A New Process for Reducing the Chlorinated Effluent of a Vacuum Salt Plant

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ABSTRACT

The Compagnie des Salins du Midi et des Salines de l'Est operates a refinery at Varangeville, the nominal capacity of which is 600,000 metric tons of salt per annum. Until July 1978 all effluent from the mine was cycled back into the natural surroundings, which caused pollution of more than 4 kg of chlorine ions per second during periods of operation.

Since then this pollution has been reduced in two consecutive stages to about 0.5 kg of chlorine ions per second. This was achieved by:

- *Causing the cleansing water from the evaporators functioning in crude brine (high suspension and rich in calcium chloride) to react with the cleansing water from evaporators supplied with purified brine containing sodium sulfate. After sedimentation and filtration this effluent is recycled in the production process*
- *Using the bulk of the other contaminated factory effluents to produce saturated brine for the drillings made in the Keuper salt deposits in Lorraine.*

INTRODUCTION

Compagnie des Salins du Midi et des Salines de l'Est (C.S.M.E.) operates a vacuum plant at Varangéville, near Nancy, in France, with a yearly capacity of 600,000 tons of salt. This vacuum plant is located on the banks of the Meurthe River, which is a tributary of the Moselle, itself a tributary of the Rhine River (Chart 1).

In 1977, all the effluent from the Varangéville vacuum plant was discharged directly into the natural environment and polluted the Meurthe, Moselle and Rhine Rivers with chlorine ions contained in this effluent. At that time, the waste constituted 3.3 kg/s of chlorine ions and represented one per cent or all chlorinated pollution of the Rhine.

The processes described in this paper, and put into operation between 1978 and 1981, have reduced this pollution figure to one sixth of its original amount, which is by now no more than 0.52 kg/s of chlorine ions (Chart 2).

OUTLINE DESCRIPTION OF THE VARANGEVILLE VACUUM PLANT

The Varangéville vacuum plant consists of two evaporation units—a thermo-compression unit and a quintuple effect unit. For historical reasons the quintuple effect is comprised of eight evaporators, one for each of the first and second effects, and two evaporators for each of the three last effects (Chart 3).

High pressure steam is produced by two coal-fired boilers. All mechanical power, most of the electrical power and all low pressure steam required for plant operation are generated by the expansion of this high pressure steam in a reaction-type turbine, which drives an alternator and a steam compressor on the same shaft. The low pressure steam is mainly used to feed the quintuple effect system. The mechanical energy of the steam compressor operates the thermo-compression unit. Electric current generated by the alternator feeds the ancillary equipment.

The brine used by the Varangéville vacuum plant comes from brine fields, 8 kilometers distant, which are supplied by water from the Meurthe River (Chart 4). The raw brine from these brine fields is fed directly to seven of the nine evaporators. The magnesium contained in this brine is eliminated by a lime treatment carried out in the evaporators:

$$CaO + H_2O + MgSO_4 \longrightarrow CaSO_4 + \underline{Mg(OH)_2}$$

$$CaO + H_2O + MgCl_2 \longrightarrow CaCl_2 + \underline{Mg(OH)_2}$$

The evaporators operate under high suspension. The solid impurities (calcium sulphate, magnesium hydrox-

