PRODUCTION OF MARINE CHEMICALS IN PAKISTAN
Part III. Studies on the Recovery of Magnesium Sulphate by Chilling

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Results are reported on recovery of $MgSO_4$ by chilling of sea water bittern using the design of the chiller as well as cooling temperatures as the two important variables. Data are presented for chillers of four different capacities from which it appears that $MgSO_4$ can be effectively recovered by cooling bittern to $-5°$, the temperature at which the concentration of this salt reduces to zero. These studies also indicate that recoveries can be enhanced if [1] arrangements are made for speedy removal of the crystals from the bulk phase of the liquid and [2] jackets are provided instead of coils in the chilling units.

Statistical analysis of the data reveals that during cooling of $MgSO_4$, there exist linear relationships between [1] concentration and temperature and [2] recovery and temperature which holds good to 95% confidence level. In the former case, the relationship is independent of initial feed concentration and the equipment design whereas in the latter the concentration range is a parameter. Nevertheless, heating affects the two relationships.

Key words: Chilling, Sea bittern, Reaction design.

INTRODUCTION

Sea water bittern, the residual concentrated liquor after the recovery of solar salt is allowed to be discharged back into the sea in Pakistan, although it is known to contain quite valuable chemicals. Earlier publications [1, 2] dealt with the status of sea salt production and reasons for deterioration of its quality. It was pointed out that admixtures due to formation of metastable phases are invariably noted if solar evaporation is continued beyond 29-29.5°Be. They consequently impart impurities to the sea salt. Since the chemicals which form the impurities are recoverable from bittern, an integrated process was reported [2] for obtaining them on pilot plant scale.

Sea-water bittern is a very sensitive and complex ionic mixture of typical inorganic compounds. The crystallization behaviour and subsequent composition of various salts and residues in the mother liquor at different stages of processing are constrained by the previous history, particularly the weather conditions. Changes in the composition raise a number of problems relating to equilibrium data on phase separation. This is perhaps the reason for adopting convenient methods such as the following for obtaining the various chemicals from this important but neglected resource: chilling [3-10], solvent extraction [11-13], passage through ion-exchange resins [14, 15], treatment with lime/caustic soda [16, 17], or an odd combination of these methods [18-20].

Chilling and solvent extraction from the basis of some of the major studies in this area. Experiments on low temperature separation of $MgSO_4$ have been reported for 12° [7, 8, 10], 0°, or –5° [3, 5, 6]. These investigations are rather silent on optimizing the temperature and composition conditions which are pertinent to recovery of magnesium sulphate and of the chemicals extracted subsequently. The only study [7] specific for the production of $MgSO_4$, by chilling, though elaborate, lacks appropriate correlation with composition and is restricted to bench scale experiments. Additionally, studies by various authors [2, 21, 22, 23] on the recovery of $MgSO_4$ by chilling to different low temperatures were aimed at evolving an integrated process for the recovery of different chemicals from sea bittern. The present studies have been undertaken to establish low temperature as a driving force for the separation of $MgSO_4$, since this step is critical for the success of the subsequent operations. Accordingly experiments have been designed to establish recovery parameters from laboratory scale (1-6 litre batches) to different pilot plant scale operations viz. 25 to 400 litres, to strike correlation of temperature with the other parameters such as composition and recovery and also to note the effect, if any, of the design of the equipment thereon.

EXPERIMENTAL

Laboratory and pilot plant studies were carried out in

the following four sets of experiments on a progressively increasing order with the scale-up factor between various steps ranging from 1:2 to 1:8 (i) Laboratory experiments on 1-6 litre batches, (ii) Mini pilot plant scale experiments on 25 litre batches, (iii) Medium size pilot plant operations on 200 litre batches and (iv) pilot plant studies on 400 litre batches.

(1) *Laboratory scale chilling.* Raw bittern obtained from salt works was concentrated to about 33°Be, either by solar evaporation or by heating. The concentrate was taken in a beaker equipped with a mechanical stirrer and the contents were kept constantly stirred. Cooling was effected externally by immersing the beaker an ice bath. On attaining the desired temperature level the contents were filtered off and the filtrate and solids were analysed. Size of the batch was varied from 1 to 6 litres. The results of the experiments are listed in Table 1.

