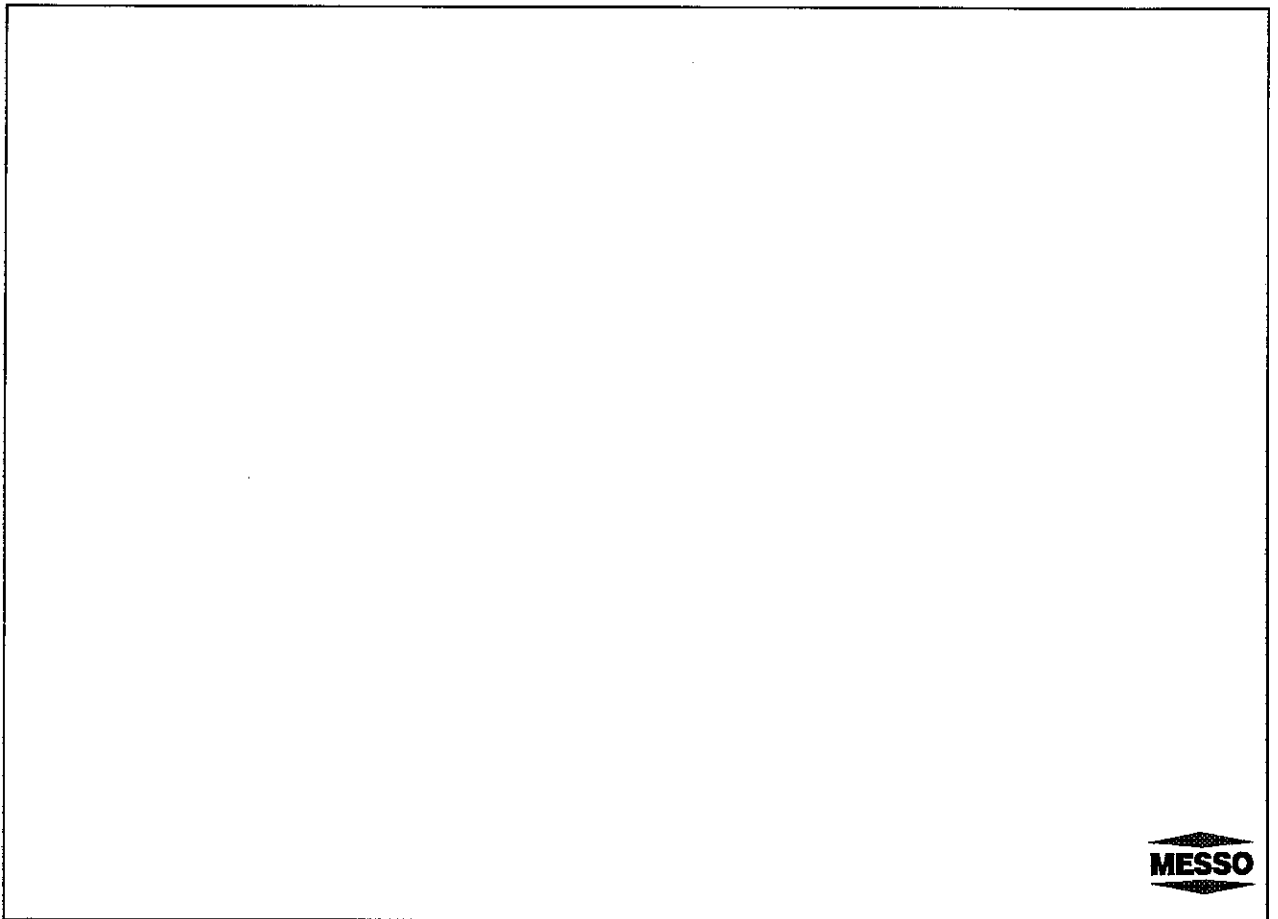


Application of the Thermal Process Technique to Effluent Problems

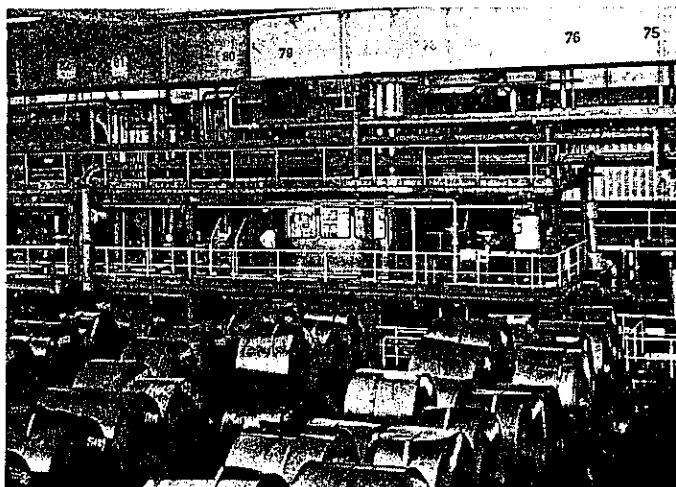
J. Driesen



The theme of this article is thermal treatment of some special and common effluents encountered in the processing field and the recovery of marketable products from them.

The treatment of caprolactam process effluents, of spent pickling liquor and spinning bath liquor are some of the problems solved by the evaporative techniques described in this article.

by M. DRIESEN*



Application of the thermal process technique to effluent problems

CONCERN about increasing pollution of waters has led to stricter regulations in all industrial countries throughout the world. Hence, the treatment of effluents becomes ever more important, especially to the expanding chemical industry.

Although governments are prepared to grant tax relief, and subsidies, for the construction of plants where effluents are treated, there are still financial problems. Clearly, a production plant cannot be seriously considered if the cost of eliminating the residues makes it uneconomic. Hence, the cost of treating effluents is of primary importance and must be kept to a minimum.

The recovery of chemicals from the discharge of chemical plants is of particular interest because this may reduce, or even cover, the cost of treating the effluents by selling the recovered products or reusing them. Such recovery sometimes yields a net profit, as the following examples show.

Concentration of mercerising liquor

Certain textiles are treated with a soda lye of 28 to 32° Bé concentration. During this mercerising process, the solution is highly diluted and so it cannot easily be used for other purposes. Today, there are many factories where the dilute liquor, normally obtained at a concentration of 5 to 7° Bé, is discharged to waste pollution and loss of NaOH are the consequences.

Modern evaporation plant can solve both problems economically. When using the vapours of the last stage, warm water can be