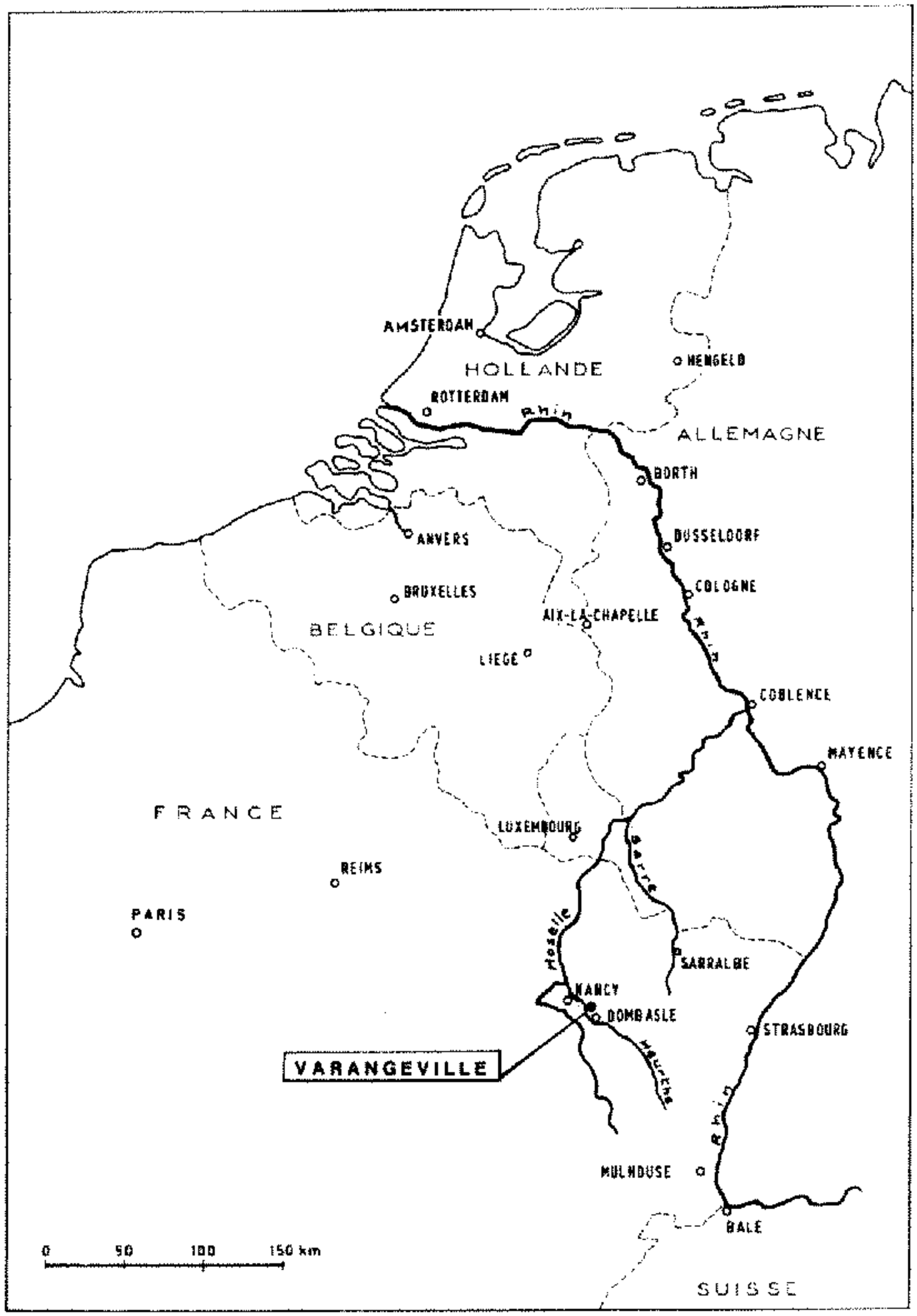

Chart 1. Location of the Varangeville Vacuum Salt Plant

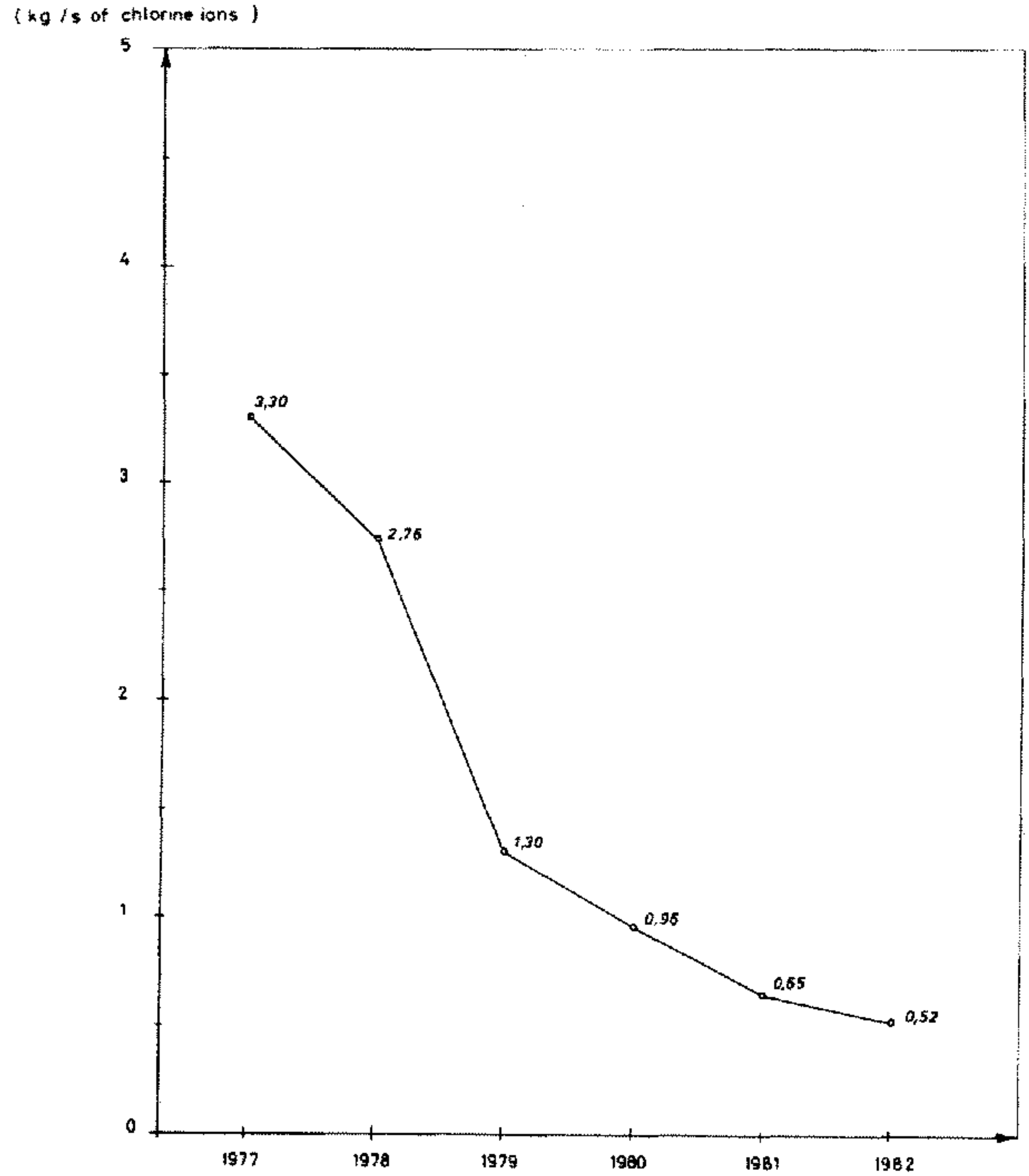

Chart 2. Evolution of the Chlorinated Effluents from Varangéville Vacuum Plant

ide) are held in suspension in the evaporator. A bleed maintains the impurity content of the evaporating brine at a constant level. To save energy and reduce the total amount of bleeds (the solubility of calcium sulphate decreases with temperature), the bleed from the thermocompression unit is discharged into the third effect, that from the first effect into the second one, that from the second effect into the third and that from the third effect into the fourth one.

The two other evaporators making up the fifth effect are fed with purified brine. This purified brine is produced by eliminating the calcium and magnesium ions contained in the raw brine by addition of sodium carbonate (Na_2CO_3) and lime (CaO).

$$CaO + H_2O + MgSO_4 \longrightarrow CaSO_4 + \underrightarrow{Mg(OH)_2}$$

$$CaO + H_2O + MgCl_2 \longrightarrow CaCl_2 + \underrightarrow{Mg(OH)_2}$$

$$Na_2CO_3 + CaCl_2 \longrightarrow 2NaCl + \underline{CaCO_3}$$

$$Na_2CO_3 + CaSO_4 \longrightarrow Na_2SO_4 + \underline{CaCO_3}$$

After decantation of the insoluble matter (magnesium hydroxyde, calcium sulphate and calcium carbonate), the purified brine contains only sodium sulphate in solution. This content is maintained at a constant level in the evaporator by bleeding.

