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DESIGN AND CONSTRUCTION OF A PILOT PLANT  
FOR UTILIZATION OF CESANO BRINE

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Introduction

On the base of conclusions obtained from a preceding study and experimental runs carried out on Cesano 1 well, a pilot plant has been designed and its assembly is foreseen to be accomplished in the present year.

A brief description of two possible processes for chemical and energetical exploitation of the resource is given.

Afterwards the type of flow of the brine has been characterized (annular and dispersed flow) and consequently choice criteria for separators have been given.

An equipment flow diagram, including regulation and control systems, is reported; choice criteria for instrumentation and regulation valves are suggested.

Geofluid characteristics

For a better comprehension of the following considerations, the chemical characteristics of Cesano 1 brine are given in Table 1.

As the ions present in the solution are mainly  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{--}$ , the saline system can be considered as a system of four reciprocate salts:  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ . In such a way it is possible to use literature data for system  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{--}$ ,  $\text{H}_2\text{O}$  and to utilise Janecke diagrams for studying the path of different processes which can be proposed.

The Janecke diagram at  $75^\circ\text{C}$  is reported in Fig. 1.

Point A represents initial composition of brine and number associates with each point gives " $\text{H}_2\text{O}$  moles/Salt moles" ratio at saturation conditions.

Table 1

## Chemical Characteristics of Cesano 1 brine

Chemical constituents		p.p.m.	Dissolved gases	p.p.m.	
Calcium	Ca <sup>++</sup>	208	Ammonia	NH <sub>3</sub>	86
Magnesium	Mg <sup>++</sup>	27,1	Hydrogen sulfide	H <sub>2</sub> S	Ass.
Sodium	Na <sup>+</sup>	51000	Carbon dioxide	CO <sub>2</sub>	1650
Potassium	K <sup>+</sup>	64000	Boric Acid	H <sub>3</sub> BO <sub>3</sub>	+5800
Lithium	Li <sup>+</sup>	165	Cesium	Cs	42
Iron	Fe <sup>++</sup> +Fe <sup>+++</sup>	4,5	Arsenic	As	4,3
Ammonium	NH <sub>4</sub> <sup>+</sup>	90			
Rubidium	Rb <sup>+</sup>	280			
Mercury	Hg	0,0030			
Bicarbonate	HCO <sub>3</sub>	2290			
Metaboric acid	BO <sub>2</sub>	4000			
Chloride	Cl	20000			
Sulfate	SO <sub>4</sub>	140000			
Silica	SiO <sub>2</sub>	113			
	F <sup>-</sup>	55			

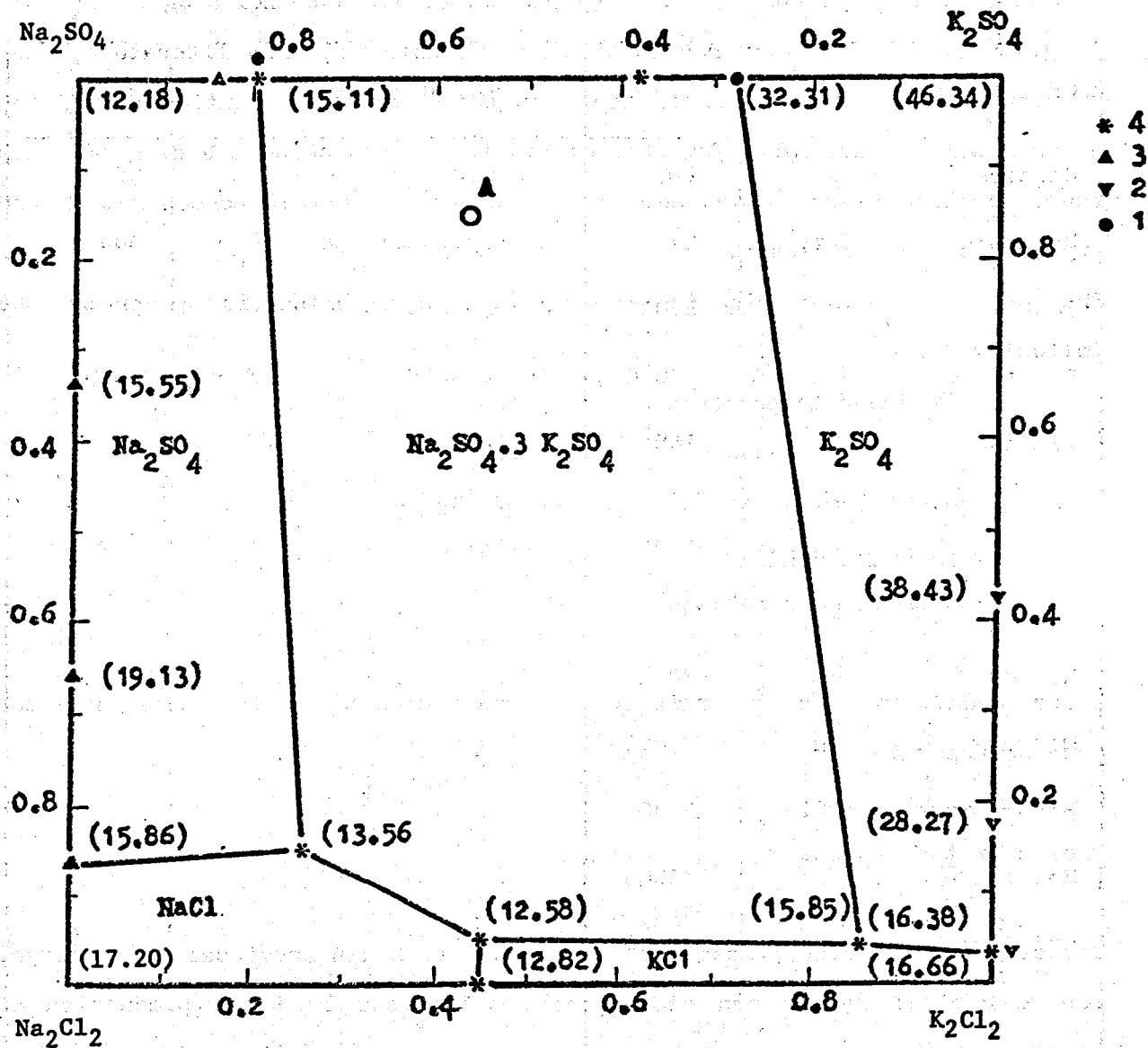


Fig. 1. Janecke diagram at 75°C.

