Seventh Symposium on Salt, Vol. I 577–582 (1993)
Elsevier Science Publishers B.V., Amsterdam

A New Magnesium Sulfate Production Plant at Salin de Giraud

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ABSTRACT

The Compagnie des Salins du Midi et des Salines de l'Est has been producing magnesium sulfate (epsomite) at the Salin de Giraud Saltworks for many years, in parallel with its production of salt. This rather small-scale production was unable to meet the growing demand for magnesium sulfate. The sulfate was obtained simply by cooling bitterns in storage ponds during the winter. The tonnage produced obviously depended on climatic conditions, and could not be predicted in advance. In order to overcome these constraints, the Compagnie des Salins du Midi et des Salines de l'Est developed an artificial process for cooling bitterns, making it possible to produce magnesium sulfate all year round. This procedure consists of cooling the bitterns in a crystallizer with a large number of compartments. Each compartment is cooled using trays in which cooling liquid from a refrigeration machine circulates. The bittern solution circulates from compartment to compartment with the crystals and is continuously cooled, so that the growth of crystal size can be controlled throughout the circuit. With this procedure, tonnage production is constant, and the crystals are chemically pure and of the right size.

INTRODUCTION

The Compagnie des Salins du Midi et des Salines de l'Est (C.S.M.E.) operates the Giraud Saltworks located in the French *commune* (smallest territorial division) of Arles. The saltworks is capable of producing 800,000 tonnes of salt in an average year (Fig. 1).

This saltworks was established in 1856 by Henri Merle, founder of the Companie Péchiney, since when it has manufactured bittern-derived products. Having decided to manufacture these products, Henri Merle called upon the renowned chemist Jérôme Balard, who had already discovered a new chemical element — bromine — from the bitterns of saltworks.

By applying Balard's inventions, it was possible to extract a great number of salts from the bitterns:

- Gauber's salt ($Na_2SO_4 \cdot 10H_2O$)
- Epsomite ($MgSO_4 \cdot 7H_2O$)
- Kainite ($MgSO_4 \cdot KCl \cdot 3H_2O$)
- Carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$)

plus various specific or non-specific blends of the above-mentioned salts.

However, from the beginning, this activity required a great deal of effort in terms of research and development. The conditions for economically profitable extraction were never truly attained, and the discovery of potassium mines in Germany and subsequently in Alsace put an end to research undertaken in this area. All the procedures concerning the mining of potassium salts were abandoned.

The extraction of bromine, practised since the First World War on a very small scale, was also abandoned in 1982 under the pressure of competition from much larger producers. Only the production of magnesium sulfate was continued. The evolution of requirements in terms of quality and productivity led to improvements in the original procedure. These improvements constitute the subject of this paper

THE PRODUCTION OF MAGNESIUM SULFATE

The natural cooling method

The basic principle of this procedure was applied from the very beginning of the Giraud Saltworks. However, the procedure has evolved in numerous ways over the years in terms of the methods used for harvesting and purifying the magnesium sulfate deposited in the bittern ponds during the winter. The procedure implemented at the Giraud Saltworks until recently is outlined below.

