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DISCUSSION: (Rapporteur Mr. L.J. Carpentier, IFA)

Q - Mr. F. ACHORN (NFDC/TVA, USA).

You showed increased movement of urea and anhydrous ammonia over ammonium nitrate. I wonder: Has nitrogen solution become a factor in this area as it has in other areas ?

A - The question is : Does it relate to liquid fertilizer ? In most figures, I included the nitrogen, ammonium nitrate and urea, that was used in the liquid fertilizer. Liquid fertilizer has had some impact in Western Canada and there is a growing interest in it; however, it is still not a major part of the market. The trend now, very definitely, is to band liquid fertilizer in our market area, and that has helped increase the acceptability of liquid fertilizers. It has improved their performance, and their acceptance in the market.

Q - Mr. CARPENTIER (IFA, France).

1/ In your paper, you mentioned very low nitrogen rates of application as compared to what we have in Europe and other parts of the world. What kind of yield level do you reach with such rates on the most important crops, such as wheat, barley, and rapeseed ?

2/ You mentioned the switch-over from ammonium nitrate to urea and anhydrous ammonia in recent years. I am rather surprised at this trend because of your climatic conditions and short growth period. Is mineralization and nitrification sufficiently quick to allow for an efficient use of these fertilizers ?

3/ You said that one of the reasons for the good effect of urea is band placement to reduce the losses, but would you not reach the same results by applying ammonium nitrate top-dressed, for example, after tillering ?

A - 1/ The average yield for wheat ranges from 20 bushels to 40 bushels per acre or about 1.2 to 2.5 tons per hectare. There are farmers who exceed those yields. This past year in Alberta, yields have been higher under dryland conditions. However, in the Southwest corner of Alberta and Southern Saskatchewan, there were many fields that were planted this year that were not harvested at all, and some fields yielded as little as 5 bushels per acre.

Barley yields range at, say, from 50 to 90 bushels per acre, or 2.5 to 6 tons per hectare. However, in Alberta, just South of Edmonton, in our test plots where we used some growth regulators and fungicides, we have managed to achieve 180 bushels per acre, or 9.7 tons per hectare. So, in the better moisture area parts of Alberta, certainly - and Manitoba as well - there is potential for increasing those yields considerably. Rapeseed yields, another important crop of ours, will be 25 to 40 bushels per acre or 1 to 2 tons per hectare. Again, we have achieved yields of 70 to 80 bushels per acre under irrigation, but, under dryland, 50 bushels probably is a realistic goal.

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Climate, the impact of climate, will change yields a great deal from year to year.

2/ The second question was related to ammonium nitrate and whether urea and anhydrous ammonia are effective replacements. In our cereal trials, we have not found any advantage for ammonium nitrate, in spite of cold spells in the spring of the year, over urea, if they are equally applied. In this case, they are band applied. So mineralization does not seem to be a problem. The conversion from ammonium to nitrate occurs rapidly enough, even though our soils are cold, to meet plant requirements.

It appears that ammonium nitrate does have a significant advantage as a forage fertilizer. In fact, in many cases, urea as a forage fertilizer will only be average 70% as effective as ammonium nitrate. So that means that you are sacrificing a lot of urea. Despite that fact, many farmers continue using urea, and I think that part of it has had to do with the dealer system and the manufacturing system switching to urea and anhydrous ammonia. It appears that, despite the advantages that ammonium nitrate has agronomically, it has not been able to retain its market share. Part of this has been raised at market, manufacturing and transportation costs and also the environmental problems associated with producing ammonium nitrate.

3/ The last question was related to top-dressing ammonium nitrate. Again, we have compared top-dressed ammonium nitrate, urea and liquid fertilizers as well and, if conditions are not favourable - and by that I mean dry weather and very warm winds - we can get severe losses of that fertilizer.

However, if immediately after application we get rainfall, top-dressed fertilizer can, at times, work very effectively. Unfortunately, under our conditions, it is very difficult to predict whether we are going to get rainfall or not. Our weather forecasts have a lot to be desired. If that could be improved, then I think that top-dressing might come into vogue, with ammonium nitrate, although it is declining as a source. There are conditions under which, if moisture conditions improve after seeding, we will recommend that farmers top-dress the nitrogen, but there is an inherent risk involved in that kind of a technique.

DISCUSSION (Rapporteur Mr. J.M. BIRKEBAEK, Superfos Fertilizers, Denmark)

Q - Mr. K. GOVINDARAJAN (Southern Petrochemical Industries, India)

1/ Have you experienced any caking of fertilizers with a granule strength of 50 N₂ ? What is the minimum allowable granule strength to avoid caking in case of DAP ?

2/ Kindly provide details of granule size analyser for the on-line analysis of granule size distribution.

A - 1/ Caking can be observed even with fertilizers with crushing strength higher than 50 N as other parameters, for example moisture, can have influence on caking tendency. It is our experience though that crushing strength must be higher than 50 N to ensure free flowing properties.

Regarding DAP, the crushing strength must be higher than 25 N. Otherwise problems will arise during handling, but we have no particular experience in production of DAP.

2/ The samples are taken from the recycle lines and we take continuous pictures with TV cameras. By analyzing the pictures, we can calculate the size distribution and the shape coefficient and even the history of the granulation.

Q - Mr. G. KONGSHAUG (Norsk Hydro, Norway),

As a daily routine, you recommend 4 physical test samples per day. Is this frequent sampling routine caused by process variations, and why do you include the caking test in this routine ?

A - To ensure the quality and avoid variations in the product, we have to make a lot of tests, among other reasons because we have very frequent changes of grades. We have sufficient capacity in our laboratories to make this large amount of tests.

Q - Mr. D. BELLIS (SICNG, Greece).

1/ Is Kemira Oy using another method than the UV-lamp for control of the coating during the production, and if so, which method ?

2/ Which material is Kemira Oy using for control of the coating ?

A - 1/ We only use the UV-lamp method for control of the coating in the production.

2/ Anticaking materials used at Kemira are normal commercial products (with or without amine) and talc.

Q - Mr. RAHOUI (SAEPA, Tunisia).

One of the factors which increase the caking tendency is humidity. How do you estimate the impact of respectively free and bound water on the caking tendency ?

A - First, we do not know what is free water and what is bound water in the fertilizer, because we often find it impossible to determine it.

It is well known that impurities do affect the caking tendency, but who knows how the impurities bind water. As an example, I can tell that we have found grades containing 2% of water and being free flowing, whereas in other cases the same grades containing only 0.6% of water (determined by the same method) have been caked.

I think it is a difficult question to everyone in the fertilizer production how to choose the right water content when varying the raw materials.

Q - Mr. ORFANIDIS (Duetag, France).

Can you please identify the fertilizer grades shown on Fig.4 of your presentation (caking tendency related to moisture).

A - Number 1 - 5 are 16-16-16
Number 6 - 10 are 20-10-10

In all cases water soluble P2O5 was 70-75%.

Q - Mr. Roy HUTCHINS (Texasgulf Inc., USA).

You showed 10 samples of NPK in comparing caking tendency with moisture content, with markedly different caking tendencies. How do you explain the difference in the caking tendencies ?

A - Even though the same grades were set to absorb moisture under the same conditions, we see a marked difference in absorption tendency. One reason for that is difference in porosity. For example, we often find a higher porosity in grades produced in a pugmill than in the same grades produced in a spherodizer.

Q - Mr. A. BENMANSOUR (SAEPA, Tunisia).

Regarding sampling for control of the physical or chemical quality of a fertilizer, please indicate the following:

- automatic or manual sampling
- frequency
- sampling methods.

How has the question of sampling been solved ? Which influence has the sampling on the results of the control ?

A - We have automatic sampling systems in production lines and in bagging stations. The samples are taken every 30 min. and collected, which means that we do not rely on random samples.

Comparison between these collected samples and random samples shows only small variance.

According to the Finnish fertilizer law every bag must have a chemical analysis within certain limits from the declaration of the fertilizer.

Q - Mr. A. HAMDJ (ICM-SAEPA, Tunisia)

Can the secondary coating of a product take place at ambient temperature ? or is it necessary to recondition the product ?

A - We normally do not deliver products which have shown caking tendency. Secondary coating is, however, a good idea, and it should be applied at ambient temperature as heating and cooling again is an economical obstruction.

Q - Mr.P. ORFANIDIS (Duetag, France).

In relation to my previous question , can you please give some additional information about the processes in producing 16-16-16 with such dramatic caking tendency (process, conditions, raw materials, other physical characteristics).

A - The grade 16-16-16 is quite "full". The physical quality of this grade depends much on the phosphoric acid, i.e. with very pure acid the caking tendency is high.

With different potashes the quality varies a lot.

Normally caking tendency, dust and crushing strength go together. The very fast indicator for caking tendency is the drop in crushing strength.

Questions put in writing:

Q - Mr.N. GAURON (Norsk Hydro Azote, France).

My question refers to Fig. 7-9 in your paper. It is here shown that the curing of NPK fertilizer should have a positive impact on the physical properties and in particular on the caking tendency.

Have you registered the same positive impact on dusting properties or dust formation?

A - The dusting properties go often together with the caking tendency. Sometimes there is developed some dust during the curing time, but after the final screening, it is very low. When stored in a dry place, the dust formation is about nothing.

Q - Mr. R. HUTCHINS (Texasgulf Inc., USA).

Were the tests relating caking tendency to moisture content with 10 samples of two grades of NPKs run under constant humidity conditions ? What were the test conditions ? Granted that differences in physical properties could affect caking between samples of the same grade. Were there chemical differences as well which could have contributed to the differences within the grades ?

The comparison of H₂O content by various methods did not distinguish between "bound" and "free" water. Would not some of the procedures measure both and some only "free" water and some part of the "bound" and all of the "free" water ?

A - The samples were originally from the the delivery (0 level). Then, in the research, the absorbed moisture in constant conditions, i.e. + 25° C and 70% relative humidity. Between the samples the main chemical differences were small, the differences within the grades were more in the physical properties and the granulation methods.

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From H₂O analysis, it is really difficult to say what is "free" and what is "bound" water. We prefer the extraction method to give free water results, but anyway the best method to "get back" the added water has been the oven method.

Water is bound in and on the particles by many different ways and I do not see any really reliable method to give absolutely right values.

Q - Dr. R. NITZSCHMANN (BASF, Federal Republic of Germany).

What methods do you use to get a representative sample for automatic size-distribution measurement or automatic analysis ?

How large are these samples ?

A - The sampler is quite normal equipment which takes samples from the falling stream by cutting the stream (from conveyor belt down to another). The size of the sample for the particle size analyzer is about 1.1 kg.

TA/88/3 Effect of raw materials, process operation and conditioners on physical characteristics, chemical properties and behaviour of NPK fertilizers by A. Barbera and R. Monaldi, Agrimont, Italy.

DISCUSSION (Rapporteur J.M. BIRKEBAEK, Superfos Fertilizers, Denmark).

Q - Mr. J.D. CRERAR (Hydro Fertilizers Ltd., UK)

Please give information about the granulation pilot plant.

a/ What size/capacity ?

b/ Continuous or discontinuous operation ?

c/ Costs and manpower needed.

d/ How are heat losses compensated for in calculating the heat balance ?

A - a/ When the plant runs, the capacity is 200 kg/day (i.e. approx. 13 kg/hour).

b/ The pilot plant is running continuously 16 hours per day.

c/ The cost of the pilot plant was about 500 mio Lire. Manpower in the plant is 3 persons/shift.

d/ The plant is very well insulated. We have measured the heat loss and we compensate all data obtained by this figure.

We have found excellent correspondence to data obtained in the full scale plant.

(Q.d was answered by Mr. G. BRUSASCO).

Q - Mr. H. HERO (Kemira Oy, Finland).

1/ How do you measure the real viscosity in situ (in reactor ?)

2/ Have you a method to measure the crystal size in the (oversaturated) slurry ?

3/ How do you see the relationship between crushing strength of granules and caking tendency ?

4. Do you see any dilemma between capacity and physical quality, especially concerning slurry viscosities ?

A - 1/ The measurement of the slurry viscosity is of special importance in the spouted-bed granulation process.

The apparatus we have installed is a rotary type viscosimeter, i.e. a rotor situated in a coaxial cylinder. We measure the "strength" (i.e. torque) to maintain a constant speed of the rotor.

2/ We do measure the crystal size in the slurry. It can be measured by optical microscopy, electronic microscopy, Coulter counter, etc.

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In particular, we measure the nucleation rate and the growth rate of the gypsum crystals coming from the wet-process phosphoric acid. We do this by screen analysis and optical microscopy.

3/ Caking is reduced by producing large granules whereby the number of contact points between granules is reduced.

Mechanical weakness of granules usually promotes excessive caking as these granules tend to deform in the storage and form relatively large contact areas. In this case, Thompson mechanisms and capillary adhesion has a most important role in fertilizer caking. Also fracturing granules can form fines that promote caking.

4/ Yes, since it is difficult to have high plant capacities and good quality of the fertilizer.

To reduce problems, lots of experiments must be done in pilot and industrial plants to control all parameters in the right way.

Q - Mr. G. KONGSHAUG (Norsk Hydro, Norway).

Your coating system contains a fluorescent substance giving the possibility of measuring the coating efficiency.

Can you tell us more about the fluorescent substance - the chemical composition and the amount ?

A - A fluorescent substance can be added, but, if the coating substance contains aromatic compounds, then generally there is enough fluorescence.

Q - Mr. B. CHRISTENSEN (Superfos Fertilizer, Denmark).

1/ By what equipment or method are the viscosity and plasticity measured ?

2/ Can you explain the reason for decreasing the cigar-burning effect (S.S.D.) by adding DAP to NPK 12-9-27 ?

A - 1/ We measure the viscosity in a rotary viscosimeter with continuous flow of slurry. What we measure is the strength necessary to rotate the rotor at a constant speed in the drum.

2/ Addition of DAP reduces the cigar-burning effect because it absorbs heat. DAP can also be used in forest fire fighting.

Q -Mr. ORPHANIDIS (Duetag, France).

1/ What is the explanation for the high insoluble P2O5 increase with time for N/P mole ratio between 0.6 and 1 as shown in Fig. 3 ?

2/ What happens with solubility retrogradation beyond 6 hours (24,48,...) ?

3/ Can you please give more details about the Argirec applications shown in Fig. 9 (temperature of granules, temperature of Argirec, cooling of granules after spraying, size/RPM of coating drum).

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A - 1/ In this pH-range are precipitated a lot of different insoluble phosphates, for ex/ Al, Mg, Fe and others.

2/ In the equilibrium state a lot of insoluble phosphates are present. The equilibrium is reached in days not in hours, so the solubility loss is higher in equilibrium than shown after 6 hours.

3/ The data presented in Fig. 9 are based on laboratory test.

We heat 10 kg of fertilizer in a rotary drum for 30 min., and have the possibility of varying many different parameters as shown.

The temperature during treatment in the plant is 70-80° C, and the product is cooled to below 40° C.

We use at present "Argirec" powder, but are going to change to liquid and only liquid coating materials.

Q - Mr. R. HUTCHINS (Texasgulf Inc, USA).

What is the anticaking agent "Argirec", and how would one go about getting samples for evaluation ?

A - The anticaking agent "Argirec" is an inert powder, clay type. Samples for evaluation can be got from:

Blancs Minéraux de Paris, 40 rue de Vignobles, 78400 Chatou, France.

TA/88/4 The use of N-P solid raw materials in the production of compound NPK fertilizers by N. Louizos, Hellenic Chemical Products & Fertilizers Co., Greece.

DISCUSSION (Rapporteur P.H. Moscham, Esso Chemical, Canada)

Q - Mr. T. KOIRUMAKI (Kemira Oy, Finland).

Why are compactors not available for production rates higher than 400 tpd, and have you made any development to improve the shape of the product, other than the polishing drum ?

A. Well, as far as the size of the plant is concerned, we could not find any compactor above this size on the market. I do not know why. Perhaps this is for historical reasons, but this is the biggest size that we could get, at least for fertilizer use. For the improvement of the shape of the product, we do have the polishing drum, as you mentioned, and we know that there is already developed technology for producing spherical granules, but we have not used this technology so far.

Q - Mr. K. GOVINDARAJAN (Southern Petrochemical Industries Corp., India).

Can you indicate whether the concept of GPF (granulation predictability factor) is applicable to DAP production in a pipe reactor ? If so, what is your experience with DAP production ?

A - Unfortunately, we do not produce DAP, so I do not have any experience of that or the concept of GPF in this case. But we can calculate this and see what results we would get.

Q - Mr. J.D. CRERAR (Norsk Hydro Fertilizers, UK).

Can you explain why DAP is superior to MAP for compacted fertilizers, what size range of feed is used and have you used Miniphos ?

2/ Also, have you any comments on the merit of powder MAP compared with DAP for conventional granulation ?

A - 1/ The first question concerning the use of MAP compared with DAP for compacted fertilizer is related to the second question about the size range of the feed we use. The DAP we use is granular DAP, whilst the MAP is not granular, so I suppose this is the reason why we get better product. We have used powdered MAP, but not Miniphos.

2/ On your second question, regarding the use of the same materials in conventional granulation, we have used these materials, but we did not see any difference apart from the difference in cost.

Q. Mr. F. KANGASTALO (Kemira Oy, Finland).

Could you use the granulation predictability factor in NPK process control, and what if the water content of the raw materials is varying over short periods ?

A - We are not using the GPF for process control. As explained previously, we are mainly using the concept of the GPF when we are going to switch from one formula to another, or from one raw material to another, but this is made only once, and after this we do not monitor the GPF continuously. Of course, this is something which could be done, but we

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have found that it is not necessary. We try to keep more or less stable conditions during production. Now, if the water content of the raw materials varies in short periods, then it is likely to vary, say minus or more 1%. The GPF is not sensitive to this level of variation.

Q - Mr. F. CARVALHO (SAPEC, Portugal).

You refer to some economic aspects in the introduction to your paper. According to your experience, do you have any idea about the comparative production costs of a conventional granulation plant and a compaction plant?

A - Actually, I think the answer is in the last paragraph of my paper, where I stated that, regarding the economic criteria, it should be stressed that costs can vary widely from one place to another, as they do not only involve the costs of the raw materials and intermediates, but also production costs and other local factors. So the answer refers to our case, and it is very difficult to translate it to other cases. Anyway, the production cost of a compaction plant, according to our experience, is less than the production cost of a conventional granulation plant. I would indicate a difference of the order of 5-10 dollar/ton. This includes the raw material costs.

Q - Mr. G. KONGSHAUG (Norsk Hydro, Norway).

As far as I understand, the granulation predictability factor (GPF) is a number indicating the energy balance for a given temperature and recycle ratio. In other words, a point on the granulation curve. Does this mean that you try to operate the plant at constant capacity, granulation temperature and recycle ratio, independent of raw materials and product grades?

A - Again, I think the answer is similar to the previous question about the variation in the moisture, and I think the GPF is not very sensitive to the changes that you refer to here. I would say that this should be used only as a general guide when we have large changes in the production mode, but we do not use it for process control, or in the cases mentioned in your question.

Q - Mr. P. ORPHANIDES (Duetag, France).

In Table 4, you show the abrasion resistance of the product 11-15-15, which differs considerably. What is the explanation for these large differences in abrasion resistance?

A - This is an extreme case, which I included in the table to show a very big variation. We have two different cases in the table, one is a normal case for 11-15-15, and the other is an extreme case to show that there is variation according to the screen size of the granules.

Q - Dr. S.K. MUKHERJEE (KRIBHCO, India).

1/ What has been your experience of onstream time of the compacting units?

2/ What are the constituents of N-P-K in your compacted product?

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3/ Have you used urea and ammonium phosphate for the compacted granulation process, either for commercial or even for experimental runs ?

4/ What has been the experience of the caking properties of the compacted fertilizers ?

A - 1/ Regarding the operating time of the compacting plant, the plant has been working since last year, and I cannot say that we have any particular problems compared to the conventional plants that we operate. We have more or less the same downtime for the compacting plant as for a conventional plant.

2/ From an agronomic point of view, we have checked that the results that we get, using the compacted fertilizers, are the same as the results from conventional fertilizer. Also, the analysis of the granules shows that, more or less, you have the same constituents in either case. Of course, this depends on the method of mixing of the solid products and part of the equipment we have in the compaction plant is actually used to effect proper mixing of the raw materials. The mix that is fed to the compactor is properly mixed, so there is no possibility of segregation as we have with bulk blends.

3/ Regarding the use of urea and ammonium sulphate, we do use these products, and so far have produced fertilizer containing up to 15% urea, although I do not foresee difficulties in going further. The same applies to ammonium phosphates.

4/ The caking properties of the compacted fertilizers are the same, although this depends on the granule size. We try to have a very specific granule size product from the compaction plant. The compacted granules are strictly between 3-4 mm size, so that we do not have the small granules that would help caking. If the anticaking treatment is the same as with conventional granulation plants, there is no problem with caking of compacted fertilizer.

Q - Mr. R. HUTCHINS (Texasgulf Inc., USA).

In estimating the GPF, would you use the total water content in your feed materials, or just the free water content which would not include the bound water in, say, the phosphoric acid molecule or in the gypsum molecule ?

A - We use the free water and do not include the bound water.

Q - Dr. S.K. MUKHERJEE (KRIBHCO, India).

In the compacted process, did you have any experience of using nitrophosphates (from nitric acid decomposition of phosphate rock) with other constituents in making compacted fertilizers ?

A - No we do not have such experience.

Q - Mr. P. ORPHANIDES (Duetag, France).

You mentioned that, in the comparison of a spherical granule produced

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from a conventional granulation method, and a compacted fertilizer, that there was no difference in caking tendency. Could you give any idea of the cost of the anticaking agent that is needed to obtain the same result with a compacted fertilizer as a spherical granule from a conventional plant ?

A - It is true that the anticaking treatment for a compacted fertilizer costs a little more. We have to use 10-20% more anticaking agent, due to the higher porosity of the compacted product.

Q - Mr. F. ACHORN (TVA, USA).

Did you make an economic comparison between bulk blending and compaction, since there are ways to prevent segregation ?

A - We did not consider bulk blending because, from the agronomic point of view, bulk blending is not accepted in the Greek market.

TA/88/5 Recent developments in the pan granulation process by P. Stokka, Norsk Hydro, Norway.

DISCUSSION (Rapporteur P.H. Moscham, Essochemical, Canada)

Q - Mr. A. HORKKO (Kemira Oy, Finland).

What are the NPK grades you have produced with the pan granulator process, and what can you say about the quality of the pan granulated NPK's compares to the spherodizer or drum granulated product ?

A - We have only pan granulated nitrophosphate based NPK, and besides the pure NP grades we have made grades up to 1-1-2 and down to 6% potassium chloride, which is our lower limit on the potassium side. In the nitrophosphate process the limit for the N/P₂O₅ ratio is 1-1. So we have produced NPKs with potassium from 6-25% (K₂O). We have not compared our product with drum or spherodizer produced material, but the quality is equal to that produced in our pugmill granulator at our plant in Northern Norway. Especially the crushing strength is very high and the spreadability is good; it is low in dust and it is not inferior to what is normally on the market.

Q - Mr. L.K. RASMUSSEN (Superfos Fertilizer, Denmark).

1/ What is the turndown ratio of a pan granulation process for AN and CAN ?

2/ For AN without any kind of additives, could you please give us typical values of the following parameters: untapped bulk density, hardness and porosity for the finished product ?

3/ What are the main drawbacks of the pan granulation process compared with the fluidized bed process for AN and CAN ?

A - 1/ We have a 50% turndown ratio, that is we can operate from 50 ton/hr to 25 ton/hr.

2/ For NPK the typical untapped bulk density is 1 kg/l. The hardness (defined between 2.8 - 3.1 mm) is typically 5-7 kg. We have not measured the porosity, but these are very dense particles. For AN, the typical untapped bulk density is also 1 kg/l and the crushing strength 3-5 kg. Again we do not measure porosity.

3/ From the fluidized bed we get a rounder product. I cannot elaborate further on this question.

Q - Mr. P. ORPHANIDES (Duetag, France).

1/ Is the methodology applied to explain and calculate the granulation phenomena also applicable for other melt granulation processes like drum granulation ?

2/ Have you investigated using a pan granulator with a pipe reactor ?

3/ Can you comment on the use of pan granulation for the fattening of prilled AN/urea in comparison with other fattening processes ?

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4/ For the production of 26% AN, the amount of powdered CaCO₃ is beyond the limits imposed by the mechanism of granule growth by onion type layering. Is the limit for CAN at 28% N for good onion type layering with the pan granulator ?

A - 1/ We have not used this methodology for the drum, but drum and pan granulation is very much the same, and also the results from the Fison test indicate that this can be also used for the drum. I think that the amount of liquid phase necessary to have granulation will be very nearly the same. We have applied this method to pugmill granulation and we have found that 12-15% liquid phase is necessary for our process. In general, when the energy impact increases, the necessary amount of liquid phase decreases.

2/ We have no experience with a pipe reactor.

3/ We have not tried this as a fattening process as such, but we have often used prilled material as start-up material, and this is an excellent starting material. So I think it has possibilities as a fattening process. The only problem will be that you have to satisfy the energy balance and you will need quite a lot of melt.

4/ The 26% CAN is a problem when you have a very low amount of water in the melt. When you increase the amount of water, it is easier to get more dry material into the granules during the granulation. We have not seen any limits to how much dolomite can be used. There is, of course, a practical limit, but we have not elaborated on that, because we are able to obtain the normal quality of material.

Q - Dr. S.K. MUKHERJEE (KRIBHCO, India).

1/ Has there been any commercial experience of pan granulation of 26% N product and, if so, what has been the recycle rate and the scale of operation?

2/ Have you been able to produce pan granulated product with phosphoric acid, ammonia and nitric acid, and could you get a product analysis of 25-25-0 and, if so, what is the character of the product ?

A - 1/ We have not produced 26%, but there is a plant, PFI, in Greece, which has now been operating since 1983. Someone from PFI would be the best to give you the details of the operation of this plant. As far as we know, the plant is operating. There is a problem with the recycle ratio as you mentioned. If you have a cold limestone feed, you have a very low recycle ratio and problems to close the process. It is important to have a good heating system for the lime. With that, I believe that we could operate satisfactorily.

2/ We have no experience with phosphoric acid. As I mentioned at the beginning, all our work on NP/NPK has been done with a nitrophosphate basis.

TA/88/6 High quality granular ammonium sulphate production by M. Fischbein, Esso Chemical, Alberta, Canada and A.M. Brown, Incitec Ltd., Brisbane, Australia.

DISCUSSION (Rapporteur Mr. P. STOKKA, Norsk Hydro, Norway)

Q - Mr. H. ALLYOT, Technip, France

1/ What is the N to S molar ratio of the slurry out of the pipe reactor ?

A - Unfortunately, because we are patenting the process and patents are pending, there are lots of questions that I will not be able to answer, and that happens to be one of them.

Q - 2/ Will you give more information on your gas cleaning system ? For example, what type of scrubbers you are using, the number, are there any tail gas scrubbers with water wash ?

A - Yes, we have two scrubber systems. They are the same scrubber systems that we were using previously on our MAP plant. There is a wet venturi scrubber system on the dryer. And on the granulator it is also a wet venturi system, and there is a tail gas scrubber. But the tail gas scrubber really is not required for ammonium sulphate. It does not really do anything.

Q - 3/ This question is related to the characteristics of the scrubbing liquor. Can you tell us the N/S ratio, density, the pH and especially in the case where you are using aqueous ammonia or aqueous ammonium sulphate as raw materials ?

A - Again I can't give you too many details about the scrubber liquor. I can say that we control the pH by adding sulphuric acid. That is the pH control. We do not add sulphate liquor or anything like that to it, just 93% or 98% sulphuric acid and the process reactants.

Q - 4/ In your paper, you said that sometimes you use some solution of ammonium sulphates from other plants.

A - We have not done that ourselves. Incitec in Australia has tried feeding ammonium sulphate solutions and I think they were close to saturation, roughly 40% by weight ammonium sulphate solutions, that they have as feed to the pipe reactor. As well they have tried dilute acids and they have also tried the aqueous ammonia. The concentration of the aqueous ammonia was very low, a few percent, but again I do not know the number off hand. I can provide you with that information.

