STANDARD MESSO

# RAW MATERIALS FROM THE SEA — RECOVERY OF WATER AND SALT FOR A NEW CHEMICAL COMPLEX IN LIBYA

**By W. Wöhlk, Standard Messo, Duisburg**

Special reprint from Middle East Water & Sewage July/August 1983

# Raw materials from the sea — recovery of water and salt for a new chemical complex in Libya

**By W. Wöhlk, Standard Messo, Duisburg**

The Libyan Government has embarked on an investment programme aimed at establishing new industries and improving the country's infrastructure. Central to this plan is the construction of a large chemical complex for the production of vinyl and polyvinyl chlorides. It has been built at Abu Kammash on the Mediterranean coast by a German consortium at a total cost of over DM 1000million. There are large natural salt deposits in the form of a salt lake which will provide feed stock for the plant.

Fresh water for the operation of the plant is not available locally and the requirement for potable and process water has had to be met by sea water desalination. The chlorine required for the vinyl and polyvinyl chlorides production and for the chlorination of the salt and potable water is produced within the plant, the raw material for the chlorine being the natural salt deposits of the salt lake. This natural salt is also refined to produce table salt. Fig 1 shows the basic requirements for salt and water recovery.

**Seawater - Mediterranean**

| | | | | |
|---|---|---|---|---|
| Raw Materials | Brine | $NaCl$ | min | 224g/litre |
| | | $MgSO_4$ | max | 35g/litre |
| | | $MgCl_2$ | max | 68g/litre |
| | | $KCl$ | max | 13g/litre |
| | | $CaSO_4$ | max | 0.5g/litre |
| | Water | Process water | | $140m^3/h$ |
| | | | max | 100ppm |
| | | Potable water | | $30m^3/h$ |
| | | | max | 500ppm |
| Products | Salt | Table salt | | 5t/h |
| | | NaCl | | 99.7% |
| | | Electrolysis salt | | 10t/h |
| | | NaCl | | 99.8% |
| | | Mg | max | 430 ppm |
| | | Ca | max | 150 ppm |
| | | $SO_4$ | max | 750 ppm |

**Fig 1 Plant requirements**

A multi-stage flash (MSF) plant was chosen for water recovery and a three stage sequentially arranged evaporation crystallisation plant for salt production. Altogether $170m^3/h$ of water is produced, of which $140m^3/h$ is process water with a maximum of 100ppm dissolved solids and 30m23/h is potable water with a maximum of 500ppm dissolved solids. Of this total $120m^3/h$ is produced in the MSF plant and $50m^3/h$ in the evaporation plant (Fig 2). Total salt production is 15tonnes/h of which 5tonnes/h is table salt and 10tonnes/h is salt of electrolysis quality. In addition to the salt deposits at the salt lake, a brine is also available for salt recovery. 224g/litre of NaCl and almost 120g/litre of other salts are dissolved in the brine which reproduces continuously by diffusion of seawater in the lower salt layers.

