The H_2-S process for the production of heavy water

by

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This report gives the results of calculations on the H_2S-process for heavy water production with a view to a possible application in a heavy water plant in Iceland. The details of the calculations are given in a fuller report in Icelandic.

The process is based on the fact that the equilibrium constant for the isotopic exchange reaction

$$H_2O + HDS \rightleftharpoons HDO + H_2S$$

varies considerably with temperature, decreasing with increasing temperature. The only information that seems to be available at present on the variation of the equilibrium constant with temperature is from a paper by A.E. Suess[1], who gives the following expression:

$$K(T) = \frac{[HDO][H_2S]}{[H_2O][HDS]} = 0{,}871 \cdot e^{\frac{523}{RT}}$$

where R is in cal/mole, °K and T in °K. This expression for K(T) is used here in all calculations.

Water and H_2S gas flow countercurrent to each other in two towers, one hot and one cold, as shown on fig. 1. The water is enriched in D-content while flowing down the cold tower and depleted in the hot tower, where the H_2S gas is enriched. It is economical to divide the plant into stages of successively smaller size as the D_2O concentration in the water increases. The first step is by far the largest and will mainly be considered here. In order to determine the McCabe-Thiele diagram for the first stage it is necessary to calculate the equilibrium lines and the operating lines of the towers. The operating lines will be determined by economic considerations. The expression for the equilibrium lines has been derived by J. Spevack and has the following form:

[1] A.E. Suess: Isotopenaustauschgleichgewichte: FIAT Review of German Science, 1936-1946.

$$y = \frac{(1+S)(1+K_x H)\alpha}{(1+H)(S+K_x)} \cdot X \cong m \cdot X$$

where y, x are the mol fractions of D in the gas and the liquid, S is the solubility of H_2S in water, H is the humidity of the gas, α is the vapor pressure ratio of HDO to that of H_2O, and $K_x = \alpha \cdot K(T)$. The values of S, H, α, K(T) and m for various temperatures are given in table I.

Table I.

T°C	S	H	K(T)	α	m
30	0,0311	0,0022	2,33	0,938	0,437
100	0,01283	0,0536	1,94	0,975	0,541
110	0,01187	0,0796	1,90	0,978	0,564
120	0,01150	0,1111	1,86	0,981	0,585
130	0,01131	0,150	1,83	0,984	0,608
140	0,01094	0,201	1,79	0,987	0,634

The operating lines for a cold and a hot tower can be shown to have the following slopes:

Cold tower:

$$\beta_k = \frac{F}{G} \cdot \frac{1+S_k}{1+H_k}$$

where F is the water feed to the cold tower and G is the H_2S flow in the cold tower. Index k refers to the cold tower.

Hot tower:

$$\beta_h = \left(\frac{F}{G} + H_h\right) \frac{1+S_h}{1+H_h}$$

where index h refers to the hot tower.

In order to determine the equilibrium lines and the operating lines it is necessary to find optimum values for tower pressures, tower temperatures, enrichment per stage, the ratio $\frac{F}{G}$ which determines β_k and β_h, and a quantity f which may be called the fractional approach to equilibrium and is defined in fig. 2. These are now considered one at a time.

Pressure. It is economical to have the pressure in the towers high in order to decrease their volume. The steam consumption also decreases with increasing pressure, because the amount of steam required to saturate the H_2S gas at a constant temperature decreases with increased total pressure. However, a pressure limit is set by the vapor pressure of H_2S liquid which at 30°C is 22,5 atm. The pressure has to be kept safely below this value in order to prevent the H_2S-gas from liquifying. From this it seems plausible to assume an average pressure of 20 atm in a hot tower and 19 atm in a cold tower.

