Frames 274-276

Chemical composition of preheater crust. March 22, 1943.

Distinct layer structure was noticeable in the incrustation in the preheater tubes, and the different layers might have been formed during different operating periods. In Gelsenberg the crust formed three layers, with the outer layer directly upon the tube wall.

1. Outer layer: 1 mm. thick dark mass, sp. gr. 5.2 (pyrite or hexagonal FeS, sp. gr. 4.8) and is practically homogeneous.

2. Middle layer: 3.5 mm. thick, gray, very hard mass with many well formed brass-colored crystals. Sp. gr. 4.8.

3. Inside layer: 8 mm. thick, black heterogeneous mass, less hard than the other two layers. Mixture of coke and crystalline constituents. Sp. gr. 3.9, confirming the presence of coke particles.

The tube wall was brittle to a depth of 1/2-1 mm., and its appearance indicated strong corrosion.

The chemical analyses of the layers of the Gelsenberg crust show that the principal constituents in the intermediate and inner layers are Fe and S, present in proportion by weight of the compound FeS.

The presence of W, Mo, V, Cr in the crust is surprising, and they were derived from the tube material. Their amounts decrease from outside to the inside. Their presence may indicate that the metals diffuse in the solid phase from the surface attacked.

Unlike other crusts, the Poelitz crusts contained only traces of these metals, showing somewhat different conditions there. Titanium is also present in Poelitz in much smaller amounts than in Gelsenberg.

Iron in the crust cannot possibly come from the tubes, because of the very slight reduction in weight of the tubes, and must come from the coal or the catalyst. The proportion of iron and titanium in the crust and of the individual iron compounds helps in arriving at this conclusion.

	Fe : Ti
Ruhr Coal Ash	51 : 1
$FeSO_4 \cdot 7H_2O$	90 : 1
Bayer mass	8.1: 1

Assuming 4% ash in the coal and the addition of 1.2 percent $FeSO_4 \cdot 7 H_2O$ and 1.5% Bayer mass, the amounts of iron introduced are in the proportion of 0.61:0.23:0.42. Should the Bayer mass settle out and solidify, the titanium content of the crust should be higher. The inside layer of the Gelsenberg crust has however Fe:Ti ratio of 50:1. The undersigned believes therefore that the FeS in the crust is derived from iron sulfate or from the coal, where the iron, coal and titanium proportion is similar to that in the crust. Such deposits do not occur in the 300 atm. bituminous coal hydrogenation (tin oxide and chlorine) in Scholven, and neither in Leuna nor in Wesseling was catalyst deposition observed from the bog iron ore or the Bayer mass, while similar deposits were formed in extraction tests in Leuna with $FeSO_4:7 H_2O$. $FeSO_4$ may be the cause of the crust formation.

Poelitz has already observed FeS formation when preparing an oil suspension of the catalyst mixture.

Crust Composition

Crust	Gelsenberg Outer layer	Gelsenberg Middle layer	Gelsenberg Inside layer	Poelitz	N 10 steel for comparison
% total S	-	-	-	33.8	0.011
% Sulfide S	11.2	31.0	22.8	33.8	-
% Fe	73.8	60.2	44.3	59.4	
% W	0.01	0.001	0	0	0.40
% Mo	0.48	0.09	0.13	0.01	0.41
% V	0.97	0.01	0.01	0.01	0.71
% Ti	0.16	0.16	0.67	0.05	-
% Cr	4.36	0.40	0.11	0.004	2.70
% Al	0.18	0.30	3.57	0.33	-
% Ca	0.06	0.17	0.86	0.27	-
% Mg	-	-	-	0.08	-
% Na_2SO_4 + K_2SO_4	-	-	4.6	0.54	-
Total C	0.87	0.61	5.12	3.49	0.18
SiO_2	1.70	0.46	1.63	0.38	0.43
CO_2	-	-	-	0.30	

Frames 277-287

Reduction of load on the liquid-phase preheater; discussions in Ludwigshafen, March 22, 1943.

Summary

The 700 atm. gas preheaters of bituminous coal plants are mostly equipped with N 10 hairpins. To increase their life and safety in operation, and also to cause appreciable savings in fuel gas, the following measures were recommended:

1. Addition of a fifth converter to all four converter stalls, and to reach the peak preheater temperature in this additional converter.