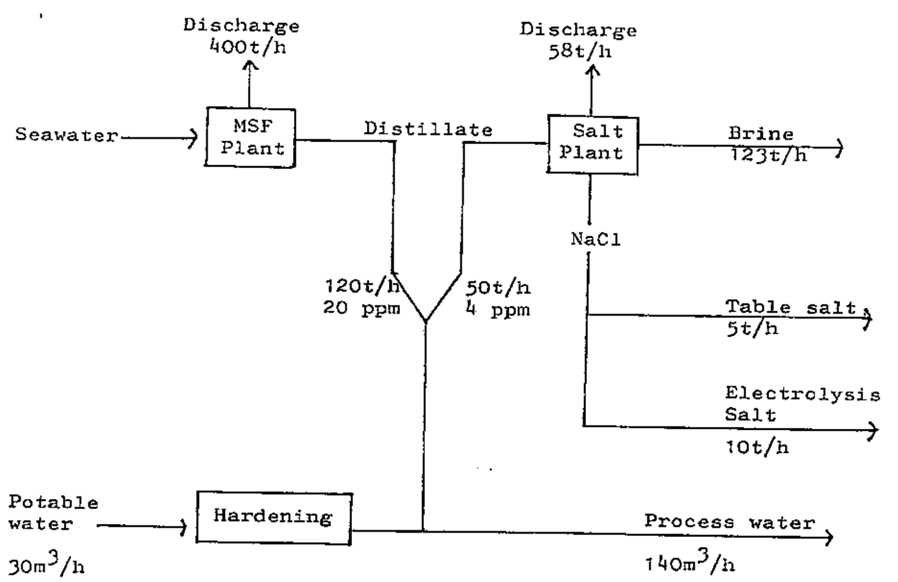



**Fig 2 Recovery of salt and potable water for a chemical complex.**

## Recovery of water using the multi-stage flash plant (Fig 3)

The total dependence of the chemical plant on the water supply meant that the MSF plant had to be designed for the utmost reliability and the processes control systems and components were all selected with this in mind. Failures in existing MSF plants were known to be due principally to incrustations and the consequent cleaning operations as well as material problems. With the Libyan plant corrosion problems were minimised by optimum material selection. The heat exchangers in the refrigeration and heat recovery sections use CuNi:10Fe tubes while the tube bottoms are made of a harder CuNi:30Fe alloy. The entire evaporation tank was made of CuNi:10Fe and Monel was selected for the demisters. A rubber-lined steel structure is used for the turn-round caps and water chambers in the seawater section and for the brine circulation section. The use of these materials has resulted in corrosion-free operation.

The demand for long trouble-free operation has also affected the process plant layout and in this context the double arrangements of the condensation and heating sections deserve special consideration. The heat exchanger surface for the plant was split into two units (Fig 4) which could be operated independently. Each half has its own cooling water inlet, its own circulation pump and its own end heater and this enables the heat exchanger tubes to be cleaned without interrupting the operation of the plant.

During normal operation the plant has a maximum brine temperature of 90°C. With one heat exchanger disconnected the plant will be operating with only 50 per cent of the normal condensation surface. However, the plant can still be operated to 85 per cent of its full capacity by raising the brine temperature to 98°C. Thus, cleaning or maintenance work on the condensation section can be carried out without significantly affecting

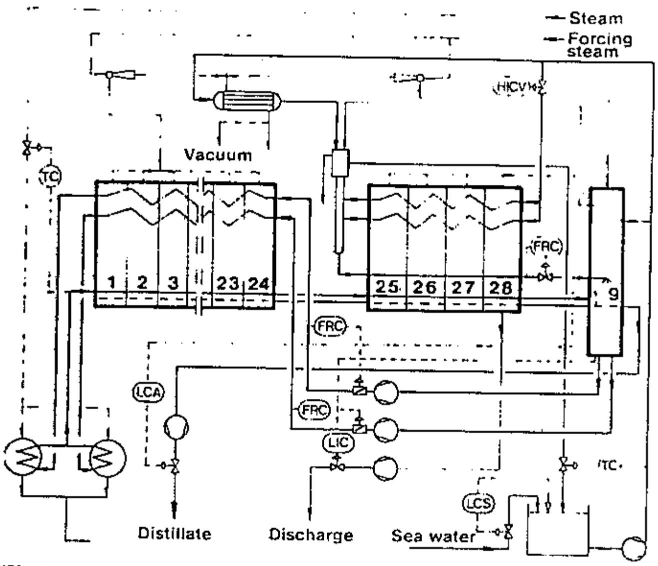



**Fig 3 MSF plant-double arrangement.**

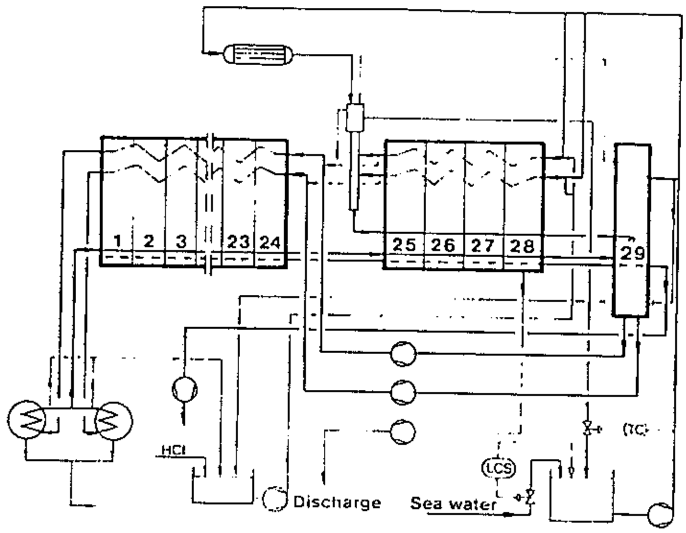



**Fig 4 MSF plant was split into two units which could be operated independently.**

distillate production. A special cleaning control was built-in to enable heat exchanger surfaces that had become encrusted with carbonates or hydroxides, to be cleaned chemically. The two lines can be cleaned independently of each other, with diluted HCl and this allows one line to be on full production whilst the other is being cleaned. Solution sides of the heat exchangers are set in a two way arrangement (Fig 5) in order to give a flow velocity of 1.8m/s and this results in a horizontal arrangement of the brine overflow lines from stage to stage (Fig 6). In order to equalise the flow and evaporation rates in Stage 1 the heated brine is fed in parallel via five feeding tanks.