Q - 5/ This question is related to the recovering of ammonia. What fraction of ammonia do you recover in the scrubbing system ? I mean the ratio between the amount of ammonia which is recovered in the scrubber and the total amount of ammonia fed to the plant.

A - It is very small. We have not done any measurements to determine exactly what it is. Our ammonia slip is negligible to the atmosphere. Our feeling is that the ammonia slip from the pipe reactor is very small, based on sulphuric acid that we feed to the scrubber system.

Q - 6/ But you also feed some ammonia directly into the drum granulator ?

A - Yes, and there is a very little slippage from that. The largest part

.../.../...

of it is absorbed in the granulator. It is only a few percentage points that actually slip into the scrubber system.

Q - Mr. P. ORPHANIDES, Duetag, France

1/ Can you please give the full analysis of the product ? In terms of ammonium sulphate, ammonium bi-sulphate, moisture, pH and other if any components.

A - I could tell you that the nitrogen analysis varies between 20 and 21. Sulphate analysis is typically 24%. The moisture content is about 0.1%. The pH also can vary anywhere from 3 to 4.5.

Q - 2/ To make the balance, there is something else in the product ?

A - We add a granulation aid to the process, and that is part of Incitec proprietary technology and that is part of our patent, so I cannot tell you what it is.

Q - 3/ In the flowsheet, it is not indicated that there is a granulating agent coming in.

A - There should be, it is mentioned in the paper.

Q - 4/ What is the pipe reactor material you use and what is the lifetime of such pipe reactors ?

A - Again I cannot comment on the material we use, but we improved dramatically on the lifetime that Incitec used to get. We can run for a couple of months without any failure. When we started out we were looking at monthly failures.

Q - 5/What is the granulation bed temperature you are working with ?

A - It runs between 200 and 230 ° F

Q - Mr. B. CHRISTENSEN, Superfos Fertilizer, Denmark

1/ Can you tell to what extent crystalline ammonium sulphate can be absorbed in the process.

A - We have not actually tried to do that again it has been tried in Australia by Incitec. I would think 20 or 30% crystalline or more. There are technologies developed by TVA in which they use up to 80% crystalline and only 20% sulphuric acid and ammonia. So I am very conservative when I say 20 or 30%. I am sure it is a lot more, but we have not personally tried it.

Q - 2/ Can you tell what is your Size Guide Number compared to Sherritt Gordon's ammonium sulphate ? They stated that it was the grade 19:3:0 with something like 20% sulphur.

A - According to Sherritt Gordon, their product contains about 3% ammonium phosphate and has a size guide number of about 250, which is approximately the same size as our product.

Q - Mr. H.J. HERO, Kemira Oy, Finland

1/ How do you control or adjust the crystal size of ammonium sulphate

before granulation ?

A - There are no crystals that are visible to the naked eye formed in the process. There is some crystallization in the scrubber liquid and that is controlled by controlling the pH and density of the liquid. But the product itself does not have any visible crystals at all.

Q - 2/ Can you say what is the liquid-solid ratio for the granulation ?

A - After the pipe reactor, I do not know what the liquid-solid ratio is in the slurry. We put in stoichiometric amounts of sulphuric acid and ammonia that we need, and roughly 0.7 ton of water for every ton of product. The water flushes off so the moisture content would be very low in the slurry as it exits the pipe reactor.

Q - 2/ Is any additive used for granulation, if so what type ? Could you tell anything about the type, if it is a surfactant or something else ?

A - I cannot really discuss the type. There is a whole family of materials that can be used and be fed into the liquid system or into the solid system. It is commonly and readily available, but I cannot really discuss the chemistry of it.

Q - 3/ You mentioned that your material is very free flowing, what is your coating agent ?

A - We do not use a coating agent at all. We had occasionally to lightly oil it because we oil our phosphate products occasionally to suppress dust. But with ammonium sulphate, as far as I know, we do not typically oil it, so there is typically no coating agent at all. If we use one it is a fraction of a percent of oil.

Q - Mr. A. BARBERA, Agrimont, Italy

1/ Have you ever granulated ammonium sulphate derived from organic production ?

A - No we have never done that. We only use fresh sulphuric acid that we manufacture and ammonia that we manufacture.

Q - 2/ Can you describe problems, if any, encountered to optimize ammonium sulphate high quality production ?

A - We encountered a lot of problems. The optimization centered quite a bit around the solids handling system. If the process is not run exactly at the right optimum operating point, you end up with excessive amounts of dust being formed and that was probably one of our biggest problems when we first started the plant up. There was a tremendous amount of dust being formed, plugging up our cyclones, and even getting into the air in the building where we had leaks and things were not sealed up well. So it is primarily a dusting problem and maintaining the product size. But we do not have a lot of corrosion problems, we do not have those types of problems. The service factor right now is very high. The plant is extremely easy to start up and shut down. And once we start up and run it, it stays running. We do not have a lot of maintenance problems. The service factor is probably as good as or

.../.../...

better than it is for making ammonium phosphate in that plant.

Q - Mr. D.S. LOVELACE, Allied-Signal Inc., USA

1/ Do you have a cooler ?

A - Yes we do.

Q- 2/ Is that your basic reason for not having caking ?

A - No

Q - 3/Is it the low moisture content then ?

A - Until our patents are approved I can only say at this point that it is a combination of everything really. It is not one specific item. You can readily cake with a cooler or without one. Both Incitec and Esso have had caking problems before understanding how to run properly. We have a cooler, they do not, so you can cake with or without one. Certainly, if your moisture content goes high, you will cake, that is not a secret, that is quite obvious.

Q - 4/ So your granulated product functions differently in moisture heat relationship to caking than does crystal ammonium sulphate ?

A - We have not really done any comparative testing. We have basically done caking test under specific conditions, but I have not compared them specifically to crystalline. I would say, qualitatively the answer is yes, it does perform better.

Q - 5/ What test method did you use to determine crushing strength ?

A - We use Pfizer hardness method. I think it is 50 granules, -7, +8 size, and we crush them and take the average crushing pressure, using a Pfizer hardness tester.

Q - 6/ Do you run SGN on your crystalline by-product ? And, if so, what is it ?

A - We do not manufacture crystalline by-product. We used to purchase it and resell it. We purchased actually yours at a time.

Q - Mr. J. PRIAT, Grande Paroisse, France

1/ What is the concentration of the sulphuric acid you introduce in your pipe reactor ?

A - We use both 93 and 98%.

Q - 2/ Another question about the concentration or the density of the liquid going from the scrubbers and that you recycle to the pipe reactor.

A - I cannot comment on that point.

Q - 3/ What is the humidity of the product at the exit of the granulator ?

A - Again, I cannot comment on that. It is very low. The product has 0.1% moisture, and the humidity at the granulator is part of our technology

so I cannot reveal that.

Q - 3/ Do you use gaseous or liquid ammonia ?

A - Both can be used. It does not make a difference.

Q - 5/ What is the temperature in the pipe reactor ?

A - As an order of magnitude, about 300 ° F.

Q - 6/ What is the consumption of fuel or gas per ton of product ?

A - I do not know the answer to that.

TA/88/7 Montedison's IDR (isobaric double recycle) process - Process improvements and applications in the urea plant retrofitting/revamping by G. Brusasco and L. Mariani, Agrimont, Italy

DISCUSSION (Rapporteur K. Farmery, ICI Fertilizers, UK)

Q - Mr. P. ORPHANIDES (Duetag, France)

For an urea plant operating on the basis of a conventional CO₂ stripping process, do you think there are incentives to revamp (in order to improve capacity and/or energy consumption) by applying the IDR process ?

What could the expected results be ?

A - The lower limit for revamp is when the steam consumption is around 1.2 te steam/te urea. As most CO₂ strippers consume around 1000 kg steam/te urea, the process is not likely to be beneficial for steam saving.

Thus, this approach is best thought of for capacity increases, not energy improvement.

For ammonia stripping processes, we have looked at revamping for urea capacity increase of up to 50% with moderate investment. In this case, most of the HP equipment can be re-used (eg the reactor, the strippers and the condensers), and the large size of the medium and low pressure purification sections can be profitably used also to give significantly higher output.

Q - Dr. S.K MUKHERJEE (KRIBHCO, India).

1/ How do you reduce energy consumption in the IDR process ? What are the key steps ?

2/ What is the ammonia conversion per pass in the IDR process ?

3/ What has been your experience of "on-stream time" for the IDR process ?

4/ What are the effluent specifications in the IDR process in terms of both free ammonia and total N in the effluent ?

A - 1/ It is easy to see how the steam consumption is reduced.

a/ Because of the very high CO₂ conversion efficiency in the reactor, there is less unconverted product to be converted by steam later downstream of the reactor.

b/ Steam produced in the medium pressure purification stages is utilised by condensation to heat the urea solution sent to the vacuum section. This means that all the surplus heat from the first decomposer and the medium pressure decomposer is used in two stages.

2/ Normally, the ammonia conversion efficiency is not so important. I do not remember the numbers but, roughly, the heat consumed is 430 kilocal/kg CO₂ (as carbamate) against 150-170 kilocal to evaporate each kg of free ammonia. Thus, we have established a limit, roughly

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of 4 moles of ammonia for 1 mole of CO₂ beyond which it is not beneficial to increase the ratio between ammonia and CO₂.

3/ The only plant using this technology is the one near Genoa in Italy, which has been running since 1981. There, the on-stream factor is similar to the best others I know, and is around 8000 hours per year. We have found no corrosion or other unusual problems preventing achievement of such on-line time.

4/ The liquids from this plant are not different from those from any other process (e.g. Snam, Stamicarbon). The most frequently used procedures are ammonia stripping and urea hydrolysing. Thus, the liquid effluent from the vacuum section is sent to a rectification column to recover ammonia and then sent to a urea hydrolyser. This method can give 2 ppm NH₃ and 2 ppm urea or 30 ppm NH₃/30 ppm urea depending on operating conditions or client requirements. This is all well-known technology. We have installed 3 such effluent systems, one of which is in India and is well known to Dr. Mukherjee.

TA/88/9 A new process for the production of concentrated ammonium nitrate solutions by P. Chinal, G. Cousserans, J.B. Peudpiece and J.F. Priat, Société Chimique de la Grande Paroisse, France

DISCUSSION (Rapporteur Mr. A.F. Porneuf, Société Chimique de la Grande Paroisse, France)

Q - Mr. A. HAMDJ (ICM/SAEPA, Tunisia).

1/ Can you adapt a pipe reactor to an existing plant without too many alterations in order to lower the technical minimum and increase production ?

2/ With a 58% nitric acid solution, can you obtain a 95-96% ammonium nitrate solution ?

3/ What is the order of magnitude of investments for a 500 t/d unit ?

4/ What is the reason for the investment being 50% lower than for a conventional unit ?

A - 1/ The pipe reactor can indeed be adapted to an existing plant and we have projects under investigation to implement that possibility. The existing equipment on which the pipe reactor will be grafted must have a sufficient size, but this is normally the case. One can generally use the neutralizer of an old plant as a separator by grafting a pipe reactor on it.

2/ Can we obtain a 95-96% solution with 58% nitric acid ? No, I think that today we can obtain a 93-94% solution according to the temperature of the acid. It is the limit because, if we try to heat up the nitric acid too much, corrosion problems appear. Then with the technology and the materials available today, we do not think we can go higher. But, in a second stage, the one we are now investigating, we may succeed in gaining 1 or 2% concentration without heating the nitric acid any further.

3/ I do not remember the figures for the investment in a 500 t/d plant. However, the cost for a 1000 t/d plant amounts to about US \$ 2 million. But it is always risky to announce such figures since local conditions are always an important factor.

4/ Why is the investment cost 50% lower ? It is mainly due to the weight of stainless steel used. A pipe reactor weighs a few tens of kg. A conventional saturator or a neutralizer can weigh 2 tons or more. In addition, circuits are much more complicated in a conventional plant. There are many more exchangers, then much more stainless steel and engineering. This is not a figure we have estimated. When our management decided the construction of a new 1000 t/d plant at our site in Rouen, we compared the two processes; the conventional process was almost double.

Q - Mr. B.K. JAIN (FAI, India).

Considering the safety aspects, what will the capacity restriction be of the new AZF pipe reactor ? Kindly indicate the construction materials used for the pipe reactor and the expected life under normal conditions.

.../.../...

A - The material used for the whole plant, except for the nitric acid heater - if it exists, which is not always the case - is 304 L type stainless steel. The lifetime was mentioned to you in relation to our industrial experience at Mazingarbe. We had a pipe reactor which was two years in operation and was then replaced not because it was corroded, but because we wanted to produce more. I cannot tell you that it lasted for 10 years, because we do not have 10 years of experience, but two years for sure. In addition, I do not think that replacing a pipe reactor is a serious problem. It is only a piece of pipe.

Q - Mr. J.D. CRERAR (Norsk Hydro Fertilizers, U.K.).

It surprised me a little to see the title of this paper: "The new AZF process for ammonium nitrate", because it seems to me that the process has many similarities to the Stengel process to which you refer and to the Improved Stengel process which we have operated in England for about thirty years. The only difference, as far as I can see, is the fact that your reactor is horizontal compared with a packed vertical reactor.

1/ The recoveries of nitrate and ammoniacal nitrogen, which you have quoted, are unlikely to be acceptable to most industrialized countries and, therefore, the optional scrubber which you mentioned is very likely to be required. Could you give me the ammoniacal and nitrate content of the condensate from your process when that optional scrubber is included, please ?

2/ Could you tell me which of those plants that you listed in France, in Scotland and in Australia, have the scrubber fitted ?

A - Concerning your remarks about the Stengel process, I think there is more difference than you mention, since, in that process, there is an internal packing inside the reactor. In the original Stengel process, as I know it, there was a hot air steam in the separator to reach the expected concentration. But I do not believe it is worthwhile starting a debate on the Stengel process.

Concerning the ammoniacal and nitric nitrogen in the condensate, I think you have the answer in the written paper. Indeed, there is no steam scrubbing in the plants at Mazingarbe and in Scotland, since it was not necessary in order to reach the 99% concentration requested.

However, we are installing one in our plant under construction at Rouen. It is actually a steam scrubbing system we have transposed from our old atmospheric pressure process and a few are operating in our plants. There are five working in the USSR, but I do not have the reference list. It is not only something on paper, but something which actually operates and which we simply transposed from our old process because we were satisfied with it.

Q - Mr. G. JUIF (Technip, France)

What is the maximum capacity we can expect from one single pipe reactor ?

A - At present, I would say 1000 t/d. I feel we should be able to reach 1500 t/d with one single pipe reactor. If we had to build in one of our plants a 1500 t/d unit, I think that today we would take the risk

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of building it with our new process.

Q - Mr. L. RASMUSSEN (Superfos Fertilizers, Denmark).

1/ Could you please tell us the yield you have been using in the cost comparison mentioned on page 12 in your paper ?

2/ If a yield of 99 or 99.5% is required, would that affect your comparison dramatically ?

3/ What is the turndown ratio of the process ?

A - 1/ In the comparison of investment costs mentioned on page 11 of our paper, we assumed that the efficiency of each plant was the same. We compared our pipe reactor process including gas scrubbing with another process under pressure also including gas scrubbing. The conditions are the same.

2/ I do not know how to answer your second question, because it is possible to reach 99-99.5% efficiency theoretically. However, I think that, to measure the efficiency, we must measure the losses very carefully.

Q - Mr. G. KONGSHAUG (Norsk Hydro, Norway).

Can you indicate the retention time and flow speed in the pipe reactor ?

A - The retention time in the pipe reactor is less than one second. The speed depends on the flow coefficient per square cm adopted. It differs if we operate in the lower part of the possibilities of the pipe reactor or, conversely, close to the maximum, and this depends on the operational pressure. But the speed inside the pipe reactor is about 200 m/sec. It is difficult to answer that question because feedstocks, such as nitric acid, which enter in liquid form, have a low speed. Ammonia enters in the gaseous form at a relatively higher speed. Then the reaction takes place. Part of the water in the nitric acid evaporates gradually when progressing in the pipe reactor and the speed increases. Then it depends at what point the speed is actually measured and, at present, we are not able to measure it. It can only be evaluated.

Q - Mr. P. ORPHANIDES (Duetag, France).

1/ The first question concerned the material of the pipe reactor, but it was already answered. The nozzle is also in ordinary 304 L ?

A - In fact, we did two experiments. On one pipe reactor we used a higher quality and more expensive material. But, in view of the results obtained, the 304 L is the adequate material.

2/ What are the improvements to be expected in revamping an existing plant with atmospheric neutralization applying your process in respect of higher efficiency and increased concentration capacity ?

A - I cannot give you a general answer, since it depends on the type of process we have to operate with. I have in mind conventional processes working very well, but where the potential of concentration of nitrate produced is somewhat wasted, because, for reasons difficult to understand, the solution is often rediluted during production. I know

an old plant where 60% nitric acid was produced and where, in fact, we realized that this acid was used at 55%, because it was diluted with condensates. In other plants, it is not the same thing and, in that case, I think we can gain concentration capacity e.g. that normally with 58% acid 92-93%, even 94%, nitrate can be produced according to the temperature at which the nitric acid is heated.

3/ What is the concentration to be expected in the case of 60% acid, when, as indicated in your flowsheet, liquid effluents from the scrubber are introduced in the reactor ?

A - When we introduce again the steam scrubbing solution in the pipe reactor, we lose about 1% concentration.

Q - It means that with a preheated acid of 60% maximum concentration after recycling, what nitrate concentration do you reach ?

A - I do not have the balance, but about 95%.

Q - If you continue recycling ammonium nitrate produced, as you do during the starting stage, can you improve the final concentration ?

A - No. In fact we do not recycle anymore, since the plant starts immediately after we press the button.

Q - What is the concentration of the scrubbing solution ? Is there no risk of crystallization ?

A - The ammonium nitrate solution used as scrubbing solution contains 30% nitrate and there is no risk of crystallization. When the plant stops, it is not emptied. It needs no dilution when restarting.

Q - My question concerned the recycling of part of the concentrated solution, 95%, to gain a little ?

A - It is the way we started operating the process, because we did not dare, in the first place, to have nitric acid and ammonia alone in the reactor and we began to recycle a previously produced nitrate solution. As a result, there were three inlets in the pipe reactor for nitric acid, ammonia and recycled nitrate solution. We realized that with a recycling of less than five we managed to avoid the mist. But that recycling did not satisfy us and we tried to gradually reduce the recycling by changing the operating conditions in the pipe reactor and we realized we could completely do without recycling.

Q - Mr. H. HERO (Kemira Oy, Finland).

1/ Your process shows very high yields and high capacities, but can you give us some figures of your nitrous values after a pipe reactor, and in your stack gases ?

2/ What has been your experience in using phosphoric acid together with nitric acid in your pipe reactor ?

A - 1/ I shall answer your first question in writing because I do not have the data here.

.../.../...

2/ Concerning the use of phosphoric acid in our pipe reactor, we have a long and old experience since, at present, there are 56 pipe reactors operating or under construction in the world following our process. It is indeed because we have the experience of making ammonium phosphate or sulphate-phosphate in a pipe reactor that people in our company had the idea, because they needed ammonium nitrate solutions, to use a pipe reactor available in our pilot plant. We also used a mixture of phosphoric acid and nitric acid in a pipe reactor in a granulation plant.

Q - Mr. V. BIZZOTTO (NSM/Norsk Hydro, Belgium).

Page 9 of your presentation you stated that ammonium nitrate solution process surprisingly did not take advantage of the modern nitric acid plant capacity of producing 60-65% acid. May I just inform and remind you that NSM did develop its own ammonium nitrate solution process using the maximum available concentration of 62-63%.

The first industrial plant, 2,000 t/d, went into operation in 1977 at Sluiskil in the Netherlands. The second one, 3,300 t/d in 1985 at Sluiskil and the third one, 3,000 t/d in 1987 at Immingham. All three were under pressure with a clean-steam production, zero pollution, 96-97% final concentration, no corrosion.

TA/88/10 Large nitric acid plants using the Grande Paroisse process: Improvements and experience by P. Gry, Société Chimique de la Grande Paroisse, France.

DISCUSSION (Rapporteur Mr. A.F. Porneuf, Grande Paroisse, France).

Q - Mr. G. KONGSHAUG, Norsk Hydro, Norway.

The problem of tail gas colour increase with increasing plant capacity due to larger stack diameter. How do GP meet the requirements of colourless tail gas from large acid plants ?

A - The problem was raised in England and in Scotland where regulations are 1000 ppm colourless gas. Hence, we had to solve that problem first at ICI and, taking account of the capacity of 1000 t/d, from our calculations, the tail gas content was 120 ppm. In Scotland, at Scottish Agricultural Industries, with a 500 t/d capacity, tail gases contained 130 ppm, so that we complied with the existing rules and gases were colourless. As a result, the higher the capacity, the lower the content of the tail gases, since the colour is due to the NO₂ content.

Q - Mr. T. LAINTO (Kemira Oy, Finland)

1/ Would it be possible to build a single line nitric acid plant with a larger capacity than 2000 t/d ? What are the critical design factors ?

2/ Can you tell us what is the difference in thermal efficiencies between a nitric acid plant with a capacity of 500 t/d and one with a capacity of 1500 t/d ?

A - 1/ I believe it is possible to build plants of more than 2000 t/d capacity, but it is not only a problem of process. There is a problem of equipment, in particular with regard to the diameter of the burner. The burner is voluminous and it raises a transport problem.

There is also a problem of machines which we are now considering with the suppliers of equipment. It is an important point. We cannot only develop the process by itself, but we must do it in association with the suppliers.

2/ There is no difference between a 500 and a 1500 t/d capacity plant, if they are built according to the same process, the double pressure. But one could build a 500 t/d single pressure plant and a 1500 t/d double pressure plant. There, we may find differences. We now build 500 t/d plants based on single pressure, but, in some cases, we might use double pressure. It depends on the operational costs, investments, payback, etc. We recently made a survey in the US for a 600 t/d plant and found that double pressure is more economical than single pressure; each case must be considered separately.

Q - Mr. P. ORPHANIDES (Duetag, France)

1/ What is the maximum burner capacity you have so far designed for a double pressure HNO₃ plant ?

2/ What is the catalyser net effective diameter for such a burner ?

3/ What are the limiting factors to increase further the burner capacity in double pressure plants ?

.../.../...

- A - 1/ It relates to a single burner 1000 t/d plant, but the design for a 1200 t/d is being completed.
- 2/ The cloth diameter is 5.5 m.
- 3/ There are mainly construction problems.

Q - MR. S.K. MUKHERJEE (Khrisco, India)

Would you like to comment on adopting design based on extended absorption tower against relatively smaller absorption tower followed by catalytic combustion in both cases to obtain emission standard at below 200 ppm max NOx, and large capacity nitric acid plants of approximately 1000 t/d (100% basis). The comparison may be on relative investment cost and ammonia efficiency ?

- A - It depends on the existing situation; it is necessary to carry out a complete survey to see if one absorption tower is sufficient. There are several possibilities. There is not only one absorption tower. One can have one absorption tower, one catalytic combustion or one small absorption tower followed by a catalytic absorption, it depends on the cost of raw materials and on the existing installation, in particular its pressure. If that pressure is not sufficient, the absorption tower will not be recommended. The solution would be one absorption tower and one catalytic combustion or a catalytic combustion alone. On the other hand, in the US, in the 70's, we installed 7 or 8 absorption towers. There was enough pressure - 7 to 10 bars. Consequently, nitric acid was recovered and the tail gas content was reduced from 4000 ppm to 200 or 400, according to the regulations in the country. There, the absorption tower was interesting but there is no systematic answer. Each case must be studied with all the factors involved.

Q - Mr. S. ORMBERG (Norsk Hydro, Norway)

You indicated moving and revamping one HNO₃ plant in France in 1989. What is the saving in investment compared to building a new plant ?

- A - We did not have the money to build a new 1000 t/d plant and the actual budget saving is about 30-40%, since part of the equipment to be used in that plant, which will be completely changed, will be recovered. All the compressor line - a single pressure unit operating at 5 bars; for the oxidation we are going to replace the burner. There were three burners, we are going to install one. The three existing absorption towers will not be transported and will be replaced by two and, since the pressure is not sufficient, we are going to install two absorption towers followed by a catalytic combustion to fall below the French standards. The line of exchangers remains the same. Hence, only the burner and absorption tower will be replaced, saving about 30-40% investment.

TA/88/11 Cadmium in the soil-plant-human environment. A short review by O. Gunnarsson, Supra, Sweden.

DISCUSSION (Rapporteur Mr. B. Persson, Supra, Sweden).

Q - Mr. G. BRUSASCO, Agrimont, Italy

You reviewed well the problem of cadmium and its ecological impact, so we are concerned about the influence on the fertilizer business.

Can you please:

1/ indicate the limits imposed by the authorities in your country

2/ comment on the influence of the phosphate market

3/ summarize the state of development of the technologies for removing Cd from phosphates.

A - 1/ There are, as far as I know, no limits imposed by the authorities.

A - Mr. B. PERSSON, Supra, Sweden

A limit of 125 mg Cd/kg P was proposed. It was never imposed due to the low Cd-content in our fertilizers.

A - Mr. O. GUNNARSSON

On the influence on the phosphate market, I would say that the optimum dosage of P2O5 cannot be given very precisely.

If the farmer is aware of the Cd problem, there will a tendency that he chooses the lower limit in the range of optimal P2O5 dosage. This means a somewhat lower use of P2O5.

Q - Mr. L.J. CARPENTIER, IFA

Are there any losses from the soil either by leaching or by volatilization of cadmium compounds ?

A - As far as I know, there are no losses by volatilization, but there are, of course, some losses by leaching. It is measured in Sweden and it is lower than 1 g Cd/ ha/year. But I suppose that it will be higher if you apply easily soluble cadmium.

Q - Mr. R.A. HUTCHINS, Texasgulf Inc., USA

Where were the samples of vegetables referred to in your overheads taken ?

A - They are based on a Finnish survey, so it is representative of Scandinavian conditions or at least Middle and North Scandinavian conditions.

Q - Mr. R. PERANDER, Kemira Oy, Finland

Can you give a brief review about the cadmium legislation situation in different countries ?

.../.../...

A - Mr. B. PERSSON, Supra Sweden.

With reservations for new or changed propositions, we believe that the current existing or proposed legislation is as follows:

<u>Norway</u>	no legal limit proposals:	mean 100 mg/kg P over 3 year period NH preferred 150 mg/kg P over 5 year period
<u>Sweden:</u>	similar position to Norway	
<u>Denmark:</u>	proposals	Max. 200 mg/kg P from July 1990 150 mg/kg P from July 1995 110 mg/kg P from July 1998
<u>Finland:</u>	legal limit	100 mg/kg P from 1989
<u>West Germany:</u>	voluntary	90 mg/kg P205 (200 mg/kg P)
<u>Austria:</u>	statutory	120 mg/kg P205 from 1987 (275 mg/kg P)
<u>Japan:</u>	statutory	150 mg/kg P205 (343 mg/kg P)
<u>Switzerland:</u>	proposed	50 mg/kg P from 31 August 1996
<u>France:</u>	no proposal	
<u>U.K.:</u>	no proposal Wait for EEC action.	

Q - Mr. G. MARROU, World Bank, USA

1/ Can you confirm that some of the commercial phosphate rocks with the highest Cd are in the US (Idaho, Montana, Wyoming) ?

Do you - or any other person in the audience - know what is the perception of that problem over there ?

What is the position of E.P.A. Any solutions ?

2/ Do you consider that Cd in phosphate rock is a real problem or a false problem ?

A - 1/ I cannot comment on that.

2/ For me, it is not an alarming problem and today it is not a real problem. But in some soils it may be a long-term real problem.

Q - Mr. A. BARBERA, Agrimont, Italy.

1/ Can you say something about which crops absorb Cd more than others ?

2/ How and where do you in your country use compost, sludges and so

.../.../...

on, that are the major sources of Cd and other toxic metals ?

A - 1/ I think that figure 5 answers your first question. It will be included in the proceedings. Grain absorb small quantities and leafy vegetables absorb quite a lot.

2/ Because of transport costs, some sewage sludge is used close to the cities, but there are restrictions on the content of Cd. It is about 10 g Cd/ton dry matter. The sewage sludge is used on less than 10% of the total agriculture area.