Table 1. Changes in concentration of magnesium sulphate in bittern during chilling. (size of the batch 2-6 litre)

Expt. No.	Initial			Final			
	Densi-ty °Be	Tempe-rature °C	Percent MgSO$_4$	Density °Be	Tempe-rature °C	Percent MgSO$_4$	Percent recovery
1.	33.2	34.0	10.32	30.35	5.0	5.41	46.43
2.	33.2	18.0	10.82	30.46	2.0	5.54	46.64
3.	33.2	18.0	10.46	30.73	2.0	4.84	49.0
4.	33.2	19.0	10.46	29.64	1.5	6.24	47.0
5.	33.03	19.0	10.35	29.00	1.5	5.65	8
6.	33.2	19.0	10.70	32.70	5.0	6.01	46.47

(2) *Chilling unit, 25 litre capacity.* A 25 litre capacity chiller, comprising essentially a jacketted vessel provided with a 144 rpm stirrer of standard geometry according to the tank size, inlet outlet, temperature controller and sight glasses was designed and fabricated on the basis of the laboratory studies. Cooling was effected by Freon-12 gas compressor of 0.25 H.P. moter, capable of removing heat at a rate of 50-70 Kj/hr/kg from the charge.

Raw bittern of known density (32.85°Be to 33.2°Be), was placed in the chiller and cooling with stirring was started. Samples of the solid-liquid mix were pipetted out at the desired time intervals, and after separating one from the other the filtrates were analysed. The results of analysis are shown in Table 2. Bittern collected during winter was invariably low in MgSO$_4$ and it had to be heated to 110° to 114° to obtain a density of 32.9 to 33.2°Be. Results for these experiments are listed in Table 3.

(3) *Chiller, 200 litre capacity.* The chiller consisted of [1] a double walled 750 mm diameter 18-8 SS vessel provided with cover and [2] a compressor unit capable of re-

Table 2. Changes in concentration of magnesium sulphate in bittern during chilling (25 litre experiments).

Exp. No.	Density °Be	Temperature °C	MgSO$_4$ %	Recovery %
1.	33.20	20	6.25	00.00
		15	6.14	1.76
		13	5.41	13.44
		12	5.17	17.28
		11	4.94	20.96
		9	4.41	28.80
		7	3.73	40.32
		5	3.08	50.72
2.	33.11	20	6.14	00.00
		12	5.54	9.77
		10	4.74	19.54
		9	4.69	23.61
		8	4.54	31.6
		6	3.42	44.29
		4	2.9	52.75
3.	33.11	20	6.32	00.00
		12	5.65	10.60
		10	4.60	27.21
		9	4.42	30.06
		8	4.08	35.44
		5	2.88	54.43
4.	33.11	20	6.28	00.00
		14	5.8	7.6
		12	5.5	12.40
		9.5	4.81	23.40
		6	3.61	42.51
		4	3.01	52.07
5.	32.94	20	5.29	00.00
		12	5.25	1.7
		11	4.80	9.3
		9	4.33	18.14
		6	3.25	38.56
		4	2.76	48.20
6.	33.03	20	5.65	00.00
		12	5.45	4.50
		10	4.70	16.80
		8	4.15	26.50
		6	3.61	36.10
		4	2.53	55.00
7.	32.85	20	5.54	00.00
		12	5.41	2.34
		10	4.75	14.25
		8	4.08	26.35
		6	3.48	37.18
		4	2.77	50.00

Table 3. Changes in concentration of magnesium sulphate in bittern during chilling.

Exp. No.	Density °Be	Temperature °C	MgSO$_4$ %	Recovery %	Remarks
1.	33.2	20.00	7.85	0.00	Bittern heated to 114°C
		14.00	6.62	15.62	
		11.00	5.54	29.42	
		9.0	5.05	35.46	
		7.5	4.18	46.75	
		6.5	3.85	50.95	
		5.0	3.37	57.07	
2.	33.2	20.0	7.82	0.00	Bittern heated to 114°C
		13.0	6.62	15.35	
		10.0	4.99	36.189	
		8.5	4.69	40.03	
		7.5	4.52	42.19	
		5.0	3.25	58.4	
3.	33.1	20.0	8.18	0.00	Bittern heated to 110°C
		15.0	7.52	8.06	
		13.0	6.75	13.81	
		10.0	5.29	35.33	
		9.0	5.17	36.79	
		7.0	4.12	49.63	
		5.0	3.16	63.20	
4.	32.94	20.0	8.06	0.00	Bittern heated to 110°C
		12.0	6.25	22.45	
		10.0	5.25	36.35	
		6.0	3.68	55.17	
		5.0	3.01	62.66	
		4.0	2.64	67.25	

Table 4. Changes in concentration of magnesium salts in bittern during chilling (200 litre experiments).