The plant started operating in March 1980 and reached full capacity within 24 hours of start-up. During acceptance test all design parameters were met without exception (see Fig 9). The remarkable improvement of the performance ratio, from 8 to 9.4, is attributable to the fact that the heat exchanger surfaces were not at this stage encrusted, ie the fouling factor included in the calculations, but not required during the acceptance test, has a surface enlarging effect. The heat exchanger surfaces have not deteriorated to date, that is to say that no incrustation has occurred during the past two years of operation.

## Recovery of salt in the evaporation plant

As mentioned previously, a 3-stage evaporation crystallisation plant was chosen for salt recovery. The third stage consists of two

| | Design parameters | Operating results |
|---|---|---|
| Distillate production | 120t/h | 122.6t/h |
| Heating steam consumption | 15t/h | 13t/h |
| Power factor | 8kg/kg | 9.4kg/kg |
| Purity of distillate | 20 ppm | 10 ppm |
| Heating steam pressure | 0.9 bar | 0.7 bar |
| Max brine temperature | 90°C | 90°C |
| Concentration factor | 1.3 - 1.8 | 1.45 |

**Fig 7 MSF design parameters.**

**Fig 5 MSF plant during construction.**

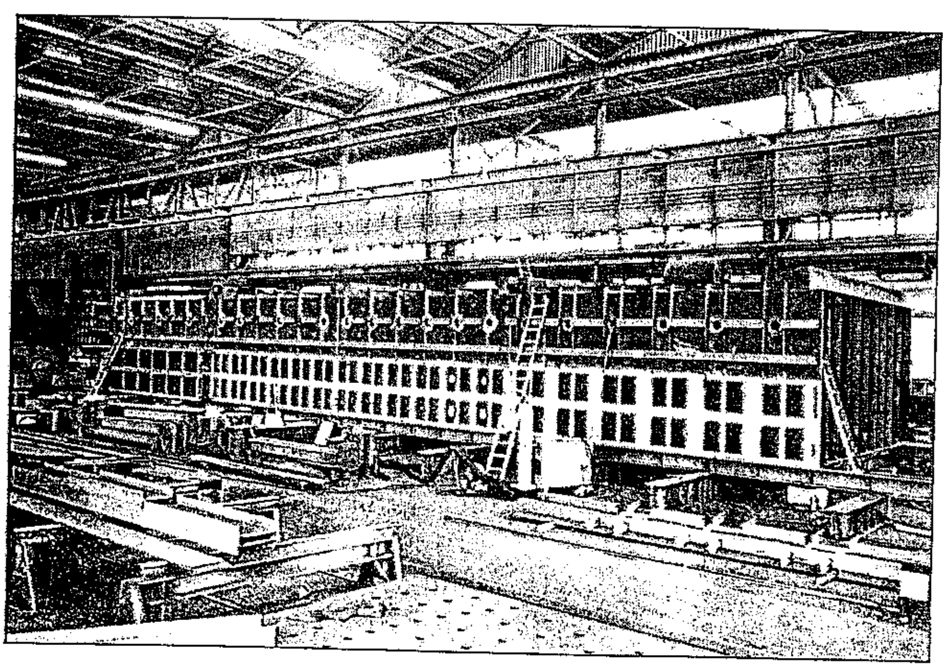
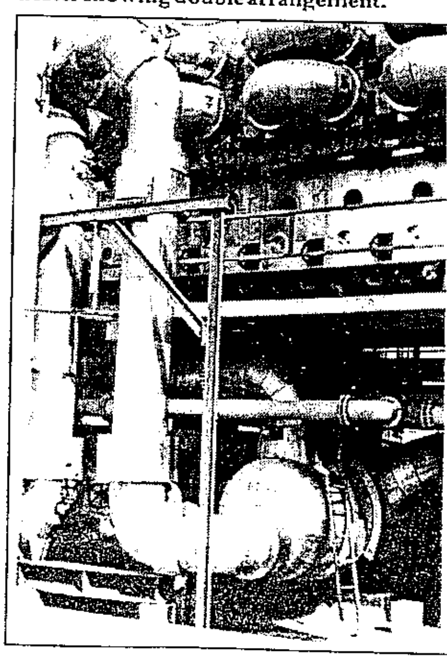


**Fig 6 Head of MSF plant with brine end heater showing double arrangement.**



evaporation units which, on the vapour side, are arranged in parallel. In all four stages, the fresh brine is fed in parallel. The evaporation output of 50tonnes/h is reached by applying 19tonnes/h of live steam.