Q - Mr. B.K. Jain, FAI, India

DAP produced from our source of imported rock contains 44-49 ppm of Cd. Is this Cd content in DAP likely to build up to undesirable Cd accumulation in the soil ?

A - It is not so easy to answer that question. A medical expert would consider it undesirable. I do not consider it to be a problem today.

Q - Mr. P. BECKER, Duetag, France

There is a very interesting information on the cadmium content of the kidney cortex in development since 1988. Can you give the references of this information ?

A - They will be given in the proceedings (see below) N) 1 ref Friberg et al.

Q - What are your suggestions as regards the approach to the problem of reducing cadmium in fertilizers ?

A - I am not a decision-maker today, but, as I said in my conclusion, we should try to keep balance between input and output on a natural level.

Q - Mr. G. KONGSHAUG, Norsk Hydro, Norway

Is the crop uptake dependent on the fertilizer type ?

1/ e.g. when nitrogen is given as ammonia, the pH in the rhizosphere becomes 1-2 pH-units lower than when the nitrogen is given as nitrate.

Should this difference also reflect the cadmium uptake ?

2/ In TSP about 90% of the Cd is water soluble and in NPKs like NPK 16-16-16 only 10-20% is water soluble.

Should this difference reflect the cadmium uptake ?

A - 1/ Yes, somewhat because of acidification (ref. Fertilizer Research vol 4 N° 1, 1983, p. 63-74, Dijkshoern et al).

2/ Yes, immediately, because the immediate source is the water soluble part, but, as I see it, the cadmium problem is the long-term accumulation and looking at that, I do not think that there are big differences.

.../.../...

Q - Dr. W. RITTINGER, BASF, Germany

1/ What will be done in Sweden to reduce the atmospheric deposition ?

2/ You remark that some people may reach the critical value of 200 µg Cd/g wet weight in the kidney cortex. We know from examinations in Germany in a region with Cd emissions over a long time, that no differences were found except for a few people who were very heavy smokers.

Have you knowledge from other examinations, in which it is distinguished between smokers and non-smokers ?

A - 1/ It is going on. The emissions from industries and power plants are reduced (see figure 9).

2/ I think there are references in my literature showing that (ref N° 1).

Q - Mr. EZAHR, OCP, Maroc.

Studies seem to show that Zn affects the rate of Cd uptake from soil to plant.

What is your opinion on that question ?

A - Short-term experiments (hours) have shown that Cd uptake is depressed by increased levels of Zn (Plant and Soil, N° 44, 1976, p 179-191).

TA/88/12 Nitrophosphate plants: the recycling concept to minimize pollution of air and water by L. Diehl, BASF, Western Germany.

DISCUSSION (Rapporteur Mr. P. Stokka, Norsk Hydro, Norway).

Q - Mr. R. PERANDER, Kemira Oy, Finland

Could you tell something about the fluorine balance in the process ?

A - You could say that 99% of the fluorine remains in the process and approximately only 1% of the fluorine goes in the air.

Q - Mr. J.M. BIRKEBAEK, Superfos Fertilizers, Denmark

You state in your paper that the ammonia content in the off-gases from the alkaline part of the Odda process, and from the drying process is well below the official limits. What are the official limits in Germany and Belgium.

A - Dr. R. NITZSCHMANN, BASF, Germany

We have in Germany in our off-gases no limits for ammonia. But it was proposed that the fertilizer industry reduces the ammonia outlet in the off-gases. For new plants it was first spoken about a limit of 50 mg. At the moment there are discussions about values between 100 and 300 mg.

Q - Mr. J.M. BIRKEBAEK, Superfos Fertilizers, Denmark.

Have you measured the content of ammonium nitrate aerosols coming directly from the NP neutralization stage ?

A - Dr. R. NITZSCHMANN, BASF, Western Germany.

We have made many investigations on this point. It turns out that if you choose a good pH of this washing fluid, and this pH depends on the temperature of the gases and the ammonia content of the gases, you can avoid absolutely all aerosols.

Q - Mr. J.M. BIRKEBAEK, Superfos Fertilizers, Denmark.

How large a percentage of air from the drying or the spherodizer are you able to recirculate ?

A - Dr. R. NITZSCHMANN, BASF, Western Germany.

About 30 to 50%

Q - Mr. J.M. BIRKEBAEK, Superfos Fertilizers, Denmark.

My last comment is that I am greatly impressed that you are able to run a cyclone battery so that the dust content is reduced to less than 5 ppm.

A - Dr. NITZSCHMANN, BASF, Western Germany.

Low dust content coming from cooling and coating drums in the CAN process.

.../.../...

Q - Mr. G. KONGSHAUG, Norsk Hydro, Norway

To clean waste water containing nitrate, you are using ion-exchangers. What is your operational experience with this cleaning process, and have you experienced deposit problems since the waste water also contains P and F components ?

A - We worked together with a company named Christ AG, Switzerland, CH-4197 Aesch, and this company has great experience with this way of cleaning water. There are plants in Yugoslavia, Bulgaria and Romania where this process has been in operation for many years.

Q - Mr. B. CHRISTENSEN, Superfos Fertilizers, Denmark.

1/ Has BASF proved the use of by-product sand for building material, and to what extent has the pollutant to be washed out and what kind of filter is used.

A - To the last part of the question, we have belt filter from the companies Pannevis, Netherlands, 3542 Utrecht and BHS AG, Western Germany, D-8972 Sonthofen. The sand has indeed been used as building material for 15 years, and it is a good building material.

Q - Mr. B. CHRISTENSEN, Superfos Fertilizers, Denmark.

Does the possibility of this filtration of sand lead to use of low grade rocks ?

A - Yes, but you must use a big sandfilter.

Q - Mr. B. CHRISTENSEN, Superfos Fertilizers, Denmark.

I think you did not answer fully the first question. To what extent do you have to wash out the pollution from the sand ?

A - We have a pH neutral sand. It is washed very thoroughly. All these soluble things are acid. We have phosphoric and nitric acids in the sand, and if we come to a pH of 7, we have washed out all these things.

Q - Mr. G. BRUSASCO, Agrimont, Italy.

Have you realized all the reported environmental protection units in your plants ? If so, what were the investment and the increasing of the production cost of NPK ?

A - We have realized the environment protection units from figures 4, 8 and 10. We are constructing the protection unit from figure 5. We are planning the unit from figure 6 and the units from figure 7 and 9 exist as technical concepts. The investment costs depend on the plant volume and also regulations.

Q - Mr. S. ORMBERG, Norsk Hydro, Norway.

You stressed that you are trying to have a balance between chalk and ammonium nitrate to make calcium ammonium nitrate. Would you not be more flexible if you, for instance, sell some of the calcium carbonate to the farmers as liming aid ?

A - Oh yes, in Germany there are at the moment trials to do such things.

TA/88/13 Nitric acid production, improvements by revamping by W. Freitag, R. Schallert and E. Scheibler, Uhde GmbH, Federal Republic of Germany

DISCUSSION (Rapporteur K. Farmery, ICI Fertilizers, UK)

Q - Mr. P. ORPHANIDES (Duetag, France)

When you say in your paper that the performance reserves of the absorption section of a nitric acid plant is often around 10%, what is the limiting factor ?

Is it:

- absorption efficiency ?
- removal of absorption heat ?
- hydraulic performance ?
- the pressure drop impact due to the rest of the plant ?

A - The main factors are design features like weir heights, the number of holes (i.e. the dry pressure drop), the cooling surface area (which cannot be modified in an existing tower) etc. All limit the extent to which the capacity of an existing plant can be increased. In general, therefore, these limiting features are those which are the most difficult to change - the mechanical design features.

Q - Dr. S.K. MUKHERJEE (KRIBHCO, India)

First a comment. The revamp options for optimisation of a plant in India (800 tpd capacity - 100% acid basis - 53% product strength) have been studied. The plant was built in 1958-59, and has been in operation for nearly 30 years. The revamp option, briefly, is for partial replacement of the absorption section, now 4 bar absolute - single pressure, to high pressure (10 bar-12 bar) in order to obtain:

- i/ 68% acid
- ii/ 200 ppm NOx emissions against 2500 ppm NOx now
- iii/ better ammonia efficiency.

The compression and combustion sections are in good condition and need no technology changes. It seems to be only the absorption section which needs extensive redesign. The project, as described, has been taken forward for implementation. Would Mr. Freitag comment on the project.

My question: will a change of packing improve the absorption capacity of an existing plant where the current packing is normal 35 mm x 35 mm ceramic Raschig rings ?

A - First a comment on the revamp proposal. I know the project quite well. Many options have been considered. All the options involving splitting into parallel streams or adding sieve-tray absorption are expensive. It is hard for me to say from here which would be the best, most reliable solution. A lot of thought and calculation are needed for each option. In addition, the decision has to be made on the basis of payback time, interest rates, etc. However, on balance, I suspect that a complete revamp/replacement of the absorption section is probably the best solution, not adding a sieve-tray tower.

As to your question about changing the packing, I doubt that approach will be profitable.

.../.../...

Q - Mr. G. KONAPHAIS (Norsk Hydro, Norway).

Our experience leads us to conclude that the dew point in nitrous gas is closer to 140° C than 115° C as you indicate in your paper. Will you recommend increased heat recovery in this temperature region when you have had problems with corrosion at the inlet of the cooler condensers in some of the plants you have built ?

A - We know that the inlet nozzle of the cooler condenser in new plants is equipped with a feedwater preheater in advance of both nozzles, so that they have the same temperature as the inlet of the cooler condenser itself. Corrosion in the cooler condenser can be completely prevented, therefore, by adding additional cooling facilities to the inlet portion of the cooler condenser itself.

In this way, we can expect the dew point - whether it is 140° C or 115° C - to be handled in the feedwater preheater, which is designed to handle it.

TA/88/14 Investigations into the initiation of a detonation of molten ammonium nitrate by falling objects, by A.H. Heemskerk, P. Schuurmann and A.C. v.d. Steen, TNO, Netherlands

DISCUSSION (Rapporteur Mr. P. Stokka, Norsk Hydro, Norway).

Q - Mr. N. ROBINSON, Hydro Fertilizers Ltd., UK

I understand that organic matter catalyses the ammonium nitrate decomposition. Can you comment on what type of organic matter is the most harmful? Am I right in assuming the most harmful things are graphite, or does it not matter as long as it is organic matter?

A - In our investigations, we did not change the type of organic matter. Coke was used only. Also in the Canadian work coke was used. In previous work, we performed some thermal stability tests where oil was added to the molten ammonium nitrate, however at lower temperatures. At the surface of the liquid a reaction was observed, but no self ignition. Since the addition of organic matter has not been investigated systematically by us, I cannot really answer your question.

Q - Mr. P. ORPHANIDES, Duetag, France.

My question is not addressed to you, but to Mr. Ormberg as Chairman of the Safety Working Party. What are the conclusions you have drawn out of the work done and the conclusions presented concerning the detonation of ammonium nitrate?

A - Mr. S. ORMBERG, Norsk Hydro, Norway.

For new projects, as for existing stores, the authorities frequently put forward questions like: What happens with AN if the warehouse burns and the roof falls in? Existing papers and reports have mainly evaluated sensitivity to high energy impacts (bullets, boosters, etc.). The present project was initiated to get results from simulated scenarios, like falling debris onto molten and overheated AN.

The conclusion of the work is just as Mr. Groothuizen said at the end of his paper. The probability of detonation of molten AN during a fire in a storage by falling debris is very unlikely to happen, as long as you use the knowledge and experience we have today for production and storing.

A - Perhaps I can comment on this. The weights we have used compared with parts of building constructions are perhaps a little low, but, in theory, the pressures are the same. The pressures which come into the molten ammonium nitrate by a dropweight, are not dependent on the weight itself. They depend on the velocity at which the weight strikes the molten ammonium nitrate and they depend on the impedance of both the dropweight and the molten ammonium nitrate. So if you have a weight, say 1000 kg, then the pressure will be the same as for the weight of 50 kg.

Mr. Groothuizen's presentation ended with this conclusion: It can be concluded that molten ammonium nitrate is less sensitive than nitroglycerine. As a consequence of this research project it is unlikely that a detonation of molten ammonium nitrate may be initiated by falling debris from a collapsing building.

TA/88/15 Safety requirements in fertilizer plants, by Dr. B. PURUCKER, BASF, Western Germany.

DISCUSSION (Rapporteur Mr. P. STOKKA, Norsk Hydro, Norway).

Q - Mr. H. HERO, Kemira Oy, Finland

You consider that NPKs are free of explosive danger. But still they are possible to use as explosives with oil. Is it essential to take into account this hazard ?

A - I think we do not have NPK formulas which, in the limits of maximum 0.4% organic mater, are able to detonate.

Q - Mr. H. HERO, Kemira Oy, Finland

What I mean is exactly that. If there are some impurities in oil, and if there is a danger in some places that it is possible that the oil mixes with, for example, 20:10:10, it can explode then. Have you taken into account that kind of hazard ?

A - We exclude oil impurities in combination with our products, and until now, I do not know of any case that 20:10:10, with the composition of our product, is going to detonate.

Q - Mr. H. HERO, Kemira Oy, Finland

Have you taken any precautions in case of stoppages of spraying nozzles inside of the drum, especially spherodizers ?

A - In the case of drum granulation, we have no special arrangements.

A - Dr. J. ENGERMANN, BASF, Western Germany.

In the case of the spherodizer, we have two things. We have measured the quantity of fluid going to the nozzles. If they are going down, we can clean with vapor very quickly. And the second thing is, when it is not possible, we must drill out the nozzles. The people who are working with this have special clothes to avoid that melt hits the body.

Q - Mr. H. HERO, Kemira Oy, Finland.

Is it the reason you have changed the product from triple 15 to triple 16, that triple 15 made by Odde process is in so called B class ?

A - No, it is not the case. We can also make triple 15 as type "C" fertilizer (free of self-sustaining decomposition).

Q - Mr. H. HERO, Kemira Oy, Finland.

But have you any safety reasons to that change ?

A - No, we have no safety reasons for that change.

Q - Mr. B.K. JAIN, FAI, India

1/ The quantity of the product can be adjusted by the use of internal inorganic stabilizers. Would you please elaborate on what is this internal stabilizer.

.../.../...

2/ The determination of porosity has been mentioned as the indication of the safety. In India, we make 25% N ammonium nitrate. Would you recommend that determination of porosity for that product ?

A - 1/ It is an inorganic salt which does react with the product and stabilizes the product against volume changes by means of temperature changes.

2/ You can measure porosity in your CAN as indication for the safety. But I think in the case of CAN, slight increases in porosity do not change your product to an unsafe product, but you must do the trials.

Q - Mr. A. HAMDI, ICM/SAEPA, Tunisia.

1/ Can you, without any risk, proceed to grinding blocks, approximately 100 to 200 mm, of 33.5% ammonium nitrate ? If so, with which type of grinder ?

2/ Can you recycle low quantities of ammonium nitrate fines in the DAP manufacturing loop ?

A - Dr. ENGELMANN, BASF, Western Germany

1/ I think it is no problem. We use normal centrifugal crushers for this type.

2/ We have no DAP manufacturing loop and I cannot answer your question.

Q - You state that detonation can come from shocks. Is this statement not in contradiction with content of preceding paper ?

A - Dr. R. NITZSCHMANN, BASF, Western Germany.

I think there is a difference between pure ammonium nitrate, and ammonium nitrate from the Odde process having impurities coming from the phosphates, for example Cl-, organic C. So we have higher safety requirements on this ammonium nitrate within our process. And I think the speech given before is only correct for ammonium nitrate which comes from a synthesis of ammonia and nitric acid.

A - Dr. B. PURUCKER, BASF, Western Germany.

Yes, I think I have discussed some differences between types of ammonium nitrate containing material in my paper. The behaviours of pure ammonium nitrate and CAN and NPK are quite different.

Q - Mr. A. BARBERA, Agrimont, Italy

If I have understood you correctly, you do not use oils in the coating drum. How do you assure the quality of products especially for dustiness ?

A - We use our own method and we have as coating material something like waxtype. We have no oils. Because I think the sensibilisation of ammonium nitrate containing product to go to cigar burning is depending on the incorporation of any organic materials which you bring on the outside of your product. We have done trials with antidusting oils and we could show that, depending on the chemical composition of the NPK product, you can bring safe products with antidusting oil to cigar burning.

Q Mr. G. KONGSHAUG, Norsk Hydro, Norway.

1/ About safety, I feel you are talking very much black and white. In the beginning of your paper, you say that the greatest potential danger lies in the ability of ammonium nitrate to detonate when subjected to mechanical shock. This is the property that has led to a number of serious accidents. Can you tell us more about these accidents ?

2/ You are talking about self-sustaining decomposition and burning due to local overheating in the drying unit. The burner test is a classification test, and I think that we shall stay with that, and not talk about the cigar burning test. Because when you have local overheating, all NPK will decompose. At the end of your paper you say that the best method to minimize the potential hazard is to produce safe products. Can you mention any product which is not safe ?

A - Let me begin with your last question. I think products we produced were capable of cigar burning and capable of cigar burning at a high speed. In my opinion, these are not sufficiently safe products, in respect to storage of fertilizers and accidents which may occur by the burning of stores for instance. If I have understood your question right, overheating in drying drums and smouldering - let me say smouldering - decomposition of products is not excluded when we go to products that in the trough test do not show cigar burning. But I think the potential of decomposition is lowered significantly also in this case. We have set up some other safety rules to lower the danger of decomposition in the drying drum as I have shown this in my paper: some construction details which I have not mentioned in detail, that overcome the risk of overheating in the product inlet of the drying drum.

The potential danger of ammonium nitrate. I wanted to give you an overview of the safety aspects of ammonium nitrate containing fertilizers. I have taken some points out of the literature, and this is a point you can read in the literature according to ammonium nitrate. I do not know in the special case the influence of very little trace amounts, as for instance organic carbon, in so-called pure ammonium nitrate, for the detonation ability and therefore I cannot tell you more.

Q - Mr. J.M. BIRKEBAEK, Superfos Fertilizers, Denmark.

I would like to know how you avoid the potential risk of decomposition of dust in the ductings when you recirculate air from the dryer back to the front end, I suppose you mix that with hot air coming from the burner.

A - The recycled dust amount is very low because it is equal to the amount of dust going out of the plant, and this dust is decomposing in the burner. And you get slightly higher amounts of NOx for instance in your off-gas as without recycling gas, but it is not very significant.

TA/88/16 Prayon industrial experience of manufacturing merchant grade phosphogypsum by A. Bourgot and P.A. Smith, Prayon-Rupel, Belgium

DISCUSSION (Rapporteur A. Davister, Prayon, Belgium)

Q - Mr. ROBINSON (Norsk Hydro Fertilizers, UK)

1/ The main effect of recrystallisation is to reduce the level of coprecipitated P2O5 in the calcium sulphate. It does not have a significant effect on the levels of fluorine, sodium, potassium and organic matter. All of the impurities affect the properties of plaster products. In view of this, I find it a little strange that no further purification is required with Central Prayon calcium sulphate. Could the authors please explain ?

2/ Crystal shape also has some effect on the properties of plaster products. Agglomerated crystals are not so suitable compared to plate crystals. In view of the fact that Central Prayon process can produce agglomerated crystals, what are the authors' comments ?

3/ What levels of P2O5, F and other impurities can be tolerated in the authors' opinion in the feed to:

- a/ cement retarder
- b/ plaster boards
- c/ plaster blocks.

4/ The sale of wet process calcium sulphate has always presented difficulties due to the competition from natural gypsum. Could the authors please indicate from their experience what the key factors are in establishing such a market.

Has the work carried out by Rhône-Poulenc helped in this direction ?

A - 1/ Yes, the role of all impurities is important, but the acidic impurities P2O5 and F are by far the most important.

P2O5 is present in three forms: acid, cocrystallized, unreacted. Acid and cocrystallized forms are largely decreased by the recrystallization and nearly qualitatively precipitated during the rehydration after neutralization into the harmless tricalcium phosphate form.

F is largely given off due to the high temperature and acidity of the recrystallization stage and, similarly to the P2O5, the decreased amount present is precipitated as the calcium salt, harmless CaF2.

The less important impurities like sodium, potassium and organic matter are brought below the right limits by a proper selection/blending of raw materials.

2/ You are right and the crystals ex-filter are of a large agglomerated type, but the Central Prayon wet hemihydrate expands during its rehydration by natural combination with its own moisture and this expansion gives an enormous increase of the grain's surface which makes it a product essentially dry and ideally sized for feeding to a plaster plant.

3/ Generally, sales of phosphogypsum have to complete or compete with natural gypsum sales. As such, phosphogypsum must normally comply with existing legislation for natural gypsum and not the requirements to

.../.../...

produce an end product within specification. Some countries have no natural gypsum and, thus, the specification for phosphogypsum is more lenient than those where no such interest exists. In short, the specification greatly depends on the final product required and the country in question. However, some general guidelines follow:

a/ Cement retarder

Depending on the type of cement required, the quality of gypsum can be more or less strict.

For general cement, the following specifications normally apply:
0.1% F or more and cocrystallized P205 of 0.1 to 0.2%.

Note soluble F and P205 to be essentially zero:

- the colour is not important
- the size specification and water content must be compatible with existing handling and feeding equipment;
- the radioactivity is not important.

The hemi-alpha from Central Prayon Process is completely neutral, soluble F and P205 are zero, cocrystallised P205 less than 0.05%, the free moisture is 2-3% after rehydration and can be in the form of pellets 5-20 mm or bulk (ground - 80 mm).

b/ Plaster boards

The requirements for phosphogypsum are as in a/, with additional requirements, such as:

- a limit on radioactivity (dependent on country);
- % Na₂O (from 0.2 to 0.4 max.);
- the organic content level should be low;
- the surface area of the gypsum should be high.

Alpha-hemihydrate from Central Prayon with a correct selection of phosphates to reduce the organic content and the radioactivity can fulfil all the conditions, save the last one, which can be easily satisfied after rehydration. Total P205 is less than 0.3%, cocrystallized less than 0.1% and F within the range 0.1 - 0.3%.

c/ Plaster blocks

The requirements are similar to b/, but there are important additional requisites with respect to the setting time (initial and final), the porosity and other physico/chemical requirements of the plaster.

Alpha-hemihydrate dried and ground by itself or mixed with beta-hemihydrate enables production at lower cost levels. Dihydrate produced by rehydration of alpha-hemihydrate can be calcined to produce beta-hemihydrate too.

4/ I cannot evaluate the influence of Rhône-Poulenc's work, but the simple fact that Prayon has built up a market for several hundred thousand tons per year of merchant grade phosphogypsum shows that, if you manufacture a product constantly controlled to satisfy the specifications agreed with the users, it is possible to sell that product, provided that your operation is economically competitive.

Similar experience with the CPP process has been shown by Boliden in Sweden and several Japanese plants.

Q - Mr. BARLOY (Krebs, France)

1/ Could you explain the influence and the concentration limits of water soluble, cocrystallized and unreacted P2O5 and F on the phosphogypsum quality ?

2/ When would you recommend the selection of Central-Prayon Process ?

A - 1/ Please see written answer to Mr. Robinson's question N° 3

2/ In every case where the user wants to sell merchant grade gypsum, Central Prayon is the obvious choice, as it produces dry gypsum without drying costs (nor investment cost nor operation cost).

In all cases where the plant operators want or must be "good neighbours", i.e. careful of their environment, high yield multiple crystal processes are required, and if the phosphate rock is igneous, the conversion from dihydrate to hemihydrate is much safer, simple and less expensive. Sometimes where difficult or low grade phosphates are to be treated and dihydrate efficiencies are very low, the two-stage CPP process can be interesting, due to its very high efficiency.

Q - Mr.C. VINCKE (Windmill Holland, Netherlands)

On page 9 of your paper, you give a specification of the alpha-hemihydrate. Could you also indicate what the contents are of impurities in relation to the phosphate rock used ?

Is the product neutral or slightly acid or slightly alkaline ?

A - a/ The other impurities can be commented as follows:

- heavy metals are no serious problem,
- radium is very important.

b/ Rock mix plus additives control quality and colour of the alpha-hemihydrate. For instance, presently, the right radium content is obtained by blending Bu-Craa with igneous ruck (Bu-craa is simply screened while igneous rock is fed as received).

c/ The alpha-hemihydrate is neutralized prior to drying and is essentially neutral.

Q - Mr. V. HORKKO (Kemira Oy, Finland)

1/ What are the results when processing a mixture of sedimentary and igneous phosphate in Central Prayon Process ?

2/ Have you thought about changing the Puurs Nissan hemi-di-process to di-hemi (Central Prayon) to get a better quality gypsum ?

A - 1/ That is precisely the operation described in the paper.

2/ This is a very interesting question. At Puurs, we operate a low strength Nissan H process, and have for many years operated a wet purification process as described in the first part of the text.

We have studied the conversion to the CPP/Central Prayon Process (DH/HH) and also to the PH3 (HH/DH/HH) process, thus reducing the gypsum

.../.../...

purification and producing a stronger acid (CPP 35-37% P2O5 and PH3 42-46% P2O5). However, reductions in the oil price have reduced the potential savings, plus the fact that our main market (Holland) of by-product gypsum from Puurs has reduced allowable radioactivity levels in the phosphogypsum, and have made the conversion unjustifiable for the present time.

Q - Mr. P. BECKER (Duetag, France)

The original Central Prayon Process used centrifuges for the first solid/liquid separation. Would you, today, use the same type of equipment ?

A - The choice is mainly defined by local conditions.

- If you use a centrifuge and want to have clear acid, you must add a settler. The couple "centrifuge + settler" may be more expensive (investment cost and/or operation cost) than the filter.

- If you require a clear acid, the centrifuge alone is cheaper and more compact than the filter.

- The CPP is now able to produce a stronger product acid strength and, in this case, filters can separate the acid more efficiently.

Q - Mr. P. ORPHANIDES (Duetag, France)

1/ What was the phosphate used in the pictures you have shown during your presentation ?

2/ Are the purity values of the gypsum mentioned based on the use of Kola phosphate or other less pure phosphate ?

A - 1/ Rock was a blend 50/50 of Phalaborwa and Bu-Craa.

2/ We annex typical values obtained with various phosphates in the CPP process: Kola - Morocco - Florida - Togo - Phalaborwa

.../.../...

PROCESSING OF DIFFERENT PHOSPHATES IN THE CENTRAL PRAYON PROCESS

VARIOUS ANALYSES

	PHOSPHATE KOLA 86 BPL			PHOSPHATE MAROC NON-CALCINE 75 BPL			PHOSPHATE MAROC CALCINE 80 BPL		
	Phosphate	Ac. produit	Hexihydrate	Phosphate	Ac. produit	Hexihydrate	Phosphate	Ac. produit	Hexihydrate
Densité		1,410			1,393			1,383	
H ₂ O total			6,0			6,0			6,2
	sur base sec 100°		sur base sec 250°	sur base sec 100°		sur base sec 250°	sur base sec 100°		sur base sec 250°
P ₂ O ₅	39,4	35,0	0,15	34,0	33,0	0,25	36,0	35,0	0,09
CaO	51,4	0,24	39,20	51,8	0,33	39,75	56,2	0,36	40,1
SO ₃	0,05	0,7	56,00	1,6	0,6	57,74	2,00	0,8	57,60
SiO ₂	2,50	0,70	0,30	2,0	0,8	0,80	2,10	1,30	0,20
Na ₂ O	0,43	0,08	0,20	0,63	0,11	0,25	0,54	0,07	0,32
K ₂ O	0,16	0,03	0,07	0,05	0,03	0,05	0,05	0,02	0,02
Cl	0,02	0,02	0,00	0,02	0,02	0,00	0,01	0,01	0,01
F	3,35	2,20	0,10	4,1	2,2	0,20	4,30	2,80	0,59
Fe ₂ O ₃	0,60	0,43	0,10	0,26	0,26	0,01	0,22	0,20	0,02
Al ₂ O ₃	0,40	0,20	0,13	0,38	0,12	0,08	0,44	0,36	0,04
H ₂ O	0,45	0,4	0,00	0,30	0,30	0,00	0,40	0,40	0,00
CO ₂				3,5			1,20		
C.org.		0,02		0,19	0,06		0,02	0,02	0,02
TiO ₂				0,03					

	PHOSPHATE PRALABORNA PTROMENITE 80 BPL			PHOSPHATE TOGO 80 BPL			PHOSPHATE FLORIDE NON-CALCINE 77 BPL		
	Phosphate	Ac. produit	Hexihydrate	Phosphate	Ac. produit	Hexihydrate	Phosphate	Ac. produit	Hexihydrate
Densité		1,397			1,416			1,415	
H ₂ O total			5,7						6,0
	sur base sec 100°		sur base sec 250°	sur base sec 100°		sur base sec 250°	sur base sec 100°		sur base sec 250°
P ₂ O ₅	36,4	34,2	0,19	36,6	36,0	0,20	34,9	34,4	0,18
CaO	53,20	0,23	41,0	51,0	0,32	35,1	49,5	0,3	39,9
SO ₃	0,00	0,82	58,3	0,1	0,8	58,0	0,50	0,9	56,8
SiO ₂	2,60	0,90	0,5	3,7	0,30	2,1	3,9	1,26	1,8
Na ₂ O	0,11	0,05	0,05	0,20	0,02	0,13	0,36	0,04	0,25
K ₂ O	0,04	0,03	0,02	0,03	0,00	0,02	0,05	0,03	0,03
Cl	0,04	0,03	0,02	0,09	0,07	0,03			
F	2,30	1,70	0,04	4,0	1,70	0,55	4,03	2,88	0,35
Fe ₂ O ₃	0,19	0,18	0,02	1,10	1,00	0,02	0,93	0,81	0,04
Al ₂ O ₃	0,19	0,15	0,08	1,06	0,31	0,31	1,12	0,68	0,26
H ₂ O	1,20	0,90	0,00	0,1	0,10	0,00	0,2	0,20	0,0
CO ₂	3,42			2,1			3,2		
C.org.	0,55	0,01		0,05	0,02	0,03			

Questions put in writing:

Q - Mr. E. Uusitalo (Kemira Oy, Finland)

What kind of rock phosphate have you used, and is it possible to use magmatic phosphate also ?