Expt. No.	Initial Density °Be	Initial Temperature °C	Initial Percent MgSO$_4$	Final Density °Be	Final Temperature °C	Final Percent MgSO$_4$	Percent recovery
1.	33.11	29.5	4.64	31.06	4	2.82	46.04
2.	33.46	25.0	5.52	31.36	4	3.06	71.52
3.	33.96	23.0	5.52	31.36	4	2.27	46.60
4.	33.28	24.0	5.20	30.19	4	3.08	47.43
5.	33.20	30.0	6.03	30.01	4	3.41	46.22
6.	33.88	31.0	5.58	30.55	4	3.40	58.56
7.	32.90	34.0	8.17	29.46	4	4.04	56.80
8.	34.31	34.0	7.34	30.55	4	3.40	60.94
9.	35.06	30.0	7.28	31.36	4	2.63	67.70
10.	34.90	30.0	7.30	30.82	4	2.84	60.39

moving 70-85 Kj/hr/kg, complete with 2 HP motor and a temperature controller, connected with suitable pipe to a cylindrical double walled immersion type cooler integrated with a stirrer in its centre. The diameter of the stirrer was 50 mm and it revolved at a speed of about 1430 rpm. Approximately 200 litre sea bittern of known composition and density (32.90 to 35°Be) was charged into the chiller and

Table 5. Changes in concentration of magnesium sulphate in bittern during chilling.

Exp. No.	Density °Be	Temperature °C	MgSO$_4$ %	Recovery %
1.	32.66	20.0	8.02	0.00
		15.0	6.41	20.06
		12.5	5.48	31.67
		10.0	5.18	35.39
		4.0	4.75	40.77
2.	32.17	20.0	8.03	0.00
		17.5	8.03	0.00
		15.0	6.30	21.54
		12.5	6.27	21.91
		10.0	5.74	28.41
		4.0	5.41	32.51
3.	33.2	20.0	8.03	0.00
		17.5	7.34	18.59
		15.0	6.25	22.41
		12.5	6.23	22.16
		10.0	5.33	33.62
		4.0	5.31	38.87
4.	32.25	20.0	8.02	0.00
		17.5	8.02	0.02
		15.0	6.43	19.93
		12.5	5.89	26.55
		10.0	5.71	28.80
		4.0	5.18	35.41
5.	32.3	20.0	8.02	0.00
		17.5	7.54	5.98
		15.0	6.98	12.96
		12.5	5.92	25.43
		10.0	5.90	26.18
		4.0	5.35	33.29
6.	32.2	20.0	7.88	0.00
		17.5	7.88	0.00
		15.0	7.88	0.00
		12.5	5.98	24.02
		10.0	5.52	29.94
		4.0	5.16	34.56

when the desired temperature was attained, solids were filtered off and analysed. The size and design of the agitator was observed to effect vigorous agitation around the cooling surface from where the heat transfer was satisfactory but the overall agitation achieved in the tank was mild with the result that the solids kept settling at the bottom, suggesting that the mixing was not sufficient uniform. Only initial and final composition of raw material and final products could therefore be estimated. The results of the experi-

ments are shown in Table 4.

(4) *Chiller, 400 litre capacity.* It consisted of an insulted cylindrical SS tank provided with inlet, outlet, sight glasses, thermometer etc., complete with a stirring system comprising an agitator of standard geometry, a moter, gearbox fixed with step-down pullies to obtain three variations of speed at 210, 240 or 300 rpm and SS cooling coils which in turn were connected to a Freon-12 compressor unit fitted with a 7.5 HP moter which could achieve a cooling rate of 120-135 Kj/hr/Kg from the charge, and a temperature controller. About 400 litre bittern of 32.2 to 33.2°Be was charged into the tank and the rest of the experimental procedure was similar to that of the 25 litre experiments. Results of the experiments are recorded in Table 5.