The raw brine to be purified is first pumped into a tank where it is mixed with a lime milk; it is then fed into a second tank where it reacts with sodium carbonate to eliminate the calcium ions. It is finally decanted and filtered before being stored in a 2,500-cubic-meter tank (Chart 5).

ORIGIN OF EFFLUENTS

Effluent from the Varangéville vacuum plant originates mainly from four sources:

- bleeds from evaporators containing raw brine
- bleeds from evaporators containing purified brine
- sludges from the brine treatment plant
- unsaturated brine from washing the plant equipment, and from dissolution of the salt dust produced when drying the salt.

The first three effluents are saturated with sodium chloride and contain soluble and insoluble impurities. But the last mentioned effluent is not saturated and contains only a few soluble or insoluble impurities. The following table 1 shows the amounts of effluent discharged into the Meurthe River in 1977:

TABLE 1

Effluent: Initial Situation

	Insolubles (t/h)			Solubles (t/h)			
	$Mg(OH)_2$	$CaSO_4$	$CaCO_3$	Ca^{2+}	Na^+	SO_4^{2-}	Cl^-
Bleeds from raw brine evaporators	—	—	—	0.57	6.33	0.14	10.73
Bleeds from purified brine evaporators	—	—	—	—	0.81	0.17	1.08
Brine treatment plant sludges	0.06	—	0.26	—	0.50	0.02	0.76
Other salted effluents	traces	traces	—	—	1.87	—	2.88
Total	0.06		0.26	0.57	9.51	0.33	15.45