2. Installation of a gas heat exchanger which would utilize the heat contained in the distillate gas mixture.

3. The cold paste methods of operations.

4. Several other measures, which will be less effective.

Load would naturally be greatly reduced when the gas heat exchange is used for thin paste heat exchanging.

Some chemical means were also proposed, notably such which would reduce the crust formation.

A. Engineering

The heating of the liquid phase stalls in different plants is shown in table 1.

We may distinguish between 4 groups of processes depending on heat exchange: Heat transferred by heat exchange amounts to 35% in group 1 (gas heat exchange in Gelsenberg) and reaches 84% in the group 4, Leuna, in which the H.O.L.D. is heat exchanged in addition to all the rest.

A thin paste is heat-exchanged in Blechhammer as in Poelitz, and this amounts to 32% in the former with the recovery of 14 M.kcal./hr. because of their high throughput with a 70% efficiency of the preheater. The heat of combustion of 1.5 tonnes of oil with a similar heat of reaction will produce 12 M.kcal./hr. (440 kcal./kg. converted m.a.f. coal).

Troubles with the N 10 steel necessitates paying renewed attention to the hairpin wall temperatures. The inside wall temperature of the hottest hairpins of the 700 atm. bituminous coal preheater under new conditions is 470° C., and the outside temperature 485° C. The recycle gas in Blechhammer is at 600° C., or 40° higher with the new preheater, leaving almost no safety margin in the recently established upper temperature limit for N 10 steel of 520° inside the hairpins.

Incrustations in the Gelsenberg and Poelitz hairpins reached a thickness of 10 mm. in the hottest part of the preheater, and the temperatures were 30-50° higher than in the uncrusted state. These temperatures were determined with thermocouples and agree fairly well with computations if the heat transfer of the crust is assumed to be 1.5 kcal./°C., $m.^2$, hr.

The recycle gas temperature can be correspondingly raised as long as the preheater is not used to its limit, i.e. if its temperature limit has not been reached.

Gelsenberg has, in addition, greatly reduced their intake temperature into converter I from 425 to 390° C. with a resulting great reduction in the preheater load. The throughput will have to be lowered only when a limit is here reached, but computations of economy show that shutting down the stall and cleaning the preheater will prove more economical than reduction of throughput.

A reduction of the preheater load, in particular of the Blechhammer preheater, is urgently needed. The following means were provisionally suggested.

I. Recommendations to reduce the preheater load:

1. The installation of a gas heat exchanger to heat the total inlet gas to 200° would permit elimination of gas hairpins. The heat economy will amount to 3 M.kcal./hr. or 150,000 x 10^9 x 10^6 kcal./yr. and stall, so that the additional heat exchange will be amortized in less than 1 year.

2. Raising the concentration of thin and heavy paste will reduce the amount of thick paste for the same coal throughput. Dr. Wissel is of the opinion based on the Poelitz experience that the thin paste may contain 41% coal and no objection was raised to 53% concentration of the thick paste.

3. Efforts must be made to heat exchange the H.O.L.D. in 700 atm. operations, similarly to the way it has been done in Leuna at 200 atm., where part of the inlet gas is heat exchanged in double coils against H.O.L.D. Heat exchanging of H.O.L.D. against paste (Josenhans' proposal) was not yet tested industrially, and it is desirable at present to use the heat contained in the distillate gas mixture as completely as possible.

4. Cooling H.O.L.D. in a wet steam cooler, as is already done in Blechhammer, is one way of solving the problem. Such a cooler will recover 3 M.kcal./hr. in steam, and will actually increase the efficiency of the Blechhammer preheater from 52 to 68%.

II. Addition of a fifth converter to the stall:

The preheater outlet gas temperature in the Gelsenberg stalls can be reduced from 425° C. to 390° without interfering with the reaction. The circulation of the charge inside the converter will raise the temperature by about 40° and greatly hasten reaching the reaction temperature. Gelsenberg and Leuna have found that 50-60% of the total heat of reaction, amounting to 3 M.kcal./hr., is liberated in the first converter, and the reaction temperature of 478° C. will be reached at the outlet from the first converter. For safety reasons, the converter inlet temperature will be lowered to 400° instead of 390°. This will naturally result in a considerable reduction in preheater load through lowering the peak temperature from 425 to 400°. The recycle gas inlet temperature in Blechhammer could then be reduced from 600 to 540° for the same number of hairpins, lowering correspondingly the tube wall temperatures.