produced without additional heating which is, in any case, required as wash water in textile and mercerising factories. In addition, a flash stage can be connected to the evaporation plant to cool the strong liquor normally leaving the evaporation plant at a concentration of 25 to 35° Bé. Fig. 1 shows the operation principle of a three-stage mercerising liquor-evaporating plant with cooling stage.

As to materials of construction where the concentration are up to 30° Bé, normal mild steel (St 35 or St 45) can be used. At greater concentrations steel resistant to caustic embrittlement (L St 45-8) must be used. This steel requires a special after-treatment and it is often difficult to obtain in small quantities. Usually, the concentration of the mercerising liquor does not exceed 35 to 36° Bé.

Profitability calculations for a typical plant with production of warm water and a treatment capacity of 3,000 kgs/hr of dilute liquor show that the total costs (consumption of energy, wages, depreciation, capital yield, overhead expenses and repairs) amount to £20,000 per year. The value of the recovered soda lye is £37,000. The energy required to produce warm water would cost a further £5,000, i.e. the total value would be £42,000. Hence a sum of £22,000 per year can be saved by using an NaOH evaporation plant. This calculation does not allow for any fee charged by municipalities for discharging the liquor to sewers.

Regeneration of spent solutions in the synthetic fibre industry

In the production of staple fibre, rayon, cellophane film, etc., the viscose leaving the nozzles solidifies on contact with the spin bath, with the soda lye from the viscose, leads to an enrichment of sodium sulphate (the reaction of H_2SO_4 contained in the spin bath). Therefore, the baths must be discharged and prepared again, or they must be regenerated. The discharge of the spin bath, results in the loss of sulphuric acid, zinc sulphate and sodium sulphate and the polluting of waters.