A - The phosphates processed in the CPP plants are listed hereunder. Their hemihydrate production was (or is) valorized as dihydrate after neutralization or "dry" rehydration.

Phosphate mixtures enabled us to balance out impurities, to reduce additive consumption, if necessary, and to produce the calcium sulfate wanted.

The processing of an igneous phosphate, which is not very easy for DH, is very interesting for CPP because phosphogypsum is usually white, has a low radioactivity and a high filtrability.

PHOSPHATES USED IN PRAYON PLANTS
CENTRAL PRAYON PLANTS

<u>ENGIS:</u> (74- 88)	KOLA	100%	
	KOLA + TOGO	50% - 50%	70% - 30%
	KOLA + KHOURIBGA	68% - 32%	
	KOLA + BUCRAA	50% - 50%	
	PHALABORWA + TOGO	70% - 30%	
	PHALABORWA + BUCRAA	0% - 50%	70% - 30%
	ORON + TOGO	70% - 30%	
	ORON + CALC. KHOUR. + TOGO	30% - 30% - 40%	
	N.CAROLINA	100%	
	N.CAROLINA + TOGO	70% - 30%	
	ZIN	100%	
<u>OTHERS:</u>	C.FLORIDA	TOGO	KHOURIBGA
	CALC. KHOURIBGA	KOLA	PHALABORWA...

Q - Mr. M. GAURON (Norsk Hydro Azote, France)

What is the cadmium distribution between the acid and the hemihydrate in the Central Prayon Process ?

A - If the phosphates used contain more than 10 ppm Cd, the amount of Cd in hemihydrate remains low, between 1 and 3 ppm, calculated on the basis of solid anhydrite (CaSO₄).

Q - Mr. R. HUTCHINS (Texasgulf Inc., USA)

1/ What rock is used ?

2/ Are additives used to (a) reduce scaling on the filters and hemi slurry piping and (b) control the rehydration rate of the hemi crystals to dihydrate ?

3/ How does recovered gypsum from your operation compare in costs with natural gypsum ?

4/ What effect would organics in the rock have on the process and quality of the product ?

A - 1/ See answer to Mr. Uusitalo (Kemira Oy, Finland)

2/ We use no additive to control scaling on the filter and in the slurry piping. We control the parameters only to filter and pump a stable hemihydrate. After solid discharge, the filter is washed according to Prayon technology.

During the "dry" rehydration of alpha-hemihydrate, soluble and cocrystallized P2O5, and soluble F, must be neutralized by adding lime.

The reaction is controlled by the amount of lime added.

3/ The cost of processing alpha-hemihydrate of suitable quality is competitive as compared to natural gypsum. For a price below the selling price of natural gypsum, a profit is obtained which partly justifies the interest of the process.

The sale of gypsum results in a 10% increase of the added value over and above the cost price of phosphoric acid (for instance the added value increases from 19 to more than 29% for 54% acid).

4/ The process technology enables the control of the organic matter content during the plant operation. It does not affect process efficiency or plant maintenance.

Concerning product quality, it is affected by the amount and nature of the organic matter. The limits on organic matter content depend on the final use of calcium sulphate (see the answer to question 3 by Mr. N. Robinson, Norsk Hydro, UK)

Q - Mr.K. GOVINDARAJAN, Southern Petrochemical Industries Corp. Ltd., India)

1/ How well is the phosphogypsum in hemihydrate (or) dihydrate form accepted in cement industries compared to natural gypsum ?

2/ Southern Petrochemical Industries Corp. Ltd. - a fertilizer company located at Tuticorin, Southern part of India - having a phosphoric acid plant of 165 MT/day adopting Nissan's hemihydrate/dihydrate process producing about 800 MT/day of phosphogypsum of following specification:

Constituent

CaO	32.50 plus or minus 0.2
SO3	44.20 plus or minus 0.3
Combined water	22.50 plus or minus 0.2
SiO2	1.07 plus or minus 0.1
Total fluoride	0.56 plus or minus 0.3
Total P2O5	0.30 plus or minus 0.2

Is it suitable for use in the building industry ?

A - 1/ See answer to question 3 by Mr. N. Robinson (Norsk Hydro, UK)

2/ On the basis of the limited analysis given, it is difficult to answer. In addition, we do not know the client's requirement (see answer to question 2 by Mr. N. Robinson). To valorize this product, it should probably be washed, processed, filtered again and eventually dried, as was described in the first part of the paper on the humid treatment in Puurs.

The Puurs plant uses the Nissan H Process, but the phosphate used, Khouribga, gives a phosphogypsum of a different specification from the above-mentioned one.

A test is necessary to evaluate the humid purification process.

Q - Mr. K. HALASELL (JPMC, Jordan)

1/ What type of radioactive impurities are found in your phosphogypsum ?

2/ What are its contents ?

3/ Are there any regulations in Belgium limiting radioactive content?

A - For the phosphates we use, the radioactivity of gypsum from alpha-hemihydrate is due to Thorium, Potassium and Radium. The latter (radon emission) is less important than Thorium.

2/ Total radioactivity is lower than 10 pci/gr.

3/ Presently, in Belgium, there is no regulation in that respect giving standards for the use of phosphogypsum.

Q - Mr. M.A. HAMDJ (Groupe Office Chérifien des Phosphates, Tunisia)

1/ On page 14 you state that the Prayon units for P2O5 are the most economical owing to the valorization of phosphogypsum and other coproducts. What are these coproducts ?

A - Downstream of phosphoric acid production, we have the following products

a/ The products resulting from the processing of fluorine recovered as H₂SiF₆, such as:

NaF, Na₂SiF₆, MgSiF₆, K₂SiF₆ and other fluorine salts.

b/ The production of high grade and partially purified acid. This technical quality acid is for sale and for feeding phosphoric acid purification units.

c/ Pure phosphoric acids (P, P5, Codex) and different products such as:

- monoammonium phosphate
- technical monoammonium phosphate
- diammonium phosphate
- liquid monoaluminium phosphate
- sodium tripolyphosphates
- sodium and potassium phosphates.

TA/88/17 Hemihydrate operating experience at Brunswick Mining and Smelting Fertilizer facilities by T. Gravestock, Brunswick Smelting and Fertilizer, Canada

DISCUSSION (Rapporteur Mr.C.M.H. Vincke, Windmill Holland, Netherlands)

Q - Mr. T. LAINTO (Kemira Oy, Finland)

I have two specific questions concerning your plant:

1/ Do you have any limitations on the discharge of gypsum into the sea today and how do you see that situation in the future ?

2/ I understand that you are running your plant five days a week. How does this affect the P205 losses ? And do you have some special arrangements to decrease these kinds of losses ?

A - The first question was the environmental impact of gypsum. With the dihydrate process, our gypsum bed was increasing at a normal rate of 11% per year. When we did convert to hemihydrate we ran into a problem. The actual rate increased to 40%. We definitely do have environmental restrictions, environmental policies in New Brunswick. We have had to do many different surveys, medical surveys, lobster studies for fluorides and this is still continuing with the participation of the government. In order to start the dredging process, we did have to get a special permit because there is lobster fishing just approximately 1,000 meters off the point of discharge.

2/ We have special arrangements to decrease losses. The plant operates on a five-day basis mainly because our sulphuric acid is received from the smelter next door and our operating policy is to consume all the acid produced by the smelter. We are also pursuing other sulphuric acid sources, looking for waste acids and looking at Noranda's intention to expand in the future. There is no doubt that P205 losses are greater shutting down on this weekly basis. You lose them on start-ups, because, essentially, over the week-end, the reactor contents cool from 100° C down to about 65° C. So initially you have to restart up on steam to 80° C, start your reaction, and it takes about four hours before the filter gives you the higher efficiencies. On the shut-downs, basically, there are no particular losses.

Q - Mr. L. RASMUSSEN (Superfos Fertilizers, Denmark)

1/ About process economy, in table one, you have summarized the achieved savings. What is the steam price used in your calculation ?

2/ Filter loss calculations can be based on filter cake samples or gypsum slurry samples. You indicate that the recovery, based on filter cake samples, is approximately 93%. Have you made loss calculations based on continuous gypsum slurry samples and, if so, what are the results ? Have you any reliable figures for the overall plant P205 recovery for the two processes ?

3 In your table 1, you have given no credit for a better acid quality. Did you not get any ?

4/ Have you any plans for the introduction of a two-stage process in your plant ?

A - 1/ The steam price, generally, when we first started off in the evaluation, was \$ 8 per thousand pounds of steam. Naturally, over

.../.../...

the two-year period, when we decided to go hemi, energy prices dropped. I evaluated the steam savings by taking actual 1985 operating data, correlating it to 1987 pro rata per tonnage changes and costs to form a comparative base.

2/ The gypsum efficiencies are based on a continuous sampling of gypsum cake. We have an automatic sampler which takes samples approximately every fifteen minutes. The sample is taken to a lab on a 24-hour basis. As an example, the P205 in cake has been running 1% versus 0.8% with the dihydrate process. We also look at overall P205 efficiency. With the dihydrate process, our normal efficiency across the plant was about 88%, and with the hemihydrate process, we are getting about 87.2%.

3/ I took credit for acid quality. Definitely, there is a credit for acid quality because, in this particular process, the aluminium content of the 40% acid is approximately 5%. With the lower impurities in the acid, we found that what we tried to do is to start with 120 c.f.m. plus. We found that adding sulphuric acid to control grade, we still had high results. We then went to 180 c.f.m. plus to bring the solids up. The other thing we found was that we used two different types of rock from Florida. We used an Estech rock and a Mobil rock. One particular rock we had to clarify to 1% levels. The other rock, we could let go to 2.5% and still make grade. And, naturally, you could use solids to make DAPs more economically.

4/ As far as our future plans go, one of the reasons we were able to, essentially, sell the idea of hemihydrate to our Board of Directors, was that we indicated that the first step of this technology was a hemi process with future plans to go into dihydrate conversion. As you know, we receive rocks from Florida, so it is expensive and there is some economic benefit to then take it a step further to the dihydrate route. So there are no plans at the moment to go that way, but there definitely could be in the future.

5/ Gypsum slurry loss is calculated basically on the standard calculation of cake. It is gypsum-cake efficiency based on a mature balance of P205 and calcium oxide.

Q - Mr. R. HUTCHINS (Texasgulf Inc, USA)

1/ You mentioned that you use Florida rock. Do you grind the rock ?

2/ You mentioned in the paper that the antiscalent system that you use is proprietary, but could you tell us what you can about that system and what antiscalent agent you use ?

3/ Do you use an additive to control your rehydration rate ?

4/ You indicated that your filtration rate had been excellent with rates up to 110% being achieved. What is that a percent of ?

5/ How does that compare with the filtration rate when you are operating in the dihydrate system ?

A - 1/ Yes, we do grind the rock.

2/ Unfortunately, I cannot discuss the antiscalent agent, but I can mention that, initially, we started off with the antiscalent at the

.../.../...

levels recommended by Norsk Hydro. Every month, we took apart the central valve at the filter, checked the down legs for scale and found there was no scaling. So what we started doing was withdrawing the use of antiscalent in these areas. The last two months before our summer shutdown of this year, we took the antiscalent off totally. We found that, basically, if you have hot water strategically located at the proper locations, you do not get scaling in the hemi process. So our antiscalent addition right now, instead of being as recommended 1.2 is in the area of 0.2 to 0.3 kg per ton.

3/ We do use an additive to control our rehydration rate, this is the purpose of it, to inhibit conversion to dihydrate.

4/ The design filtration rate is 500 tons/day P205.

5/ In the dihydrate system, we had problems at 500 short tons/day. Our previous dihydrate system was a 500 ton/day plant generally running at 95.5% efficiencies, but when we pushed the plant beyond this 500 tons/day, our efficiencies dropped off pretty quickly. With this particular process, we can get up to 600 metric tonnes and maintain the hemihydrate efficiencies. We believe that it is mainly due to the nature of the crystal that we are getting which we also feel is the result of grinding the rock.

Q - Mr. P. SMITH (Prayon, Belgium)

How much effect do you think the modification the Prayon filter has made to the number of tons/day that you can get across the filters ?

A - I think that is definitely a factor, because, when we got approval to go from dihydrate to hemihydrate, we know we were going to upgrade our plans from a 316 to 317 sloped bottom. Prayon had indicated to us that basically sloped bottom pan configuration would improve efficiencies by 0.5%. So when we got the approval, we actually bought the pans about six months prior to the start-up of the hemihydrate conversion, and we put them in during one of our Christmas shutdown periods to observe the effect on the dihydrate process, and we did see some improvement in filtration. We like the sloped bottom pans. We also have not observed any build-up whatsoever in the pans. The only times you run into problems on the filtration side is if you allow holes to get into the cloth which results in scaling up of the pans.

TA/88/18 The prediction of rock dissolution rates in the Norsk Hydro hemihydrate phosphoric acid processes, by N. Robinson, Norsk Hydro Fertilizers, U.K.:

DISCUSSION (Rapporteur Mr.C.M.H. Vincke, Windmill Holland, Netherlands)

Q - Mr. N. YAMANAKA (Nissan Chemical Industries Ltd., Japan)

There are other parameters than dissolution rate of rock in the first stage to design a phosphoric acid plant with a rock the nature of which is not known. Do you think that this design method is sufficient to completely eliminate a continuous small-scale test in designing a plant with new rock ?

A - I think the question relates to whether, in fact, this method of design is the complete story when designing a reaction system for the hemihydrate process. And the answer, of course, is that it is not. It is only one aspect of it, but it is an important aspect in that there is no point in designing a reactor for optimizing crystal growth or minimizing foaming or anything else if you do not dissolve the rock. You must dissolve the rock, and this is one of the parameters which must be satisfied, but it is not to say that this is the only parameter.

Q - Mr. P. SMITH (Prayon, Belgium)

Does the acid viscosity affect the dissolution rate ? If so, what is the relative magnitude of the viscosity and particle size effects ? Can the rates be compensated for ? Can you compensate for the effect of viscosity ? Similarly, does the slurry viscosity affect the dissolution rate ?

A - The question is: Is the slurry viscosity more important than particle size distribution, and will it affect dissolution ? The answer is yes. The viscosity of a slurry can affect the dissolution rate particularly if it affects the mixing efficiency. Really, it is a question of what design of agitator you have, what the residence time is, what the mixing time is, etc., but the higher the slurry viscosity the harder it is to achieve a good mixing.

I think, personally, that a particle size redistribution has a bigger effect, has a quicker effect. The slurry viscosity is taken into account by the determination of a dissolution constant which, as I have mentioned, must be determined practically. I am not recommending that you try to calculate a dissolution constant from theoretical principles. We did try to do this many, many years ago, and it really is just not accurate enough.

TA/88/19 Phosphoric acid evaporation process improvements increase production by utilizing a new heat exchanger circulating system featuring a new alloy, by W. Conti, Industria Sicilliana Acido Fosforico SpA, Italy and R. Boillat, Chas. S. Lewis and Co.Inc., USA

DISCUSSION (Rapporteur Mr. A. Davister, Prayon, Belgium)

Q - Mr. R. BARUT (Norsk Hydro Azote, France)

Have you measured corrosion rates for LEWMET 25 in phosphoric acid produced from Togo ore having the highest chlorine content ?

A - At the time of industrial testing, we did not use that particular rock, but in the lab test, we have tested acids with concentration of Cl up to 1200 ppm with corrosion rates less than 5 mils per year.

Q - Mr. P. ORPHANIDES (Duetag, France)

1/ What is the material used for the construction of the metallic evaporator heat exchanger ?

2/ Have you any scaling problems ? Is it still necessary to clean these scalings by so-called boil-out ? What is the chemical nature of the scalings ?

A - 1/ Alloy is SANICRO 28

2/ Yes, boil-outs (65° C, 5% H₂SO₄ solution washing by means of recirculation) remains necessary, but less frequently than before. Let us say once per week to once per ten days pending on the type of phosphate rock used. The scaling is made of gypsum and other solids.

Q - Mr. M. ALOUANE (Industries Chimiques Maghrébines, Tunisie)

1/ The first modernization actions aimed at the substitution of graphite heat exchangers by alloy-type exchangers. It is due to the bad quality of graphite exchangers or for maintenance reasons ?

2/ What are the concentration limits of the acid concerning sulphide, chloride and fluoride that are acceptable for LEWMET 25 ?

A - 1/ The substitution main reason was to reduce maintenance.

2/ We do not know exactly what are the practical limits, because in industrial operation we never reached these limits, as our alloy has always performed satisfactorily. In the lab, some tests with acid containing up to 10 000 ppm Cl⁻ were acceptable.

Q - Mr. P. BECKER (Duetag, France)

1/ What units are used for corrosion levels in table 4 ?

2/ What is the liquid velocity in the heat exchangers ?

A - 1/ Units are mils per year

2/ Velocity is 2.4 m/sec.

Q - Mr. V. HORKKO (Kemira Oy, Finland)

.../.../...

1/ What are the cleaning intervals of the heat exchangers after installing the LEWMET pumps ? What is the on-stream factor ?

2/ What is the solids content of the concentrated acid ?

A - 1/ Intervals between cleanings : 6 to 10 days pending on rock.

On-stream factor after three years operation is 90-93%.

2/ Solids content is 2 to 3%.

Q - Mr. M. BARLOY (Krebs, France)

1/ What is the cost of LEWMET 25 compared to existing alloys like Ferralium, Sanicro 28, Alloy 20...?

2/ What is the difference between LEWMET 15 and chromium containing cast iron manufactured in France by Creusot-Loire for 15 to 20 years ?

A - 1/ LEWMET alloys contain more than 85% of alloying (non-iron) metals, so they must be more expensive and we can say that LEWMET 25 is 10-15% more expensive than LEWMET 15.

2/ I do not know that Creusot-Loire alloy.

All I can say is that LEWMET 15 is an alloy developed on the basis of research results of an American laboratory.

Q - Mr. N. ROBINSON (Norsk Hydro Fertilizers, U.K.)

1/ How important is nickel in giving resistance to chloride corrosion ? Is there a minimum level ?

2/ What sort of corrosion rates would be expected at temperature of 100°C ?

3/ What is the erosion resistance of LEWMET 25, say in comparison with Ferralium, which has been developed specifically to resist erosion, but has not a very good resistance to chlorides ?

A - 1/Ni is the base metal of this alloy and it has a better corrosion resistance than iron. But, as the acid gives oxidizing conditions, there is a specific corrosion by halogens, that is called "pitting". For that reason, cobalt and molybdenum are added to fight that "pitting" corrosion. Nickel is only used to balance it and serves to obtain a fully austenitic phase.

2/LEWMET has operated safely at GELA at temperatures between 65 and 80° C. In another plant, we have pumps operating for 7 years on 54% P205 acid and 110° C.

3/ The erosion resistance is excellent; it is so good that machining is difficult and tools have a hard work.

For instance, with a tip speed of 25 m/sec., we have no trace of erosion after three years.

TA/88/20 Strategy for saving water in a fertilizer plant situated in an arid region where water resources are scarce and limited by A. Benmansour and H. Essebaa, SIAPE, Tunisia.

DISCUSSION (Rapporteur Mr. A. Davister, Prayon, Belgium).

Q - Mr. P. ORPHANIDES (Duetag, France)

1/ Have you investigated the possibility of reducing cooling water requirements by utilizing the absorption heat in your sulphuric acid plant for boiler feed water heating or for phosphoric acid evaporation?

2/ Did you re-evaluate that possibility later on?

3/ Water is a very rare and useful commodity in desertic areas. Other people should be able to use it, for instance farmers. What is your opinion?

Is it good or not to have accepted the pressure of local authorities to install your plant far from the sea and in a desertic area?

A - 1/ No, we did not, as the supply of water was expected to be satisfactory. It is only after the start-up that we had those difficulties that reduced the water supply.

2/ No, we did not do it.

3/ An official state organization is controlling and regulating the use of water resources. We have complied with their rules and have been controlled constantly.

Yes, we have followed the opinion of the ecologists when we decided to install the ICG plant in a desertic area, but we are satisfied with our decision. It has led to some savings, and now the average cost price is lower than the cost price obtained in our factories located on the sea-side.

Q - Mr. T. KOIVUMAKI (Kemira Oy, Finland)

1/ You have used cooling towers to cool the recycled water and these evaporate 135 m³/h of water. Why do you not use cooling systems that do not evaporate water like air cooling or ammonia or freon?

Is it a question of investment cost?

A - Before building the plant, we studied air cooling, but the size of the air-cooled exchangers would have been like a football ground and the cost was of course excessive.

As far as ammonia is concerned, we do not use ammonia on that site.

Q - Mr. P. BECKER (Duetag, France)

1/ What was, approximately, the increase of that corrosion rate due to the mixing of brackish water with fresh water and the resulting increase in chloride content?

2/ What is the type of soil where you made your gypsum pile? Have you any idea of water evaporation and leaching? Did you use any means

.../.../...

to make your pond impervious ?

A - 1/ SIAPE operates with a level of chloride in the range of 1100 ppm. In ICG, even with the current mix of water, the chloride level is lower, in fact less than half the SIAPE level. Of course, exceptionally and only to avoid a shut-down of the plant, we have used quantities of brackish water bringing the chlorine level up to 2000 ppm, but this was for very short periods and we have not measured the corrosion rates at those periods.

2/ We did not use any artificial process to make the soil impervious, and during the first months, all the water was leached into the soil, but after a while, the gypsum itself has become impervious and we have been able to recover and recycle water that is used to pulp the gypsum. This is a self sealing procedure.

**HIGH QUALITY GRANULAR AMMONIUM
SULPHATE PRODUCTION**

Milt Fischbein
Esso Chemical Canada, Alberta Canada

A. M. (Tony) Brown
Incitec Ltd., Brisbane Australia

PRESENTED TO THE IFA CONFERENCE
EDMONTON, CANADA, SEPTEMBER 1988

by
Milt Fischbein

SUMMARY

In 1986 Esso Chemical's market research group identified a need for a form of sulphur which was to have the following characteristics:

- a) The sulphur had to be in the sulphate form so that it would be readily available to the crops as a nutrient.
- b) It had to have physical characteristics that would make it easy to handle and apply with conventional farming equipment.
- c) It had to be size compatible and readily blendable with existing products such as MAP and Urea, and could not segregate during shipping and handling.

It was felt that the only product which would have all of these characteristics was a granular form of ammonium sulphate.

A world wide search was carried out by Esso Chemical Canada's Agricultural Chemicals Technology Division New Products Group, to determine if such a product was being commercially produced. Incitec, an Australian company, was the only commercial producer identified.

In the summer of 1986, Esso purchased Incitec's technology and in December of 1986, nine months after the initial "New Product" suggestion was brought forth, Esso was commercially producing a high quality granular ammonium sulphate. The product has been in commercial production ever since.

HISTORY

Ammonium sulphate was originally produced as a by-product from the coking of coal, the refining of nickel, and also from the production of caprolactum. The synthetic production of ammonium sulphate became popular just before World War I when ammonia became commercially available in large quantities.⁽¹⁾ Currently about 47% of the world's ammonium sulphate is synthetically produced, the rest is produced as a by-product.⁽¹⁾

By-product crystalline ammonium sulphate was initially used as an inexpensive source of nitrogen. As more concentrated forms of nitrogen, such as urea with 46% nitrogen and ammonium nitrate with 34% nitrogen became available, ammonium sulphate became less popular as a nitrogen source. Currently, ammonium sulphate is becoming popular as a source of "plant available" soluble sulphur. It has found particularly strong acceptance in Western Canada, as a sulphate source for canola crops.

In North America, virtually all tonnage quantities of ammonium sulphate are produced as by-product. The largest producer is Allied-Signal, who manufactures about 1,200,000 metric tonnes per year, or 36% of the 3,350,000⁽¹⁾ tonnes produced annually in North America.

In Western Canada there are three producers of ammonium sulphate: Sherritt Gordon Mines, which has a capacity of 200,000 tonnes of by-product crystalline ammonium sulphate per year; Cominco, with an annual capacity of 125,000 tonnes of by-product crystalline ammonium sulphate; and Esso Chemical with an annual capacity of about 225,000 tonnes of synthetic granular ammonium sulphate.

Esso Chemical Alberta Limited is the only commercial producer of synthetic granular ammonium sulphate in North America. All other North American producers manufacture by-product ammonium sulphate in the crystalline form.

Granular products have a distinct advantage over crystalline products because of their superior blending and handling characteristics.

Over the last three decades there have been numerous attempts at producing a high quality granular ammonium sulphate. In 1964, Burns patented a process for granulating synthetic ammonium sulphate in a drum granulation plant where fresh ammonia and sulphuric acid were fed to, and reacted in, a conventional granulator.⁽²⁾ TVA patented a process in 1969 which was analogous to the pre-neutralizer process currently used to manufacture DAP.⁽³⁾ Sulphuric acid and ammonia were reacted in a pre-neutralizer to a mole ratio of 1.1 to 1, N to S. This highly corrosive mixture was then pumped up to the granulator where further neutralization was carried out.⁽⁴⁾ Due to a variety of problems including high corrosion rates and unstable granulation, neither of these processes is in commercial use today.

As the abundance of small sized by-product crystalline ammonium sulphate increased, attempts were made to co-granulate these crystals into granules to improve their quality and make them more saleable. TVA has recently developed a process in which crystalline ammonium sulphate is co-granulated with fresh sulphuric acid and ammonia. This final product contains about 80% by-product crystals and the other 20% is made up of fresh reactants.⁽⁵⁾ This process was recently commercialized in the United States, but has been experiencing some start up problems.⁽⁹⁾

In 1977, Incitec, an Australian company, developed a pipe reactor process for producing a high quality granular ammonium sulphate in a conventional drum granulation plant. They have been using this process commercially for over ten years at two Australian granulation plants, and currently produce over 100,000 tonnes per year.

In 1986, Esso Chemical licensed ammonium sulphate technology from Incitec. The plant was started up in December of 1986, and Esso has been producing granular ammonium sulphate ever since. Esso and Incitec have made a number of improvements to the original process and as a result have jointly filed patent applications on both the improved process and the improved product.

PROCESS DESCRIPTION

Incitec's process was retrofitted into Esso's conventional drum type granulation plant which, at that time, was only producing MAP. The retrofit was designed such that both ammonium sulphate and MAP can be made on the same granulation train, with very little downtime required to switch product grades.

The process as described below is typical of the one used at Esso's plant in Redwater and both Incitec plants in Australia.