In summer, the sodium chloride deposited by the

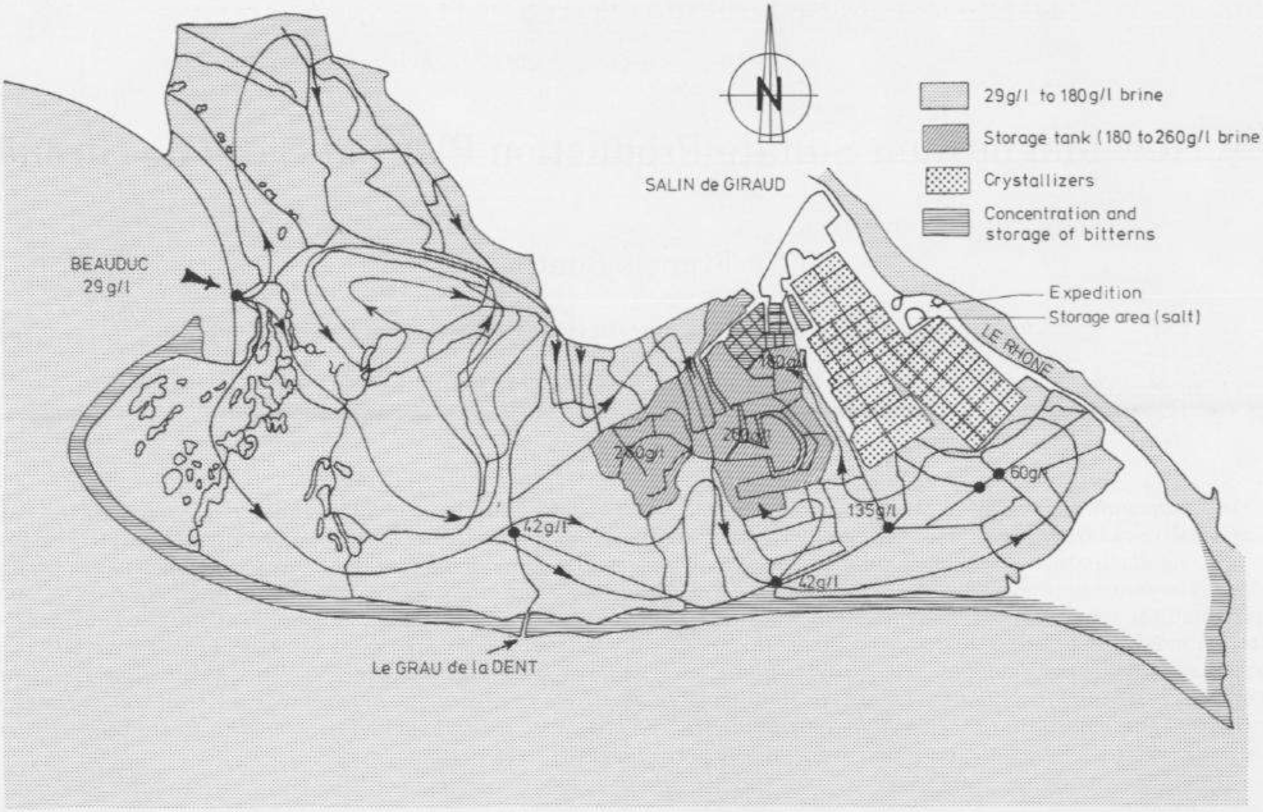

Fig. 1. The Salin de Giraud Saltworks.

bitterns on the saltworks, were spread in a thin layer (10–20 cm) over evaporating surfaces containing a natural concentration of heptahydrate magnesium sulfate of up to approximately 240 g/l (the concentration of hexahydrate magnesium chloride was thus around 430 g/l). These bitterns were then stored in ponds of about 4 m high, open to the air, throughout the winter. During this period, the temperature of the bitterns could drop to around 5°C, but this depended on the harshness of the winter and was variable from one year to the next.

The solubility of magnesium sulfate depends on temperature; the cooling of the bitterns produced a deposit of magnesium sulfate in the bottom of the ponds (see Fig. 2 for graphs showing the solubility of magnesium sulfate at different temperatures).

At the end of the winter, the ponds were simply emptied of the bitterns and the sulfate (deposits were mechanically harvested (using a bulldozer or hydraulic excavator).

The crystals harvested had to be purified in order to eliminate the remaining bitterns, as well as any sand or clay picked up during harvesting. This was done in a special plant by dissolving the magnesium sulfate in a hot saturated solution and then recrystallizing it by cooling at ambient temperature.

THE DRAWBACKS OF NATURAL COOLING

Although the procedure described above is relatively easy to implement, it has many drawbacks:

– The practical yield of the operation is very low; at the cooling temperature indicated above, only 35% of the magnesium sulfate that could theoretically be deposited by the bitterns is actually recovered.

– The tonnage obtained varies a great deal from one year to the next, depending on the lowest winter temperature reached.

– Despite purification in a plant, purity of the finished product left much to be desired, in particular with regard to the presence of insoluble matter (especially clays).