When planning the salt plant, the tendency to incrustation of the brine being processed and the high purity required for the NaCl were given particular attention. Incrustation is mainly calcium sulphate (gypsum) which precipitates in the course of NaCl crystallisation. To avoid these incrustations, a gypsum circulation is established round the whole plant so that CaSO4 suspension density of several per cent is achieved. Gypsum crystallisation is thus controlled and incrustation of the heat exchanger surfaces does not occur.

In order to recover a pure vapour condensate, demisters were incorporated into all evaporation stages which ensure impurities of less than 10ppm dissolved solids. The distillate produced is conveyed to the desalting plant. Starting from the salt lake brine, with simple evaproative crystallisation and subsequent separation in a centrifuge, a salt would be produced which contains six times the amount of calcium sulphate and about 10 times the amount of magnesium that is permissible. The magnesium impurities reach the salt via the surrounding mother liquor, whilst calcium sulphate and NaCl exist as crystalline solids. With a special cleaning control the salt from the evaporator is improved to the required quality. NaCl and calcium sulphate are separated from each other in the hydrocyclones and the solid impurities removed by the multi-stage counterfow washing process, using sea water. The salt destined for the electrolysis is conveyed whilst still wet to the saturators. The salt required for the table salt market is dried and sprayed with anti-caking additives and is packed.

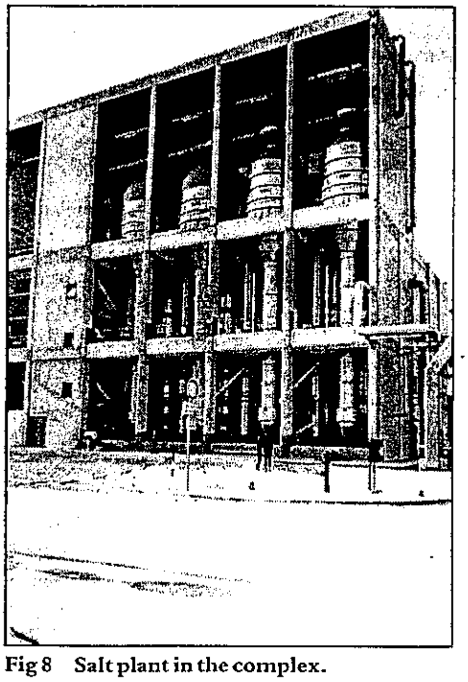


**Fig 8 Salt plant in the complex.**

Fig 8 shows the 4-stage plant solution side which extends to a height of 29m and covers, including salt preparation, drying and packing, an area of approx 1000m². In the heater circuit there is a circulating pump at each stage, which delivers 4000m³/h of suspension through the heater tubes maintaining a velocity of 1.5m/s. If no brine is available, the discharge from the MSF plant can be used for salt recovery, with a repectively higher evaporation capacity. Plant of this type is extremely liable to incrustation as a result of the large amounts of gypsum precipitated. However with specially developed controls it is possible to avoid incrustation altogether. Firstly, the pre-concentrated seawater from the discharge solution of the MSF plant is further concentrted by multi-stage evaporation up to saturation and in the final stage crystallisation of NaCl takes place.

The prerequisite for an incrustatiôn-free operation of the evaporation section is the existence of gypsum crystals in the evaporators. Supersaturation-producing incrustation can be avoided if, on one hand the suspension density is maintained at approximately 10 weight per cent and on the other hand the especially suitable $CaSO_4 - ½H_2O$ is being crystallised. The precipitation of $CaSO_4 - ½H_2O$ is adjustable in salt solutions by choosing corresponding concentration/temperature fields. According to the operation scheme shown in the semi-hydrate is the precipitating and constant solid phase due to the kind of solution flow in the first two evaporation stages. In the third evaporation stage, however, preconcentration takes place but not crystallisation. After separation and partial return of the $CaSO_4 - ½H_2O$ crystals into the pre-evaporators, the desired sodium chloride in electrolysis salt quality is finally produced in the last stage. Incrustations with $CaSO_4 - ½H_2O$ have not yet occurred in plant arranged in this way.

So far three such salt plants are operating worldwide. The largest of these plants, in the Arabian Gulf, produces 100tonnes/h of distillate and 4.5tonnes/h of electrolysis salt from the discharge brine of an MSF plant.

The plant is of a 3-stage design consisting of three fixed circulation evaporators, *ie* two concentration stages and one crystalliser. The evaporators have diameters of 4.8m, 6.5m and 6.5m respectively and use heat exchangers with an exchange surface of 900m² each. The vapours of the last stage are condensed in an end condenser with an exchange surface of 1200m².

S21e 1000/1.84 printed in England by N & W Litho Limited