RESULTS AND DISCUSSION

$MgSO_4$ recoveries. The value of recovery of $MgSO_4$ range from 45-50% in bench scale experiments, 50-55% for 25 litre batches, 46-71% for 200 litre batches and 32-40% for the 400 litre batches. Generally the average recovery was higher for the 200 litre batches, possibly because the major portion of the crystallized $MgSO_4$ was continuously settling thus enhancing the recovery. The reason for the differences among the various scales of operation particularly the low yield for the 400 litre batches may be due to the onset of a dynamic pseudo-equilibrium which apparently depends on the design and construction of equipment used and the rate of cooling.

$MgSO_4$, concentration in bittern vs temperature. The plot of $MgSO_4$ concentration against temperature is apparently a temperature-equilibrium composition diagram. Fig. 1 and 2 indicate that the curves in the three sets are almost identical excepting the last portion pertaining to the 400 litre batch. The concentration in this particular instance becomes asymptotic to x-axis indicating that the temperature is no longer a driving force below 5°. In cases where the temperature exceeds 20°, the first cooling does not appear to effect change in the initial composition in all the three instances and the diagrams suggest that the process comprises at least three phases. The first phase is represented by the portion of the curves which remain parallel to the x-axis, when equilibrium condition exists, with reference to composition during the initial stages of cooling. Withdrawal of heat beyond this stage results in mass transfer being manifested by crystallization of $MgSO_4$ indicating that temperature is the driving force for the stage of process of separation. This second phase corresponds to the start of crystallization, initially at a slow rate, marked by non-linear relationship. The fall is so sharp that no useful solution except on the initial crystallization temperature and corresponding composition can be worked out from this part of the curve. However, in the case of percent recovery vs temperature curves the change is very distinct particularly with reference to the composition change of the feed. The percent recovery is insignificant during this stage. The third phase sets in here after and is characterized by a linear relationship which on extrapolation, indicates complete $MgSO_4$ recovery at 5°.

The linear portion of the curves obtained from the comprehensive data collected during different scales of operations forms the basis of the present investigation.
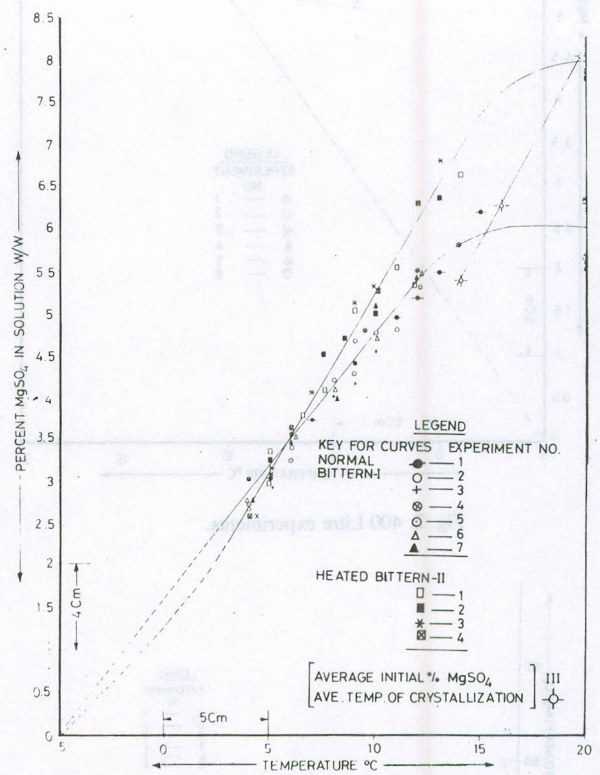

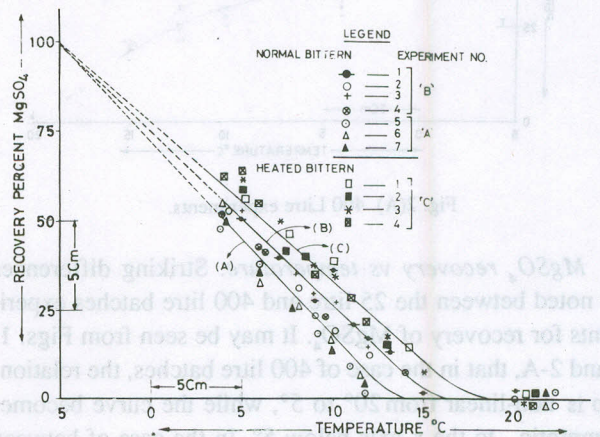Fig. 1. 25 Litre experiments normal and heated bittern.

