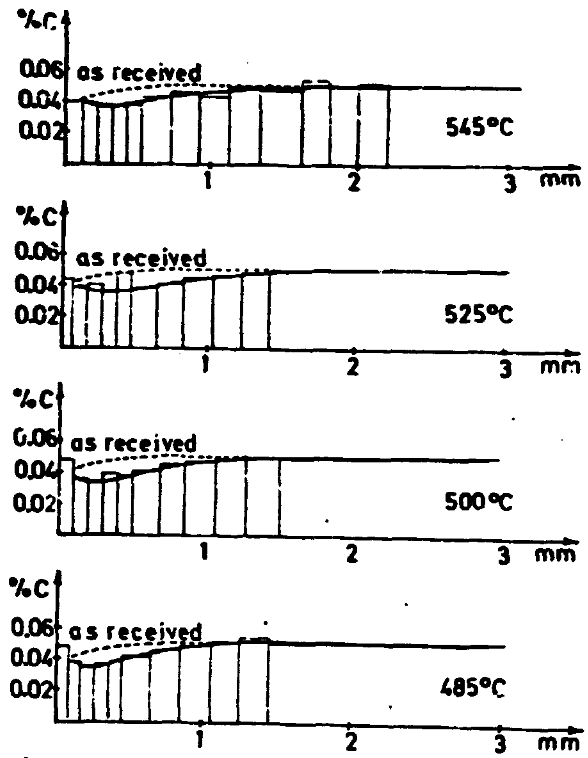

Fig.6. Decarburisation of 2¼Cr1Mo(0.048 %C)

Examinations reveal a significant decarburization of the steel with the higher carbon content at 545°C. In contrast, the low carbon steel is only slightly decarburized. For the two types of steel the extent of the decarburization is decreasing with the temperature. Assuming that decarburization is a phenomenon dependent on $\sqrt{t}$, rate constants for the decarburization process have been calculated as :

$c = 5.9 \cdot 10^{-8}\ g.cm^{-2}.s^{-1/2}$ at 545°C
$c = 2.2 \cdot 10^{-8}\ g.cm^{-2}.s^{-1/2}$ at 525°C
$c = 1.8 \cdot 10^{-8}\ g.cm^{-2}.s^{-1/2}$ at 500°C
$c = 1.5 \cdot 10^{-8}\ g.cm^{-2}.s^{-1/2}$ at 485°C

for the high carbon 2 1/4 Cr - 1 Mo steel.

For the low carbon 2 1/4 Cr - 1 Mo steel the calculated rate constants are :

$c = 1.3 \cdot 10^{-8}\ g.cm^{-2}.s^{-1/2}$ at 545°C
$c = 0.8 \cdot 10^{-8}\ g.cm^{-2}.s^{-1/2}$ at 325°C and 500°C
$c = 0.5 \cdot 10^{-8}\ g.cm^{-2}.s^{-1/2}$ at 485°C

Analysis of available decarburization data was performed by ARMIJO (1). He has calculated the corresponding decarburization rate constants and he has plotted these values as a function of 1/T. Nearly all values are contained between two lines. Figure 7 shows the two lines of ARMIJO and the values of the rate constants calculated from our results. It can be seen from this plot that the values of these rate constants are comparable to those obtained elsewhere, in tests where the thermohydraulic conditions have often been widely different (i.e. both static and isothermal dynamic experiments.) It appears therefore that decarburization is not sensitive to the thermohydraulic conditions, at least in the range investigated in those experiments.

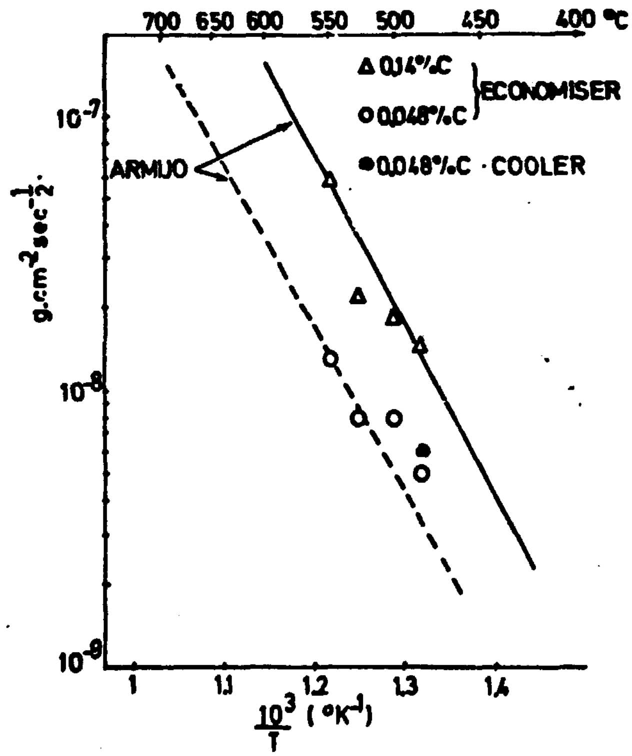

Fig.7. Decarburisation rate constants

REMARKS

1) For a given sodium activity, the rate constants as calculated above may depend on the bulk carbon content of the materials and on the metallurgical structure. For the specimens studied, it can be seen that, at the various temperatures, the ratios between the rate constants corresponding to the higher and to the lower carbon materials are roughly equal to the ratio between the carbon contents. This result could be expected as it has been pointed out above that the metallurgical structure of the various specimens are of the same type. Other tests carried out by

ture. The PHENIX parameters retained in the CARNACIER A loops are :