In Table 2 data relative to considered Janecke diagram are given. Other data on the Na - K - SO<sub>4</sub> - Cl system equilibria are given in literature (4-12).

A qualitative tridimensional representation of the Janecke diagram at 75°C is given in Fig. 2; such representation was obtained from literature data, knowing the water content present in the saturated solution along the diagram borders and in a few characteristic points inside the diagram. This representation gives a good help to the comprehension of concentration and crystallisation processes.

The physical characterisation of the Cesano 1 brine is given by the following data

Wellhead temperature	185°C
" pressure	125 bar
Overall mass rate	27 Kg/sec.
<u>Vapor mass rate</u>	0,51
Overall mass rate	

These conditions can be assumed as input conditions for designing the process apparatus.

#### Choice of the process

Use of Cesano 1 brine, whose chemical composition has previously been given, for electrical and/or non electrical applications leads to production of large quantities of waste water and consequently injection problems in deep wells arise.

As a large quantity of salts crystallizes after cooling due to brine energetical exploitation, addition of fresh water shall have to be provided. A process which allows a salts recovery together with a reduction of waste water should offer many advantages for integral use of this resource.

Many alternative processes for salts recovery have been considered (13-14),

Table 2

Data relative to Janecke diagram at 75°C

References	Solid phase	grams for 100 grams of saturated solution				Molar Ratio				H <sub>2</sub> O moles	} Na <sub>2</sub> <sup>++</sup>	} K <sub>2</sub> <sup>++</sup>	} Cl <sub>2</sub> <sup>=</sup>	} SO <sub>4</sub> <sup>=</sup>
		NaCl	KCl	Na <sub>2</sub> SO <sub>4</sub>	K <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> Cl <sub>2</sub>	K <sub>2</sub> Cl <sub>2</sub>	Na <sub>2</sub> SO <sub>4</sub>	K <sub>2</sub> SO <sub>4</sub>	Salt moles				
1	N+G			27.84	7.38			0.822	0.178	15.11	0.822	0.178		1
"	K+G			5.64	16.43			0.296	0.704	32.31	0.296	0.704		1
2	K		10.00		8.77		0.571		0.429	38.43		1	0.571	0.429
"	K		18.70		4.47		0.830		0.170	28.27		1	0.830	0.170
"	Ka+K		32.30		1.42		0.964		0.036	16.39		1	0.964	0.036
3	N+Na	25.3		4.95		0.861		0.139		15.42	1		0.861	0.139
"	N	16.5		10.2		0.663		0.337		19.13	1		0.663	0.337
"	N	7.76		19.7		0.324		0.676		19.65	1		0.324	0.676

N=Na<sub>2</sub>SO<sub>4</sub>; K=K<sub>2</sub>SO<sub>4</sub>; Na=NaCl; Ka=KCl; G=Na<sub>2</sub>SO<sub>4</sub> · 3K<sub>2</sub>SO<sub>4</sub>

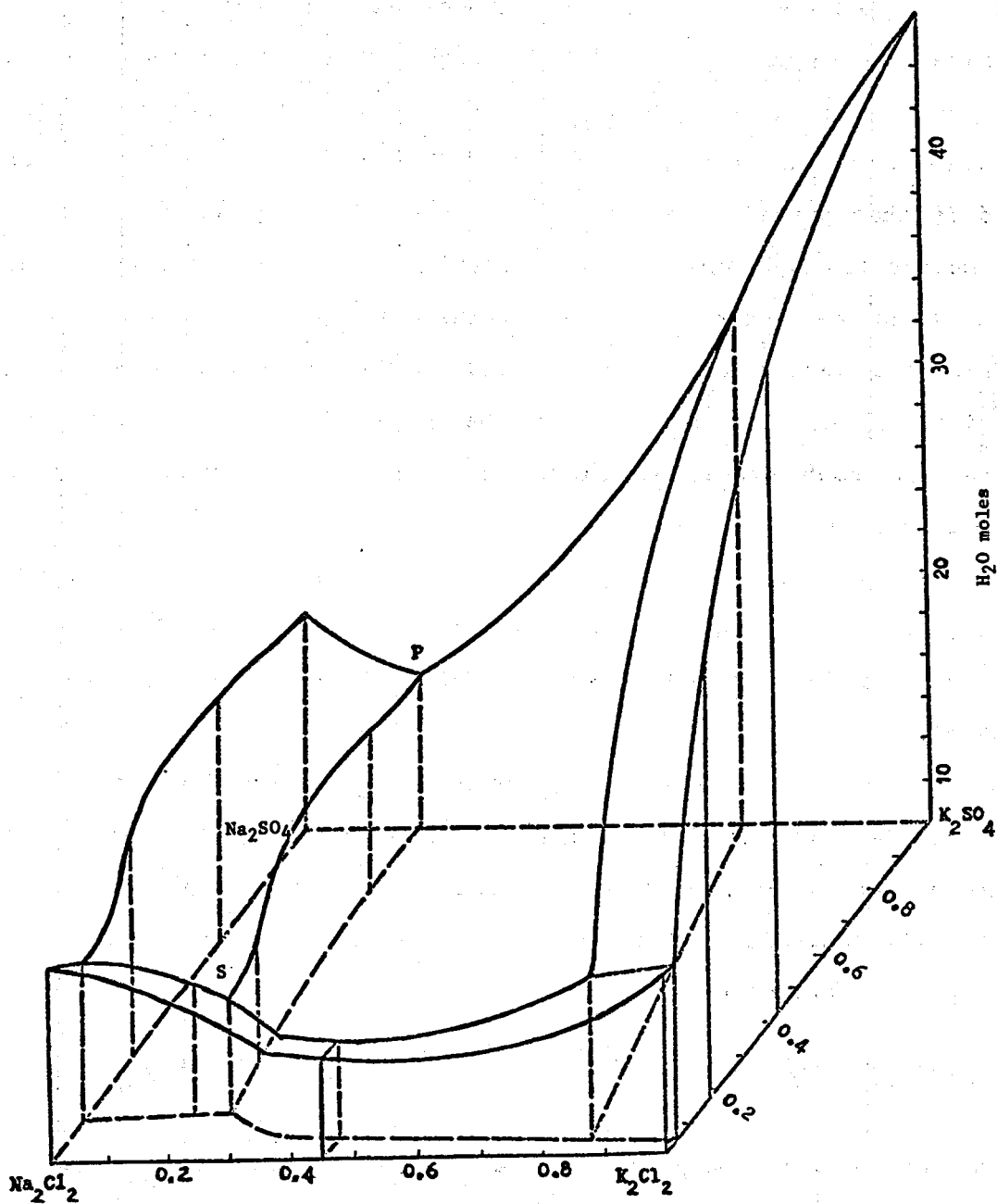


Fig. 2. Tridimensional representation of Janecke diagram at 75°C.

but a few of these were not compatible with energetical use of the brine. The two taken into consideration for practical application are shown in Figures 3 and 4. The flow diagram illustrated in Fig. 3 could be suggested whether the boric acid recovery were economically convenient.