Temperature. It is desirable to have the temperature difference between the hot and the cold towers large in order to obtain a large recovery of D_2O from the feed water. The lower temperature is limited by the possibility of H_2S hydrate formation (H_2S, $6H_2O$). Above 30°C this hydrate is not formed. The lower temperature is therefore chosen as 30°C. Regarding the higher temperature, an economic balance has to be made between increased recovery and increased steam consumption as the temperature is raised. Preliminary estimates seem to indicate that this value is around 120°C, which will be used here. This is based on the very low cost of steam in Iceland (0,11 $/ton of 150°C steam). In other countries where steam cost is much higher the optimum hot tower temperature is lower and the recovery therefore less.

Enrichment per stage. By using many stages with a low enrichment in each the total volume of the towers of all the stages is decreased. On the other hand energy costs, pumps, pipes and heat exchanger costs are increased somewhat. An estimate seems to indicate that the total cost does not greatly vary with enrichment in the interval from 5 to 10. Here the enrichment per stage is chosen as 6 to 7.

The ratio F/G. In order to determine the optimum value of this ratio we have to assume a value of f, and we here take f = 0,985. Then the number of theoretical plates in a hot and a cold tower can be calculated for various values of F/G. The optimum value of F/G is chosen where the numbers of theoretical plates in a hot and a cold tower are equal, which is very near to the value for a minimum total number of plates in both hot and cold towers. Thus $(F/G)_{opt} = 0,470$ (F and G in moles).

The fractional approach to equilibrium f. The optimum value of f is determined by an economic balance between tower volume and steam consumption, using the above found values for tower pressure, temperature, enrichment per stage and the ratio F/G. It is assumed that Spraypak is used as tower packing and that (HETP) = 2 feet. The tower cost per unit volume is about 800 $\$/m^3$. Annual costs are assumed 15% of capital cost. The cost of steam is \$ 0,11 per ton at 150°C and is is further assumed that 50% heat recovery is obtained in heat exchangers. With these assumptions the minimum total annual cost is obtained for f = 0,989.

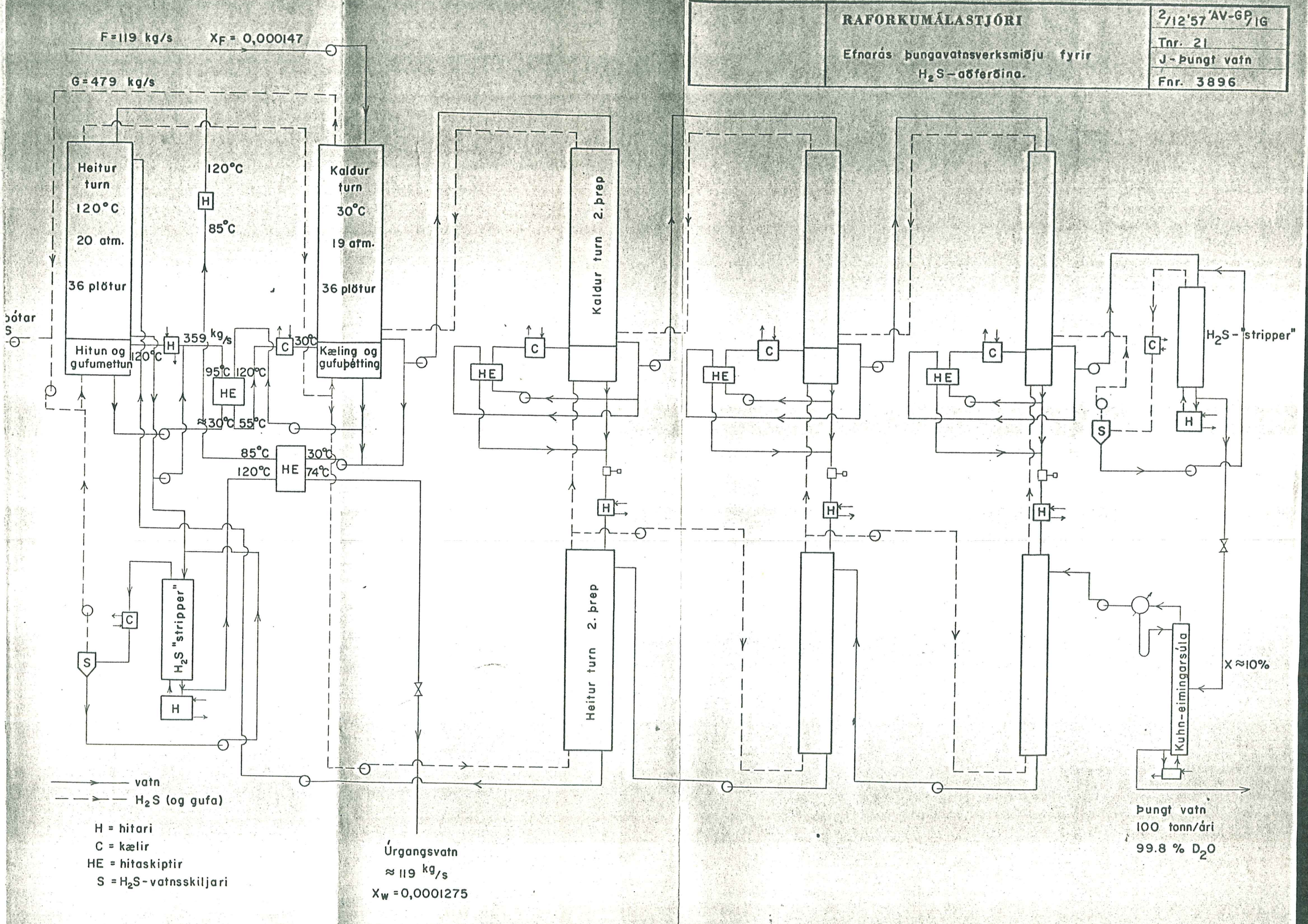
It is now possible to draw the McCabe-Thiele diagram for the first stage of the plant and this is done in fig. 3. In order to be able to draw a flow diagram of the plant it is necessary to find the best arrangement of heat exchangers. In studying this the following conclusions have been reached.