The process is shown in Figure #1. The conventional pre-neutralizer has been replaced by a pipe reactor with a mixing tee. Scrubber liquor and ammonia are combined in the first stage of the mixing tee. This mixture is then further combined with sulphuric acid in the second stage of the mixing tee, and is fed to the pipe reactor where the reaction runs almost to completion. The resulting ammonium sulphate/bisulphate slurry then discharges onto the granulation bed which contains recycled fines and crushed oversized particles. Ammonia is fed into the granulation bed via a sparger, to bring the bed up to the final mole ratio of 2:1, N:S. The product then exits the granulator and is fed to conventional drying, screening, recycle, and cooling equipment.

Flashing steam and ammonia slip are exhausted to the scrubbers, which are maintained slightly acidic by the addition of sulphuric acid to the scrubber liquor circulation tank. The scrubber liquor is then recycled back to the pipe reactor mixing tee. An additive is introduced into the granulator to promote good granulation.

The process was designed to produce 30 tonnes per hour. This rate has been commercially demonstrated and uprates of up to 50 tonnes per hour are feasible with some equipment modifications. Both of the Australian plants were originally designed to operate at 15 tonnes per hour but they have since been uprated. The Gibson Island Plant produces 35 tonnes per hour, and the Greenleaf Plant produces 20 tonnes per hour. Further uprates are planned as needed to meet market requirements.

PROCESS CONTROL

The granulation of ammonium sulphate is a docile, easily controlled operation. Control of the granulator is obtained by adjusting liquid feeds to the mixing tee and not by control of the solids recycle ratio. The solids recycle ratio is typically in the range of 3:1 to 10:1. The recycle ratio is generally determined by granulation efficiency and size requirements, and not by moisture limitations in the granulator.

While control of the process is relatively simple, straying outside of the specified control range can result in one of the following two conditions:

- a) Product size in the granulator is lost, and the plant begins to fill up with fine sulphate dust which can slip through the scrubbing system. In this situation, it is often necessary to dump the contents of the solids system and reseed the plant to start up again.
- b) A hard, good-looking product will be produced, but after a few days it will set up solidly in the storage building and require extreme measures to break it up.

UTILIZATION OF WASTE STREAMS

The process chemistry is simple and well documented in the literature.



The highly exothermic nature of this process yields some interesting advantages. The reaction liberates enough heat to evaporate about 0.7 tonne of water for every tonne of product produced. The plant can, therefore, consume significant quantities of dilute aqueous streams such as waste sulphuric acid, aqueous ammonia, or ammonium sulphate liquor. In fact, one of Incitec's plants was successfully retrofitted to consume aqueous ammonia from an adjacent urea plant. This resulted in a considerable amount of energy savings, as steam was no longer required to strip the ammonia from this solution.

A computer model, developed by Incitec, has shown that a 30 tonne per hour ammonium sulphate plant can consume approximately 20,000 kilograms per hour of 20% aqueous ammonia from a urea plant, or about 18,000 kilograms per hour of ammonium sulphate liquor from a by-product plant. Incitec's simulation can be utilized to determine the effects of introducing other aqueous streams into the pipe reactor.

PRODUCT QUALITY

The granular ammonium sulphate produced by this process is hard, low in dust levels, consistent in size, free flowing, and non-caking. Esso's major objective in producing a high quality granular ammonium sulphate was to produce a granule which would be completely blend compatible with Esso's other granular products. The problem with local crystalline ammonium sulphate is that it tends to be small and irregularly shaped and will not blend uniformly with other products such as urea and ammonium phosphate. Once blended, crystalline ammonium sulphate will segregate during handling. This results in unpredictable, non-homogeneous blends being applied to the fields, causing non-uniform distribution of nutrients to crops. Esso's granular ammonium sulphate does not segregate from blends during handling and, therefore, always results in consistent uniform distribution of nutrients to crops.

Table #1 shows the size distribution range and size guide numbers (SGN) of various North American ammonium sulphates versus granular urea. Products whose SGN vary more than 10% will tend not to blend together well.(7) Therefore, in order to form a non-segregating blend with urea, a fertilizer must have a size guide number of about 230-280. Esso's granular ammonium sulphate has a SGN of 253 and, therefore, will blend very well with urea and other quality granular products, while domestic ammonium sulphates have SGN ranging from 123 to 213 and will segregate during handling.

Figure #2 is a representation of what happens to a typical 50/50 blend of crystalline ammonium sulphate and MAP after some handling. The blend has segregated badly. The blend in Figure #3 is 50/50 granular ammonium sulphate and MAP. This blend did not segregate during handling.

Esso's granular ammonium sulphate has a crush strength two times as high as any other granular ammonium sulphate reported in literature. In addition, it is low in dust levels, it is free flowing, consistent in size, and does not cake in storage.

In Australia, Incitec's granular ammonium sulphate is sold at a premium price over crystalline sulphate and has virtually displaced the traditional crystalline sulphate market. Because of its unique non-caking characteristics, it is blended with super phosphates and used as an alternative to DAP, especially where sulphur deficiency occurs. Table #2 shows a comparison of Incitec's granular ammonium sulphate size versus other Australian products. Note that the typical Australian product is smaller than typical North American product.

Demand for Esso's product has increased steadily since initial start-up 22 months ago.

This strong market demand demonstrates the farmers desire for a high quality, free flowing, non-caking, blend-compatible source of ammonium sulphate.

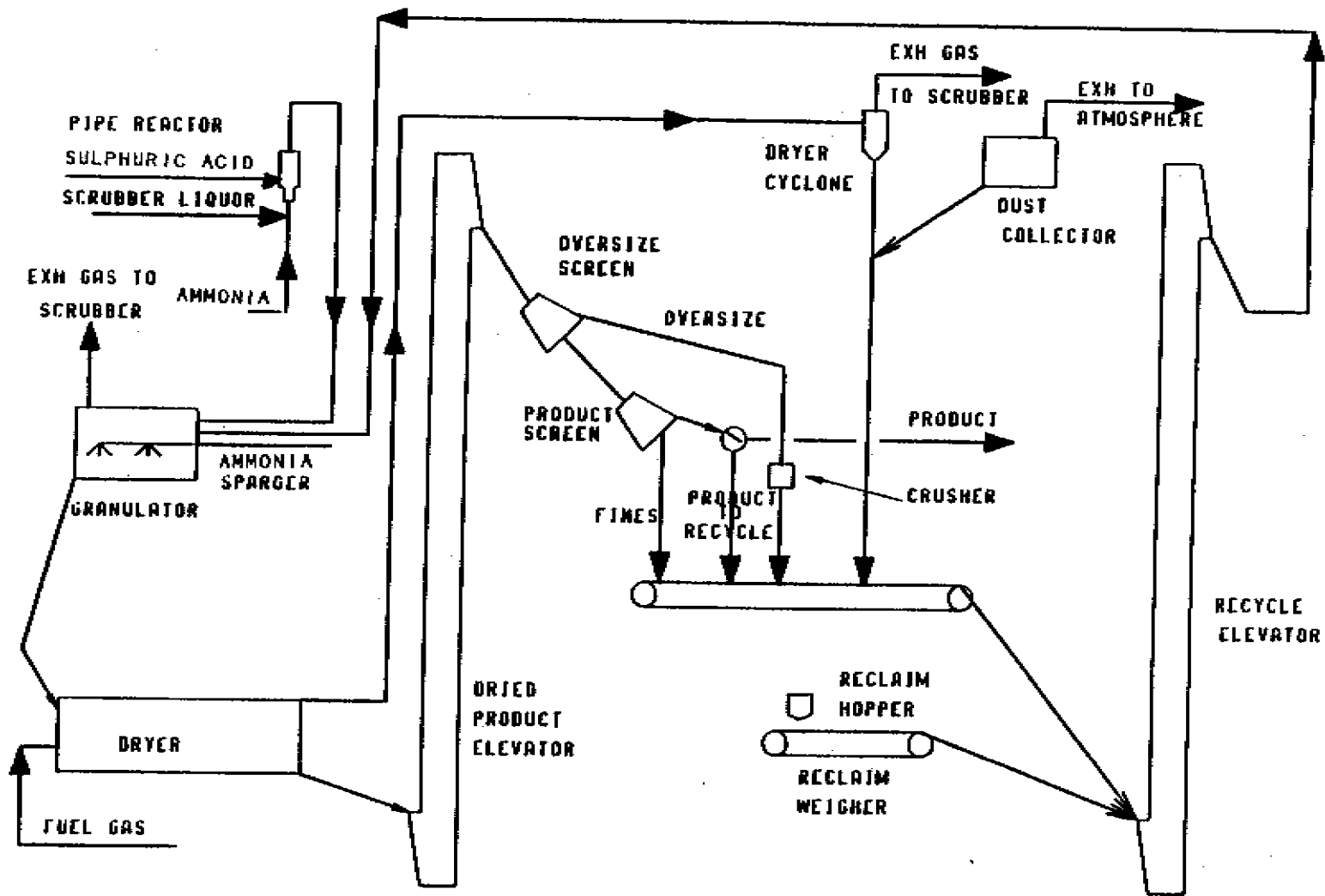
PRODUCT AND PROCESS IMPROVEMENT

Esso has worked to dramatically improve the quality of their granular ammonium sulphate. As shown in Table #2, Australian product size requirements are smaller than in North America. Therefore, Incitec had no need to produce larger product, because there was no market demand for it. When Esso approached Incitec, to purchase their technology, it was recognized that the product size would be an issue. To resolve this concern, Esso worked improve the process and thus the quality of the product. The result of this effort was a larger, harder, rounder granular ammonium sulphate than ever before produced, which was still free flowing and non-caking. This is shown in Table #3 which compares Esso ammonium sulphate to original Incitec ammonium sulphate.

Esso and Incitec have jointly filed patents on the improved product and on the process improvements which have been made to Incitec technology.

LIST OF REFERENCES

1. Ammonium Sulphate: Past Performance, Future Prospects, British Sulphur
2. Burns, W. L., Ammonium Sulphate - Ammonium Bisulphate Fertilizer and Method of Making. U. S. Patent #3,351,455 Nov. 7, 1967
3. Hicks, G. C., Process for Production of Granular Ammonium Sulphate, U. S. Patent #3,464,809 Sept. 2, 1969
4. Hicks, G. C. et al, Development of a Granular Ammonium Sulphate Process, Agriculture and Food Chemistry,, Vol 17, No. 2
5. Granular Ammonium Sulphate from By-Product Crystals, TVA Article
6. Harrision et al, Granulation of Crystalline By-Product Ammonium Sulphate, U.S. Patent #4,589,904 - May 20, 1986.
7. Canadian Fertilizer Institute, The CFI Guide of Material Selection for the Production of Quality Granular Blends.
8. Allied Chemical, Product Guide, SULF-N45
9. Peru Indiana: Ammonium Sulphate Plant Stopped After Emissions Problem, Green Markets July 11, 1988
10. Peru Ag. Products, Products Guide, G-N-S.



PROCESS FLOWSHEET

FIGURE 1

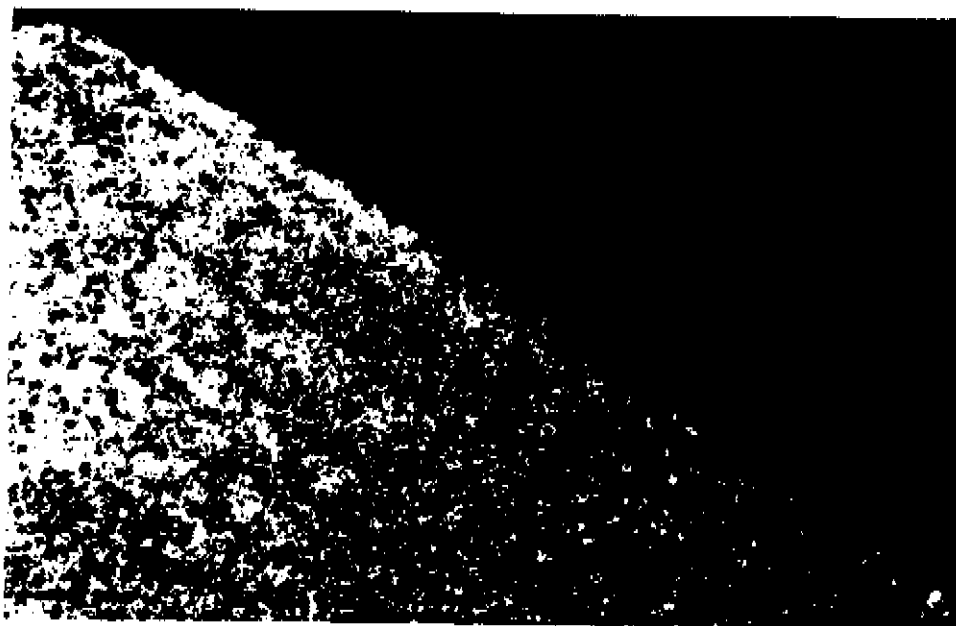


FIGURE 2 Here's a typical blend with regular 21-0-0-24 crystalline ammonium sulphate. Segregation is evident.

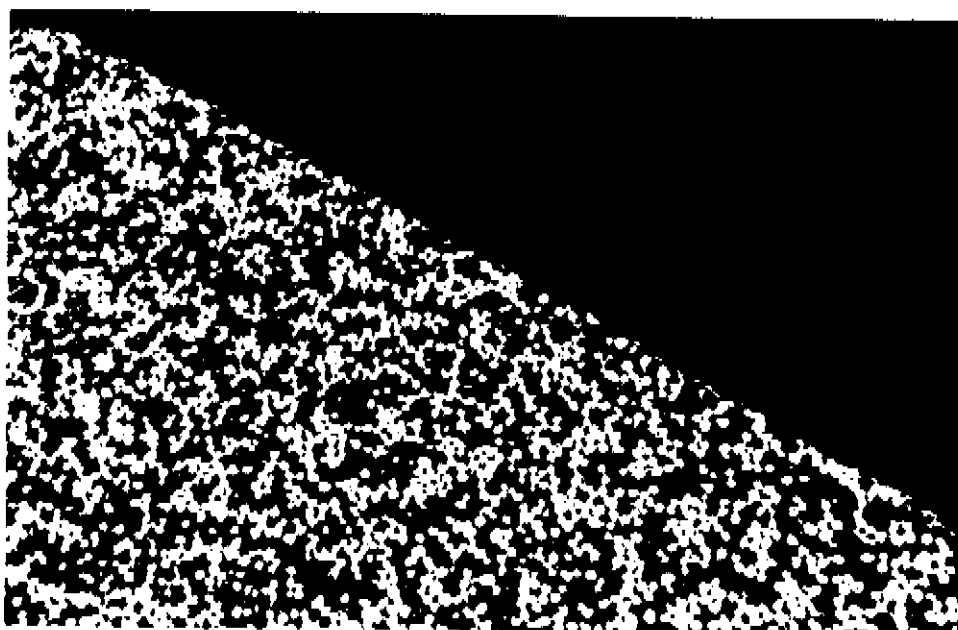


FIGURE 3 Minimal segregation of 20-0-0-24 ENGRO granular ammonium sulphate blend due to similar granule size.

Table #1

AMMONIUM SULPHATE PRODUCT QUALITY COMPARISON

Cumulative Particle Size Distribution		<u>Esso Granular Urea</u>	<u>Esso Granular Ammonium Sulphate</u>	<u>Domestic Crystalline Ammonium Sulphate</u>	<u>Imported Screened Crystalline Ammonium Sulphate⁽⁸⁾</u>	<u>TVA Granular Ammonium Sulphate</u>
<u>MM</u>	<u>Tyler Mesh</u>					
+3.4	(+6)	1	4	0	4-10	-
+2.4	(+8)	60	61	8	15-40	-
+1.7	(+10)	98	97	-	40-70	-
+1.4	(+12)	100	100	55	80-90	-
+1.0	(+16)	Tr	Tr	85	95-99	95(10)
+0.6	(+28)	-	-	98	-	-
Size Guide Number		255	253	123	155-213	220(10)
Crush Strength (Kg) Pfizer Hardness -2.4MM +2.8MM		-	4.5-5.7	-	-	2.3(6)

Table #2

AUSTRALIAN PRODUCT SIZE COMPARISON

Cumulative Particle Size Distribution		<u>Incitec Prilled Urea</u>	<u>Incitec Granular Ammonium Sulphate</u>	<u>Australian Crystalline Ammonium Sulphate</u>
<u>MM</u>	<u>Tyler Mesh</u>			
+3.4	+6	-	3.5	0
+2.8	+7	1.5	10	0
+2.0	+9	39	45-75	0
+1.7	+10	67	80	1.0
+1.4	+12	89	90	-
+1.18	+14	95	95	10
+0.85	+20	99	99	19
+0.5	+32	100	100	50
+0.25	+60	-	-	90
SGR		187	196	50

6 - 11

Table #3

**COMPARISON OF ESSO'S GRANULAR AMMONIUM SULPHATE
TO INCITEC'S GRANULAR AMMONIUM SULPHATE**

Cumulative Particle Size Distribution		Esso (Improved Grade) <u>Granular Ammonium Sulphate</u>	Incitec (Regular Grade) <u>Granular Ammonium Sulphate</u>
<u>MM</u>	<u>Tyler Mesh</u>		
+3.4	+6	4	3.5 maximum
+2.4	+8	61	10
+2.0	+9	-	45-75
+1.7	+10	97	80
+1.4	+12	100	90
+0.85	+20	-	99
SGN		253	196
Pfizer Hardness (Kg) -2.4 +2.8		4.5-5.7	1.6-3.1
% Water		0.1	0.1-0.2

**CADMIUM IN THE SOIL-PLANT-HUMAN ENVIRONMENT
A SHORT REVIEW**

O. Gunnarsson, Supra, Sweden

RESUME

Mining and processing of phosphate rocks to fertilizers may be considered as a transfer of the essential element phosphorus from biologically passive to biologically active reservoirs (from rocks/mines to soils, plants, animals and human beings). But "impurities" in the rocks such as cadmium may also unintentionally be transferred to biologically active reservoirs where they may cause harmful effects on organisms.

About the toxic effects of cadmium on human beings the kidney is the critical organ first showing pathological symptoms. Severe bone diseases is a result of very high doses.

Acute toxicity of cadmium caused by heavy exposure is well known since long but is rare today since we know how to avoid it.

The problem that concerns medical scientists today is instead possible effects of comparatively low but long term exposure due to "normal" intake via food, water, inhalation and smoking.

Food is probably the most important cadmium source for the normal population at least for non smokers. Food originates directly or indirectly from plants.

Considering cadmium content of plants there is a very wide variation among species and also between different botanical parts of a plant.

Plants take their cadmium mainly from the soil but also to some extent directly from the atmosphere.

The reactions of cadmium in soils are very complex and there is no simple relation between plant uptake and amounts in the soils. The pH of the soil is an important factor. Low pH means high availability and high pH the contrary. All other plant and soil factors equal the plant uptake increases as the amount in the soil increases.

There is always a considerable but widely varying "natural" content of cadmium in soils due to geological background. But agricultural soils also receive new cadmium from different sources -atmospheric deposition, manure, sludge and phosphate fertilizers. As an average this total input exceeds the net output via agricultural products and leaching in most industrialized countries. That means - at least theoretically - a slow long term accumulation. Cadmium in fertilizers is probably not the most important input. Its effects on plant uptake has proved to be insignificant in long term field experiments with normal fertilization.

The cadmium input via fertilizers is not an acute health problem but the long term effects of a slow accumulation in the soils are worrying environmental and medical authorities and there is an increasing pressure on the industry to reduce the cadmium content of fertilizers.

ECOLOGICAL ASPECTS

Global ecological models consider chemical elements as belonging to either **biologically passive** (unavailable to organisms) or **biologically active** (available to organisms) reservoirs.

The activity of the fertilizer industry may from an ecological point of view be considered as a transfer of essential elements (nitrogen, phosphorus, potassium, sulphur and so on) from biologically passive reservoirs (atmosphere, rocks/mines) to biologically active reservoirs (soils, water, plants, animals, human beings). This transfer has generally been of very great value to mankind. The activity has made it possible to produce more and better food and fibre. Increased fertilizer use has been and is an essential prerequisite for feeding the increasing world population.

During the last decades, however, some negative consequences of this transfer has been paid increasing attention. One is that plant nutrients (specially nitrogen and phosphorus) may leak to ecosystems such as water sources where they have caused pollution and eutrophication. The role of fertilizers for pollution and unwanted eutrophication of water sources is however far from clearcut but will not be discussed further here.

Another environmental and health problem related to fertilizer use is that essential elements in the passive reservoirs may be mixed with elements which are harmful to plants, animals and human beings even in very small amounts. These biologically harmful elements may also (unintentionally) be transferred to soils and plants during the industrial and agronomic operations. Cadmium in rock phosphate is one example of such an element (Figure 1).

But cadmium is also transferred to biological active reservoirs via combustion of fossile fuels and via mining of other cadmium containing minerals and use for a number of industrial purposes such as metal alloys, colour pigments, plastic stabilizers and batteries. Production and consumption of these products have increased considerably since the beginning of this century. Only a minor part is recycled. Some of it has in one way or another contaminated the biological active reservoirs. Thus atmosphere carried cadmium is deposited on plants and soils. Compared to cadmium released from combustion and industrial uses the total content of phosphate fertilizers is small but it is more or less directed to a sensitive system - the food chain.

MEDICAL BACKGROUND

The fundamental biochemical and physiological effects of cadmium are at best incompletely understood. The toxic effects are thought to be performed by the cadmium ion (Cd^{2+}) which has similar chemical properties as zinc ions. Zinc ions play an essential role in many enzymatic systems. As zinc ions are replaced by cadmium ions these enzymatic processes are inactivated.

Human beings are exposed to cadmium from a large number of different sources. Considered one by one their effects may be negligible but the integrated effect of them all may be significant.

The main routes of exposure are inhalation and ingestion (Figure 2).

Absorption after inhalation varies between 10 and 60% depending on particle size.

The average absorption after ingestion is of the order 5%, but varies due to diet conditions. Thus low calcium intake, low vitamin D intake and low protein intake may increase the intestinal absorption up to 20-30%.

Figure 2 shows the various chronic effects developing with increasing doses. The kidney is the organ first showing pathological symptoms. Severe bone diseases is a result of very high doses.

Acute toxicity of cadmium in human beings due to comparatively heavy exposure is well known since long.

High incidence of illness among industrial workers exposed to heavy cadmium oxide exposure is well documented. Well known is also the "Itai-itai" disease in Japan where heavily cadmium polluted water from mining and melt activities was used for irrigation of rice which was an important part of the diet of the affected population. Unsatisfactory intake of protein, calcium and vitamin D was probably cofactors for the development of this disease.

Such acute cases as mentioned above are however rare and can be avoided based on today's knowledge.

The problem that concerns medical and environmental scientists today is instead possible effects of comparatively low but long-term exposure to cadmium due to "normal" intake via food, water, inhalation and smoking.

Cadmium has a long biological halflife in the human body (10-40 years). That means that it is accumulated up to an age of about fifty. The accumulation takes place especially in the liver and in kidney cortex. The content of the kidney cortex is often used as a criteria of exposure. 200 g Cd per gram wet weight of

kidney cortex is considered to be a critical content above which pathological changes may appear. The average content of cadmium in kidney cortex is of the order $50 \mu\text{g}/\text{gram}$ wet weight for 50 year old individuals in industrial countries but it has been shown that this content has increased considerably during the last 100 years. There is also a wide variation among countries and among individuals and it may be postulated that some people have reached or passed the critical value $200 \mu\text{g}$ (Figure 4). It is also postulated that the number of individuals reaching the critical value will increase if nothing is done to reduce cadmium pollution in biologically active ecosystems.

CADMIUM IN PLANTS AND SOILS

Food is probably the most important cadmium source for the "normal" population (at least for non-smokers). Food originates directly or indirectly from plants.

Figure 5 shows averages and ranges of Cd-concentrations in dry matter of a number of agricultural and horticultural crops in Finland.

There are very large differences in cadmium content among different agricultural plants. The content also differs between botanical parts of the plant. The content is generally higher in roots and vegetative parts than in fruits.

It has also been shown that there are differences between varieties of the same crop, for example between wheat varieties. Striking also is the wide yearly variation for the same crop grown on the same soil. Comparatively wet climate seems to give higher content than dry conditions.

Plants take their cadmium mainly from the soil but also to some extent directly from the atmosphere.

Cadmium and zinc have a similar chemistry and are often found together in approximately the same proportions in geochemical and biochemical systems. A danish experiment indicates that a grasscrop received 30-40% of its cadmium from the atmosphere by leaf absorption.

Soil reactions of cadmium are very complex. The exchangeable cadmium (as Cd^{2+}) in the soil is considered to be the primary source of the plants. But there is no simple relation between uptake and the exchangeable amounts. The availability is dependent on many factors. Especially pH should be mentioned. Availability increases with decreasing pH.

Figure 6 shows the effect of increased amounts of Cd applied as sludge and of liming (= increasing pH) on content of Cd in fodder rape. The effect of increasing amounts applied to the soil is nearly linear but moderate. Increasing pH from 4,8 to 6,0 reduced cadmium uptake to less than half. The effect of increasing pH further from 6,0 to 7,2 was less but obvious.

Antagonism and synergism between cadmium ions and other ions in the soil influence also availability and uptake.

As is obvious from the above discussion the plant uptake of cadmium is influenced by many factors. In general, however, increased amounts in the soils means increased uptake.

Considering the content of cadmium in agricultural soils (surface soil 0-25 cm) there is a very wide variation. For "normally" cultivated and fertilized soils the main part of the content may be considered as "natural". Accounted for as gram per hectare there was found a range from 100 to 3000 for Swedish soils (Figure 7). The average content was 550 g/hectare but no significant difference was found between cultivated (= fertilized) and uncultivated (= unfertilized) soils.

On the other hand it has been shown by extensive and careful soil analyses from long term field experiments that fertilizer applied cadmium over 17 years is accumulated in the soils (Figure 8). The estimated total input was accounted for very well. Half of it remained in an easily soluble form compared with 25% easily soluble of the total "natural" background content. But the increased soil content had very small if any influence on the content of wheat grain grown in the field experiments. (See the lowest line in Fig 8).

The agricultural soils receive cadmium from different sources : phosphate fertilizers, atmospheric deposition, manure and sludge. Locally the amounts put in via sludge may be considerable : 10-15 g/hectare and year. Input via manure can partly be considered as an internal circulation but the cadmium content in imported feeding stuff means a net input to the soil. The atmospheric deposition may be considerable - in the order 1-6 g per hectare and year. But there are indications based on concentration of cadmium in moss (Figure 9) that the atmospheric deposition has decreased during the last 10-15 years in Sweden. The content 1985 was only about half of what it was 1975. This is probably a result of improved cleaning of industrial and combustion effluents.

Referring to Swedish circumstances the cadmium input via phosphatic fertilizers was of the order 3-4 g/hectare and year in the early seventies. Now it is of order 1-2 g. That is the result of lower cadmium content of the fertilizers but also of decreased phosphorus fertilization.

The yearly input via fertilizers can be compared with content of exchangeable cadmium in the surface soil (0-25 cm) - for Sweden 1-2 g as compared to 550 g. That means a yearly increase of 0,2-0,4% of the soil content. From this it is obvious that the short term effect of "normal" input cadmium via fertilizers on the cadmium content of the plants will be practically impossible to detect.

The yearly output of cadmium via products which are leaving the agricultural system is of the order 0,5-3 g per hectare depending on yield level and type of agriculture. In most cases the output is less than the total estimated input and this leads to the conclusion that there is a slow accumulation of cadmium in the agricultural soils of industrialized countries.

CONCLUSION

Due to its toxic effects on the human organism cadmium is not wanted in agricultural plants which are entering the food chain. It is, however, not possible to grow plants without uptake of cadmium. There is always a background level in the soils - natural or created by human activities. A reasonable goal, however, is to keep balance between input to and output from the agricultural system and not to increase the cadmium content of the soils. Balance sheets indicate that this is not the case today on many soils in industrialized countries. The input seems to exceed the output and a slow accumulation may be postulated.