The brine (stream 1) goes to the first high pressure separator; steam is fed to a turbine while liquid to a low pressure separator; the steam rising up from this second separator is fed to an intermediate section of turbine, liquid is then passed to a crystallizer for obtaining glaserite ( $\text{Na}_2\text{SO}_4 \cdot 3\text{K}_2\text{S}_4$ ) Mother liquors coming out of centrifuge are pumped to a countercurrent double effect which performs as a crystallizer. From these two stages mixed crystals are obtained: glaserite and  $\text{Na}_2\text{SO}_4$  from the first one and glaserite, Na Cl and  $\text{Na}_2\text{SO}_4$  from the second one. In Table 3 a material balance for each stream is given as a result of detailed calculations referred in (15).

The 17th stream contains theoretically a solution of  $\text{H}_3\text{BO}_3$  from which it is possible to try a recovery. But this process is too complicated for a first trial pilot plant and the opportunity of  $\text{H}_3\text{BO}_3$  recovery must be carefully evaluated.

The flow diagram of the second process, that assumed for the pilot plant designing, is given in Fig. 4. This scheme which is quite a simplification of the preceding one, must be utilized when boric acid recovery is not economically convenient. Mother liquors after crystallization of glaserite are pumped to reinjection well.

#### Pilot plant targets

Design, construction and performance of the pilot plant are aimed at

- 1) execution of long term runs with sufficient flow rate in order to allow a correct resource evaluation.
- 2) Verification of design methods of apparatus such as control and sampling systems.
- 3) Evaluation of quantity of steam produced by flash and its characteristics



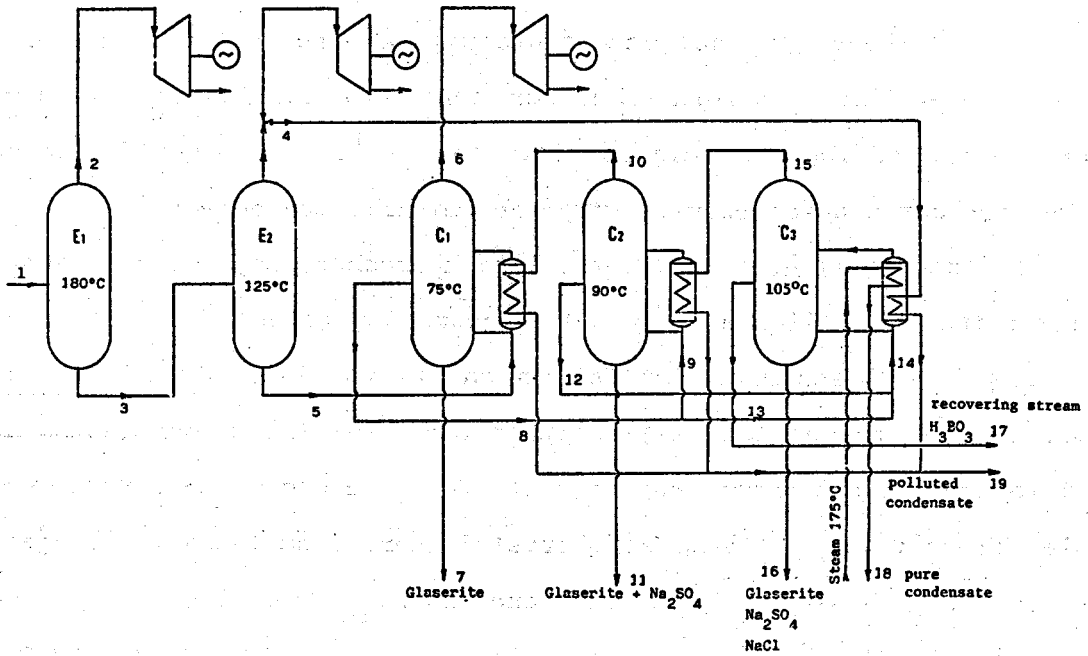


Fig. 3. Flow diagram for energetical exploitation of the resource coupled with salts recovery.

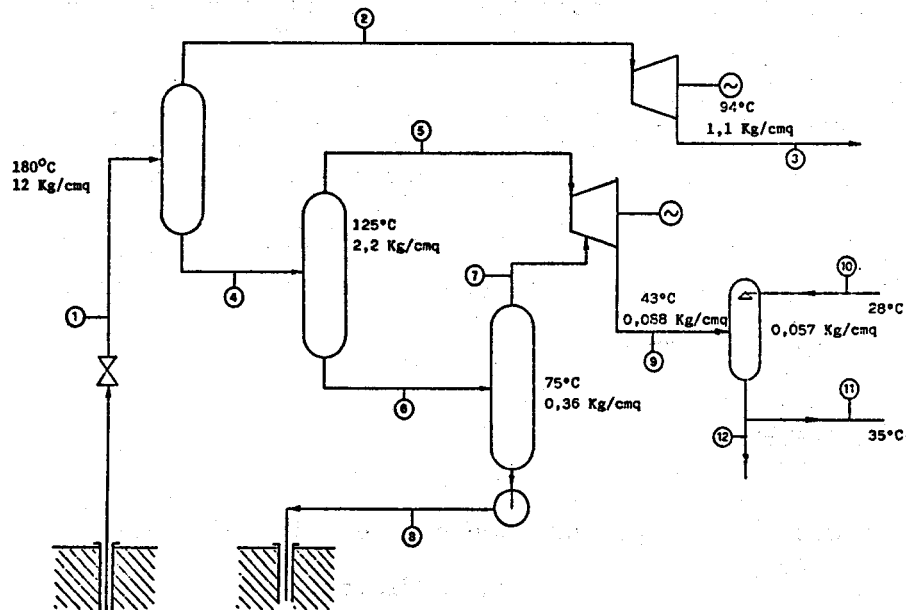


Fig. 4. Flow diagram for energetical exploitation of the resource coupled with partial salts recovery.