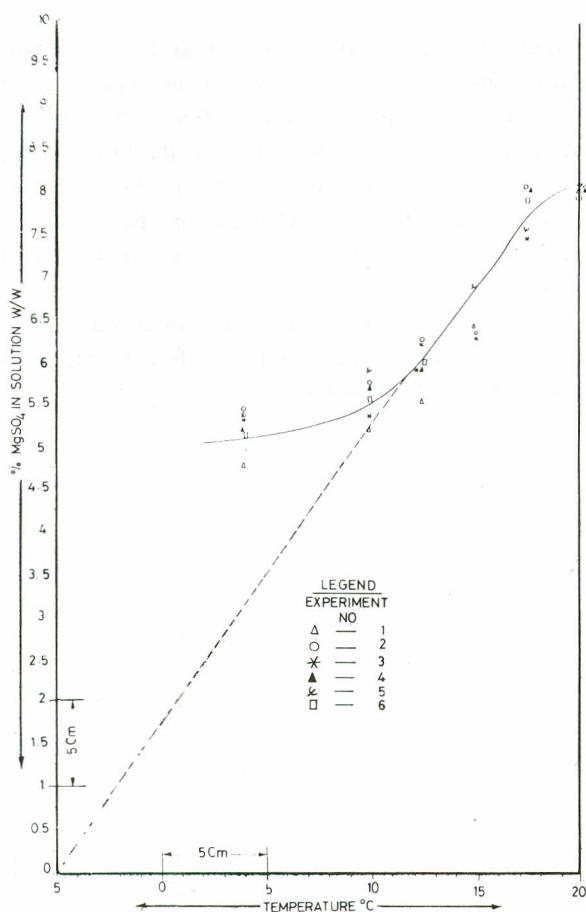Fig. 1(A). 25 Litre experiments normal and heated bittern.
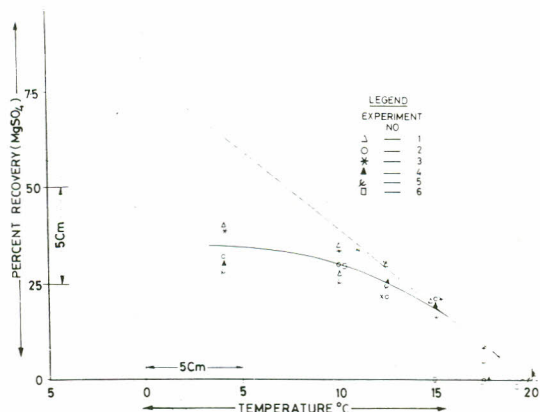
Fig. 2. 400 Litre experiments.

Fig. 2(A). 400 Litre experiments.

MgSO$_4$ recovery vs temperature. Striking differences are noted between the 25 litre and 400 litre batches experiments for recovery of MgSO$_4$. It may be seen from Figs. 1-A and 2-A, that in the case of 400 litre batches, the relationship is non-linear from 20° to 5°, while the curve becomes asymptotic to the x-axis below 5°. In the case of between

the 25 litre batch, however, despite the significant differences between the concentration of active components of the normal and heated bittern, the relationships are almost linear.

An examination of the set of curves unfolds very interesting and useful conclusions. Firstly, the linear portions of the curves converge on extrapolation to 100% recovery points indicated by dotted lines, suggesting that quantitative recovery of MgSO$_4$ at –5° is independent of the initial composition of bittern. Secondly the curves are not only characteristic of the equipment design as explained for 400 litre batches but for a given equiment they are also very sensitive to the initial composition of MgSO$_4$. The phenomenon is so pronounced that even for the same set of experiments carried on 25 litre batches, there are two distinct curves each corresponding to an initial average composition of bittern, the respective ranges being 5.29 to 5.65% and 6.14 to 6.32% MgSO$_4$.