From considerations of heat requirements, the fifth converter will prove an advantage:

1. In Gelsenberg (gas heat exchange):

The lower converter inlet temperature will hardly affect the gas heat exchange because of reduction in amount of cold gas, and the amount of heat corresponding to a temperature difference of 25° may be considered a net gain:

With 56 tonnes/hr. paste 30,000 $m.^3$/hr. intake gas, and

With 70% preheater efficiency 850,000 kcal./hr. of heat will be conserved.

2. In Blechhammer and Poelitz (thin paste heat exchange):

Heat corresponding to 25° lower temperature will reduce the heat exchange efficiency to only 80% by eliminating the cold gas. The gain in heat for the high Blechhammer throughput is 1,600,000 kcal./hr.

The more promising results in the Gelsenberg operations are based on gasoline + middle oil production, and the proportion will be different for Blechhammer because of the higher throughput than for gasoline + middle oil process.

3. Cold paste method:

Part of the paste is not passed through the preheater but is injected directly into the reaction space, and this cold paste is also heated up to the reaction temperature by recycling inside the converter. This cold paste process was first tried out in Scholven and was found satisfactory in over 1 year operation in Gelsenberg. The earlier fears of too rapid temperature rises inside the converters have not been confirmed in Gelsenberg. The amount of heavy oil excess (asphalts) has increased somewhat in Gelsenberg. No experience is as yet available for the fuel oil process, nor the effect of increased asphalt content upon the processing of residues. The coal paste might be slightly preheated, e.g. to 200° C., which would reduce the amount of additional heat necessary. This method of operation introduced no difficulties because paste pumps will not have to be reapportioned with larger throughputs.

The reduced amount in cold gas will correspondingly reduce the power requirements for recycle pumps and for the cooling water.

In figure 1, the upper part represents the existing conditions, and the suggested improvements are shown on the lower picture. The encircled figures refer to the different processes.

Figure 2 represents the temperature diagrams. The recycle gas temperature may be greatly reduced, with an elimination of 10 hairpins. Even if the preheater is not rebuilt, disregarding the savings, the recycle gas temperatures and the hairpin temperatures will become much lower. The reduction in heat requirements is remarkable and amounts to 7,000,000 kcal./hr. (at 700 atm.); the resistance of the stall is also greatly reduced by reducing the number of hairpins.

A total of 20 converter shells will be required for Gelsenberg, Poelitz and Blechhammer. The inserts will be made of lower alloy steel, as is already done in Leuna and Welheim.

B. Chemical measures

Reduction in crust formation, or even its prevention is a chemical method to reduce the preheater load. Analyses of Gelsenberg crust (see preceding article) show that W, Mo, V, and Cr are derived from the tubes, and that their amounts are lower at a greater distance from the tube walls. These metals are lower in amount in the Poelitz crust. The inside tube wall in Gelsenberg was greatly affected to a depth of 1/2-1 mm., and became very brittle. The amounts of Ti, Al, Ca and C from the coal or the catalyst increase from the outside to the inside of the crust. The iron:titanium proportion in the crust corresponds occasionally to that in coal ash and in the catalyst, leading to conclusions on substances which primarily participate in the crust formations. Iron catalysts seem to be primarily responsible for it. Such crusts were not formed so far in the 300 atm. bituminous coal hydrogenation with tin oxide and chlorine, or else reached a thickness of the order of 1 mm. Neither Leuna nor Wesseling, which used bog iron ore or Bayer mass, have so far observed such crust. On the other hand, Ludwigshafen has found crust formation when using only ferrous sulfate (extraction test).

Iron sulfate, or the interaction of iron sulfate and sodium sulfide may possibly be the principal agents in the formation of preheater crusts. A change in the method of adding catalysts may be desirable, and in particular the method tested of adding the catalyst behind the converter inlet. Poelitz will test the possibility of adding sodium sulfide or the iron catalyst directly to the converter. Another method might consist in replacing the present catalysts with iron-char. This is now being tested in Ludwigshafen.