Nowadays, the spin bath liquor from most large factories is already regenerated in continuously working cooling crystallisation plants (Fig. 2). The spin bath, usually entering the plant at a temperature of 45 to 50°C, is cooled to the final temperature required in the crystallisation plant by flash evaporation. The vapours of the warm stages are directly condensed in the condenser, whereas in the case of the cold stages, vapour compressors are installed to raise the pressure to that of the condenser. Most of the crystallisers are constructed horizontally and consist of 6 to 10 stages. As the spin bath liquor has a tendency to foam, devices must be installed, especially in the first stage. The Glauber's salt ($Na_2SO_4 \times 10 H_2O$), obtained during the cooling process is maintained in suspension by the rapidly moved liquid during evaporation, and transferred together with the continuous flow of solution to the next stage. This process is assisted by means of a dosed supply of atmospheric air. The air, and all non-condensable gases, are removed by

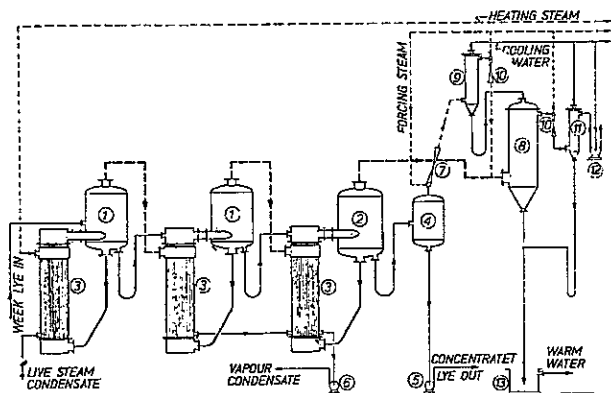


Fig. 1 Triple effect evaporation plant with cooling stage for mercerisation lye.

1, 2: Evaporator; 3. Calandria; 4. Flash recooler; 5. Concentrate pump; 6. Condensate pump; 7. Vapour compressor; 8, 9: Direct contact condenser; 10. Steam ejector; 11. Inter condenser; 12. Vacuum pump; 13. Hot well.

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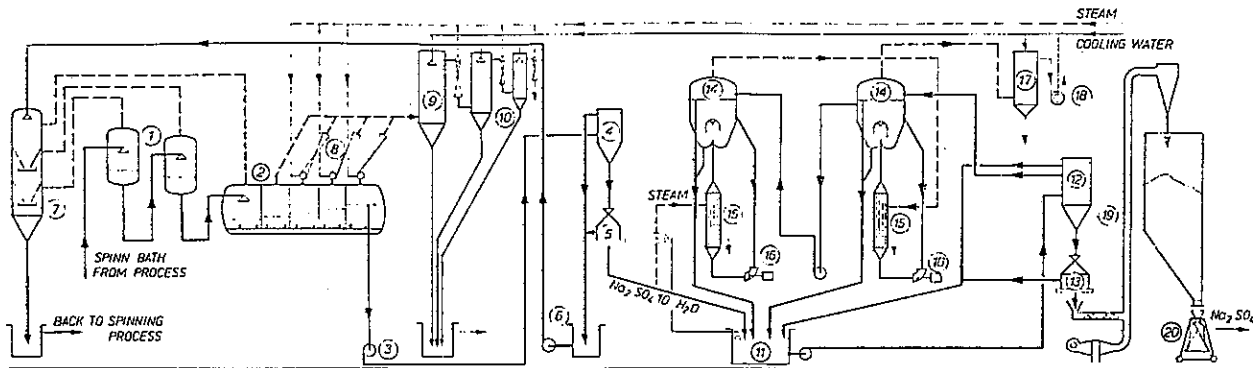


Fig. 2 Sodium sulphate recovery from spinbath.

1. Pre-evaporator; 2. Crystalliser; 3. Slurry pump; 4, 12. Pre-concentrator; 5, 13. Centrifuge; 6. Collecting vessel; 7. Direct contact condenser (heat recovery); 8. Steam ejectors; 9, 17. Direct contact condenser; 10/18. Vacuum pump; 11. Melter; 14. Evaporator; 15. Heater; 16. Circulation pump; 19. Dryer; 20. Bagging station.

water-ring pumps or by steam-jet vacuum pumps. The solution leaving the last stage of the crystalliser at a temperature of 0 to 5°C is separated from the Glauber's salt in a continuously working centrifuge. After passing a heat recovery system the salt-free mother liquor flows back to the spin bath collecting tank.

