



### OCCASION

This publication has been made available to the public on the occasion of the 50<sup>th</sup> anniversary of the United Nations Industrial Development Organisation.

TOGETHER

for a sustainable future

### DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as "developed", "industrialized" and "developing" are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

### FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

### CONTACT

Please contact <u>publications@unido.org</u> for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at <u>www.unido.org</u>



05050

### United Nations Industrial Development Organization

ĴÇD)

Distr. LIMITED

ID/WG.21/13 5 September 1968

ENGLISH ORIGINAL: RUSSIAN

Expert Working Group Meeting on Modernization and Mechanization of the Salt Industries, based on Sea Water in the Developing Countries

Rome, Italy - 25-29 September 1968

# REPORT ON THE EXTRACTION OF SALT FROM SEA WATER IN BULGARIAL

1/ The views and opinions expressed in this paper do not necessarily reflect the views of the secretariat of UNIDO. This document has been reproduced without formal editing.

id.68-3101

We regret that some of the pages in the microfiche copy of this report may not be up to the proper legibility standards, even though the best possible copy was used for preparing the master fiche.

da 197 - 198

100



Salt has been extracted along the Black Sea coast of Bulgaria, particularly in the area around Pomorie, since ancient times.

In the 18th century, salt began to be extracted from salt lakes along the sea coast. Such extraction of salt was only on the basis of small private holdings, however, and the amount extracted was small. It was only in the 20th century that the extraction of salt took on an industrial character, the first large quantities of salt (6,000 tonnes) being produced in 1909.

### Technology

Common salt is produced through the evaporation of sea water by the heat of the sun and by currents of air. In the course of this process the concentration of salt dissolved in the sea water increases, and at the end of the process sodium chloride (common salt) crystallizes out.

The water of the Black Sea corresponds approximately to a solution containing the following amounts of various substances per 1000 grammes:

NaCl	MgC12	MgS04	KCl	Mg(HCO3)2	NaBr	Dry residue
13,7412	1.6855	0.9137	0.3223	0.2461	0.0577	
		Density		1.0135 g/cm <sup>3</sup>		
		Specific gravity =		1.5 <sup>0</sup> Be (Baumé)		

The salt production facilities are located close to the sea, from which they are separated by a sandbar. The salt pans are 0.6 to 1.5 metres above sea level, so that the sea water can flow into them without assistance up special channels when required.

The soil of the area where the salt pans are located is sandy clay, and water does not seep through it. The area is sunny and swept by breezes, so that the climatic conditions are suitable for the rapid evaporation of sea water to obtain salt.

# . Systems of salt extraction

The term "salt extraction" covers the entire series of activities carried on ' in order to obtain sea salt.

The principal technological processes entering into salt extraction are the following:

- (a) The preparation of concentrated brine;
- (b) the crystallization of the salt;
- (c) the collection, washing and storage of the salt.

There may be differences in the way the above processes are carried out, depending on the system of salt extraction used. In the Bulgarian State enterprise "Black Sea Saltworks", two systems known as the "Foken" and the "Ankhial" systems are used.

Regardless of which system is used, all the technological processes are carried out between April and October. In salt extraction parlance, this period is known as the "season".

A. The "Foken" system

# Preparation of the concentrated brine

The raw material for the production of sea salt is sea water concentrated to saturation point. In order to obtain this brine, a shallow layer of sea water is admitted to the evaporation pans, through which it moves in stages over a considerable path. In order to lengthen the path of the water and thus increase its degree of concentration, the brine evaporating area is laid out in the form of basins or pans connected by channels which can be closed by wooden sluice gates. The pans are separated from each other by clay-filled wooden dykes 0.50 to 1.5 metres high. The area of the pans varies from 10 to 4,000 decares, in inverse proportion to the concentration of the brine in them.