Reducing the amount of gas in preheating might be another method to reduce the load upon the preheater. Ludwigshafen lowered the amount of gas to 0.55 $m.^3$/kg. paste in extraction tests. A reduction of the amount of gas without introducing difficulties in operations, and a method of adding gas behind the preheaters remain yet to be studied. Wesseling has found that the stall temperature rises if the amount of gas is reduced. Reducing the amount of gas affects adversely the distillation processes at the same catchpot temperatures.

The preheater gas inlet temperature could be strongly lowered by adding substances with high reaction heat, e.g. SO_2 to the first converter. 1 kg. SO_2 liberates 820 kcal. when combining with 1.1 $m.^3$ H_2, which would reduce the peak temperature in the preheater and would in addition make available the catalytic effect of the H_2S formed.

Reduction of pressure as means to reduce the load on the preheater will bring about some disadvantages for the progress of converter reactions. Reducing the pressure by 50 atm. would raise the asphalt content by about 1%.

. Materials of construction

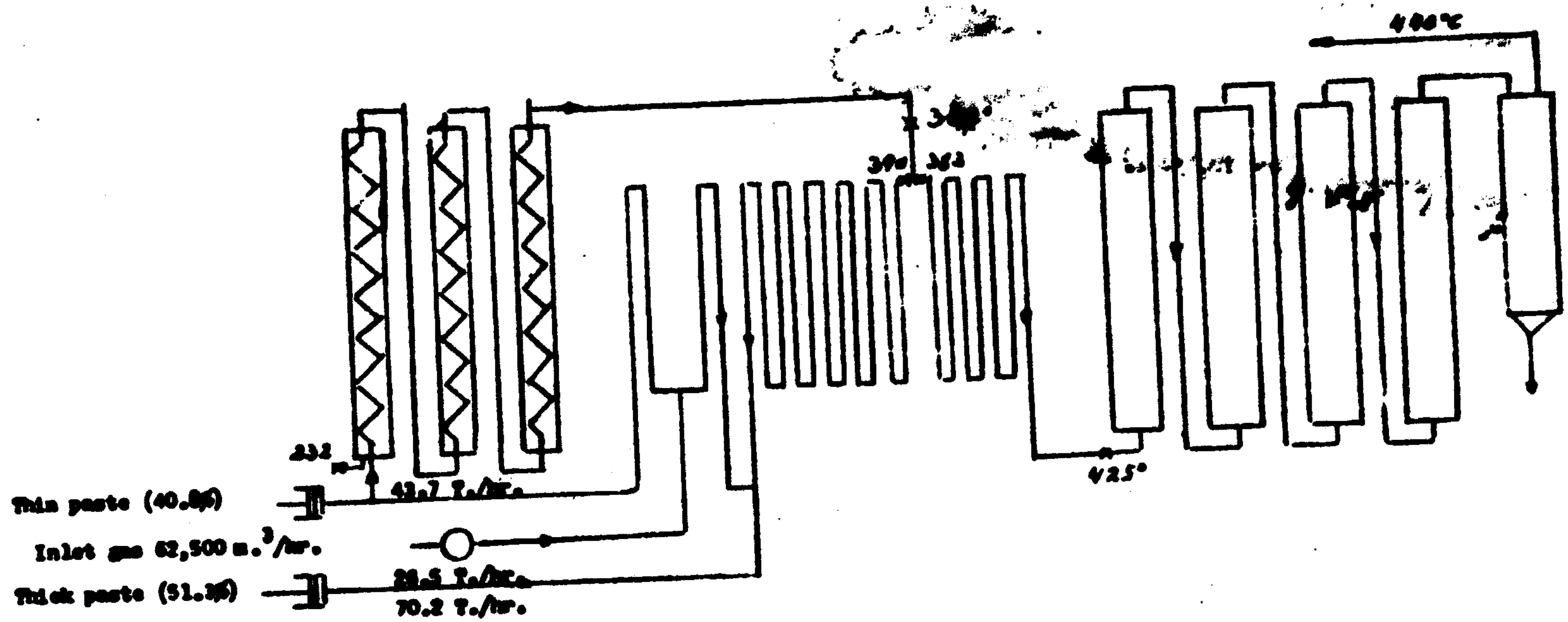
Two accidents in Gelsenberg hairpin tubes of N 10 steel after bout 2 years' operation have created fears about the safety of the airpin heaters.