- the sequence of the materials,
- the temperatures,
- the ratio $\frac{\text{equivalent diameter}}{\text{residence time}}$
- the ratio $\frac{\text{ferritic steel surface area}}{\text{austenitic steel surface area}}$

Conditions for a turbulent hydraulic regime are satisfied in all regions of the loop. The loop contains five litres of sodium with a flow rate of 480 kg/h. The three A loops have been operated for six months, one year and two years respectively. After test, carbon transfer has been evaluated by chemical analysis of 100 microns thick machined layers.

After two years of operation, the decarburization of the 2 1/4 Cr 1 Mo steel and the carburization of the 316 L steel are not practically measurable. A slight and superficial (100 microns) carburization of the 321 H steel is observed at 545°C.

2.2 - ICARE loop

2.2.1 - Description of the loop

Figure 2 shows the design of the loop. The principal sodium circuit has three exchangers : A (316 L steel), B_1 (321 H steel) and B_2 (2 1/4 Cr - 1 Mo steel) simulating respectively the PHENIX IHX, the superheater and the booster superheater, and the economiser-evaporator. In the cold region (350°C), there are an electromagnetic pump, a cold trap (120°C), a plugging-meter and a heater to regulate the temperature of the cold point (350°C) of the exchanger A. In the hot region (550°C), there is a heater to regulate the temperature of the hot point (550°C) of the exchanger B_1. Heat exchanges are made through an auxiliary sodium circuit used as an econo-

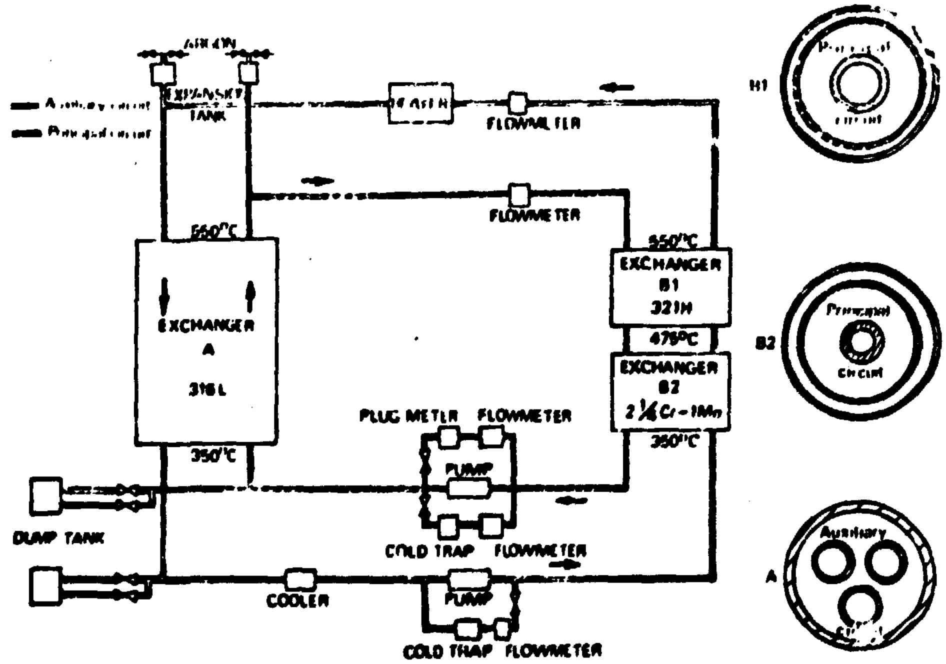

Fig 2 CARBON TRANSFER LOOP (ICARE)

miser. The PHENIX parameters retained in the ICARE loop are : the sequence of materials, the temperature, the equivalent diameter and the residence time. In these conditions, it can be shown that ratio $\frac{\text{ferritic steel surface area}}{\text{austenitic steel surface area}}$ is automatically respected. Additionaly, the main tubes of the three exchangers have the same dimensions and the same manufacturing processes than those chosen for PHENIX. The 2 1/4 Cr - 1 Mo steel is normalized-tempered and has a bainite-ferrite structure; the 316 L and 321 H steel have a normal annealed austenitic structure. The loop contains 110 litres of sodium with a flow rate of 1700 kg/h, the Reynolds number being higher than 10 000 in every section of the circuit. The loop has been operated for 10000 hours. The impurities (C,O, Fe, Ni, Cr and Ca) of the sodium were controlled periodically. The oxygen content has varied between 1 and 2 ppm, and the content in "elementary carbon" between 5 and 12 ppm; the carbonate, carbide and cyanide species were not practically measurable (< 0,1 ppm for carbonate and carbide and < 0,01 ppm for cyanide). The carbon activity, measured with Fe-Mn 20% foils, has varied between 3 and 7.10^{-3}. The contents in various metallic elements have not practically changed (Fe : 1-2 ppm, Ni < 0,5 ppm, Cr < 0,5 ppm and Ca < 2,5 ppm).