The pans are classified, according to their technological function, into evaporating pans and crystallizing pans. The most advantageous relation of the area of the evaporating pans to that of the crystallizing pans is about 10 to 1. In the evaporating pans, grains of sand and algae sink to the bottom and calcium carbonate and calcium sulphate are precipitated out, while the concentration of the brine is raised to  $24^{9}$ Be. The sea water is concentrated in the following stages:

	Concentration	Depth of brine in pan			
1.	up to 3 <sup>°</sup> Be	up to 25cm			
2.	3- 7 <sup>°</sup> Be	10-15cm			
3.	7–10 <sup>0</sup> Be	10-12cm			
4.	10–12 <sup>0</sup> Be	10-12cm			
5.	12-24 <sup>°</sup> Be	10-12cm			

After concentration, the brine is admitted to the crystallizing pans, where concentration is continued, and at a specific gravity of  $25.5^{\circ}-30^{\circ}$  Be the sodium chloride crystallizes out.

The admission of sea water to the salt pans through the channels connecting these with the sea begins in April. By the end of June the concentration of the brine has reached 24<sup>°</sup>Be and crystallization begins. In salt extraction parlance, the brine which is concentrated in the period from April to October and from which salt is extracted in the same year is called "fresh".

At the end of September, there remain surplus amounts of brine with a concentration of from 2° to 12-15°Be. This brine is admitted to the crystallizing pans from which the salt has already been collected and is then further concentrated. This brine is called "autumn brine" and is used for the production of salt in the following year. It is protected from dilution by collecting it in reservoirs called "reserve pans". Each of these pans is filled from 0.8 to 3.5 metres deep with a number of batches of autumn brine of approximately equal concentration, the brine with the highest content of sodium chloride being stored in the pans filled to the greatest depth.

## Crystallisation of salt

The crystallization of the salt begins at the end of June or the beginning of July. In order to obtain a sufficiently thick layer of salt, additional brine at 25°Be is admitted to the crystallisation pans several times during the crystallisation process. Brine at a lower concentration must not be admitted, as it would disturb the crystallisation process. When a specific gravity of ID/WG.21/13 Page 6

 $30^{\circ}$ Be is reached, about 80 per cent of the salt crystallizes out and the rate of crystallization drops sharply. In addition, magnesium salts which adversely affect the quality of the salt begin to crystallize out from the brine. The crystallization process is therefore carried on until a brine concentration of  $30^{\circ}$ Be is reached.

When the layer of salt reaches a thickness of 3-5cm (at the beginning of August), the brine is drained off and the crystallizing pans are prepared for the collection of the salt. If possible, part of the brine drained off from the crystallizing pans is admitted to other pans for the further extraction of salt of lower quality for industrial use. Some of the brine is also further concentrated in order to obtain natural and enriched magnesium chloride. Large quantities of brine are discarded in the sea, however.

# Collection, washing and storage of the salt

After the brine has been drained off from the crystallizing pans, collection of the salt begins. Workers collect the salt with paddles, pile it up in heaps, and carry it to "washing machines" which are actually anger-type grading machines in which the salt is washed with 24<sup>°</sup>Be brine containing the minimum of dissolved salts other than sodium chloride. This washing reduces the amount of magnesium salts and sand or grit particles in the salt.

The washed salt is piled up in pyramidal heaps each containing 1,500-3,000 tonnes which are called in salt extraction parlance "mows".

Salt is normally collected once a season from the crystallizing pans. It is only if there is a particularly long, hot summer that the orystallizing pans from which salt has already been collected at the beginning of August are filled again with brine and used to produce a second crop of salt.

After the collection of the salt and the removal of the "autumn" brine, the salt pans remain empty.

Rain water falling in the pans in autumn and winter is discarded in the sea. In March and April the bottom of the crystallizing pans dries out sufficiently for the work of sealing and smoothing to be carried out so as to reduce the amount of dust or grit picked up when the salt is collected later. The sealing, or, as it is also called, the "rolling" of the pans is carried out with a roller drawn by a tractor specially adapted for operating on soft ground. This rolling marks the beginning of a new season of salt production.