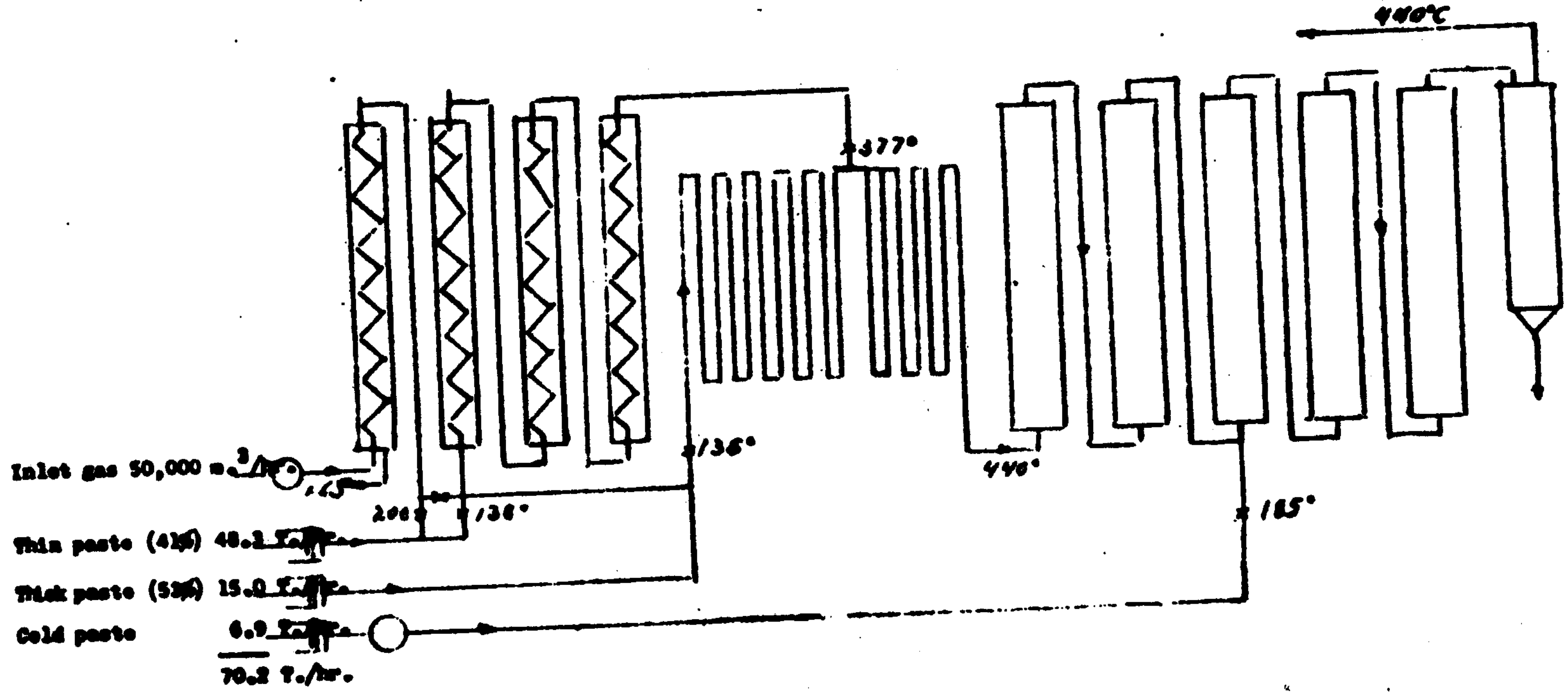
Other damages to N 10 parts have frequently occurred in the ast years, but could always be connected with defects in the composiion, structure, or mechanical strength of steels introduced by temperng. The above cases differ from the earlier ones in that such faults ere not observed. They rather indicated that the original properties f steels had deteriorated during operations. The material could not ermanently resist the full operational stresses. The usual safety argin was evidently exceeded. (The remainder of this page is not readable).