1) It does not pay to use either gas-gas or gas-liquid heat exchangers. Liquid-liquid heat exchangers should be used to decrease steam consumption.

2) Where H_2S gas has to be cooled or heated and humidfied this is best done in a direct contact dehumidifier or humidifier. These could use Spraypak and be a part of the towers.

The flow diagram for the plant can now be drawn and this is done in fig. 4. The first stage towers would have to be divided into parallell units, but in other respects the diagram shows the main parts of the plant.

	RAFORKUMÁLASTJÓRI Efnarás þungavatnsverksmiðju fyrir H_2S-aðferðina.	2/12'57 AV-GP/IG Tnr. 21 J - Þungt vatn Fnr. 3896



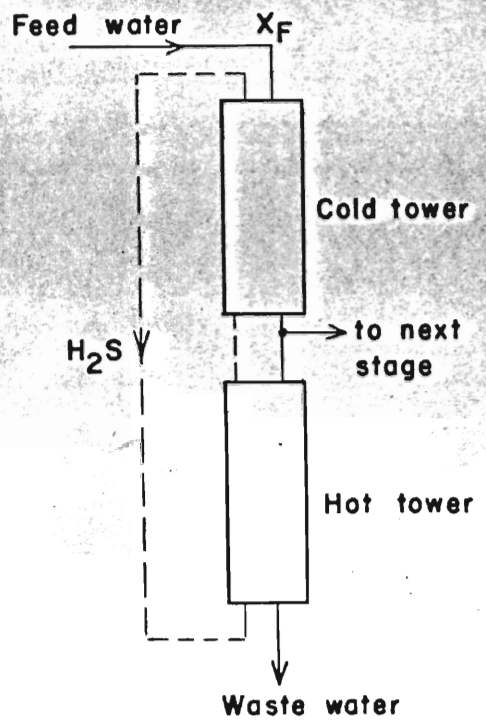

Feed water
X_F
Cold tower
H_2S
to next stage
Hot tower
Waste water

FIG. 1.