Glauber's salt can rarely be sold at a profit, except in some special cases (production of viscose sponges). Its transportation is uneconomic because of the high content of water of crystallisation of 56%. Another unfavourable factor is the low melting point of 32°C which may lead to the release of the water of crystallisation during transportation, especially at high summer temperatures.

These disadvantages are avoided when the water of crystallisation is removed by calcination. The anhydrous sodium sulphate obtained (from this process) can be sold. It is used particularly in the glass, paper and detergent industries. There are different methods of performing calcination. In particular two continuous, economic processes developed during the last 20 years and giving a high quality product have found widest application. (Both starting from the melting of Glauber's salt.)

(a) The method regarded as the classical one is the so-called mother liquor crystallisation process. The Glauber's salt obtained from the cooling of spin bath liquor is molten at a temperature of 50 to 60°C in a melting pot equipped with a heating jacket or a heating coil. This treatment releases the water of crystallisation and yields a saturated mother liquor containing abt. 16 to 17% of anhydrous sodium sulphate, in crystalline form. This then flows to a pre-concentrator, is separated in a centrifuge, which reduces the moisture to 2 to 4% before it is finally dried. The mother liquor passes into a cooling crystalliser closely resembling the apparatus required for cooling the spin bath liquor. When cooled to approx. 0°C, Glauber's salt is again obtained, which is separated in a centrifuge and fed back to the melting vessel. The remaining solution consists only of water and a low content of sodium sulphate.

(b) With the modern mother-liquor evaporating process, the Glauber's salt, obtained from the cooling of the spin bath liquor, is also melted. The mother liquor is not cooled but flows to a two- or three-stage evaporation plant. On concentrating the solution, further crystalline sodium sulphate precipitates, which is separated from the solution by centrifuging. Depending on the impurities which are fed to the sodium sulphate installation, together with the wet Glauber's salt from the spin bath crystallisation station, the total water can be evaporated, or alternatively a small part of the solution can be discharged. If the spin bath liquor contains zinc, zinc sulphate can easily be recovered from the discharged solution by means of an after treatment. As a result of this, additional savings in zinc can be made.

The sodium sulphate produced as described in (a) and (b) satisfies the highest quality requirements. According to the process and the starting solution, the purity achieved is between 99.6 and 99.9% plus of Na_2SO_4 . Generally, the costs of regeneration are ca. 20 to

40% lower than the proceeds of the sale of sodium sulphate, which were in the last few years £10 to £12 per ton. Since the beginning of 1969, however, there has been a great shortage and high qualities have prices up to U.S. \$40 and U.S. \$50 per ton.

It is worth noting how the improvement of evaporation techniques, and the introduction of new processes, have reduced energy consumption. Ten years ago, plants for the crystallisation of mother liquor (described under (a)) consumed 1.7 t of steam per ton of sodium sulphate produced. Today, new evaporation techniques with integrated heating-circulation system consumes a little more than 0.7 t steam/t of sodium sulphate.

Spin bath regeneration is an excellent example of the profitable solution of effluent problems in the synthetic fibre industry.

Treatment of pickling solutions containing sulphuric acid in the steel industry

When pickling rolling-mill products, the 25% H_2SO_4 solution becomes richer in iron sulphate. When the pickling solution has reached an iron content of 100 to 120 g/l, it must be discharged and replaced by fresh solution. The used pickling solution is neutralised in large tanks by adding milk of lime. The problems involved in the removal of residues (gypsum) are well-known. This process is not only troublesome but also expensive.