The cadmium content of fertilizers is probably not the most important input of cadmium to soils and its influence on the cadmium intake of human beings is probably negligible at least for the nearest decades. Nevertheless it is a part of unwanted total input and there is at least in Sweden an increasing pressure from environmental groups and even medical and environmental authorities on the industry to reduce the cadmium content of fertilizers. Their reason for this is a supposed long-term accumulation of cadmium in soils and increased plant uptake in the future.

Litterature

Friberg Lars, Elinder Carl-Gustaf, Kjellström Tord,
Nordberg Gunnar F: Cadmium and health: a toxicological and epidemiological appraisal.
Vol I : Exposure, Dose and Metabolism.
Vol II: Effects and response
CRC Press, Inc. Boca Raton, Florida, 1985.

Gunnarsson, Olle: Heavy metals in fertilizers, do they cause environmental and health problems?
Fertilizers and Agriculture, nr 85, sept 1983.
IFA Ltd, 28 rue Marbeuf-75008 Paris.

Nriagu, Jerome O: Cadmium in the environment.
Part I: Ecological Cycling.
John Wiley & Sons. New York Chichester, Brisbane Toronto, 1980.

Cadmium in the soil-plant environment. Lectures and discussions at a conference at the Royal Swedish Academy of Agriculture and Forestry on furse 5th 1980. Report nr 4. Stockholm 1980.

Kadmium i miljön - Bedömningsgrunder.
Naturvårdsverket. Rapport nr 3317, 1987.

Monitor 1987 - Naturvårdsverket informerar: Tungmetaller - förekomst och omsättning i naturen.

National institute of public health on environmental hygiene, Bilthoven, The Netherlands.
Appendix to report nr 758476002.
Integrated criteria document cadmium.
Effects, July 1987.

TFI Cadmium seminar Nov 20-21, 1980.
Rosslyn, Virginia
The Fertilizer Institute, 1015 18th, St N.W.
Washington, D C 20036, Dec 1980.

CADMIUM CONCENTRATIONS IN NATURALLY OCCURRING RAW PHOSPHATE OBTAINED FROM DIFFERENT COUNTRIES^{59,93}

Country	Cadmium concentration in phosphate rock (mg/kg)	Cadmium concentration in relation to the phosphate (P ₂ O ₅) content (mg/kg)
U.S. (Florida)	5.5—16	18—52
Morocco	8—30	24—96
Senegal	70—90	225—290
Togo	50	161
U.S.S.R. (Kola)	0.1—0.4	0.3—1.3
Tunisia/Algeria	—	60
Israel/Jordan	—	35

Source: Cadmium and Health a toxicological and Epidemiological appraisal. Volume I. Exposure, Dose, and Metabolism

Lars Friberg, Carl-Gustaf Elinder, Tord Kjellström
Gunnar F. Nordberg

DOSE-EFFECT RELATIONSHIPS FOR CRONIC EFFECTS OF CADMIUM

DOSE	EXPOSURE ROUTES	
	INHALATION (AIR, GASES, SMOKE)	INGESTION (FOOD, DRINKING WATER)
LOW ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ HIGH	SLIGHT RENAL TUBULAR DAMAGE SLIGHT LUNG FUNCTION CHANGES RENAL STONES PROGRESSING RENAL DAMAGE CHANGES IN C AND VITAMIN D METABOLISM OBSTRUCTIV LUNG DESEASE PROSTATIC CANCER ? LUNG CANCER ? ANAEMIA UREMIA OSTEOMALACIA AND OSTEPORISIS	SLIGHT RENAL TUBULAR DAMAGE DECREASE IN INTESTINAL CALCIUM ADSORPTION PROGRESSING RENAL DAMAGE INTENSTINAL MUCOSA DAMAGE ANAEMIA OSTEOMALACIA AND OSTEPOROSIS

OG/1988-08-29

SOME MEDICAL DATA ON CADMIUM

CRITICAL LEVEL IN KIDNEY CORTEX GIVING DETECTABLE PROTEIN URIA	~ 200 µG/G WET WEIGHT (RANGE 150-400)
--	--

WEEKLY INTAKE OVER A 50- YEAR PERIOD ESTIMATED TO GIVE THE CRITICAL LEVEL IN KIDNEY CORTEX	~ 1400 µG/WEEK
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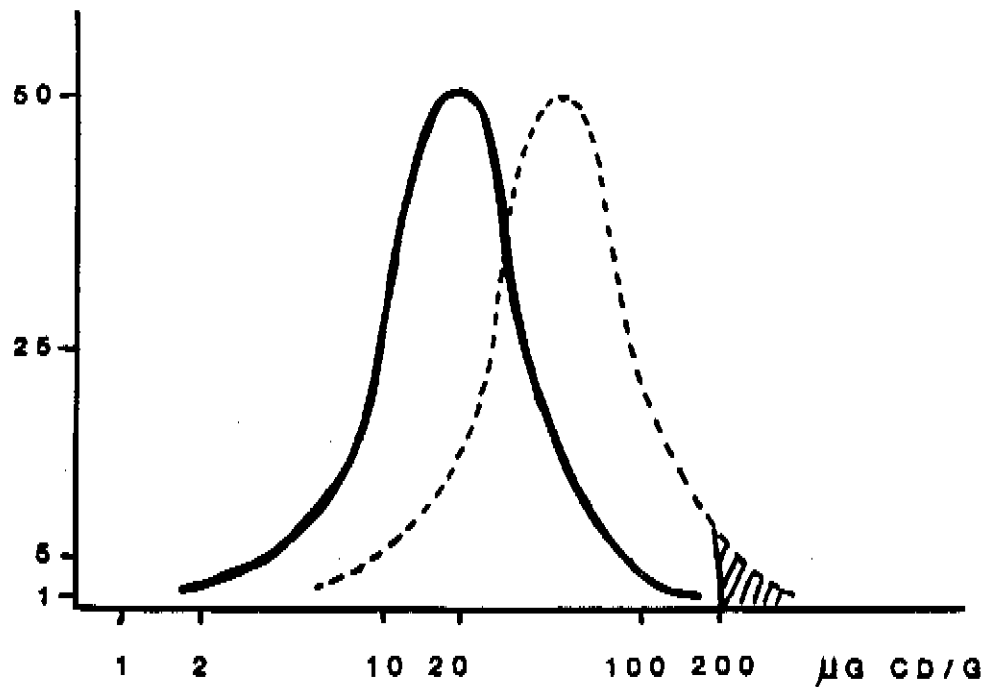
MAX-INTAKE RECOMMENDED BY WHO	400-500 µG/WEEK
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ESTIMATED AVERAGE WEEKLY INTAKE
IN SOME COUNTRIES.

	<u>µG/WEEK</u>	<u>REFERENCE</u>
UNITED STATES	273	COMPILANCE PROG. EVALUATION 1974
CANADA	364	KIRKPATRICK AND COFFIN, 1977
WEST GERMANY	336	EPA - 600/6-75-003
RUMANIA	266-448	"-"
CZECHOSLOVAKIA	460	"-"
JAPAN (UNPOLLUTED AREA)	392	"-"
SWEDEN	119	KJELLSTRÖM, 1978

FREQUENCY DISTRIBUTION OF Cd CONCENTRATIONS IN KIDNEY CORTEX IN SWEDEN 1974 (BLACK LINE) AND HYPOTHETICAL CURVE AT A GEOMETRIC MEAN VALUE OF 50 $\mu\text{g Cd/g}$ (DOTTED LINE). FROM ELINDER, ET AL, 1978.

FREQUENCY %



————— FROM ELINDER ET AL, 1976

- - - - - HYPOTHETICAL CURVE WITH A GEOMETRIC MEAN OF 50 $\mu\text{g Cd/g}$.

CADMIUM CONCENTRATION OF CEREALS AND VEGETABLES BASED ON A FINNISH SURVEY

P VARO, M NUURTAMO, E SAARI AND P KOIVISTOINEN:
MINERAL ELEMENT COMPOSITION OF FINNISH FOODS.

III. ANNUAL VARIATIONS IN THE MINERAL ELEMENT COMPOSITION OF CEREAL
GRAINS. ACTA AGRIC. SCAND. SUPPL. 22, 1980, PP 27-35.

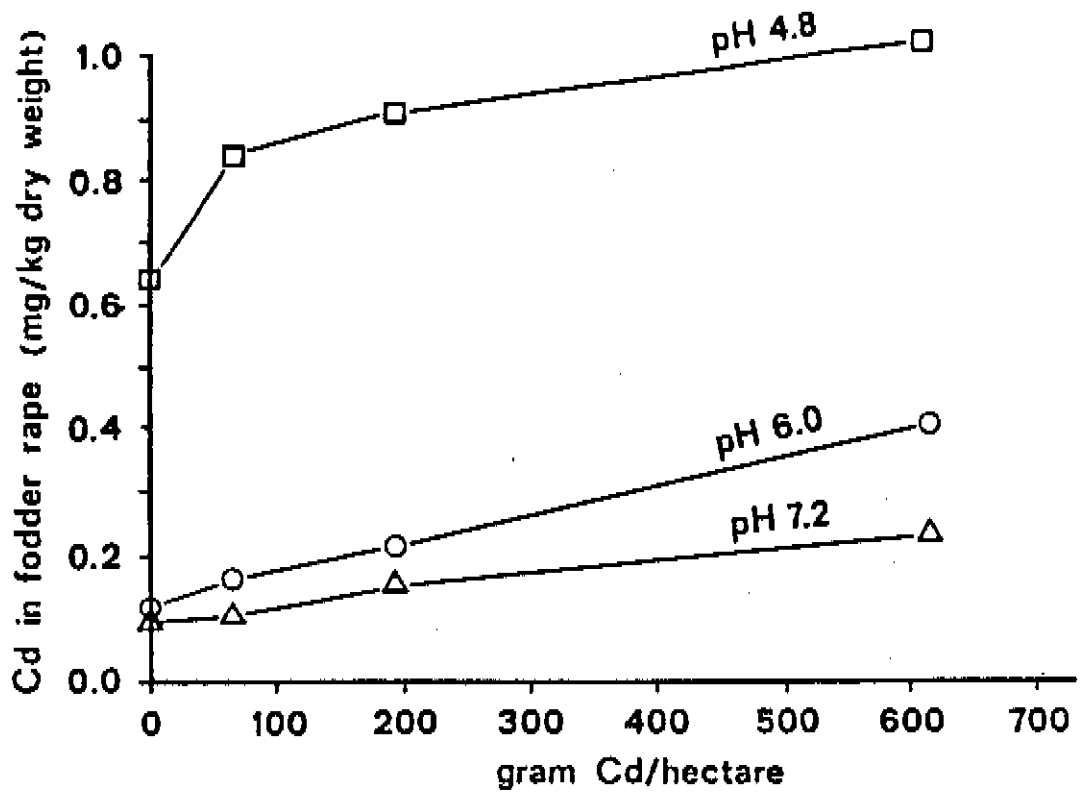
P VARO, O LÄHELMÄ, M NUURTAMO, E SAARI AND P KOIVISTOINEN:
MINERAL ELEMENT COMPOSITION OF FINNISH FOODS.

VII. POTATO, VEGETABLES, FRUITS, BERRIES AND MUSHROOMS.
ACTA AGRIC. SCAND. SUPPL. 23, 1980, PP 89-113.

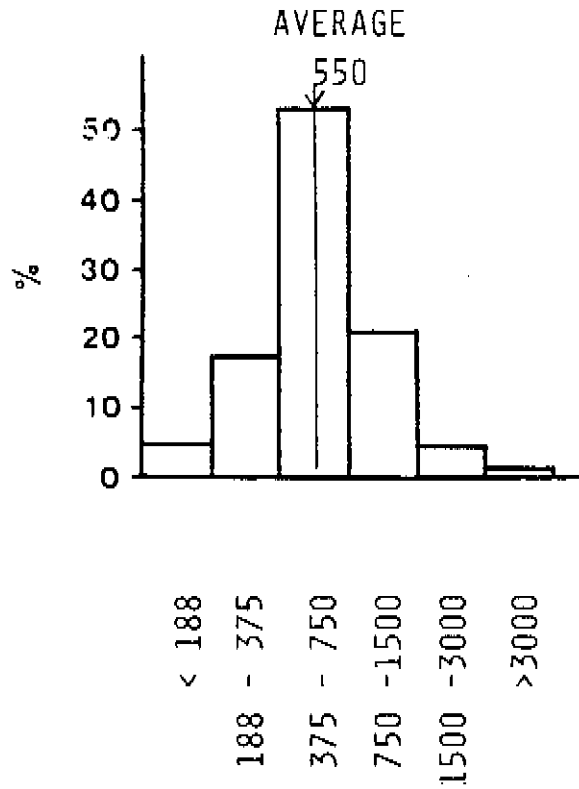
PRODUCT	NO. OF SAMPLES	NANOGRAM CADMIUM/GRAM DRY MATTER	
		AVERAGES	RANGE
GRAIN OF WINTER WHEAT ¹⁾	(34)	74	20 - 99
GRAIN OF SPRING WHEAT ¹⁾	(51)	48	29 - 79
GRAIN OF RYE ¹⁾	(50)	16	5 - 43
GRAIN OF BARLEY ¹⁾	(47)	24	5 - 43
GRAIN OF OATS ¹⁾	(36)	48	5 - 79
POTATO	(20)	50	20 - 100
POTATO, FRESH	(3)	150	100 - 300
CARROT	(5)	273	183 - 364
RED BEET	(5)	250	83 - 333
CABBAGE, WHITE	(5)	63	63 - 125
CAULIFLOWER	(5)	125	37 - 250
LETTUCE	(6)	1000	400 -2000
SPINACH	(4)	2143	714 -5000
ONION, YELLOW	(5)	231	39 - 385
PEASE	(3)	125	4 - 292

1) AVERAGE OF FIVE YEARS (1972-1976)

THE INFLUENCE OF PH ON THE UPTAKE OF CADMIUM IN FODDER RAPE FROM SOILS AMENDED WITH CADMIUM-CONTAINING SEWAGE SLUDGE. (DERIVED FROM ANDERSSON, A. AND NILSSON, K.O., AMBIO, 3, 198-210, 1974.)



FREQUENCY DISTRIBUTION OF CADMIUM IN SWEDISH SOILS. (FROM ANDERSSON, A., SWED. J. AGRIC. RES., 7.7 - 20, 1977.)



Cd/G HECTAR (SURFACE SOIL 0-25 CM)

**CADMIUM ACCUMULATION IN SOLIS DUE TO SUPERPHOSPHATE APPLICATION IN LONG TERM FIELD EXPERIMENTS.
AVERAGES BASED ON ANALYSES FROM 6 FIELD EXPERIMENTS.**

	TREATMENTS			
	A	B	C	D
P-FERTILIZATION, KG/HA/YEAR	0	15	30	45
ESTIMATED CD-APPLICATION, G/HA/YEAR 1)	0	1.65	3.3	4.95
ESTIMATED CD-APPLICATION OVER 17 YEARS, G/HA	0	28	56	84
CADMIUM EXTRACTED FROM THE SURFACE SOIL THE 17TH YEAR 2)				
1. BY 2 N HCL, G/HA (TOTAL?)	913	933	967	1 000
INCREASE RELATED TO A (CONTROL), G/HA	-	+ 20	+ 54	+ 87
INCREASE RELATED TO A (CONTROL), %	-	+ 2.2	5.9	9.5
2. BY AMMONIUM LACTATE/ACELATE, G/HA ("EASILY SOLUBLE")	221	229	250	262
INCREASE RELATED TO A (CONTROL), G/HA	-	+ 8	+ 29	+ 42
INCREASE RELATED TO A (CONTROL), %		+ 3.6	+ 13.1	+ 19.0
"EASILY SOLUBLE" AS % OF "TOTAL"	24	25	26	26
CD-CONTENT OF WHEAT HARVETED THE 15TH YEAR PPB IN DRY MATTER OF GRAIN	107	106	109	111

1) ESTIMATED CD-CONTENT OF USED PHOSPHATES: 110 MG/KG P

2) CALCULATIONS BASED ON THE ASSUMPTION THAT THE SURFACE SOIL OF A HECTAR IS 2.5×10^6 KG.

**REGIONAL DISTRIBUTION OF CADMIUM CONCENTRATION IN MOSS
(HYLOCOMIUM SPLENDERS), MG/KG DRY MATTER (PPM)**

REGION	1968/69	1975	1980	1985
SOUTH WEST SWEDEN	0.89	0.82	0.53	0.41
SOUTH EAST SWEDEN	0.81	0.74	0.51	0.36
MIDDLE EST SWEDEN	0.63	0.65	0.42	0.31
MIDDLE EAST SWEDEN	0.80	0.60	0.49	0.33
NORTH SWEDEN, COAST AREA	-	0.59	0.43	0.29
NORTH SWEDEN, INLAND	-	0.39	0.28	0.18

**SOURCE: MONITOR, THE YEARBOOK OF THE SWEDISH ENVIRONMENTAL
PROTECTION AGENCY 1987.**

APPROXIMATE: 1PPM = 1.5 - 2 G/HA

OG 1988-08-29/BB

nitric acid production - improvements by revamping

R. Schallert, E. Scheibler, M. Thiemann, W. Freitag
(UHDE GmbH, Dortmund, Federal Republic of Germany)

summary

introduction

plant capacity increase and resulting bottlenecks

- **general**
 presentation of diagram 01:
 handling following subjects:
 - investment cost versus plant capacity
 - range of normal design capacity;
 - range of max capacity increase
 - in relation to expected cost

- **origin of additional air supply for capacity increase**
 modification of the air compressor itself
 installation of an auxiliary air compressor
 addition of oxygen

- **expected bottlenecks**
 presentation of diagram 02:
 handling following subjects:
 - main plant equipment and associated pressure drop
 - pressure drop as key parameter for internal energy change of gas streams;
 - possibilities for limiting pressure drop on some equipment for gas flow;
 - effects on waste heat boiler, steam/water side;
 - tailgas turbine, volume stream;
 - absorption tower, hydraulics;

- **example from practice**
 capacity increase with auxiliary air compressor
 debottlenecking by modification of the waste heat boiler
 installation of a second absorption tower
 allocation of several heat exchangers in parallel

- **cost situation**
 investment cost and benefits if the procedure from the above example will be performed stepwise

tailgas treatment

- general
three different methods to achieve reduced NO_x emission within
revamp design
 - installation of a catalytic abatement system
 - extension of absorption volume
 - combination of both
- operating parameters
presentation of diagram 03: NH₃-residue versus NO_x in the
untreated tailgas
handling following subjects: application of the abatement system,
influence on the tailgas turbine,
opacity requirements.
 - presentation of diagram 04: tailgas No_x versus absorption volume
handling following subjects: determining influences and factors
for absorption process
Dynamic Absorption Calculation Method
(DACM)
- combination of catalytic abater / extended absorption volume
presentation of diagram 05: optimum, combination absorption /
catalytic abatement
handling following subjects: an example considering:
additional pressure drop;
additional acid production;
additional ammonia consumption;
total energy, credit or debit;
investment cost.

waste heat recovery

- plant energy analysis
presentation of tables: plant energy import / export
handling following subject: where to find recuperative energy;
energy percentage as part from the
total
 - presentation of diagram 06: recalescence curve, heat exchanger train
handling following subject: use of the process heat for different fluids;
reference to pinch method.
- example, energy tracing
increase of recuperative energy by means of
better material for heat exchangers
alteration of process flow
 - presentation of diagram 07: heat exchanger train, original;
 - presentation of diagram 08: heat exchanger train, revamped;

process control

- general
 optimized process control via computer for:
 unit-operation control;
 unit-process control;
 plant control.
 presentation of diagram 9: functions of a fully computerized control system.
- example
 unit-operation control for:
 tailgas NO_x;
 tailgas oxygen;
 ammonia / air ratio;
 gauze temperature;
 allocation of unit-process control
- expected profits
 energy savings;
 acid production increase;
 better production scheduling;
 better maintenance survey.

conclusions

INTRODUCTION

Due to the deteriorating profits in the fertilizer sector world-wide, producers have for some years been reluctant to invest in new plants.

On the other hand, there has been growing interest to investigate possible modifications of existing plants with a view to improving the energy balance, increasing the capacity within economically reasonable limits and meeting the ever more stringent environmental pollution control requirements.

Revamps have been performed for various types of fertilizer plant including the associated acid production facilities.

This paper illustrates the different revamping options for nitric acid plants using both Uhde and other proprietary processes.

PLANT CAPACITY INCREASE AND THE RESULTING BOTTLENECKS

A production plant cannot be and should not be designed exactly for the specified capacity. It is also good engineering practice to provide a certain design in order to maintain flexibility of plant operation if any design parameters should change. How much over-capacity is provided depends directly on the commercial terms and conditions and the type of plant. Nitric acid plants are usually over-rated by 3 to 5%. Engineering experience has shown that a so-called design generosity in respect of an intended capacity increase is a highly effective option. For better understanding, the relations are presented in

diagram 01 : investment cost versus plant capacity

The diagram is divided into two sections:

normal design capacity (built-in)

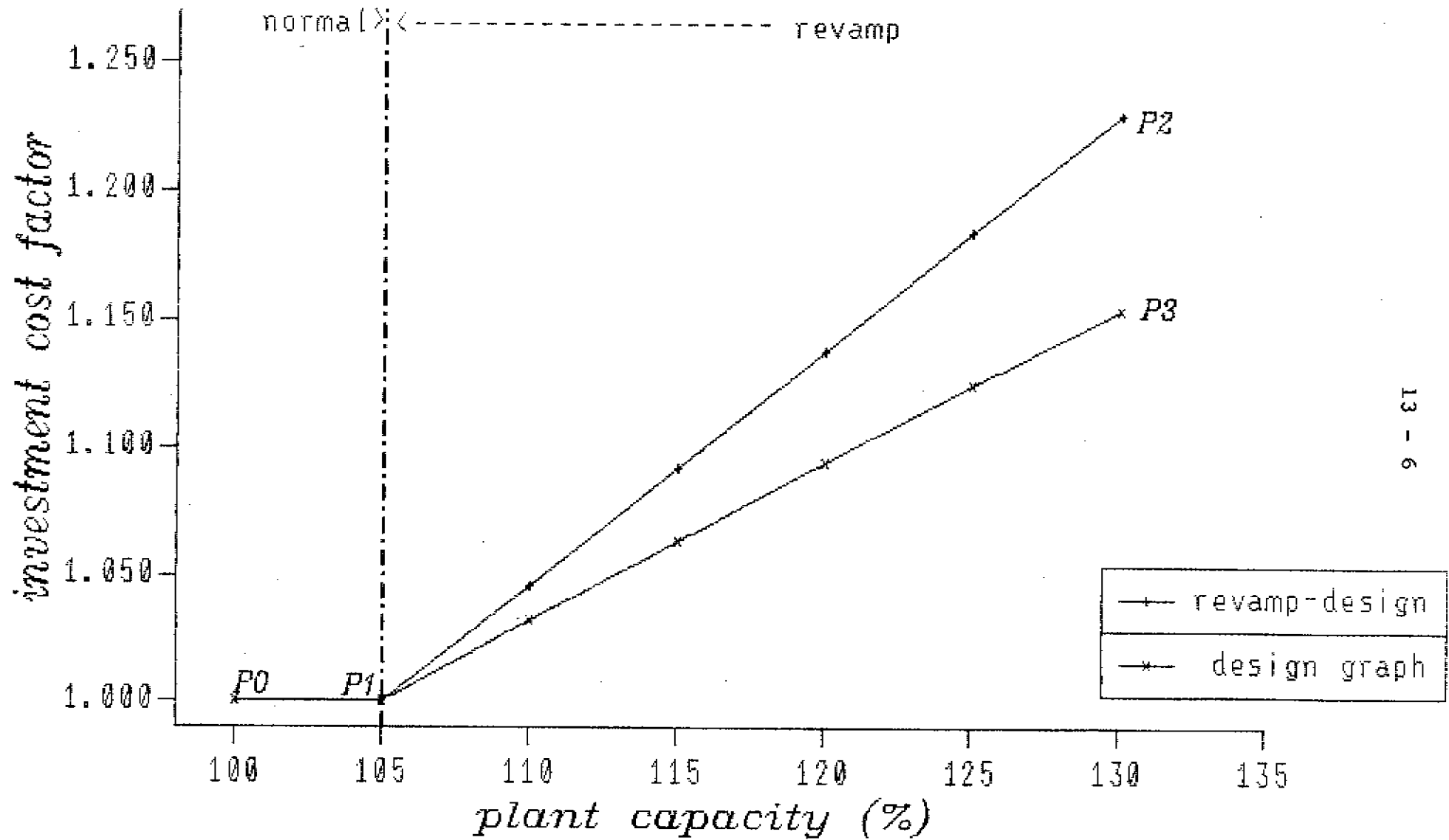
max. capacity subject to a revamp

In the design curve, plotted in blue, the part between P0 and P1 represents the over-capacity margin which can be regarded as built in. If capital-cost estimates are performed by the exponential method using plant capacity-ratio exponents based on existing cost factors for 100% capacity, the plot can be extended, for instance, to P2 corresponding to a capacity of 130%.

If a revamp is intended to increase the capacity, for instance to 130% of the original design capacity, a similar plant curve can be calculated by the exponential method, however, with different capacity-ratio exponents. Very roughly, the performance reserves for the main plant items can be summarized as follows:

compressor set	-	5 %
absorption	-	10 %
heat exchangers	-	15 %
steam system	-	20 %

diagram 01 : investment cost versus plant capacity



The sequence is also directly proportional to absolute equipment costs and represents the necessary steps for upgrading the equipment to the new plant capacity. Modifications of the compressor set cause the highest expense, whereas modifications of the steam system can be achieved at relatively low cost. The given reserve of 20% for the steam system does not mean 20% more in steam production but is related only to the heat flux.

The revamp curve presented in diagram 01, plotted in red, is based on different capacity-ratio exponents, i.e. different from the plant exponent, depending on the equipment part in which it is to be integrated. In the above example, the first 10% increase in capacity is dominated by changes in and around the compressor set. The next 10% are governed by the absorption system and pipework. In many cases, a 20% increase is the limit for justifiable expense. In the given example, a revamp from 105% to 130% could be performed but is generally not guaranteed. From the plots in diagram 01 it can be concluded that the more reserves are provided initially the greater are the expected savings if the plant should be revamped later.

The additional oxygen required for a capacity increase can be made available by modification of the air compressor, installation of a secondary air compressor or by the addition of pure oxygen. The use of pure oxygen is normally very costly and in many cases a capacity increase with more air throughput is preferred. In any case, a higher air stream requires modifications to the tailgas turbine. The question as to which method of additional oxygen feed to the process is the best cannot be answered in general and should be subject to detailed investigations. A result of this short consideration is that the compressor set certainly represents the key to all revamp activities. For a planned future capacity increase, a future-oriented design with sufficient reserve capacity of the compressor set is a good investment in capital.