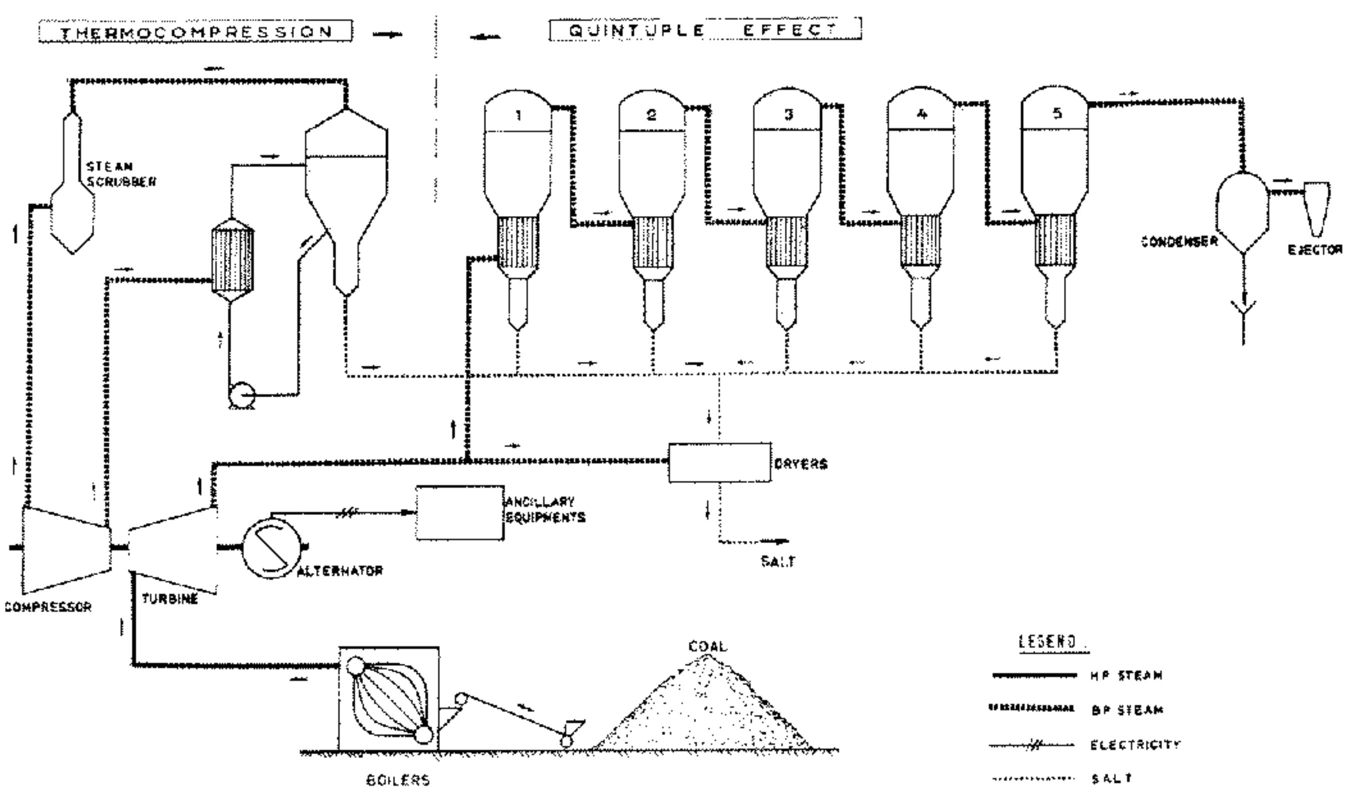

Chart 3. Flow-Sheet

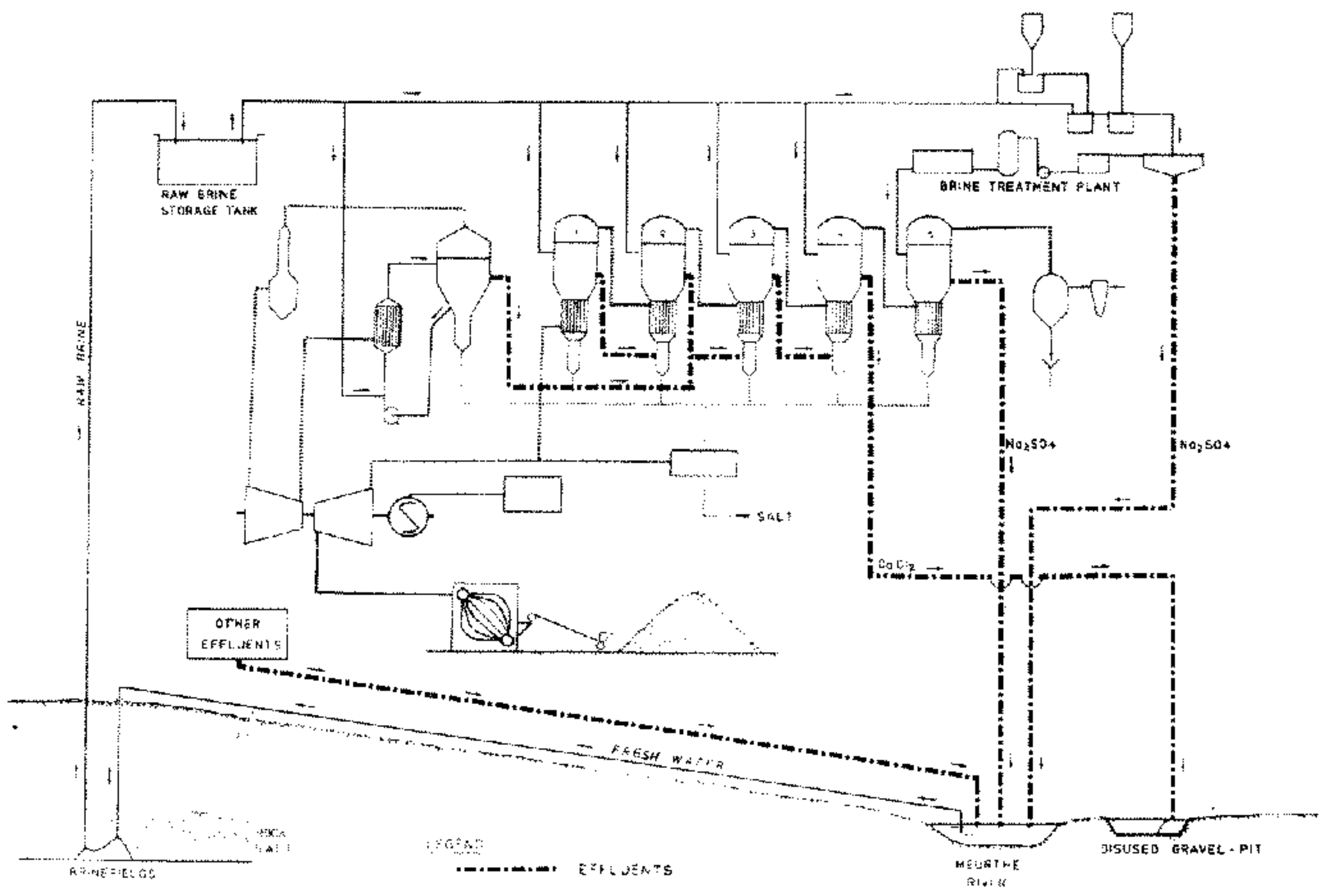

Chart 4. Initial Situation

In 1977, bleeds from the raw brine evaporators containing suspended solids ($CaSO_4$; $Mh(OH)_2$) were stored in an unused gravel pit serving as decanter, and the banks of the pit let the liquid part of theses effluents be filtered into the Meurthe River.

Bleeds from the purified brine evaporators which contain no solid impurities were drained directly into a tributary of the Meurthe River, together with discharge from the brine treatment plant and the balance of the vacuum plant effluents (Chart 4).

FIRST STEP OF REDUCING CHLORINATED EFFLUENT (Chart 6)

Two operations were carried out with the aim of reducing the chlorinated wastes from the vacuum plant:

- incorporation of a bleeds treatment plant
- injection into the brine fields of part of the salted effluents coming from the vacuum plant.

Bleeds Treatment Plant

This plant is intended for mixing together in a reactor the following:

- bleeds drained off from the raw brine evaporators which include calcium chloride ($CaCl_2$) in solution and suspended solids ($Mg(OH)_2$, $CaSO_4$)
- bleeds drained off from the purified brine evaporators containing only sodium sulphate (Na_2SO_4) in solution (Na_2SO_4) in solution
- Sludges coming from the decanter of the brine treatment plant which include suspended solids ($Mg(OH)_2$ and $CaCO_3$) as well as sodium sulphate (Na_2SO_4) in solution.

The following chemical reaction takes place in the reactor:

$$CaCl_2 + Na_2SO_4 \longrightarrow \underline{CaSO_4} + 2NaCl$$

To separate the solids ($CaSO_4$, $Mg(OH)_2$ and $CaCO_3$) from the liquid, the mixture is then transferred into a decanter after addition of a flocculating agent to make easier the precipitation of all suspended matter. Overflow from the decanter, which, in view of the proportions of the various waste fluids and their chemical composition, contains only calcium chloride and sodium chloride in