### B. The "Ankhial" system

This is a very old system. It idffers from the "Foken" system in the distribution and construction of the evaporating and crystallizing pans and also in the technological procedure followed. It is characterized by the division of the crystallizing pans into a multitude of small areas.

In recent years there has been a transition from the "Ankhial" system to the "Foken" system.

### The technical characteristics of sea salt

Crystal salt consists of cubic crystals of sodium chloride 8-15mm in size with a moisture content of from 4 to 71 per cent.

The physico-chemical characteristics of crystal sea salt are as follows:

- (a) Colour white to pale grey;
- (b) Taste pure salty taste;
- (c) Odour none;
- (d) Adulterants and metals harmful to human health, such as lead, copper, arsenic, etc. none;
- (e) Reaction in an aqueous solution neutral;
- (f) Percentage content of sodium chloride (on basis of dry substance) minimum 95 per cent;
- (g) Percentage content of water-insoluable substances (on basis of dry substance) - maximum 0.3 per cent;
- (h) Moisture content about 6.5 per cent;
- (i) Percentage content of calcium (on basis of dry substance) maximum
  0.3 per cent;

- (j) Percentage content of magnesium (on basis of ary substance) maximum,
  0.3 per cent;
- (k) Content of ferric oxide trace;
- (1) Appearance of aqueous solution after removal of water-insoluble particles - transparent.

### Processing of the salt

Part of the sea salt obtained is delivered in the form of crystal salt for the requirements of the milk processing industry.

The remainder of the salt is processed into ground salt for domestic and industrial use.

### Output

Thanks to ever-improved organization and salt production methods, the output of sea salt has risen from an average annual output of 20,000 tonnes in 1947 to about 60,000 tonnes per year in recent years.

The cost of crystal sea salt varies from 13 to 18 levs per tonne.

### Modernization and extension plans for the salt industry

The salt extraction systems still in use have become obsolete: they do not correspond to the present stage of development of other branches of industrial production and they suffer from a number of shortcomings which prevent the further development of salt production if existing production processes are adhered to.

The processing of the salt produced is carried out by machines and equipment of low productivity, and the level of development of the production and handling operations is low.

A large part of the brine which remains behind after the salt has been extracted and which is rich in other salts is thrown away into the sea. The production of magnesium chloride is only small and is carried out with obsolete technological processes and equipment.

iD/WG.21/13 Page 9

The following proposals, which involve the mechanization and modernication of the production of sea salt in Bulgaria, are aimed at reducing all these shortcomings to a minimum.

There are four alternative proposals:

1. The first alternative is based on the continued use of the existing methods for the concentration of brine and the crystallizing out of sodium chloride by the use of the heat of the sun. This alternative provides for the mechanization of the labour-consuming processes involved in the production, transport, processing, storage and despatch of sea salt. This proposed solution is based on the "Foken" system of producing sea salt. It provides for the reconstruction of the evaporating pans in order to increase the amount of salt produced and the creation of the right conditions for the introduction of suitable mechanization.

The reconstruction of the existing evaporating pans is essential, as it is planned to collect the salt with the aid of special equipment called a "salt combine harvester". This equipment requires the crystallizing pans to be located very close together in one place and to be of certain suitable dimensions, as its transport capability is limited.

2. The second alternative for the mechanization of sea salt production provides for the extraction of the sodium chloride in a multi-vessel evaporator. The main features of this method of salt extraction are the following:

- (a) The initial concentration of the sea water to 25°Be is carried out in the same way as at present;
- (b) The final concentration and crystallizing out of the sodium chloride are carried out in the multi-vessel evaporator;
- (c) The sea salt produced is processed with the aid of modern automatic requipment.

3. The third alternative provides for the production of table salt in an evaporator installation operating on the thermocompression principle.

- 4. The fourth alternative for the mechanization of salt production provides for the following:
  - (a) Mechanization of the salt production facilities at Pomorie as described in the first alternative;

(b) Construction of an evaporator installation for the production of salt in the town of Burgas along the lines set out in the third alternative.

It is envisaged that such an evaporator installation would have a capacity of 100,000 tonnes per year.