– The harvesting and purification operations were costly, which made the procedure as a whole costly.

THE ARTIFICIAL COOLING PROCEDURE: BACKGROUND

In order to avoid the disadvantages of the natural cooling procedure, and in particular to have constant control over temperature, the possibility of using a refrigeration device to obtain the negative calories necessary for cooling was envisaged very early on.

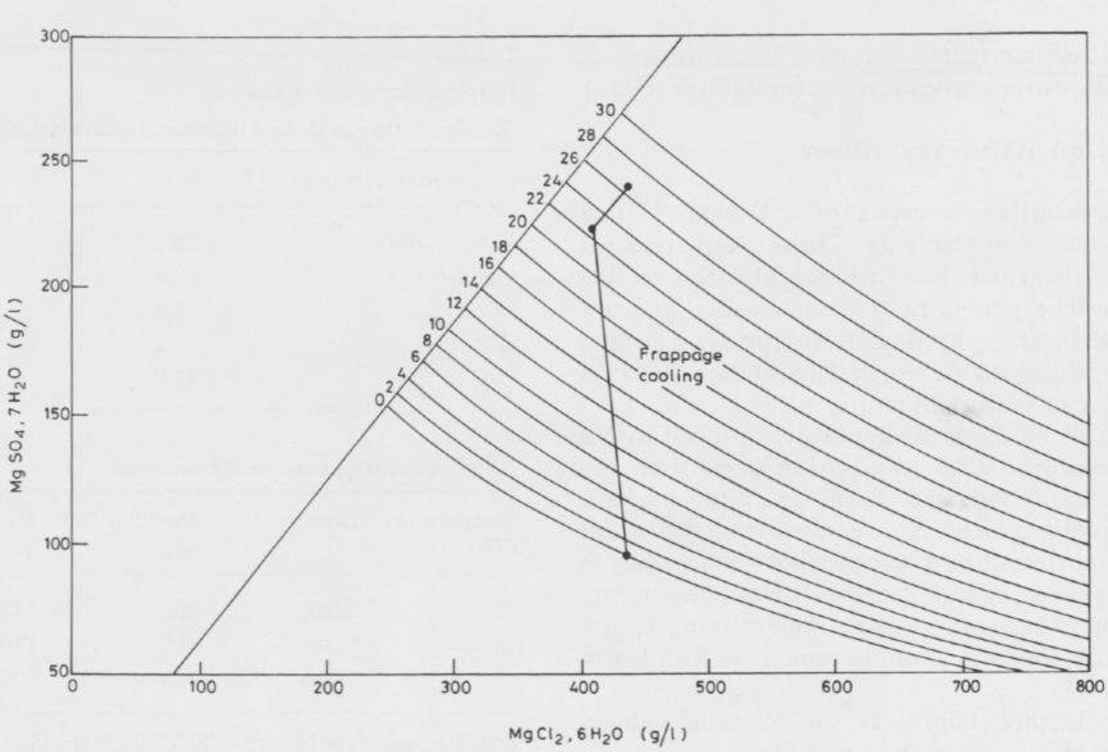

Fig. 2. Experimental data on Salin de Giraud bitterns.

A technique of this kind had already been used, with mixed success, in the last century at the Giraud Saltworks to crystallize Glauber's salt ($Na_2SO_4{\cdot}10H_2O$). Although very early laboratory tests had demonstrated the feasibility of artificial cooling for the production of magnesium sulfate, a type of crystallizer suited to the specific constraints of this product remained to be found. After many years of laboratory research and pilot projects, a special type of crystallizer was found to be the most appropriate and was successfully tested in 1983.

However, it was not until 1989 that the final decision was made to establish an industrial plant, based on the principle developed in the preceding years. This plant started operation in early 1990 and was immediately working to stated production objectives.

DESCRIPTION OF THE ARTIFICIAL COOLING PROCEDURE

General

Various types of difficulties are encountered in obtaining magnesium sulfate by artificial cooling of bitterns:

– Significant cooling of the bitterns, in general to 25–0°C, is necessary. At the same time however, the gradual crusting of the walls of the exchanger used for this must be avoided.