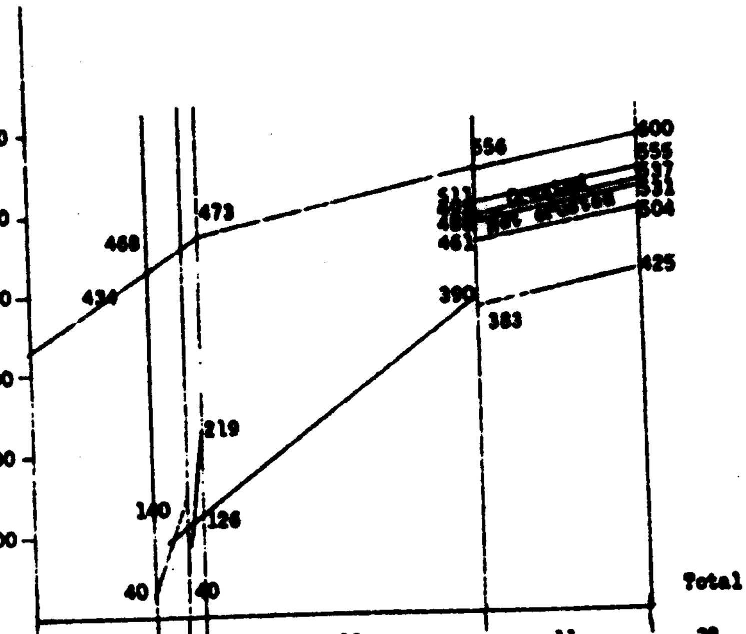
TABLE 1

Groups and characteristics	Plant	Press., atm.	Thruput, T./hr.	Intake gas, m.^{3}/hr.	Temp., °C.	Heat of reaction, kcal./hr. x 10^6	Recycle gas temp., °C.	Total heat requirements, kcal. x 10^6	From heat exchangers, Percent	From heat exchangers, No.	From preheater, In preheater, %	No. of hairpins
I. Gas heat exchange	Scholven	300	24	30,000	430	5.7	590	8.0	45			24
	Gelsenberg: New	700	30	31,000	430	8.0	560	9.8	35		65	30
	Old	700	20	31,000	350	3.3	595			1		
II. Thin paste heat exchange	Poelitz	650	40	33,000	425	6.6	595	10.8	55	5	45	21
	Blechhammer	700	70	62,000	425	12.0	600	19.4	52	3	48	53
III. Total feed heat exchange	Rheinbraun	580	46	30,000	418	6.5	560	11.5	65		35	18
	Welheim	630	33	20,000	447	4.5	570	8.8	70	3	30	25
IV. As III, with addition of H.O.L.D. heat exchange	Leuna	250	38	26,000*	420	3.8	550	8.4	84	3	18	

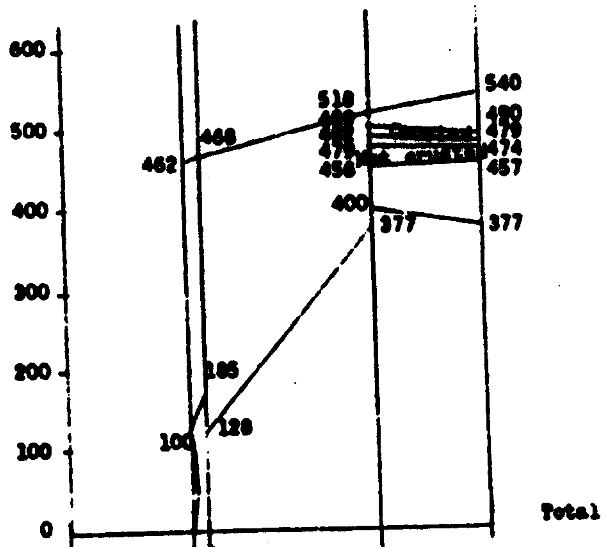
*Includes heating to 270° C. of 22,000 m.^{3}/hr. of gas by heat exchanging H.O.L.D.


440°C
425°
232
Thin paste (40.8%)
42.7 T./hr.
Inlet gas 62,500 m.³/hr.
Thick paste (51.3%)
28.5 T./hr.
70.2 T./hr.


440°C
377°
136°
440°
185°
138°
Inlet gas 50,000 m.³/hr.
Thin paste (41%) 48.3 T./hr.
Thick paste (53%) 15.0 T./hr.
Cold paste 6.9 T./hr.
70.2 T./hr.



No. of hairpins	21	18	11	32
Heat transfer, 10^3 kcal./hr.	2310	4810	2460	9580
Δ p, atm.			15.4	



No. of hairpins	1	11	7	19
Heat transfer, 10^3 kcal./hr.	315	2800	1170	4285
Δ p, atm.			7.2	