Many large pickling plants in the steel industry have therefore been adapted to continuous regeneration plants. The process is simple (Fig. 3). From the pickling vat, a certain quantity of pickling bath liquor discharges continuously at a temperature of 80 to 90°C and is cooled in a 5- to 12-stage vacuum cooling crystalliser. As it is not possible to 'condense by steam-jet vapour compressors' we suggest 'The vapours arising from the solution are directly condensed in a mixing condenser or lifted up to condensing pressure by steam-jet vapour compressors'. Through the lower solubility caused by the temperature reduction, the iron sulphate precipitates as heptahydrate ($\text{FeSO}_4 \times 7\text{H}_2\text{O}$); it is separated by centrifuging. The salt-free cold solution is used to condense the vapours of the cooling crystallisation plant. During this process, the solution is again heated up to a temperature of abt. 60°C. The system of heat

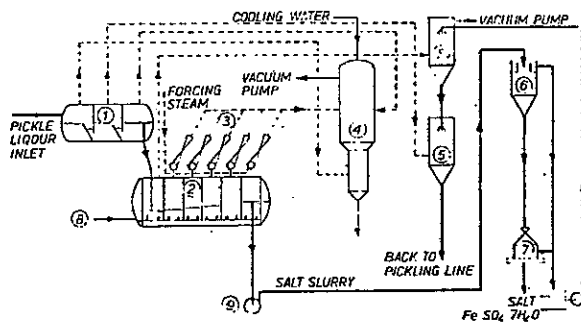
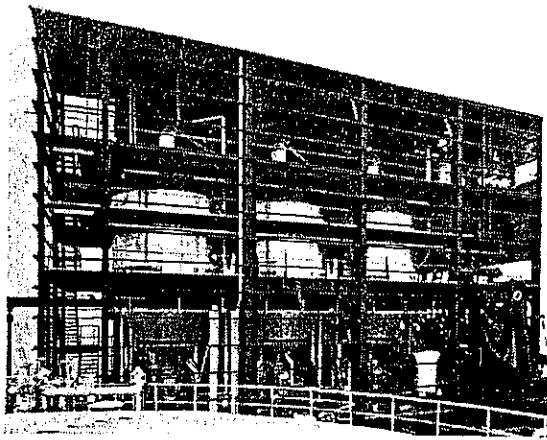


Fig. 3 Nine-stage continuous vacuum crystallisation plant for pickling bath regeneration.

1. Pre-evaporator; 2. Vacuum crystalliser; 3. Vapour compressor; 4. 2-stage vacuum main condenser; 5. Direct contact condenser (heat recovery); 6. Pre-concentrator; 7. Centrifuge; 8. Air agitation system; 9. Salt slurry pump.



A three stage crystallisation plant in the course of erection intended for the production of ammonium sulphate from effluents of caprolactam. Capacity 25 t/h ($\text{NH}_4 \cdot 2\text{SO}_4$).

recovery saves not only the considerable amount of energy required to cool the solution but also an amount of heating steam which would otherwise be needed to heat the solution to the operating temperature. The solution flowing back to the pickling line now contains approx. 5% iron sulphate and 23 to 25% of H_2SO_4 .

Since, during the cooling crystallisation, part of the solution water passes to the cooling water as vapour and as the water of crystallisation bound to the iron sulphate heptahydrate is removed, water and sulphuric acid, used in the process of chemical transformation, must be replenished. This make-up is relatively small compared with the acid lost during neutralisation. Normally, the bath to be neutralised still contains 8 to 10% of H_2SO_4 . A comparison between the effective operating costs of neutralisation and vacuum crystallisation shows the latter to amount to only approx. 20 to 30% of the neutralisation costs. However, since iron sulphate heptahydrate has only a limited sale, an additional profit from this source cannot be expected.

The treatment of acid of reaction (H_2SO_4) from the production of titanium dioxide is in the same category as the regeneration of pickling bath because, here too, iron sulphate heptahydrate crystallises and the dilute acid is concentrated by evaporation. At present, however, this process is not yet widely used since profitable production can only be achieved in combination with further treatment of the concentrated acid of reaction (production of phosphate fertilisers), and because it is still possible to discharge these effluents into the sea.