Table 3. Material balance for Fig. 3 flow diagram.

STREAM	Temp. °C	Press. Kg/cm <sup>2</sup>	Na <sup>+</sup> tonn/hr	K <sup>+</sup> tonn/hr	SO <sub>4</sub> <sup>-</sup> tonn/hr	Cl <sup>-</sup> tonn/hr	H <sub>3</sub> BO <sub>3</sub> tonn/hr	H <sub>2</sub> O tonn/hr	STEAM tonn/hr	GAS tonn/hr	TOTAL tonn/hr
1	180	12	9,59(s)	12,02(s)	29,15(s)	4,20(s)	1,10(s)	132,8(s)	6,6	4,5	200,00
2	180	12	-	-	-	-	-	-	6,6	4,5	11,1
3	180	12	9,59(s)	12,02(s)	29,15(s)	4,20(s)	1,10(s)	132,8(s)	-	-	188,9
4	125	2,2	2,2	-	-	-	-	-	15,7	-	15,7
5	125	2,2	9,59(s)	12,02(s)	29,15(s)	4,20(s)	1,10(s)	117,1(s)	-	-	173,2
6	75	0,36	-	-	-	-	-	-	47,9	-	47,9
7	75	0,36	1,69(c)	8,60(c)	14,10(c)	-	-	-	-	-	24,4
8	75	0,36	7,91(s)	3,42(s)	15,04(s)	4,20(s)	1,10(s)	69,2(s)	-	-	100,9
9	75	-	4,04(s)	1,75(s)	7,68(s)	2,14(s)	0,56(s)	35,3(s)	-	-	51,5
10	90	0,66	-	-	-	-	-	-	27,0	-	27,0
11	90	0,66	2,82(c)	1,03(c)	7,16(c)	-	-	-	-	-	11,0
12	90	0,66	1,21(s)	0,72(s)	0,52(s)	2,14(s)	0,56(s)	8,3(s)	-	-	13,5
13	75	-	3,87(s)	1,68(s)	7,36(s)	2,05(s)	0,54(s)	33,9(s)	-	-	49,5
14	78	-	5,08(s)	2,39(s)	7,88(s)	4,02(s)	1,10(s)	42,2(s)	-	-	62,9
15	105	1,1	-	-	-	-	-	-	28,8	-	28,8
16	105	1,1	3,19(c)	1,01(c)	7,09(c)	0,59(c)	-	-	-	-	11,9
17	105	1,1	1,89(s)	1,39(s)	0,79(s)	3,61(s)	1,10(s)	13,4(s)	-	-	22,2
18	125	2,4	-	-	-	-	-	-	16,5	-	16,5
19	103	-	-	-	-	-	-	-	71,5	-	71,5

(c) crystals  
(s) solution

- 4) Possibility of evaluating a helical screw expander performance.
- 5) Estimate of corrosion, erosion and scale problems.
- 6) Determination of the chemical consistency of resource in order to produce glaserite as chemical fertilizer.
- 7) Study of exhaust brines by deep well reinjection.
- 8) In a second time, if of interest, can be examined the possibility of heat recovery with new type heat exchangers.

#### Choice of operative conditions

The choice of operative conditions must be made considering

- 1) Temperature, pressure and flow rates of the brine at wellhead;
- 2) Well characteristic curve;
- 3) Presence of  $\text{CO}_2$  in the brine;
- 4)  $\text{CaCO}_3$  deposition due to  $\text{CO}_2$  stripping, caused by pressure reduction while brine is rising up;
- 5) Solubility of glaserite and other salts at different temperature.

From examination of characteristic curve an overall mass rate of about 100 t/h has been chosen because performance of well around this value of mass rate should be stable enough. Primary separator works at a pressure as close as possible to that of wellhead; consequently its operative conditions are approximatively  $p = 12$  bar,  $t = 180^\circ\text{C}$ . In this apparatus carbon dioxide saturated with steam is separated from the brine. This part of the plant, including first separator, is subjected to calcium carbonate scaling. Secondary separator works at a pressure of 2,2 bar and temperature of  $125^\circ\text{C}$ ; at these conditions crystallization of glaserite or other salts does not occur because the solution is under the saturation conditions in respect of these salts.

Crystallization of glaserite is expected to occur just in the crystallizer whose operative conditions are 0,36 bar and  $75^\circ\text{C}$ .

Under these conditions, according with Janecke diagram and a few preliminary

data obtained during a brief erosion run, practically pure glaserite is obtained.

Material balances relating to the process are summarized in Table 4.

### Choice of the separators

Liquid-vapor separators can be roughly classified in three types listed below:

- gravitational separators
- centrifugal separators
- inertial separators

The choice among these ones depends on the type of two phase flow and on the characteristics of the entrained liquid. A method based on the use of Baker's parameters has been used for a quick evaluation of the flow region. In Fig. 5 Baker's diagram is given; the obtained results with our input data are summarized in Table 5. The operating field is therefore located on the border between annular and dispersed flow region.

The type of flow suggests the choice of cyclone separators. As the input flow rate can oscillate, the bottom hold-up of the separator must be sufficiently large in order to prevent possible flooding of the apparatus.

Small diameter drops are undoubtedly entrained by the rising up steam and gas and therefore it needs to wash such stream by fresh water; moreover a demister is put on the top of the separator for removing the smallest drop still present in the steam before its entering into a turbine. Details of the primary and secondary separators design are given in (15); the schemes of such apparatus are given in Figs. 6 and 7.