The overall pressure drop in a nitric acid plant can be calculated on the basis of a system having a number of resistances in series and then the items are summed up for the entire process-relevant parts. The pressure drop represents the key parameter for the internal energy change of the process gas streams and can be calculated according to the following equation:

$$\Delta p_0 = \Delta p_1 + \Delta p_2 * (p_{des}/p_x) * (V_{n_x}/V_{n_{des}}) E2$$

- Δp_0 = total plant pressure drop, process
- Δp_1 = absorption pressure drop
- Δp_2 = pressure drop, other equipment
- p_{des} = design discharge pressure, air compressor
- p_x = discharge pressure, air compressor,
new capacity
- V_{n_x} = air flow, new capacity
- $V_{n_{des}}$ = design air flow, air compressor
- n = cubic metres (at standard temp.
and pressure) per hour

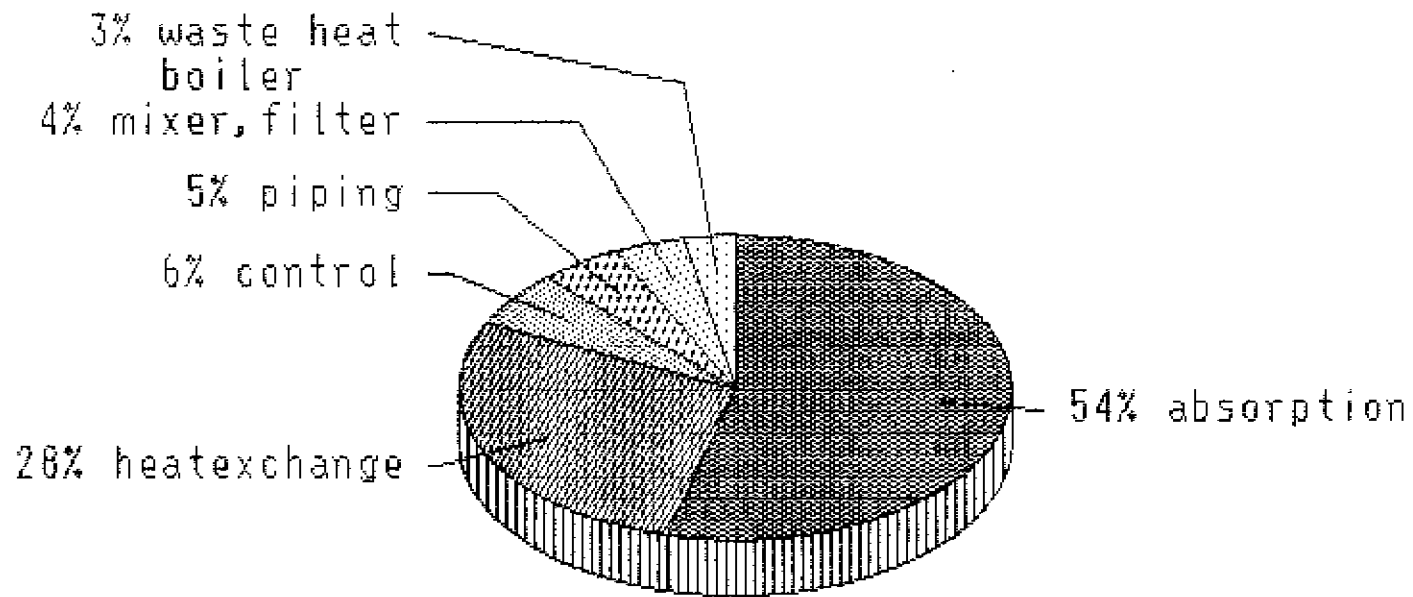
The formula is based on two parts; one half, i.e. the quadratic component, is derived from the gas stream velocity, the other half is determined by the factor from the absorption. The break-down of the total plant pressure drop by individual items of equipment at 100% capacity for a medium-pressure plant is the subject of

diagram 02 : main plant equipment and associated pressure drop

More than three quarters of the total losses occur in the absorption section and in the heat exchangers. Unfortunately, there is little chance of effective modification of these items of equipment.

The considerations regarding the pressure drop leads to the first main equipment item which should be discussed as a bottleneck, namely the tailgas turbine. The expander flow through the turbine is not only directly influenced by the pressure drop but also by the increasing process temperatures. These two limiting functions finally determine what capacity increase can be achieved. With reference to the revamp example for a capacity increase of 130%, the effective volume stream through the tailgas turbine is more than 40% greater than the original design and in most cases this means that a new rotor will be required.

diagram 02 : main plant equipment and associated pressure drop



The next major bottleneck is the absorption section, not only with respect to process gas pressure drop but also to the nitrous gas contents in the tailgas leaving the tower. This aspect is in most cases more critical than the pressure drop which is divided into a wet part related to the liquid depth on the sieve trays and a dry part reflecting the losses through the column and the sieve tray holes. The ratio between the wet and the dry parts is roughly 3:1. To keep the nitrous gas concentration in the tailgas within acceptable limits, the system pressure must be increased, but the question as to whether this is feasible depends on the particular case. There is a more detailed paper in the following chapter referring to the subject of tailgas treatment.

For the steam generation system, consisting of waste heat boiler, steam drum, economizer and forced water circulation, it is a question of how to protect the superheater and pre-evaporating coils in the boiler against the expected higher heat flux. Other measures like increasing of La Mont nozzles, providing water separators at the steam drum outlet and modifications to the forced water circulation are of an accompanying nature for debottlenecking. The outlet temperature of the waste heat boiler influences directly the inlet temperature to the turbine via the downstream tailgas heater.

As shown in diagram 02, filters, mixers, piping, valves and fittings have no significant influence on the total plant pressure drop. A great advantage in modifying these equipment items is that they can be replaced very easily and that any additional pressure drop caused by newly installed equipment can be compensated.

In the following, a revamp procedure will be analyzed on the basis of an example to determine whether there is any advantage in doing it stepwise, including a calculation of benefits and interest gain as well as investment costs. The general situation can be described as follows:

The management must consider that, due to environmental requirements, nitrous gas emission with the tailgas must be reduced to max. 500 ppm within the next two years. The actual tailgas content varies between 1100 ppm and 1400 ppm. The decision was made to install a second absorption tower in combination with a capacity increase to 130%. The additional air is supplied by a secondary air compressor because there is insufficient steam for the steam-turbine-driven compressor set.

Summary of new or modified equipment:

- motor-driven secondary air compressor
- modifications to tailgas turbine including new rotor
- extended cooler condenser
- secondary air cooler
- extended ammonia evaporation
- modifications to the steam drum and water system of the La Mont boiler
- extended absorption, cooled by chilled water

It was intended to finish the reassembly of all equipment after a shut-down period of four weeks. The investment costs for this case are shown in diagram 01, plotted in red, revamp design. The graph was calculated by the exponential method with different exponents for the equipment involved.

A stepwise procedure for the given example can be split into three sections

- I. compressor air supply
tailgas turbine modification
expected plant capacity 110%
- II. installation of new heat exchangers
modification of waste heat boiler and water system
expected plant capacity 120%
- III. installation of an additional absorption tower
with chilled water cooling
expected plant capacity 130%

The above-mentioned red curve in diagram 01 is based on a total investment of \$ 3.95 million including equipment, erection and civil works. A breakdown by sections yields:

- I. \$ 1.82 million
- II. \$ 0.75 million
- III. \$ 1.38 million

It is assumed that the shut-down period for the stepwise procedure is nearly the same as for the straight one. The investment period has been fixed at 24 months divided into three sections of 8 months each, the yearly total operating time being 8000 h. The interest rate is based on 8% per annum. Production costs are as follows:

• electric power	\$	0.07/kWh
• steam	\$	15.8 /mt (40 bar, 340 °C)
• ammonia	\$	115.8 /mt
• nitric acid	\$	47.4 /mt

The profitability of the project was checked using the following formula:

$$K_n = K_o (1 + p/100) \exp n$$

where

K_n = accumulated capital + interest after n months

K_o = investment capital

p = % interest on monthly basis

n = investment period

It was assumed that the total investment of \$ 3.95 million, corresponding to K_o in the above formula, could be invested on the money market for 24 months at an interest rate of 8% per annum. As a result of this, there would be an interest gain of \$ 0.683 million. On the other hand, if the capital of \$ 3.95 million is invested directly in the plant for uprating the capacity to 130%, the resulting gain due to increased production would be \$ 0.864 million. The comparison of the outlined figures indicates that it is more economical to invest in the plant.

In the following table 01, the expected production gain, expressed in million \$, is summarized. The right column contains the figure of 0.864 which means that, within the investment period of 24 months, the plant is operating at a capacity of 130% and \$ 0.864 million is the production gain due to the increased capacity. In the left column, those figures are summarized which can be expected if the revamp is performed stepwise and the plant is operating in periods of 8 months each at the given capacities. The total of the

figures in the left column amounts to \$ 0.605 million; therefore the question must be answered as to whether the remaining capital, which had not been invested within the 8 monthly periods, can equalize the difference by interest gains.

table 01 : summary of production data

capacity (%)	production gain (8-months basis)	production gain (24-months basis)
100	0	0
110	\$ 0.143 million	
120	\$ 0.174 million	
130	\$ 0.288 million	\$ 0.864 million

For the determination of what interest gain can be achieved, two models should be considered, table 02 for investment model 1 and table 03 for investment model 2. The difference between the two models consists of the different times when the revamp is started. Model 1 is based on investments in month 0, month 8 and month 16 and has two periods with interest gain and three periods with production gain. Model 2 is based on investments in month 8, month 16 and month 24 and has three periods with interest gain and two periods with production gain.

Under "A-capital" in tables 02 and 03 under the headline A-capital, the total investment and the remaining capital which is used for interest gain are listed by the periods in months outlined under "time". Under "I-capital", the investment is listed which corresponds to the revamp steps, see also the description on page 03.

A summary of the calculated results of the described procedures is shown in the following table 04. From the figures quoted, it can be seen that a stepwise revamp has advantages in costs according to the described investment model 2. The advantages depend on the actual interest rate and operating costs and vary from country to country.

table 02 : investment model 1

A-capital	time		I-capital
3.95 mio	t0 (0 month)	→	1.82 mio
			interest gain 0.116 mio
2.13 mio	t1 (8 months)	→	0.75 mio
			interest gain 0.155 mio
1.38 mio	t2 (16 months)	→	1.38 mio
	t3 (24 months)	→	

table 03 : investment model 2

A-capital	time		I-capital
3.95 mio	t0 (0 month)	→	0.00 mio
			interest gain 0.215 mio
3.95 mio	t1 (8 months)	→	1.82 mio
			interest gain 0.239 mio
2.13 mio	t2 (16 months)	→	0.75 mio
			interest gain 0.238 mio
1.38 mio	t3 (24 months)	→	1.38 mio

Finally, it can be concluded that it is worth considering as to whether the revamp work for a capacity increase should be spread over a prolonged investment period. The described procedures can be worked out in more detail, if requested.

table 04 : summary of production and interest gain

capital investment survey	total gain (24-month basis)
capital on the money market	\$ 0.683 million
capital invested, straight revamp	\$ 0.867 million
capital invested, section revamp model 1	\$ 0.876 million
capital invested, section revamp model 2	\$ 1.010 million

TAILGAS TREATMENT

Due to environmental pollution control regulations it has become more and more important to reduce nitrous gas emissions even from nitric acid plants which have been designed some time ago. Particularly processes with selective reduction have convincing advantages, compared with non-selective processes using the residual oxygen for combustion purposes. Such a catalytic selective abatement system which allows the nitrous gas concentration to be lowered to below 200 ppm by volume nowadays desired in most countries, is well suited, under certain conditions, to be integrated into existing plants during a revamp.

The installation of an additional absorption volume improves process economics, but 200 ppm nitrous gas emission cannot be obtained in most cases with system pressures below 6 bar abs. Alkaline treatment methods are also suitable to obtain admissible tailgas concentrations, but with combined by-products.

The best method for a revamp is the combination of absorption extension and a following selective catalytic tailgas treatment. An example for this will be described later.

The abatement system described below is under license from Messrs. BASF, Federal Republic of Germany, and operates with the following main process parameters

catalyst	• vanadium pentoxide
reactions	• $6 \text{ NO} + 4 \text{ NH}_3 = = = 5 \text{ N}_2 + 6 \text{ H}_2\text{O}$ reaction enthalpy $\Delta H = -1811 \text{ kJ}$ $6 \text{ NO}_2 + 8 \text{ NH}_3 = = = 7 \text{ N}_2 + 12 \text{ H}_2\text{O}$ reaction enthalpy $\Delta H = -2737 \text{ kJ}$
NO/NO ₂ ratio	• 50% at reactor inlet is optimum
tailgas NOx	• approx 3500 ppm max. at reactor inlet below 200 ppm at reactor outlet NOx reduction of 70 - 80 ppm results 1 in oK temperature increase of the tailgas

temperature	<ul style="list-style-type: none"> • 200 - 350 °C at reactor inlet • > 90 °C at the tailgas turbine outlet
pressure	<ul style="list-style-type: none"> • 1.5 - 11 bar abs
pressure drop	<ul style="list-style-type: none"> • typically 0.09 bar for reactor and mixers

The ammonia consumption by the system is the key parameter for an economic estimate and depends on the inlet concentration of NOx with a given degree of oxidation expressed in %, which means the existing $\text{NO}_2/(\text{NO} + \text{NO}_2)$ ratio, process temperature and pressure. Under modern design conditions, namely

reactor inlet NOx concentration 650 ppm
 reactor outlet NOx concentration 170 ppm
 degree of oxidation at reactor inlet 50%
 degree of oxidation at reactor outlet 20%
 inlet temperature 260 °C, system pressure 4.6 bar abs,

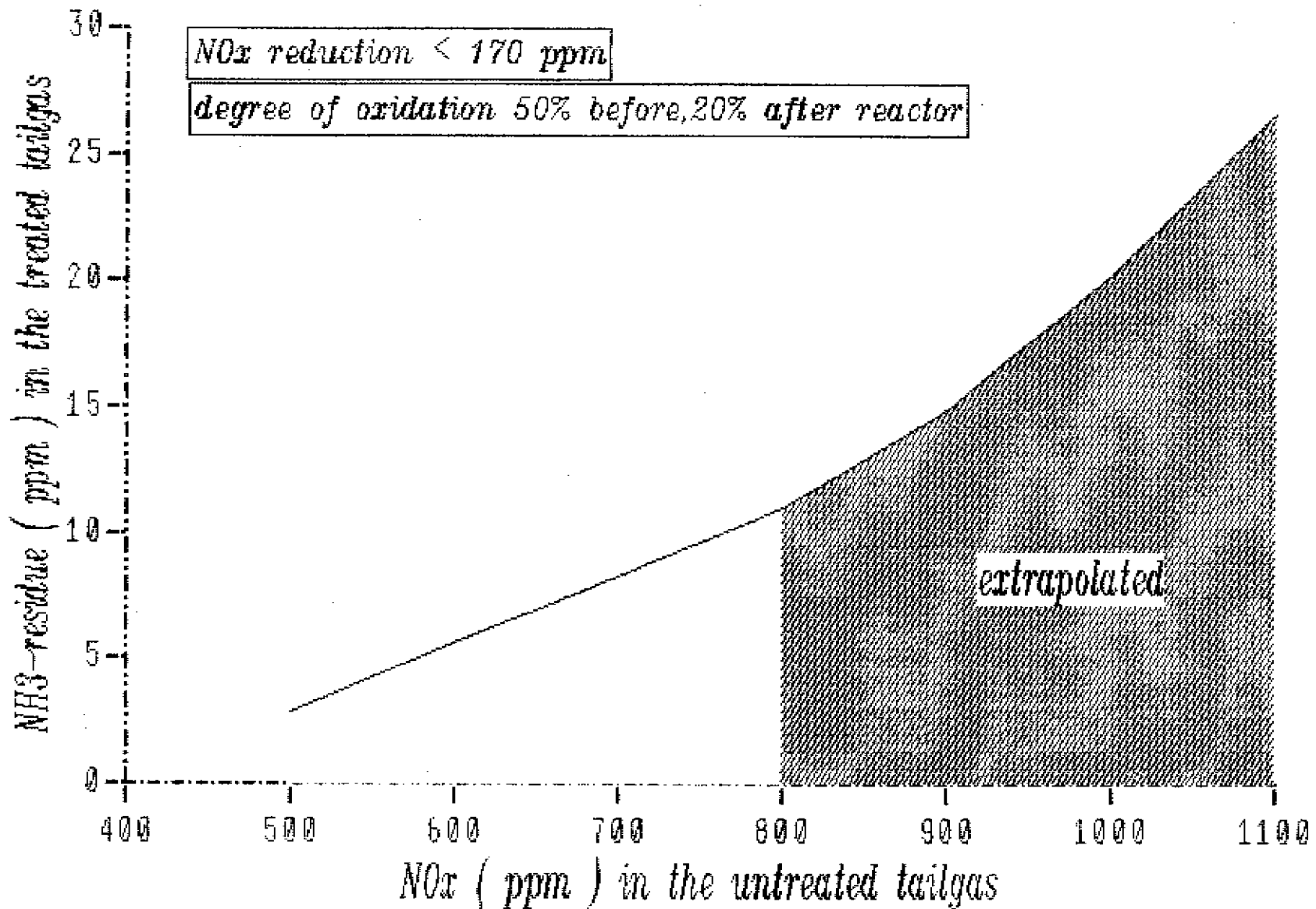
an ammonia supply of 0.36 kg NH_3 /kg NOx is sufficient to operate the system. In many cases today there is also an emission limit for NH_3 which is below 15 ppm in the treated tailgas. The relationship of NOx in the untreated tailgas to the residual NH_3 in the treated tailgas is presented in

diagram 03 : NH_3 -residue versus NOx

Diagram 03 shows the broad operation width of the whole system under the operating conditions mentioned and with a constant charged catalyst volume. For revamp purposes, each case must be designed individually. Nevertheless, it is possible to keep the residual NH_3 below the accepted limits of 15 ppm, even with considerable higher inlet NOx concentrations, but with a corresponding charged catalyst volume; see also the example quoted later.

The NOx reduction in the tailgas reactor is an exothermic process, in which the reaction enthalpy can be recovered by the tailgas turbine, as the net gain at the turbine

diagram 03 : NH_3 -residue versus NO_x



shaft equals the gain by the temperature rise minus the loss resulting from the additional pressure drop in the abatement system.

It should be noted that the catalytic selective abatement system meets the opacity requirements for tailgas according to US EPA New Source Performance Standard (NSPS) for nitric acid plants. A plant equipped with a catalytic abatement system will produce an emission level of less than 10% opacity, which means 90% of light passes through the plume. The NSPS does require continuous stack recording for NOx.

The performance of an absorption system operating at 5.5 bar abs pressure is shown in

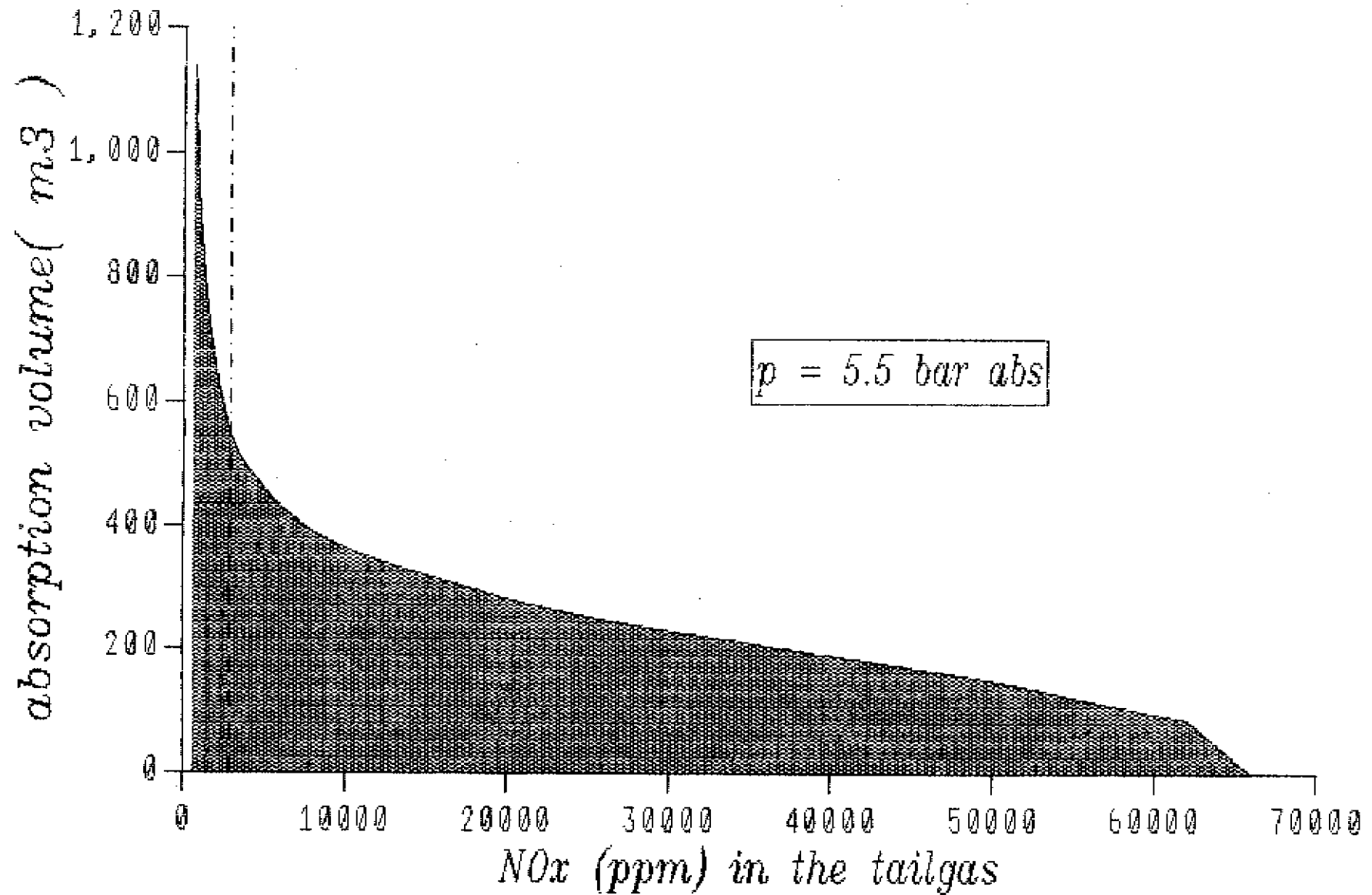
diagram 04 : absorption volume versus nitrous gas concentration

The plot is related to a modern medium-pressure plant of 500 mtpd and shows that, with nearly half the installed absorption volume, 95% of the nitrous gases are converted to acid, see reference line drawn at 2900 ppm. From 2900 to 630 ppm in this case, more than half of the total installed absorption volume is required, one third of the absorption pressure drop being related to this absorption part and approx. 14% of the total installed cooling area. There are very limited measures to reduce the absorption volume and often an advantage will be obtained at the expense of a lower process performance. For instance, an increase in tray weir heights for better absorption efficiency will entail a considerable energy loss at the tailgas turbine due to the greater pressure drop.

With reference to the liquid depth on the sieve trays in the towers designed by UHDE, a new Dynamic Absorption Calculation Method < DACM > has been developed, which allows, among other things, a more precise determination of the tray efficiency in relation to the liquid height on the trays. The example that will be shown later has been calculated with the aid of DACM and results in an improvement by 35 ppm compared with former methods using an optimization calculation for liquid depth on the trays.

Under revamp conditions it is even more difficult to obtain the desired process performance, because there is very little influence on the existing process parameters and

diagram 04 : absorption volume vs nitrous gas concentration



installed equipment, certainly with respect to justifiable economic expense. With reference to the details on the absorption volume pointed out, the following example should explain in which way an optimum can be determined between an extended absorption section and a selective abatement system. The result of this investigation yields the maximum nitrous gas concentration in the tailgas at which an extended absorption can be operated economically in combination with a selective abatement system.

The calculation considers the following process parameters:

- additional pressure drops caused by new equipment, absorption and abatement system
- additional acid production
- additional ammonia consumption
- energy, credit or debit
- investment costs for the absorption, the required absorption volume being calculated by weight only; for the abatement system only the required catalyst volume has been considered
- actual plant data, basis for revamp
 - 470 mtpd HNO_3 - 100%
 - pressure at tailgas turbine inlet 3.65 bar abs
 - NOx in the tailgas at outlet from absorption section 2500 ppm
 - (beginning of extension)
 - oxygen in the tailgas 3%

The calculation is performed in that, first, the selective abatement system is considered alone to bring down the NOx concentration from 2500 to 200 ppm. Afterwards, in steps of 100 ppm, beginning at 2000 ppm, ending at 1000 ppm, the combination of absorption and catalytic abatement system is calculated. In each case the final NOx concentration is 200 ppm. The results are summarized to form a qualitative cost factor expressed as S/mt HNO_3 (100%), based on the process parameters mentioned above. The

graphic plot of the cost factor versus NO_x concentration in the tailgas, showing the optimum is presented in

diagram 05 : optimization, absorption/catalytic abatement

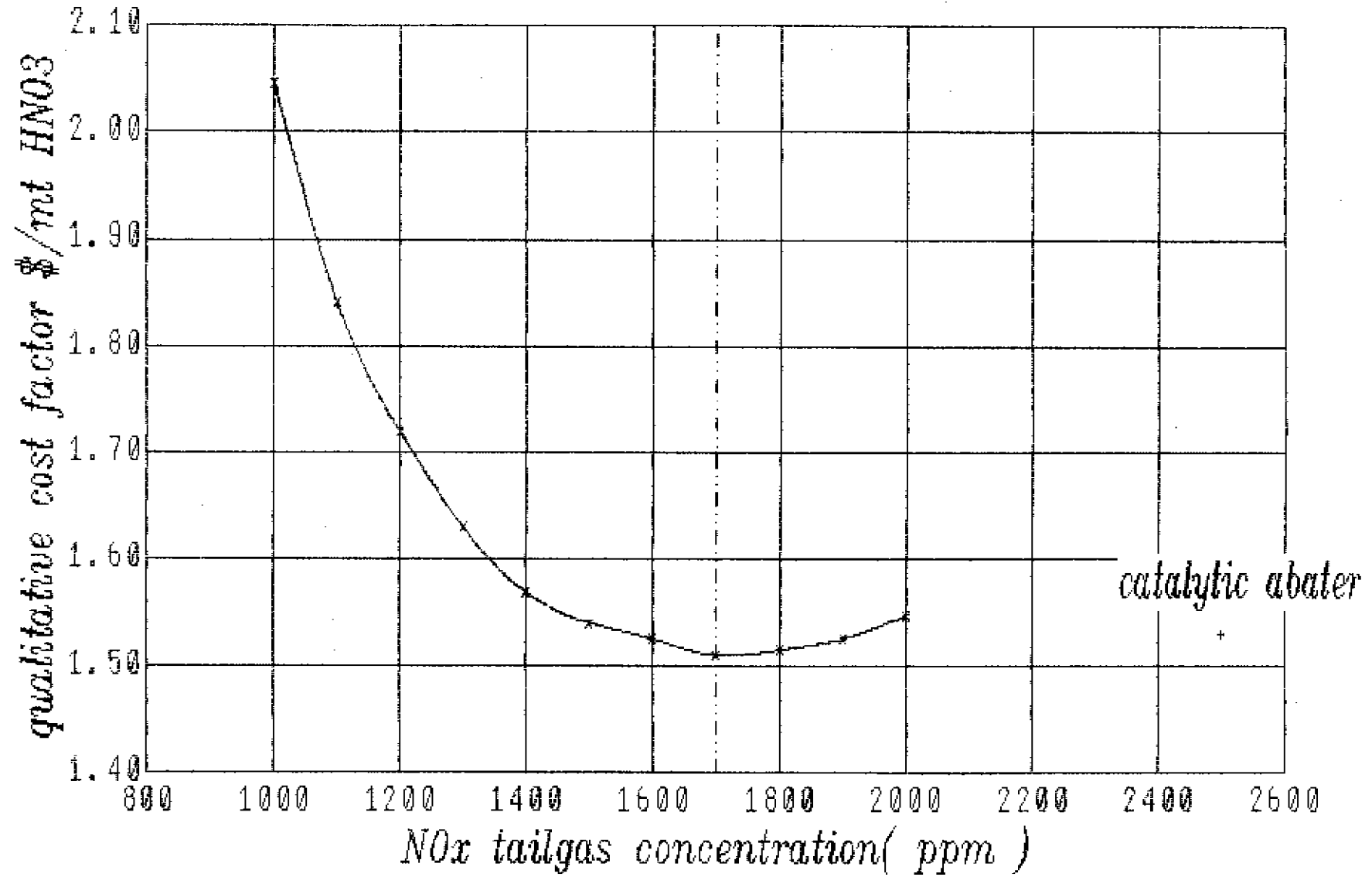
The price basis for the cost factor corresponds to European standards, viz. DM 270 DM/t NH₃, DM 100/t HNO₃ and DM 0.12 DM/kWh electric energy. Due to the considered range of the specified NO_x reduction, it was assumed that the engineering, civil works and erection would remain constant.

The plot in diagram 05 indicates that the reduction with an extended absorption is profitable to a NO_x concentration of 1700 ppm. The shape of the plot is rather flat from 1900 to 1600 ppm so that small differences in prices may shift the optimum point. Nevertheless, it is worth discussing during the revamp a combination of extended absorption and catalytic selective abatement system due to the operating cost situation.

From the example it can be seen that the cost factor for a combination of tailgas treatment, consisting of absorption and catalytic abater, is lower than the single method of catalytic abatement alone.