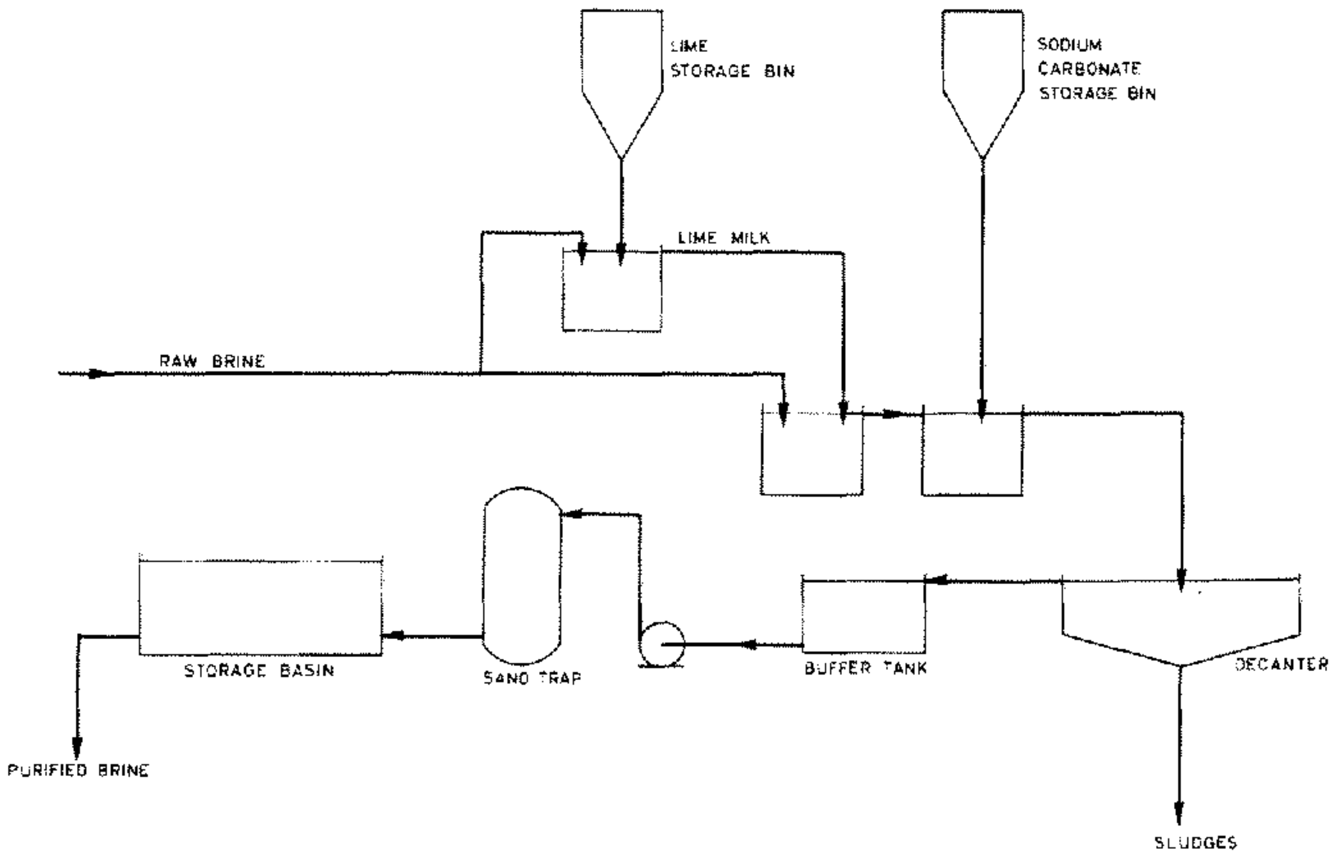

Chart 5. Brine Treatment Plant

solution, is recirculated into the raw brine evaporators. The decanter underflow, after being diluted with fresh water, is fed to the unused gravel pit serving as a decanter, where the suspended solids ($CaSO_4$, $Mg(OH)_2$ and $CaCO_3$) form a deposit.

Injection of Salted Effluents into the Brine Fields

Until July 1978, the raw brine was produced by dissolving the rock salt bed with fresh water coming from the Meurthe River. But after this date, the brine fields were partly fed by some of the salted effluent discharged by the vacuum plant. A sewage network was built to recover all salted effluents that were free of all other chemicals and to discharge them to the pumping pit that fed the brine fields.

Only wastes with a very low salt content and those containing undesirable chemicals, such as potassium ferrocyanide used as an anticaking agent for the salt, and which would interfere with the operation of the evaporators, continued to be discharged into the Meurthe River.

Upon completion of this initial phase, chlorinated effluents had been reduced by approximately 75%, and discharge of suspended solids had been completely eliminated.

TABLE 2

Effluent After First Step

	Solubles t/h			
	Ca^{2+}	Na^+	$SO_4^=$	Cl^-
Bleeds treatment plant underflow	0.02	1.16	0.02	2.00
Other salted effluents	—	1.24	—	1.90
Total	0.02	2.40	0.02	3.90
Original conditions	0.57	9.51	0.33	15.45

SECOND STEP OF REDUCING CHLORINATED EFFLUENT (Chart 7)

In order to reduce still further chlorinated effluent from the vacuum plant, a second series of operations was initiated at the end of 1981 with the aim of recovering the brine included in the underflow from the bleeds treatment plant decanter which has a flow rate of approximately 10 m^3h and a concentration of solids close to approximately 300 g/l. To this end, this underflow is centrifuged.