Treatment of effluents from the production of caprolactam

Caprolactam is an important basic material for producing synthetic fibres. In past years, production capacity in this field has been

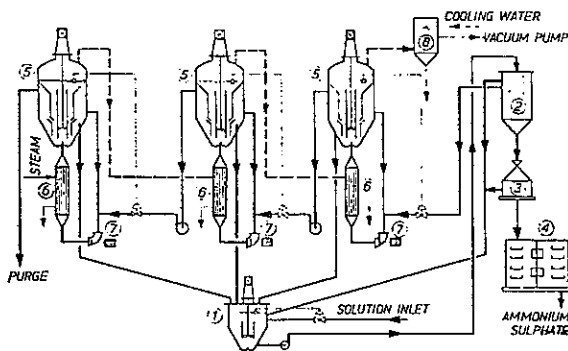


Fig. 4 Three-stage crystallisation plant for ammonium sulphate.

1. Slurry collecting tank; 2. Pre-concentrator; 3. Centrifuge;
4. Dryer; 5. Evaporator-crystalliser; 6. Heater; 7. Circulation pump; 8. Direct contact condenser.

increased considerably. Various processes are used; consequently, different amounts of effluents are obtained which generally contain 25 to 39% of ammonium sulphate. The pH values of these sulphuric acid-containing solutions range from 3 to 4.5. Frequently these solutions also contain up to 0.7% of ammonium nitrate and certain polymeric compounds. Since the quantity of these effluents, which contain a valuable product, normally amount to 25 to 100 tons/hr, as complete a treatment as possible must be used. According to the latest practice in this field, mainly three-stage evaporation crystallisers are used for this purpose. They are equipped with a forced circulation system and designed to produce crystals which satisfy internationally recognised specifications for export quality ammonium sulphate. Despite the concentration of impurities during evaporation a counterflow wash of fresh solution gives the requisite purity of the product. The specific consumption of steam, including drying, range from 0.75 to 1t/t ammonium sulphate, according to the concentration of the starting solution. Cheap low-pressure steam of less than 0.5 kg/cm² (approx. 7 psi) can be used.

When the concentration of impurities in the solution is greater due to the presence of ammonium nitrate and other substances arising from the production of caprolactam, an amount of up to 5% of the starting solution must be discharged from the crystallisation process. This quantity can either be treated or neutralised.

The selling price of ammonium sulphate is more than £20 per ton. Consequently, the plant yields a good profit and also solves the effluent problem.

Fig. 4 shows a crystalliser-plant for ammonium sulphate from caprolactam manufacture effluents.

Recovery of sylvinite from the slag of aluminium production

Though this is not an effluent treatment problem the techniques used are relevant to the solution of similar problems.

In the production of crude aluminium, sylvinite is added to the melt. When the reaction is over, slag is discharged and usually tipped. It normally contains approx. 60% soluble substances, especially NaCl/KCl and approx. 40% of insoluble substances. By means of natural precipitation, part of the substances is continuously leached out so that there is a danger of polluting the underground water. This problem is solved in the following way (Fig. 5): The slag is ground and fed into a continuous dissolving unit. The solution which has absorbed NaCl/KCl flows through a filter plant which separates the remaining insoluble matter. The solution, thus purified, passes into a three-stage forced circulation evaporation crystallisation plant. Here NaCl/KCl forms again as a mixed salt (sylvinite) which is separated in a centrifuge station. There is no need to discharge any solution from the plant because the processing eliminates the impurities remaining in the solution together with the salt. The sylvinite is then again added to the aluminium melt.

The price of crude sylvinite is about £10 per ton. The total costs (energy, personnel, depreciation, capital yield, cost for treating the slag, etc.) amount to approx. £6 per ton of sylvinite, i.e. the treatment is an economic solution of the residue problem.

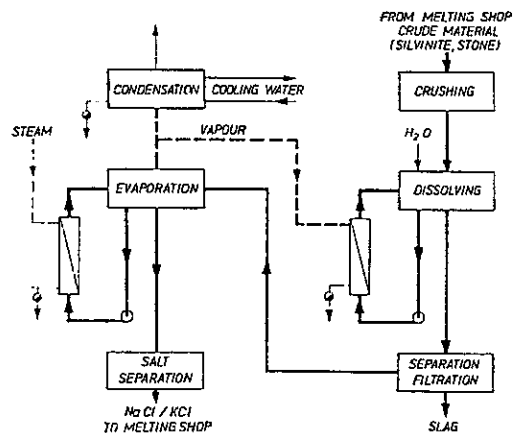


Fig. 5 Slag treatment (sylvinite crystallisation).