### Choice of crystallizer

For obtaining crystals of same size a Kristal-Oslo crystallizer has been

Table 4: Material balance for Fig. 4 flow diagram (tonn/h)

Stream	Liquid	Steam	Gas	Total
1	188,9	6,6	4,5	200,0
2	-	6,6	4,5	11,1
3	1,0	5,6	4,5	11,1
4	188,9	-	-	188,9
5	-	15,7	-	15,7
6	173,2	-	-	173,2
7	-	11,7	-	11,7
8	161,5	-	-	161,5
9	3,4	24	-	27,4
10	2000	-	-	2000
11	2000	-	-	2000
12	27,4	-	-	27,4

Table 5

Bx	By	$\varnothing$ mm	Flow
50	13600	200	annular
50	20500	125	annular
50	31000	90	dispersed

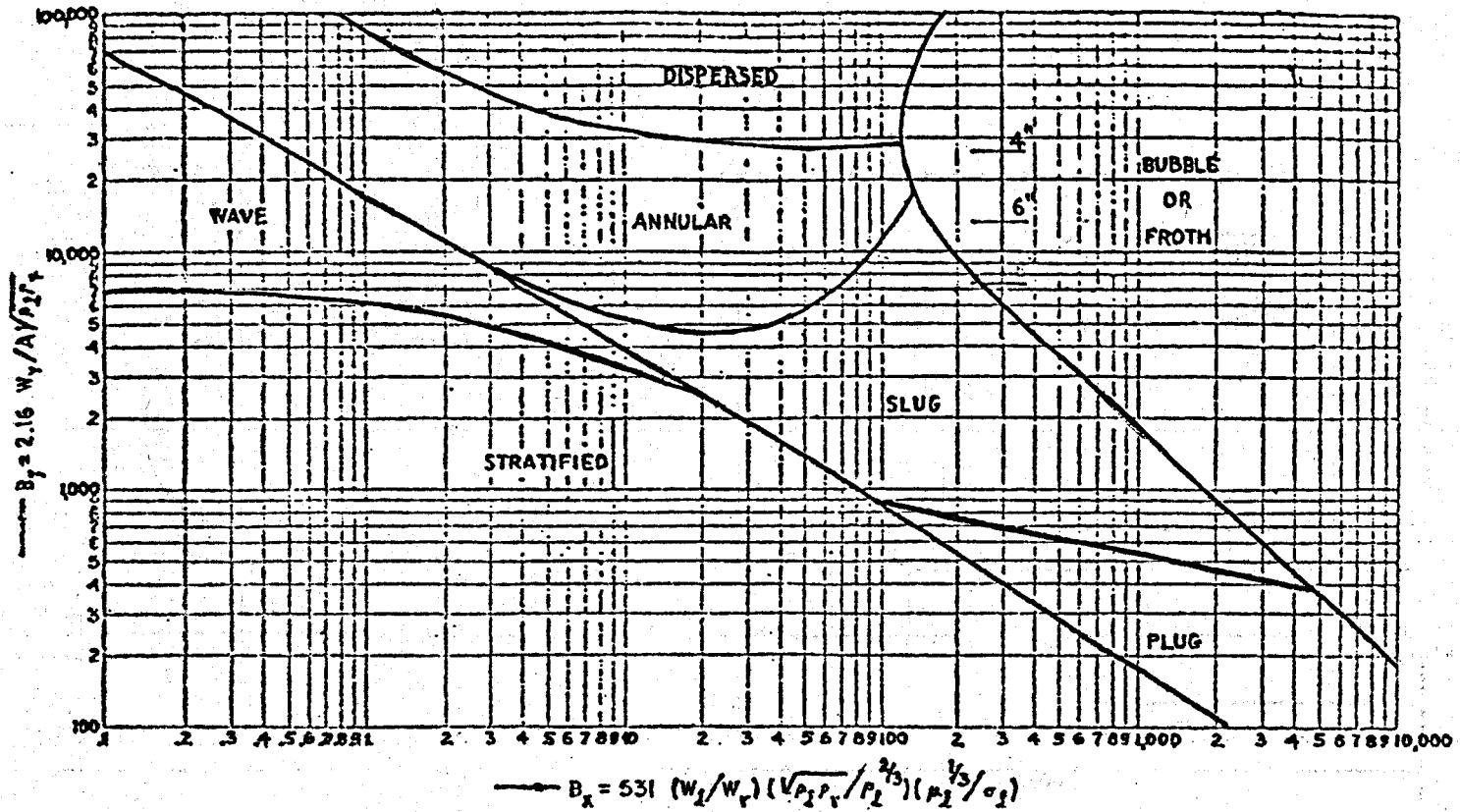


Fig. 5. Type of two phase flow as a function of Baker's parameter.