– Cooling must be controlled in order to avoid spontaneous nucleation, which would prevent the growth of the existing germs into crystals of the desired size (see Fig. 3).

– There must be sufficient mixing within the medium to ensure contact of the crystals with the bitterns, without breaking the crystals already formed.

Other difficulties include that of obtaining crystals whose average size is between 500 μm and 800 μm and that of guaranteeing that the installation's yield is sufficient — if possible around 80% of production in relation to the sulfate theoretically available

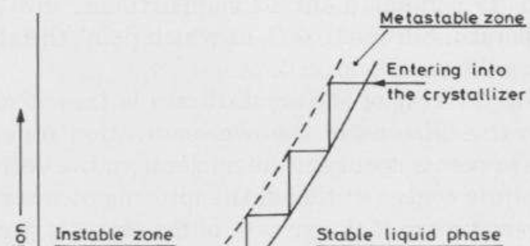

Fig. 3. Solubility diagram.

in the bitterns supplied. These problems were overcome by the use of a special type of crystallizer (Fig. 4).

Description of the crystallizer

The crystallizer consists of a U-shaped tank divided into compartments. These compartments consist of fixed panels which are also the cooling elements. The panels have double walls, and are connected together by flexible tubing. The cooling liquid circulates inside one panel and then on to the next one, thus cooling the tank.

The base of each of the panels is equipped with a small opening to allow the bittern to go from one compartment to the next, as well as a rotation shaft. On the rotation shaft are fixed mixing blades for each compartment and scrapers for each panel, so that the surface of each panel is always kept clean, thus enhancing heat transfer. The stirring blades also ensure that the crystals remain suspended in the bittern.

Under the force of gravity, the crystalline slurry flows over the length of the crystallizer.

The cooling of each compartment can be regulated by the flow of the liquid arriving onto each panel. The cooling liquid is maintained at the desired temperature by a cooling unit operating in the conventional manner (compressor, exchangers, refrigeration liquid).

Conditions of the process

The magnesium sulfate rich bitterns arrive from the ponds where they have been stored since summer (see properties of bitterns, Table 1). Their temperature is between 25°C (in summer) and 15°C (in winter), and in principle they are saturated with sulfate. They enter the first compartment of the crystallizer, where they are cooled by 1–2°C, and so on from compartment to compartment until the temperature drops to 0°C, at which point the slurry leaves the tank by overflow.

The interest of the crystallizers is that it maintains the bitterns in the over-saturation zone and thus prevents spontaneous nucleation; the decrease in sulfate concentration of the bitterns occurs naturally by virtue of the growth of the crystals present in the crystallizer.

The slow mixing ensures contact of the crystals with the bitterns, and prevents practically all breakage of crystals that have already attained full size. Thus, the bitterns can theoretically deposit 110 g/l of $MgSO_4 \cdot 7H_2O$ when they are saturated at 23°C.

The average size of the crystals is between 500 and 800 μm, but smaller crystals, i.e. those under 200 μm, are recycled in the crystallizer.

The crystals are centrifuged, then dried and conditioned.

TABLE 1

Physical properties of bitterns

Supply of bitterns (before treatment and dilution)

Standard composition	%
$MgSO_4 \cdot 7H_2O$	18.1
$MgCl_2 \cdot 6H_2O$	32.8
NaCl	4.8
KCl	3.1
H_2O	41.2

Bitterns at various stages of treatment

Temperature (°C)	Density	$MgCl_2 \cdot 6H_2O$ (g/l)	$MgSO_4 \cdot 7H_2O$ (g/l)
25	1.326	435	240
15	1.243	418	170
0	1.210	435	95

Specific heat of the bittern at 25°C: 0.62. Kcal/kg
Viscosity at 0°C: 11 cp.

Solubility of the heptahydrate magnesium sulfate in the bitterns

°C	%
0	8.96
5	10.08
10	11.35
15	13.20
20	14.96
25	17.26
28	18.98

CONCLUSIONS

The plant was built in 1989 in accordance with the principle described above, and began operation in 1990. The technique used offers significant advantages, in that it discounts the effects of external constraints (i.e. weather conditions).