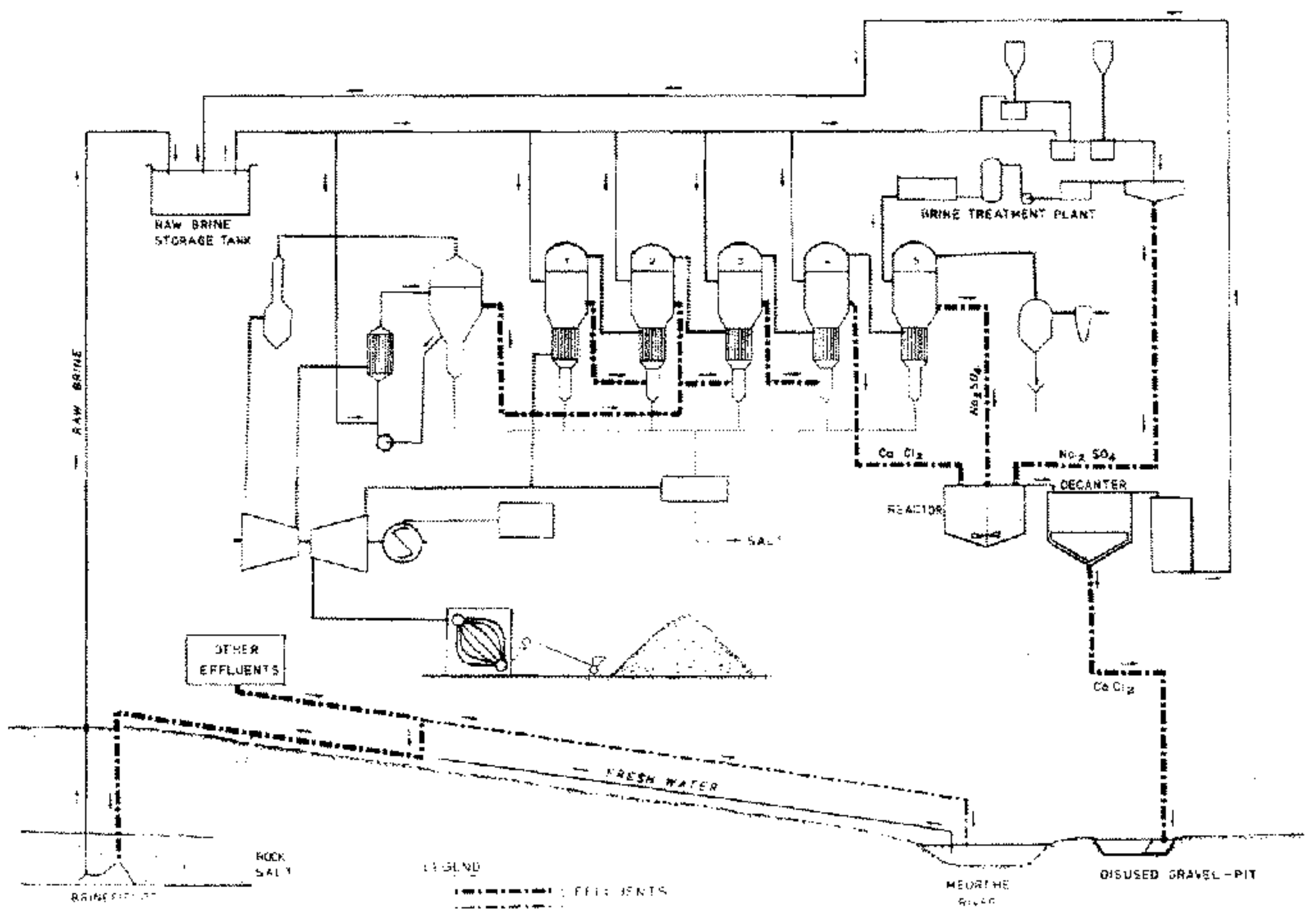

Chart 6. First Step

The liquid obtained from this centrifuging has a solid matter content of below 150 mg/l, and is fed to the decanter of the bleeds treatment plant in order to be clarified and to be recirculated in the raw brine evaporators. In order to stabilize the calcium chloride content of the brine in the evaporators, a deconcentration bleeding must be made; the bleed flow varies according to the magnesium chloride content of the raw brine and is approximately 2 m^3h. This charge containing suspended solids is fed to the gravel pit where it is decanted.

The sludges obtained from centrifuging, which have a residual moisture content of 40% in weight at the outlet of the centrifuge, are mixed with fresh water before also being discharged to the gravel pit. Upon conclusion of this second step, discharge had been reduced by 45% in relation to the first step and 86% in relation to the initial situation.