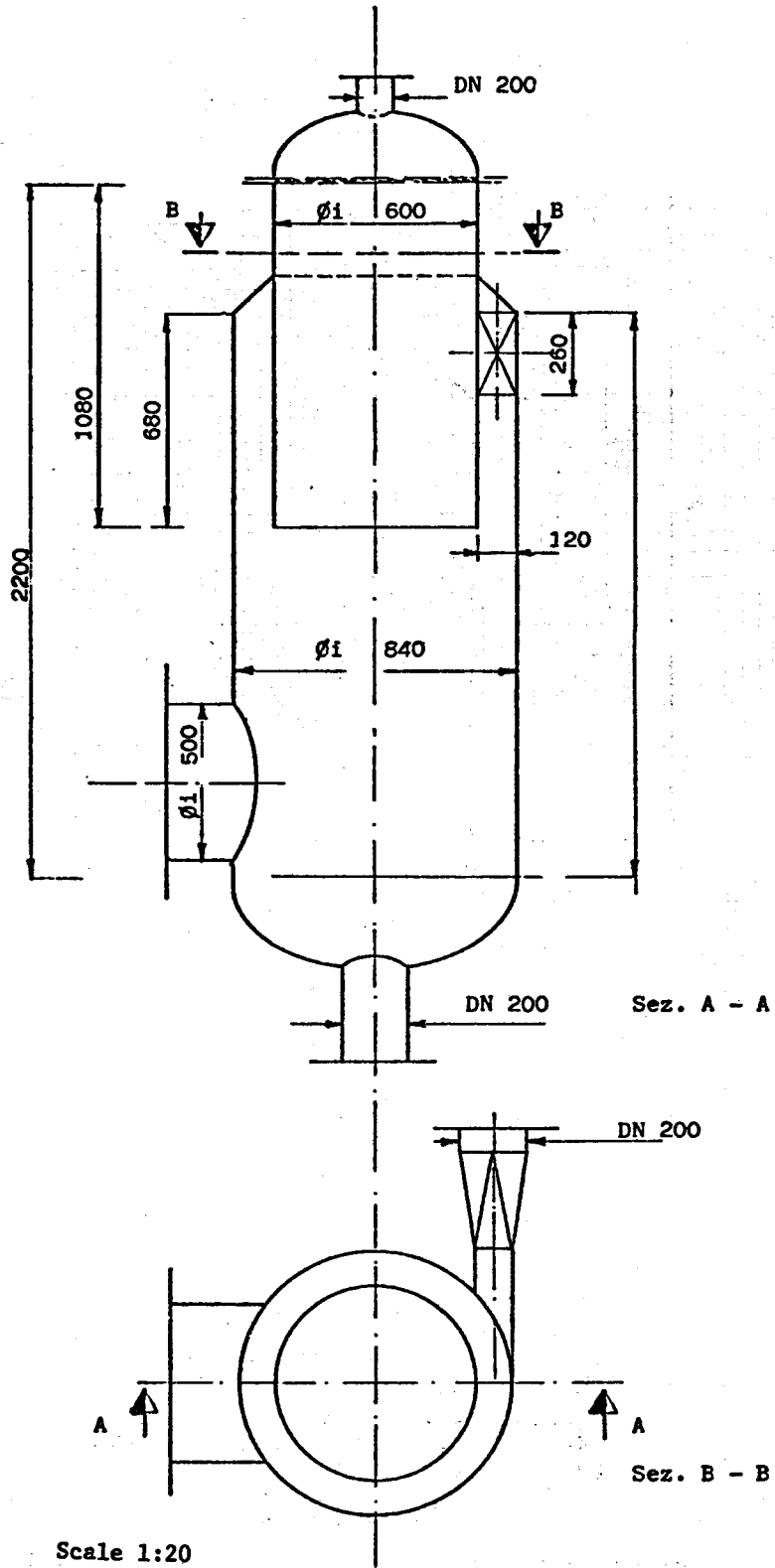


Fig. 6. Primary separator.

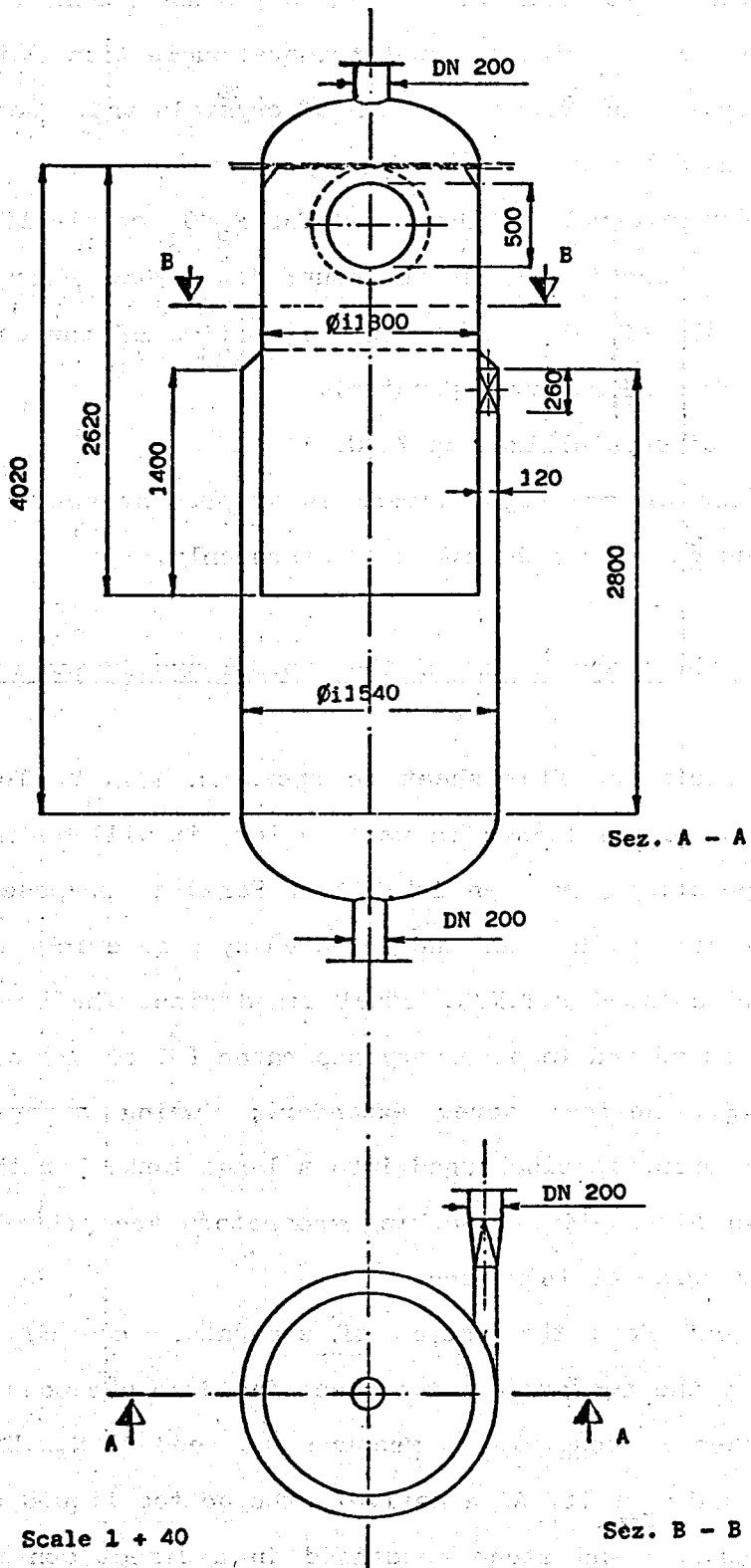


Fig. 7. Secondary separator.



chosen. Its scheme is given in Fig. 8; in the upper zone evaporation occurs together with supersaturation and primary nucleation while in the lower zone it has growing and classification of crystals and secondary nucleation.

The designing hypothesis are

- 1) Griffith number equal to that used for  $K_2SO_4$  crystallization ( $P/V = 30 \text{ Kg/hm}^3$ ;  $P =$  produced crystals for hour;  $V =$  Volume of crystallizer).
- 2) Feed flow rate of 5000 Kg/h (only a portion of the concentrated brine discharged from secondary separator).
- 3) Temperature of crystallization  $75^\circ\text{C}$ .