The product obtained is relatively pure and the size of the crystals is very satisfactory (see the technical data sheet in Table 2 for the product's main characteristics).

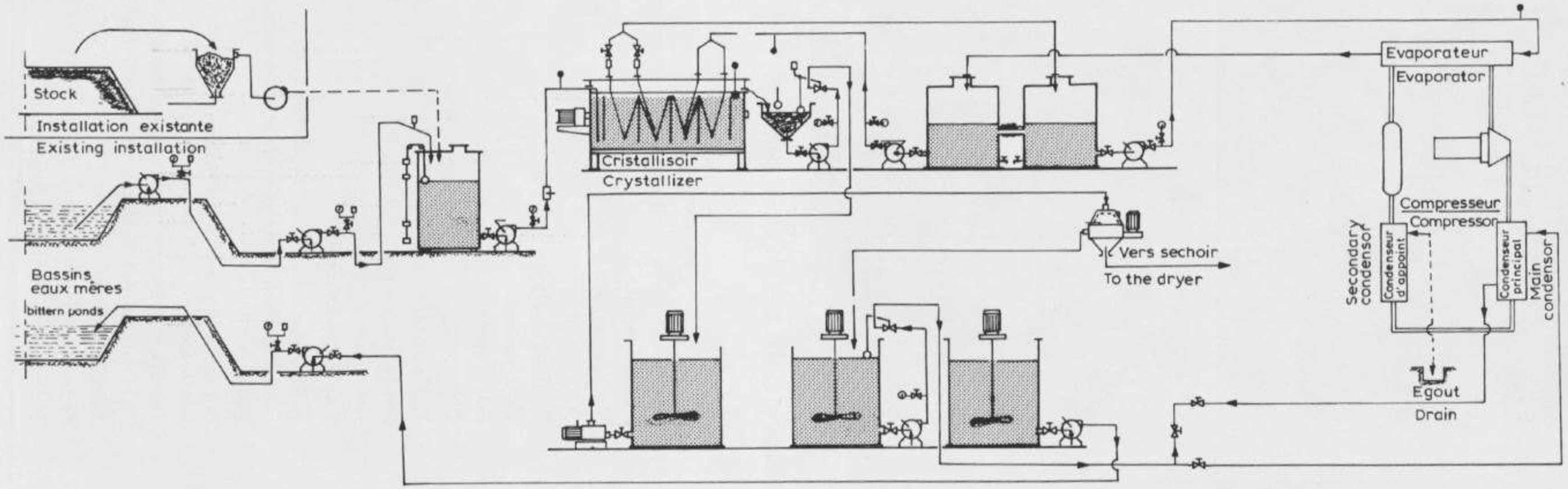

Fig. 4. Magnesium sulfate operation flow-sheet.