TABLE 3

Effluent After Second Step

	Solubles t/h			
	Ca^{2+}	Na^+	$SO_4^=$	Cl^-
Sludges obtained from centrifuging and deconcentration bleeds	0.06	0.69	0.002	1.250
Other salted effluents	—	0.58	—	0.900
Total	0.06	1.27	0.002	2.15
Situation at the end of the 1st step	0.02	2.40	0.02	3.90
Original conditions	0.57	9.51	0.33	15.45

RESULTS

The discharge of chlorine ions dropped from 3.30 kg/s in 1977 to 0.52 kg/s in 1982, as shown in Chart 2. Since July 1978, sludges from the brine purifying station containing lime carbonate and magnesium hydroxide in suspension are no longer discharged into the Meurthe River but mixed with process bleeds for treatment.

The cost of this operation, which has been partially subsidized by Agence Financiere du Bassin Rhin-Meuse, was 7.6 MF (investment and operation over a ten-year pe-

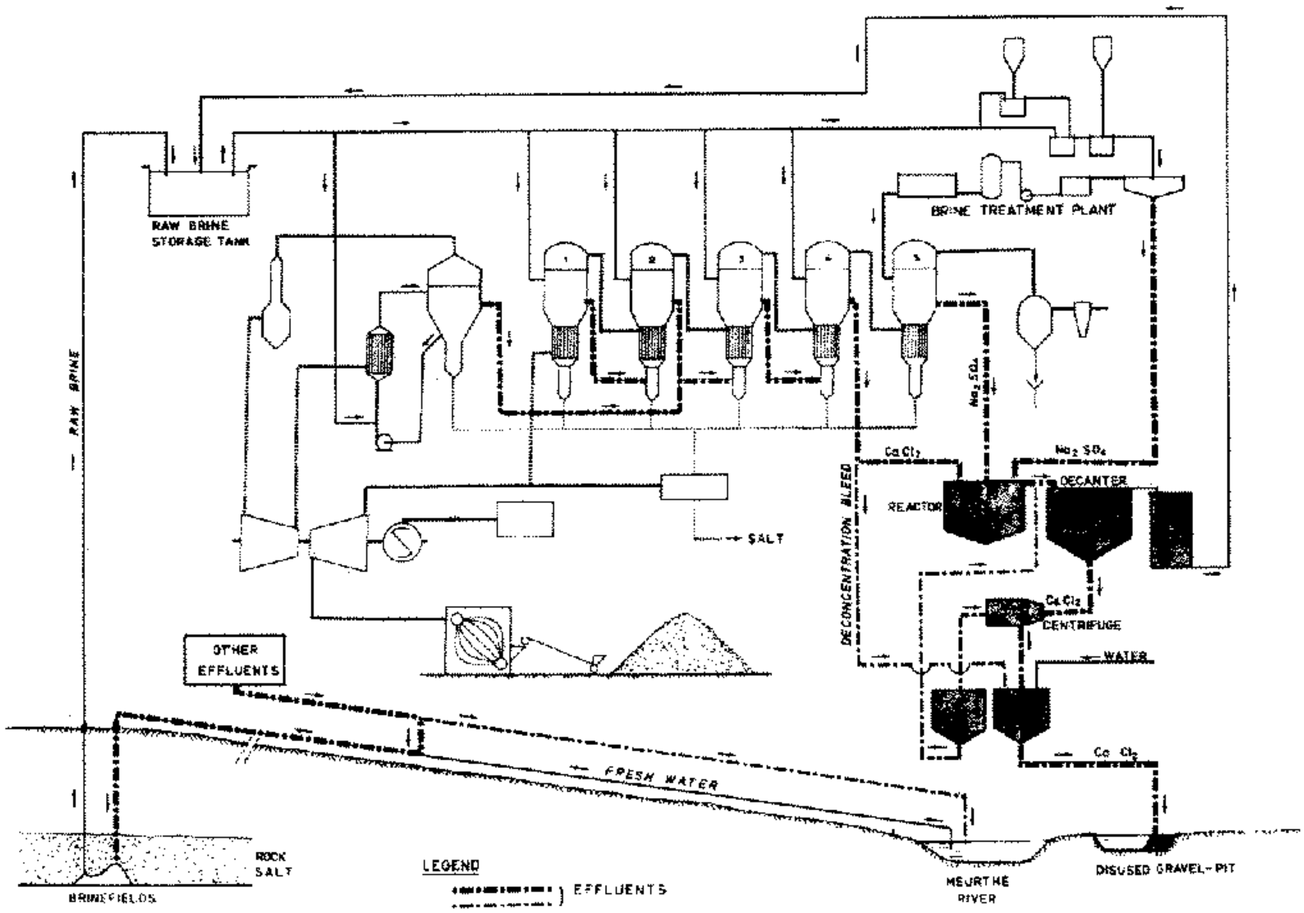

Chart 7. Second Step

riod) i.e., 2.75 MF per kg/s of chlorine ions removed. By comparison, the project for injecting salted wastes from the Mines de Potasse d'Alsace into the Grande Oolite salted water table, at present under consideration by the Rhine River International Commission, would cost over 10 MF per kg/s of chlorine ions removed.