The construction of the crystallizer is at present suspended and the runs will be carried out using the two separators only.

#### Equipment flow sheet and choice of the control system and regulation valves

A simplified equipment flow sheet is shown in Fig. 9. To reduce troubles with calcium carbonate scales in well casing, it will be tried to introduce below the vaporating level an inhibitor. For this purpose the additive is previously diluted with water and injected by a metering pump into the well through an articulated P.T.F.E. steel lined pipe. The brine coming out of the wellhead can be fed to a primary separator (S1 or S2) or to a total flow turbine (H.S.E., helical screw expander); during start-up or blow-down operations the brine is discharged into a large tank. For the first stage of separation two alternatively working separators are provided because heavy scale problems arise at this step.

Liquid drawn out from the bottom of separators can be mixed with steam flowing up from the top and the two phase fluid so produced is fed to H.S.E. Such a way makes it possible to measure the feed to H.S.E. and to vary the ratio steam/liquid in it. Alternatively the bottom liquid can be fed to the secondary separator and steam condensed in a direct contact condenser, or directly discharged into the large tank. On the primary separators the

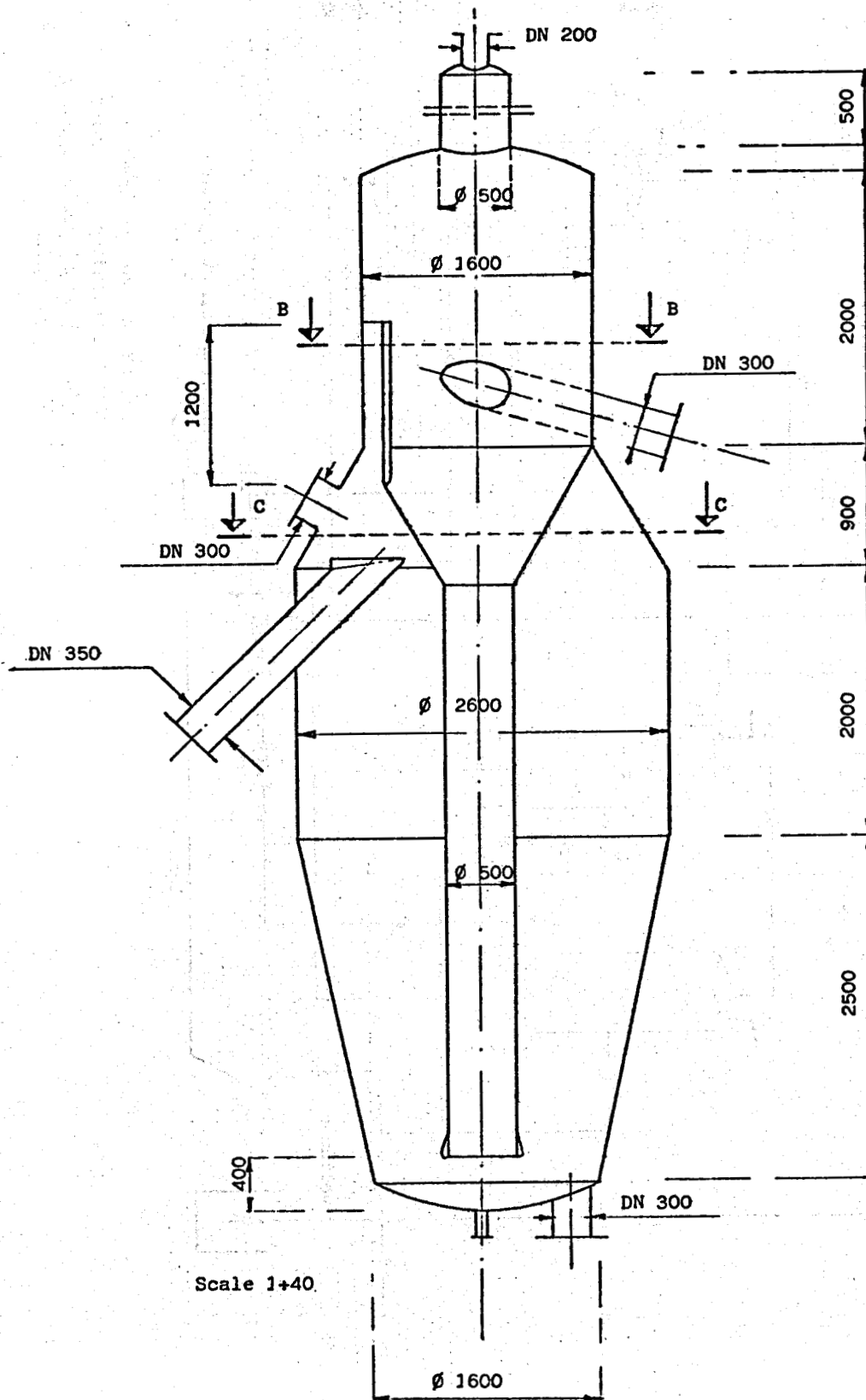
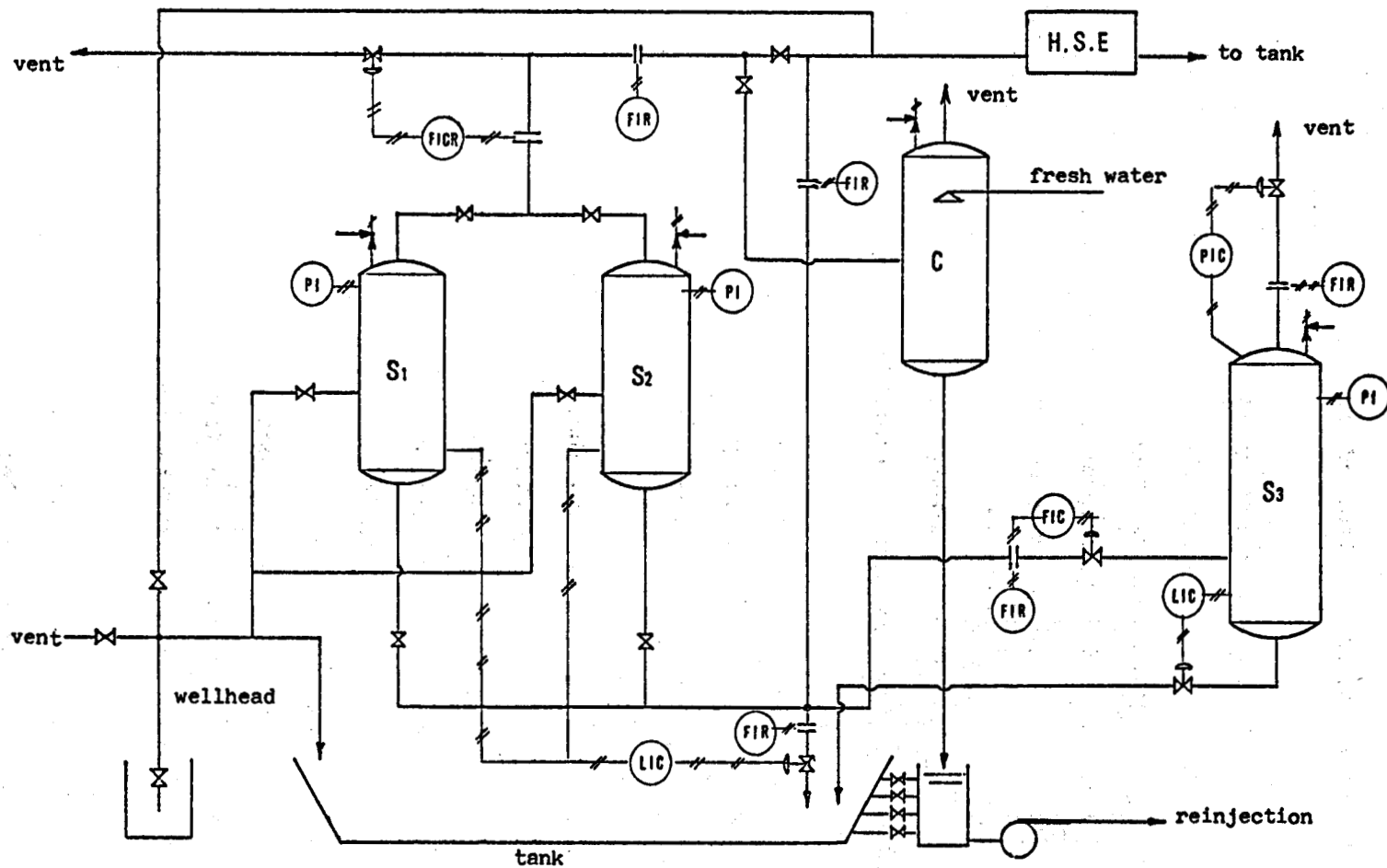