It becomes markedly evident from the recovery curves that the reduction in the initial MgSO$_4$ content of bittern causes lowering of the crystallization temperature and results in a proportional shift of the curve on x-axis in the respective cases. This shift clearly demonstrates that there exists a quantitative relationship between initial crystallization temperature and pecentage of MgSO$_4$ in bittern. Accordingly for each set of experiments an average initial percentage of MgSO$_4$ in bittern was estimated and the corresponding values of average crystallization temperature

Table 6. Magnesium sulphate concentration and temperature of crystallization.

MgSO$_4$% (Average)	Average crystallization Temp. from graph °C
5.49	14
6.25	16
7.93	19.5
8.00	19.75

Table. 7.

Set of experiments	Scale of operation	Type of bittern	Concentration range of MgSO$_4$ in bittern		Valid temperature range for linear relationship(°C)
1.	25 lits.	Normal	5.29	to 5.65% (A)	12°–4°
2.	25 lits.	Normal	6.14	to 6.32% (B)	14.5°–5°
3.	25 lits.	Heated	7.88	to 8.18% (C)	16°–5°
4.	400 lits.	Normal	7.88	to 8.03% —	—

were noted from the graph. These are given in Tables 6 and 7 and selectively plotted in Figures. The plot is linear and suggests that the relation between recovery and temperature holds good even for different lines for the same set of experiments.

The recovery vs temperature studies do suggest that temperature acts as a driving force in the separation of the magnesium sulphate heptahydrate, $MgSO_4 . 7H_2O$ phase from bittern at least down to 5°. The extrapolation of temperature vs composition curves indicates that it is possible to recover $MgSO_4$ quantitatively from bittern by cooling it to –5° but it is quite likely that in actual operation, the separation of crystals, is related by factors so far not considered important e.g. viscosity of solution, freezing of the liquid phase, formation of double salts etc.

Analytical equations. The linear portion of the plots for percent $MgSO_4$ in solution vs temperature or recovery vs temperature and the regression analysis of the related data suggest the relationship of the following type

$$N = No + mt$$

where N is the initial concentration of or recovery of $MgSO_4$; No the said quantities corresponding to 0°, it is the temperature in degrees centigrade and m the slope. The values of slopes and intercepts obtained either graphically or through regression are given in the Tables 8 and 9 and the corresponding data for % recovery against temperature is given in Table 6 and 7. An examination of the comparative data reveals that in the cases of % $MgSO_4$ in solution vs temperature, the graphical and regression data both for slopes and intercepts in respect of 25 litre batches experiment for heated as well as normal bittern are within the range of 0.5-10%. This is further confirmed by very high values of correlation coefficient for this bivariate system. The corresponding results for 400 litre batches differ by about 30% for intercepts and more than 17% for slope and the coefficient of correlation is also comparatively low. The basic reason, as pointed out earlier, lies in the design of the equipment which perhaps sets forth pseudo-equilibrium. This affects the recovery and shortens the linear portion resulting in lower values of the correlation coefficient.

There appears some degree of variation among the recovery data although it may be said to be within tolerance limits. Data variation is noticeable particularly in case of heated bittern for slopes whose value is more than 13%. Apparently major changes in process donot seem to be involved here but it may be as well be due to uneven heating which in different cases may give rise to erratic results. Furthermore it is found that for heated bittern the values of slopes for different sets of curves for $MgSO_4$ in solution vs temperature, are 25 to 30% higher than the corresponding ones for normal bittern which perhaps causes a parabolic shape to extra polated portion of the curve. Slopes in this case are a measure of the rate of crystallization and their high values are indicative of higher rate. This is supported by the figures on relative composition of $MgSO_4$ which is more in case of heated bittern. However, further studies are needed for arriving at a quantitative relation in this area.

It appears from the preceeding discussion that the recovery of $MgSO_4$ from bittern is not only dependent on temperature but also on the design of the equipment and rate of cooling, the last factor being governed by the degree of agitation. For maximum recoveries, agitation should be at such a rate that the liquid phase is well mixed and at the same time allows the solid phase to separate out from the solution. The rate of cooling if sufficiently controlled avoids formation of a concentration gradient, which, in turn, would diminish the chances of back diffusion of the crystals into the main liquid bulk and hence would enhance the recovery. If, however, the crystals are re-circulated into the solution by vigorous agitation, the recovery would be low, as has been demonstrated by experiments on the 400 litre batches model. It is also indicated that cooling coils normally used for rapid heat transfer are not favourable in this situation and hence use of jacketed cooling would be the appropriate choice.

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