The calculation method which is the basis of the plot in diagram 05 and is described in the above-mentioned example, is available as a fully computerized package. Taking into consideration all the important parameters, many examples of application can be handled.

diagram 05 : optimization, absorption/catalytic abatement



WASTE HEAT RECOVERY

The energy input required for the nitric acid process is composed of different portions, such as ammonia, air, process water, demineralized water, cooling water and electric energy for pump drivers. The percentage of these portions as part of the total is shown in table 05. Due to the chosen reference level of 25 °C and the basic enthalpy data for water of 104.77 kJ/kg, the active energy input can be reduced to ammonia and air as well as electric input for pumps.

As can be seen from table 05, the main part of the energy input is introduced to the process via the ammonia in the form of chemically fixed energy.

The given example is related to a 500 mtpd plant and represents the minimum energy input when a steam turbine drive is used for the compressor set.

table 05 : nitric acid process - energy input

	(kg/h)	(kW)		(%)
ammonia (25 °C, 15 bar)	5 889	36 220	a)	97.4
air (25 °C, 1 bar)	105 899	776	c)	2.1
process water (25 °C, 12 bar)	5 432	0	0	
demineralized water (25 °C, 8 bar)	0	0		0
cooling water (25 °C, 6 bar)	0	0		0
electric energy		198		0.5
total	117 220	37 194		100.0

basic data for calculation

reference temperature 25 °C, enthalpy 104.77 kJ/kg (water)

corrected specific enthalpy for water and steam

steam (25 °C, 1.01 bar) 2 442.51 kJ/kg

gross calorific value for gaseous ammonia

(25 °C, 1.013 bar) 22 254 kJ/kg

- symbols
- a) gross calorific value
 - b) sensible heat
 - c) enthalpy of steam in the gas stream concerned

The input energy is split into the outlet streams as nitric acid, tailgas, waste water, cooling water and export steam. The percentage of the output energy as part of the total is shown in table 06. Reference is made for this example to a 500 mtpd plant. As can be seen from the figures given, most of the energy, i.e. more than 91%, is covered by the combined energy contents of the streams. The expression 'combined energy contents' is the sum of all heat flows to either cooling water or steam generation. The split percentage into the cooling water reads 48.6% whereas 42.9% is left for steam generation.

table 06 : nitric acid process - energy output

(%)		(kg/h)	(kW)	
1.5	nitric acid (47 °C, 5 bar)	33 605	545	b)
5.6	tailgas (106 °C, 1 bar)	83 615	2 070	b + c)
0.4	waste water (60 °C, 1 bar)		162	b)
91.4	combined energy contents		34 021	b)
1.1	losses		396	
total 100.0		117 220	37 194	

basic data for calculation

Reference temperature 25 °C, enthalpy 104.77 kJ/kg (water)

Corrected specific enthalpy for water and steam

steam	(106 °C, 1.01 bar)	2 580.94 kJ/kg
water	(60 °C, 1.01 bar)	146.39 kJ/kg

symbols

- a) gross calorific value
- b) sensible heat
- c) enthalpy of steam in the gas stream concerned

In view of the energy distribution shown, the objective of revamp engineering should be to keep the heat flow to the cooling water as low as possible to favour the steam generation as recuperative energy, always with respect to given design features. Revamp work on the cooling water side promises the best energy improvement. From the given example the recuperative efficiency can be defined as 42.9%, when steam generation is intended. For other forms of energy, corresponding transformation efficiencies must be calculated.

Improvements with regard to the energy leaving the plant with the tailgas are only possible if the thermal efficiency of the tailgas turbine can be improved.

The energy losses of the nitric acid process consist mainly of vapours from the thermal deaerator and blow-down flash steam as well as the electric energy for the pumps since in this consideration temperature increase for the fluids has been neglected. The energy leaving the plant with the waste water has its origin in the boiler blow down which must be cooled to a permissible discharge temperature by cooling water. Ammoniacal water has no influence on the energy balance.

Revamp engineering for the above-mentioned items is of secondary importance; only detail improvements should be expected.

Having discussed the energy situation at battery limits, a consideration of the process conditions within battery limit should follow.

The process gas temperatures from the catalyst to the outlet of the absorption unit can be summarized to a recalescence curve representing process temperature levels versus transferred heat, see the following

diagram 06 : recalescence curve, heat exchanger train

The blue plot relates to the nitrous gas from the catalyst gauze to the absorption outlet, whereas the red plot represents different process fluids marked and explained in the diagram by legend. The curves allow a comprehensive energy-wise classification of the process. Optimum waste heat utilization is not the only desirable design purpose, but special process features and at least the economic aspect of heat exchanger design must also be considered with the same importance. An evaluation of diagram 06 with regard to how efficiently the waste heat utilization was performed, can be done by analyzing the areas under the curves.

In diagram 06, the conversion efficiency is represented by the area under the red plot divided by area under the blue plot of 49%. The same relation will be obtained if the tailgas temperature is increased by 100 °C. There are some shifts in temperature levels of several items of equipment, but the total relation of the red area divided by blue area remains unchanged. The influence of the tailgas temperature increase can be demonstrated as indicated in the following table 07.

diagram 06 : recalescence curve, heat exchanger train

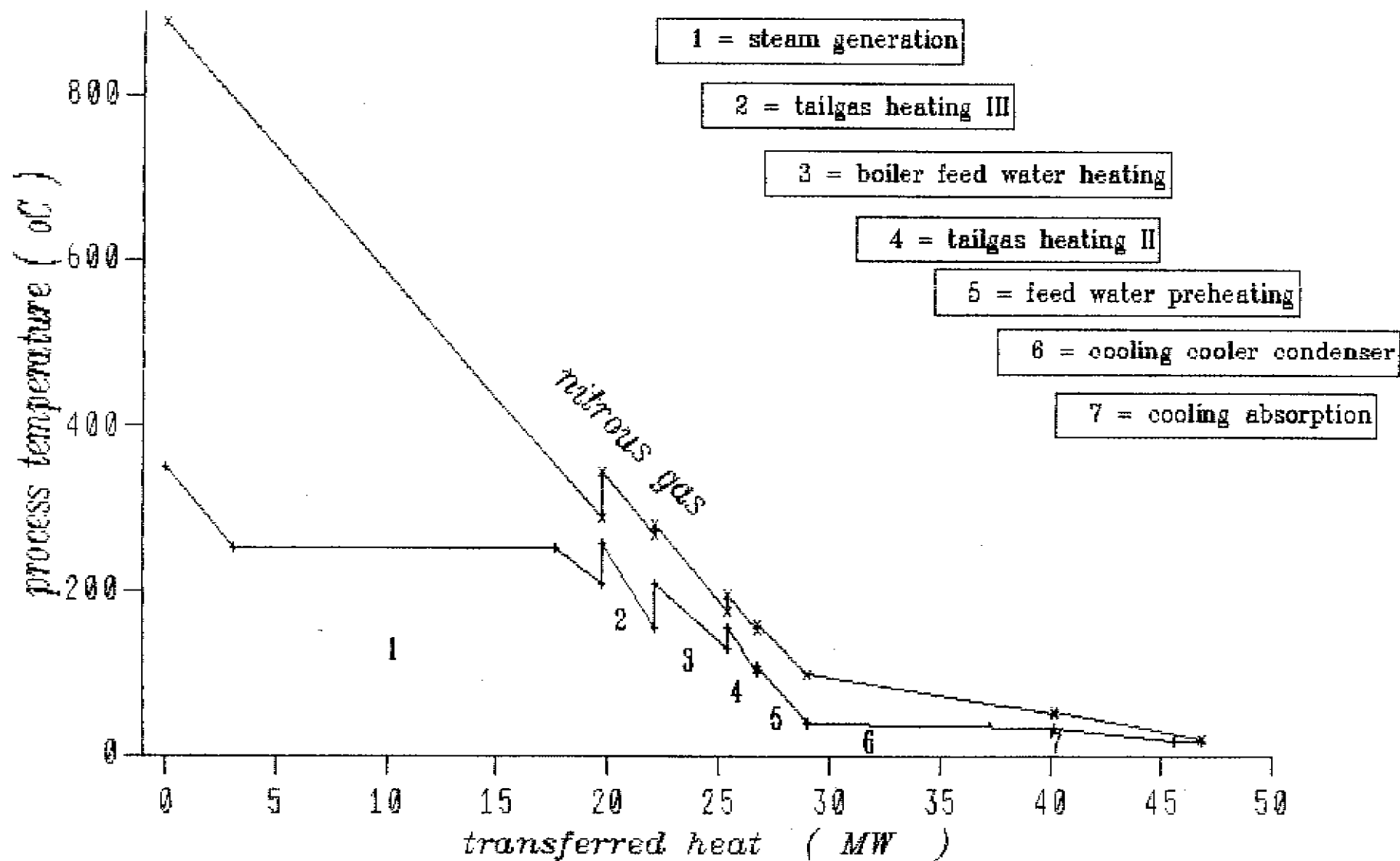


table 07 : nitric acid process - energy output

(%)		(kg/h)	(kW)	
1.5	nitric acid (47 °C, 5 bar)	33 605	545	b)
11.0	tailgas (184 °C, 1 bar)	83 615	4 101	b + c)
0.4	waste water (60 °C, 1 bar)		162	b)
86.0	combined energy contents		31 990	b)
1.1	losses		396	
total 100.0		117 220	37 194	

The result of the tailgas temperature increase is that, within the combined energy part, the percentage of the cooling water is raised slightly to 49.6% whereas the steam generation part is reduced to 36.4%. The supposedly better energy recovery in fact leaves the plant at battery limits with the tailgas after passing through the turbine.

These considerations are more important in the design phase than for revamp services. Therefore, an example will now be illustrated giving better energy recovery by application of better heat exchanger material and modified process operation. In a high-pressure plant, combustion pressure = 8 bar abs, the nitrous gas leaving the waste heat boiler is cooled in a tailgas heater and finally in cooler condensers. Due to corrosion problems, the tailgas from the absorption section is first heated by steam to 130 °C before passing through the tailgas heater where it is further heated to the final temperature required for the turbine, which should be the same after revamp. The un-revamped system is shown in

diagram 07 : heat exchanger train, original

The revamp consists of the following:

- replacement of a steam-heated tailgas heater
- additional feed water preheating
- final tailgas temperature upstream of the turbine = constant

The required energy for the tailgas and for the feed water could be taken from the nitrous gas before it enters the cooler condensers. The problem was solved by using corrosion-resistant materials of the specification

C max	Si max	P max	S max	Cr	Ni
0.02	0.3	0.02	0.015	24.5	20.5

with the result that the condensing range of the nitrous gas could be partly used for heat recovery. The extremely corrosive part-evaporation of nitric acid in the tubes, which mainly caused the corrosion problems, has been avoided by designing two smaller tailgas heaters; the first, charged with the cold tailgas from the absorption section, is located directly at the inlet of the cooler condenser, and should always operate with tube wall temperatures below the condensation point, the second with tube wall temperatures above the condensation point. This could be achieved by operating the heat exchangers according to the co-current flow principle.

The result of the revamp with respect to energy recovery is presented in

diagram 08 : heat exchanger train, revamped

and now a yield, with regard to the area units under the curves, of 42.6% compared with 27.9% for the original. In this way, the recuperative part of the combined energy content could be increased. The relationship of cooling water to steam generation has been shifted to steam generation and hence there is less heat flow to the cooling water.

diagram 07 : heat exchanger train, original

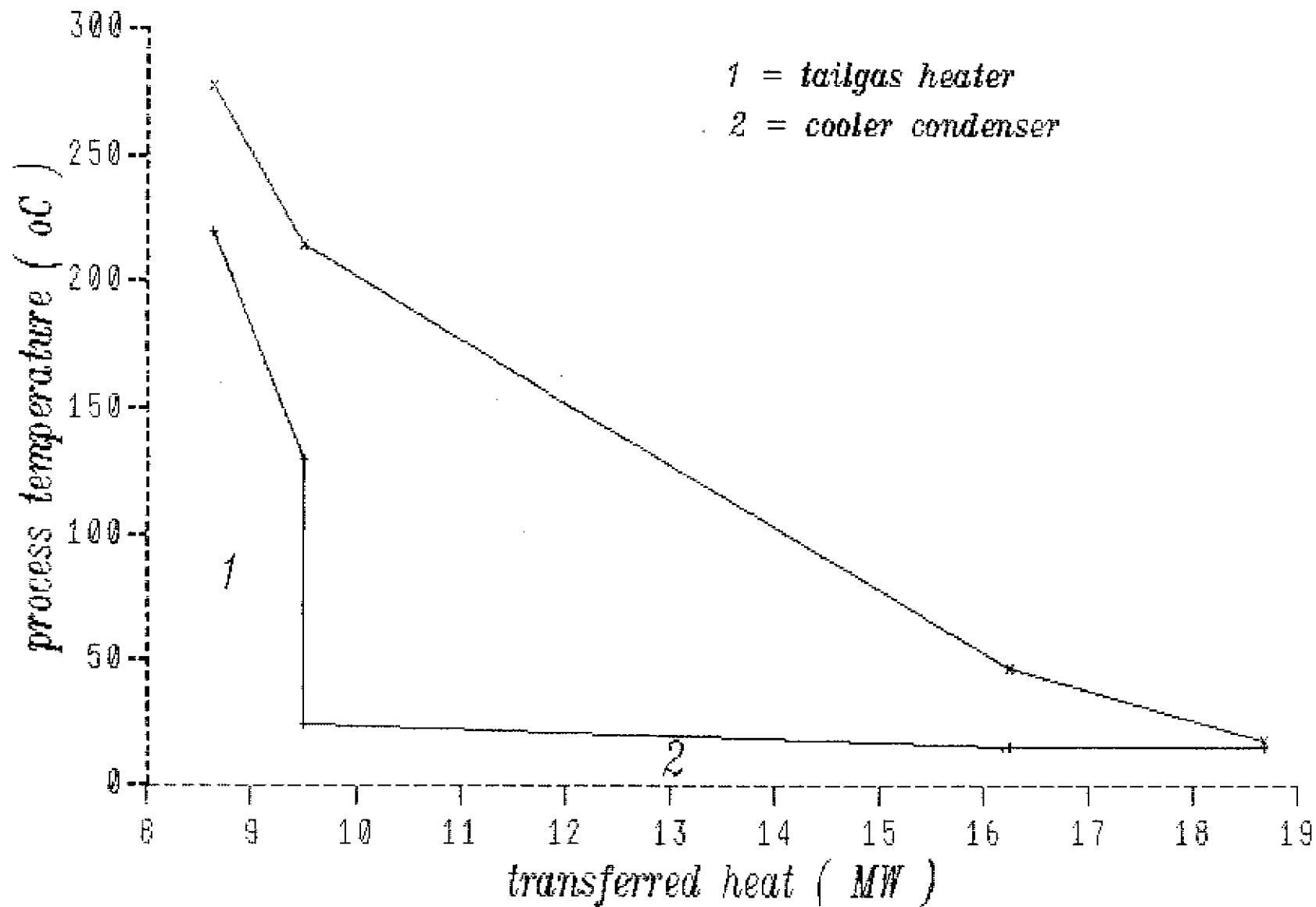
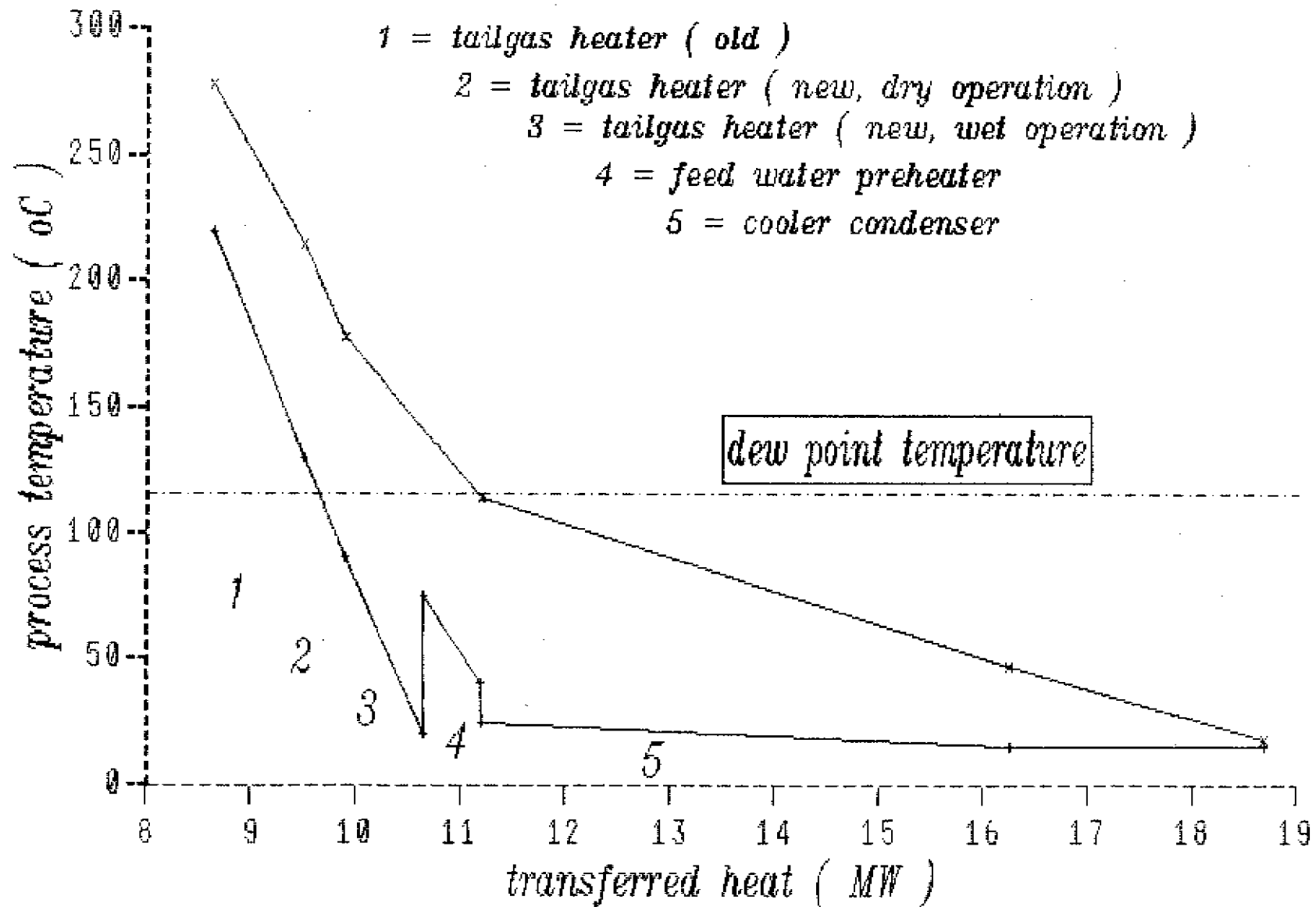


diagram 08 : heat exchanger train, revamped



PROCESS CONTROL

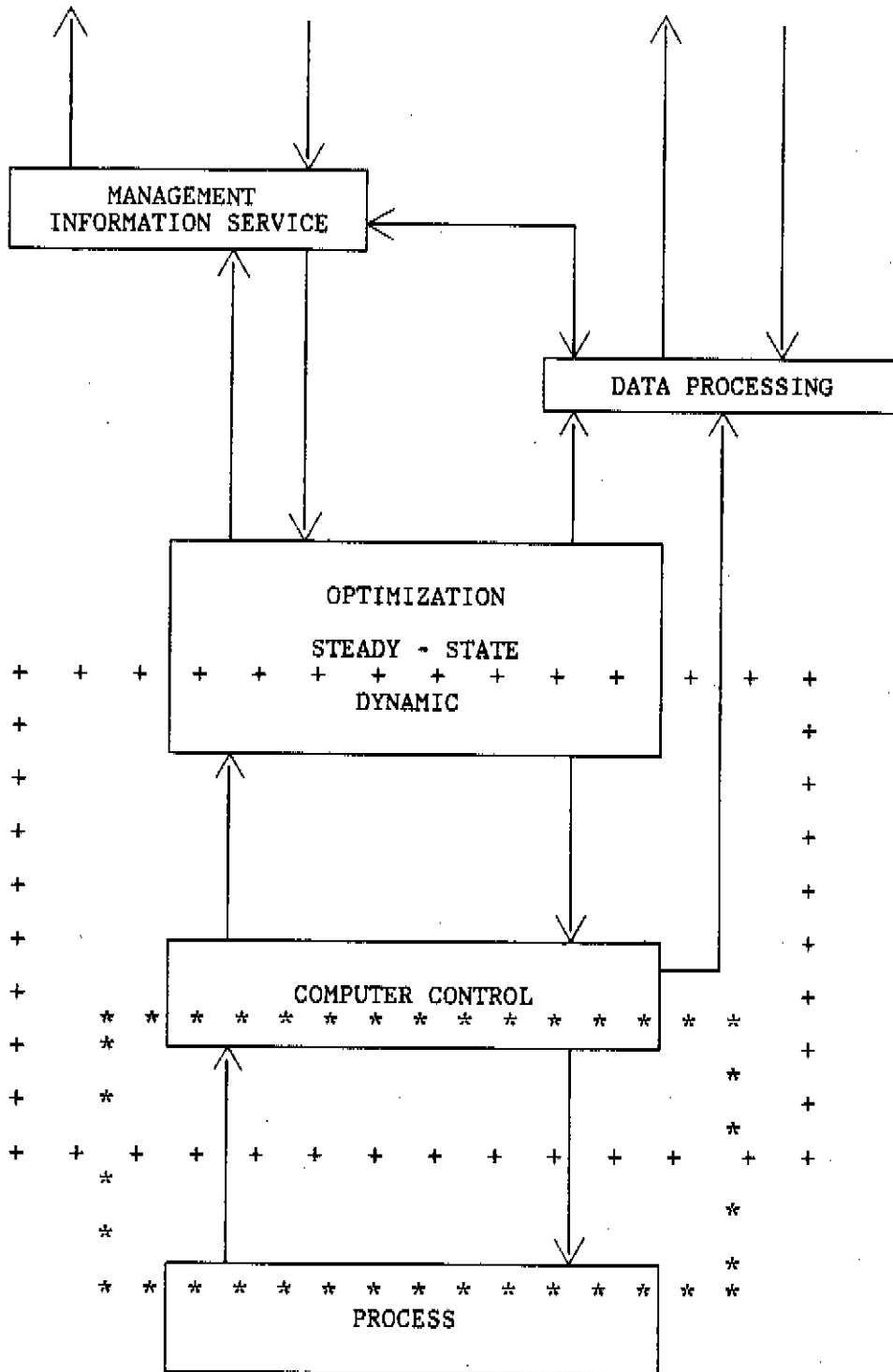
Computerized process control can today help to make profits in, and can model the performance of, plants accurately and cost-effectively. In existing plants, computerized process control is used to reduce operating costs, improve yield and increase throughput. Computerized control can be divided into different levels, the interdependence of which is listed in

diagram 09 : functions of a fully computerized control system

1. **unit operation control** means the control of individual items of equipment, such as ammonia burner, absorption tower, heat exchanger
2. **unit process control** means a combination of individual unit operations, which must be coordinated to meet plant requirements
3. **plant control** means the concentration of all process controls at one location, for instance in a central control room
4. **departmental control** means the control of a complete company division like the fertilizer group; this control level is not involved directly with process belongings
5. **company control** generally not of interest for process control, except for some plant inputs which are initiated from this level

The optimization of the nitric acid process by means of process and absorption calculations with a view to minimizing operating costs can be achieved via a 'Digital Control System' named briefly < DCS > Such a system is also suitable for integration in existing plants, it being possible to compensate the higher investment by improvements in

diagram 9 : functions of a fully computerized control system



* unit operation control *
 + process control +

plant operation. DCS can also tune the process to maximum capacity with output data reflecting the additional cost of this operating option. Improvements and expected operating profits will be listed at the end of this chapter.

The object of the optimization is to keep tailgas NO_x within the accepted limits with respect to minimum plant pressure which simultaneously represents minimum energy requirements, whereas the plant load and the actual cooling water temperature are variables. The acid profile in the absorption unit must be controlled as well as the moisture contents of the intake air. Essentially, this outlines the allocation of unit operation control to a skeleton process control.

DCS and the corresponding software available in our company contain algorithms for material transfer of different nitrous gases which are the basis for nitric acid formation on the absorption sieve trays, not only for HNO₃ formation but also for HNO₂. The interspace between the trays is used for the oxidation of NO to NO₂ where the reaction velocity is calculated stepwise and finally integrated.

The reactions are temperature- and pressure-dependent. The composition and temperature of the liquid coming from the next higher tray in the column is estimated first and balanced in the following calculation step together with the gas stream. Finally, 18 equations have to be solved simultaneously. For better control of cpu time, initially only some of the equations are solved either with the gas upstream or with the liquid downstream. The result of the calculation is an acid profile which is presented as the acid concentration on the trays versus the absorption volume. These data are available in respect of each tray for the liquid and gas stream composition and the transferred heat in the absorption unit with the installed cooling area including tray temperatures.

For optimization purposes, the program works more simply because the number of trays in an existing plant is fixed; on the other hand there is enough capacity available to integrate actual plant parameters. The actual calculation for optimization can be described as follows: Based on measured data for ammonia, air conditions and nitrous gas at some key points in the plant, for instance pressure and temperature at the cooler condenser outlet as well as at the head of the absorption column, a flow data list is calculated on a mass basis, while observing fixed input data such as tailgas oxygen and cooling wa-

ter temperature. From the flow data list, initial data are taken for the absorption unit. The calculation of the absorption system is subject to pressure variations and is repeated with respect to certain measured tray temperatures which serve as ancillary data for the program until the desired NO_x tailgas concentration is reached. The highlighted data are:

- primary and secondary air flow
- process water make up
- absorption inlet pressure
- the tray for acid condensate feed

and various other data which are useful for plant and process control, and also the complete acid profile. The input of the new rated values can be performed via an external keyboard.

The interrelationship with the second important process part, i.e. the ammonia conversion on the catalyst gauzes, is established by separate program calculations, the results being fed to the mass flow data list.

An optimized ammonia oxidation depends on several variables which can be influenced within certain limits.

- area load of catalyst gauzes
- system pressure upstream of the catalysts
- gauze temperature
- number of gauzes installed
- running period of the catalyst

Increased gauze temperatures as well as frequent shut-downs lead to untimely aging of the catalyst, as the platinum becomes eroded and must be replaced more often which represents a loss in production. The optimization yields the right time for a catalyst change and indicates the quantity of catalyst which should be replaced and gives recommendations with regard to the suitable gauze temperature. Key parameters for the calculation are the costs for ammonia and the catalyst as well as the acid requirements. Significant difficulties within this optimization result from the measurement of conversion efficiency.

UHDE has developed a physical model of the catalyst gauze which allows the determination of platinum losses and conversion efficiency. The results obtained are satisfactory and can be used via DCS.

Finally, some facts should be mentioned regarding the profits expected. These can be subdivided into two groups, one with not directly itemizable benefits and the other with same, expressed directly in terms of money. The first group can be summarized as follows:

- preventive maintenance
- medium-term capacity planning
change of catalyst
quantity of new catalyst required
ammonia consumption
(each of the above-mentioned items in
relation to the actual cost situation)
- auxiliary facilities for the training
of operating personnel
- shortening of start-up periods

For the second group, a rough estimate indicates that the investment costs for DCS can be recovered in two years of operation by a medium-pressure 370 mtpd plant with a catalytic abatement system. The direct profits are:

- savings of ammonia in the abatement system
due to closer operation at rated value with
lower oscillation
- oxygen concentration in the tailgas can be
lowered and this is directly energy saving
- continuously lower NOx emission increases
the acid production rate and saves ammonia
at the catalytic abater

- optimized capacity planning lowers production costs compared with constant operation
- preventive maintenance lowers the risk of unexpected shut-downs

CONCLUSIONS

Various options were discussed in this paper with regard to the revamping of nitric acid plants. The question as to whether individual measures or a combination of different measures are to be given preference depends on the objectives specified by the plant owners.

In most cases an evaluation of different technically feasible solutions will produce the desired results, the optimum cost-benefit ratio being obtained by comparing the investment costs required for each particular option with the achievable economic efficiency.