Fig. 8. Crystallizer.



S1, S2 primary separators  
 S3 secondary separators  
 H.S.E. helical screw expander  
 C condenser

Fig. 9. Equipment flow sheet.

venting system of the steam is controlled by the overall flow rate of the rising up steam. Such a choice has been made taking into account the well characteristic curve which, in the adopted operative conditions, is flat. In this case the classical venting controlled by pressure does not assure a constant flow rate.

Liquid level in S1 and S2 is automatically controlled discharging part of the brine into the tank; this amount is little in comparison with the main quantity which is fed to the successive stages.

As calcium carbonate scale will clog frequently the regulation valves, these have been chosen of self cleaning type and two units put in parallel and working alternatively have been provided.

The level control of S3 separator is accomplished by a regulation valve put on the bottom outlet and the pressure is controlled by a valve put on the venting pipe.

As surely glaserite and other salts crystallise on the floor of the tank, this is connected by five pipes, placed at different levels from the floor, with an external vessel; reinjection pump is connected with this one, where dilution water is also added.

For pressure and temperature measurements there are not particular problems and normal instrumentation has been provided: the same for the choice of calibrated orifices in vapour flow measurement. On the contrary these instruments cannot be used for measurement of flow rate of boiling brines as they give large errors due to vaporization inside the orifice; in this case magnetic inductive flowmeters with removable electrodes have been chosen.

The metering tube is made by P.T.F.E. and resist up to 180°C and 40 bar.

For level measurements a buoyancy type instrument has been chosen; it has provided a continuous washing of the tube where the floating element is placed.

A complete system of washing is provided in order to maintain as clean as possible pipes, valves, instruments, nozzles, etc.

Literature

- 1) Cornec E., Krombach M., Caliche 10, 59 (1928)
- 2) Hering E. - University Thesis - Srasbonrg (1926)
- 3) Chretien A. - An. Chim. (101), 12, 9, (1929)
- 4) Blasdal W.C. - J. Ind. Eng. Chem. 10, 334 (1918)
- 5) Anosov V., Bysova E.A., - I.Z.V., Sectora Fiz. - Khim. Analiza  
Inst-Obshch. Neorgan. Khim. Akad Nauk USSR  
15, 118 (1947)
- 6) Campbell A.N. et al. - J. Chem. Soc. 56, 2507 (1934)
- 7) Linke F.W. - Solubilities of Inorganic and Metal Organic Compounds  
4<sup>th</sup> Edition (1958)
- 8) Shull'gina K., Yanasteva O.K. - Zhui. Obachei Khim. 25, 234 (1955)
- 9) Gilliot A. - Bull. Soc. Chim. 992 (1951) France
- 10) Rustamov P.G. - Isv. Akad. Nauk. Azerb. 4, 33, 5, 45 (1957)
- 11) Pel'sh A.D. - Tr. Vses. Nauch. Iss. Led. Inst. Galurgii 145, 160 (1949)
- 12) Zaslavsky A.T. et at. Izv. Akad. Nauk. Su Khim 47 (1938)
- 13) Problemi per lo sfruttamento di F. Giovannini et al.  
"Problemi per lo sfruttamento di soluzioni geotermiche ad alta  
temperatura ed alta salinità per la produzione di energia elettrica".  
Relazione finale - University of Pisa 1978 March.
- 14) F. Giovannini, F. Nasti - Thesis - University of Pisa - 1977 July
- 15) G. Magozzi et al.  
"Studio e sviluppo del processo e progettazione di un impianto pilota  
per un ciclo di sfruttamento di salamoie ad alta temperatura ed alta  
salinità".  
Relazione finale - University of Pisa 1979 October.