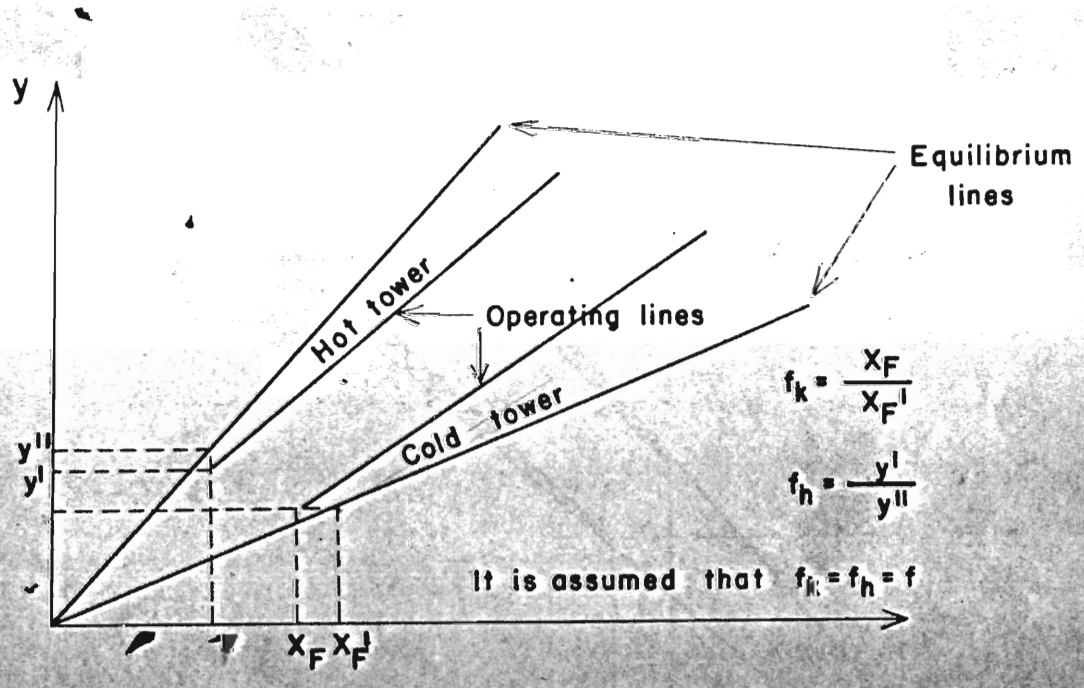

y
Equilibrium lines
Hot tower
Operating lines
Cold tower
y^{II}
y^{I}
$f_k = \frac{X_F}{X_F^I}$
$f_h = \frac{y^I}{y^{II}}$
It is assumed that $f_k = f_h = f$
X_F X_F^I

FIG. 2.

RAFORKUMÁLASTJÓRI	2/12 '57 GP/IG
Mc Cabe-Thiele línurit yfir fyrsta og annað þrep D_2O-vinnslu með H_2S aðferðinni.	Tnr. 22
	J- Þungt vatn
	Fnr. 3897

Fig. 3

MYND - 4.