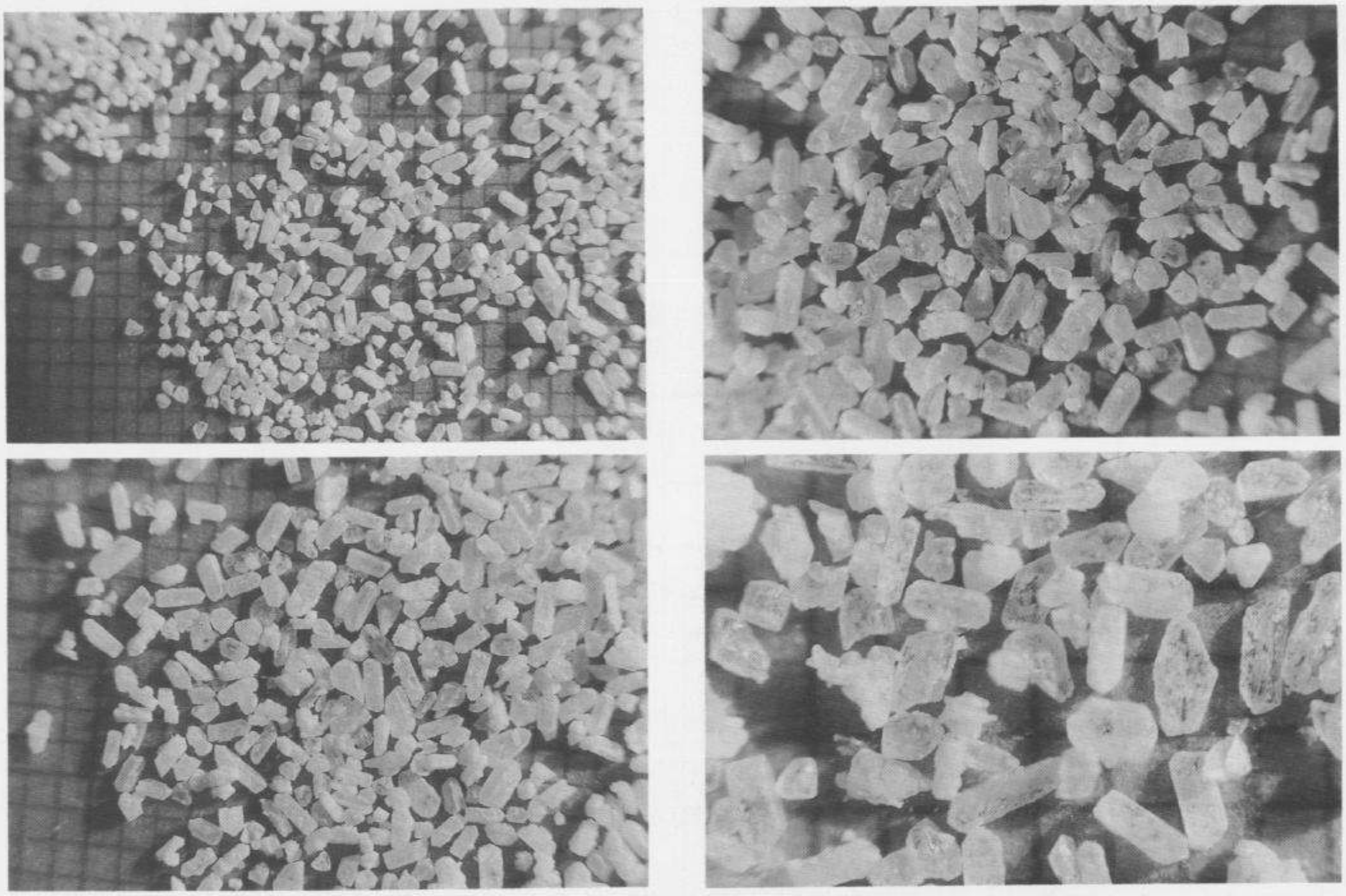

Fig. 5. Samples of the magnesium sulfate produced at Salin de Giraud Saltworks.

TABLE 2

Magnesium sulfate produced at Salin de Giraud Saltworks

General properties

Magnesium sulfate of marine origin – white crystals, very soluble in water (109 g in 100 g of water at 20°C)

Loss of water of crystallization above 50°C; anhydrous at 200°C

Density: 1.68 g cm^3

Solubility (g/100 g) of water, according to temperature

Temperature °C	g $MgSO_4 \cdot 7H_2O$
1.8	77.9
10	90.0
20	108.6
30	134.9

Density of solution at 20°C according to concentration

$MgSO_4 \cdot 7H_2$) in g into 100 g of water	Density
10	1.042
30	1.117
50	1.175
70	1.222
90	1.258
108.6	1.288

Specifications

MgO content	≥15.9%
SO_3 content	≥31.6%

Typical analysis

MgO content	16.1%
SO_3 content	32%
Cl content	0.1%
Fe_2O_3 content	0.001%
Insolubles content	0.03%
Bulk density	1.0 g/cm^3

Packing – Storage

25 kg polyethylene bags. Loaded on 1200 kg pallets

Store if possible in a cool place at a constant temperature

Uses

Source of magnesium in fertilizers and for spraying leaves. Cattle feed

Detergent industry (preparation of stabilisers for persalts)

Pulp industry (stabilization of oxygen bleaching baths)

Textile, leather

Other quality

Pharmaceutical magnesium sulfate