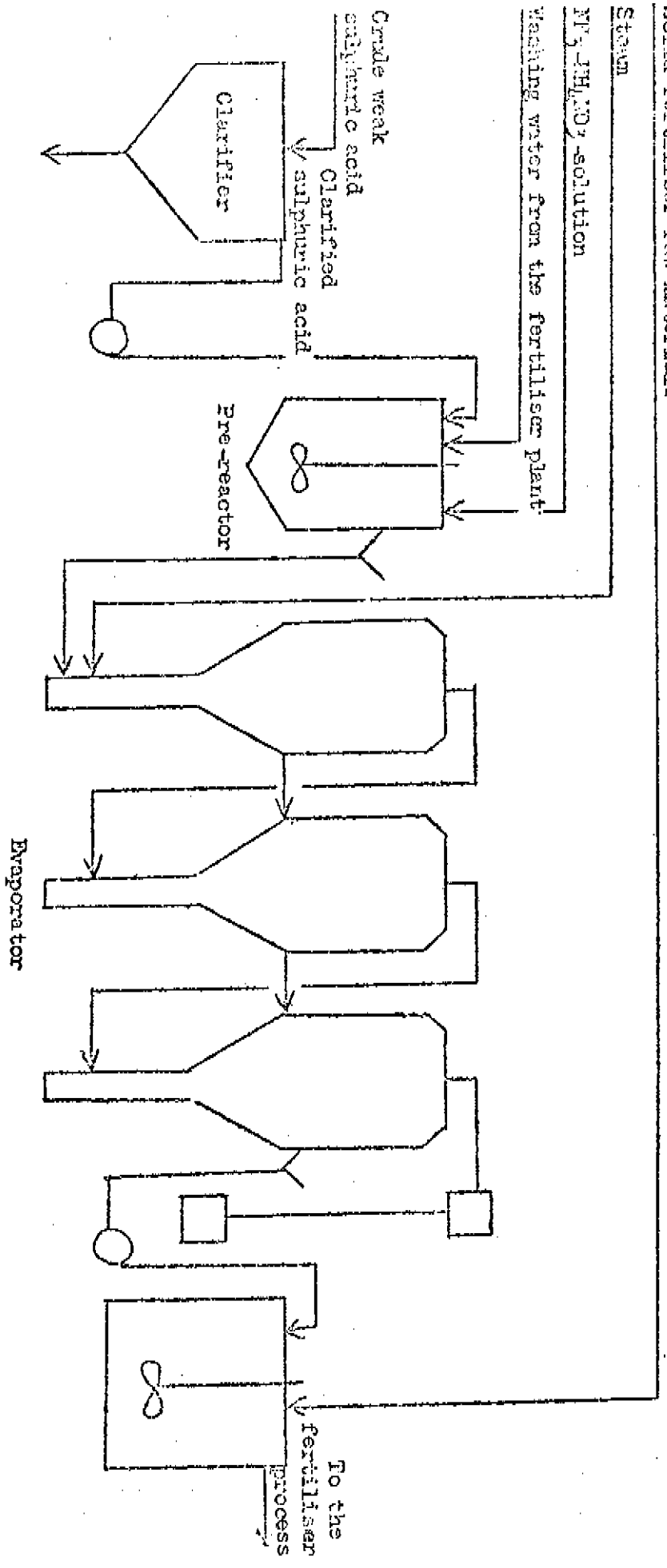


FIGURE 1 : THE USE OF CRUDE AND WEAK SULPHURIC ACID IN A FERTILISER PROCESS, FLOWSHEET