Framleiðsla: 100 tonn D_2O/ári

H_2O: F = 119 kg/s = 6610 mol/s $\quad X_F = 0.000147$

H_2S: G = 479 kg/s = 14050 mol/s

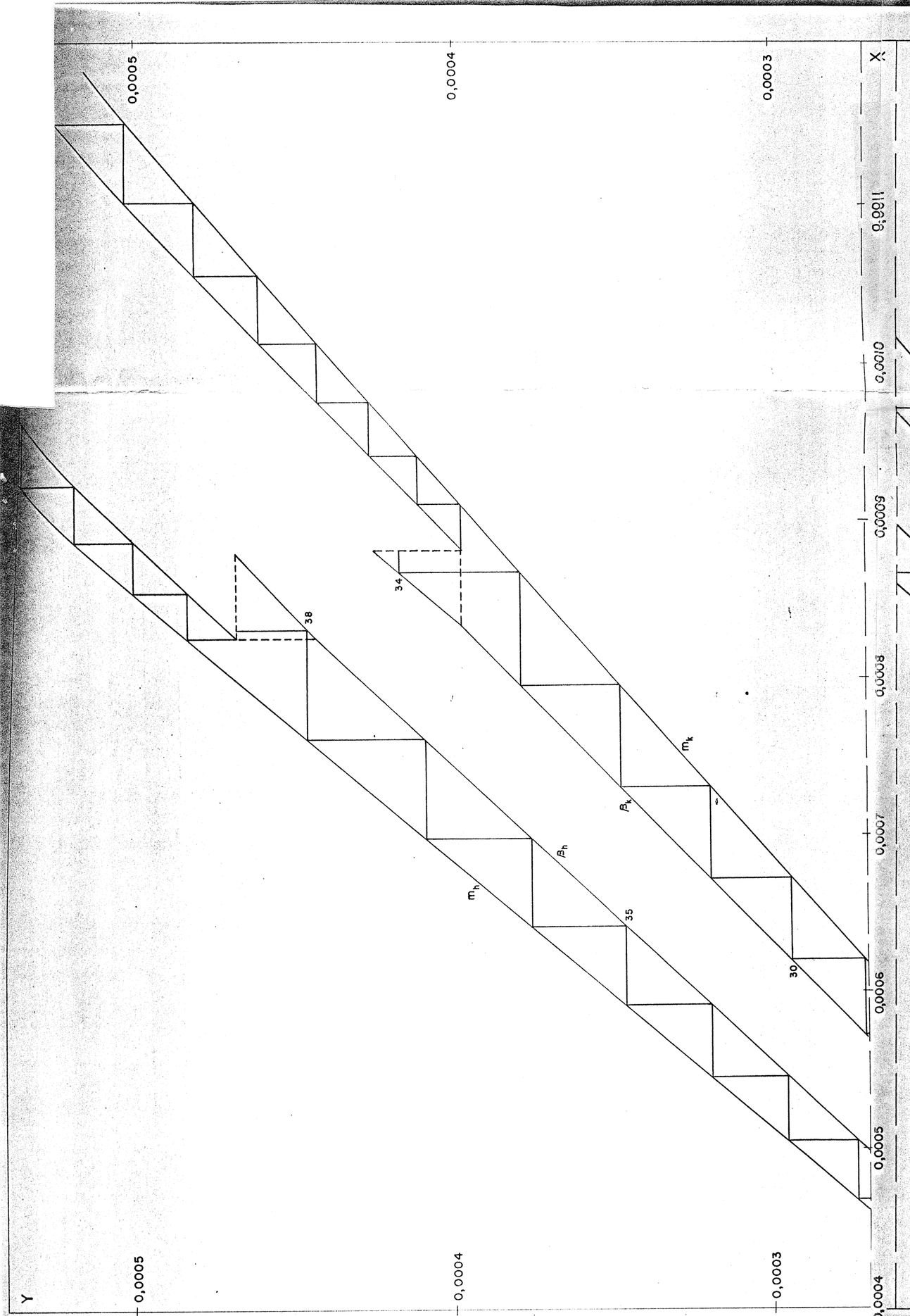
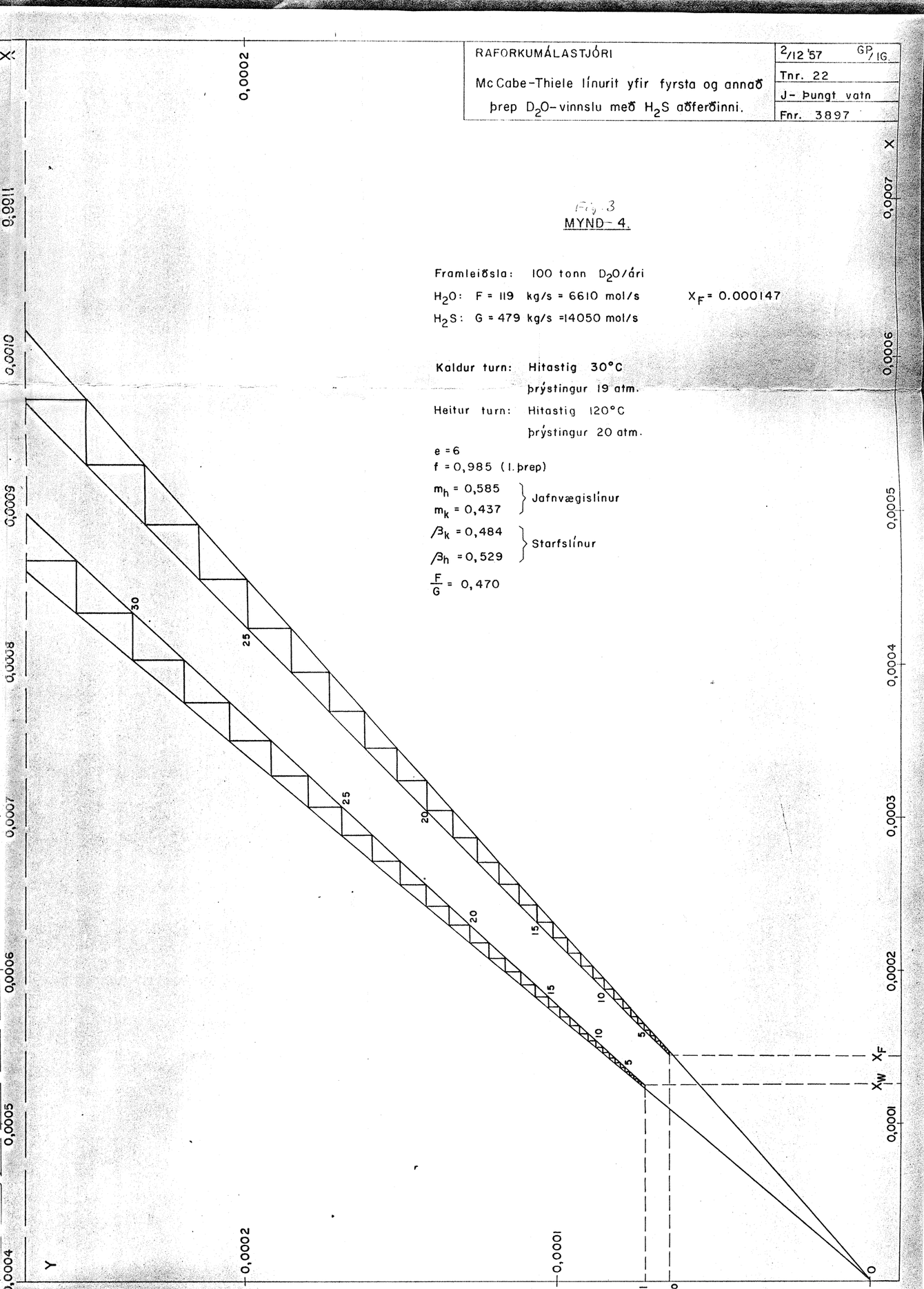
Kaldur turn: Hitastig 30°C
þrýstingur 19 atm.

Heitur turn: Hitastig 120°C
þrýstingur 20 atm.

e = 6

f = 0,985 (1. þrep)

m_h = 0,585, m_k = 0,437 } Jafnvægislínur

β_k = 0,484, β_h = 0,529 } Starfslínur

$\frac{F}{G}$ = 0,470