2.2.2 Carburization of 316 L steel

The measurements of the carbon gradient at the surface of the as received tubes indicated a slight and superficial carburization (figure 3). After test, no change in the carbon content compared to the as received tubes was observed near the I.D. for all the samples examined (corresponding to exposures at 350, 475, 510, 530 and 550°C). The metallographic examinations showed that the grain boundaries are affected on a depth of 20 microns by a precipitation of chromium carbides. Nevertheless, this effect is not due to carburization during the test, but to a structural evolution in temperature of the initially carburized surface layer.

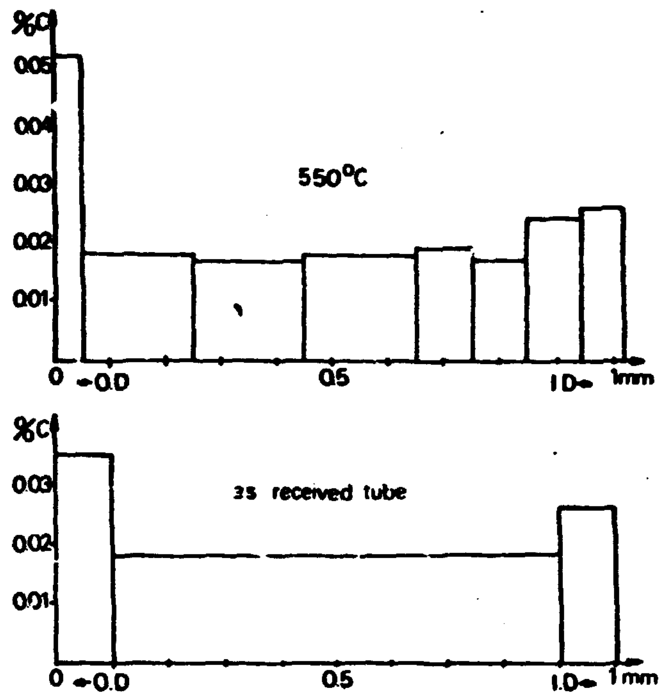

Fig.3 CARBURIZATION OF 316L STEEL

2.2.3 - Carburization of 321 H steel

Samples corresponding to the temperatures of 475, 510, 530 and 550°C were examined. The chemical analyses showed after test a carburization slighty greater than on the as received tube. This phenomenon increases when the temperature decreases (figure 4). The metallographic examinations showed intergranular precipitation on a depth of 20 microns.

2.2.4 - Decarburization of 2 1/4 Cr - 1 Mo steel

Samples corresponding to the temperatures of 350 and 475°C were examined. The chemical analysis and the metallographic observations did not show any decarburization.

3 - CARNACIER B LOOP

3.1 - Description of the loop

For a second run a CARNACIER loop (B_2) having the same thermohydraulic characteristics as the CARNACIER A loops above, but with the 321 H steel section been replaced by a

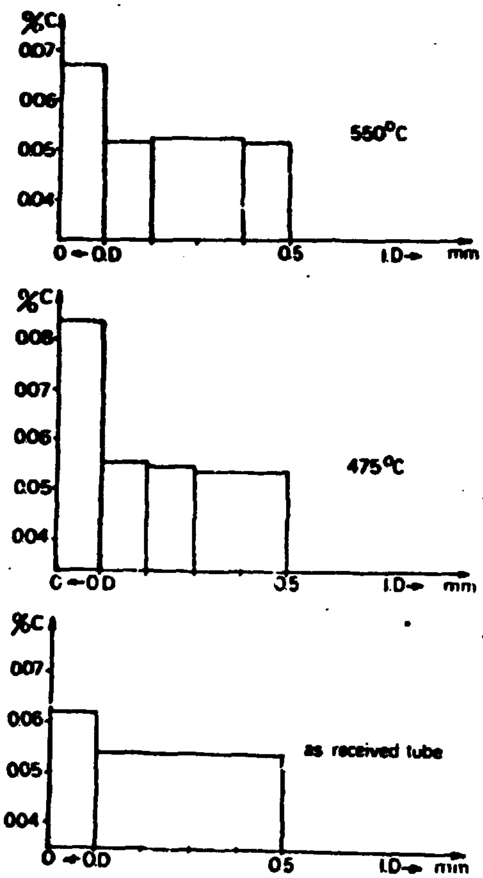

Fig 4 CARBURIZATION OF 321H STEEL

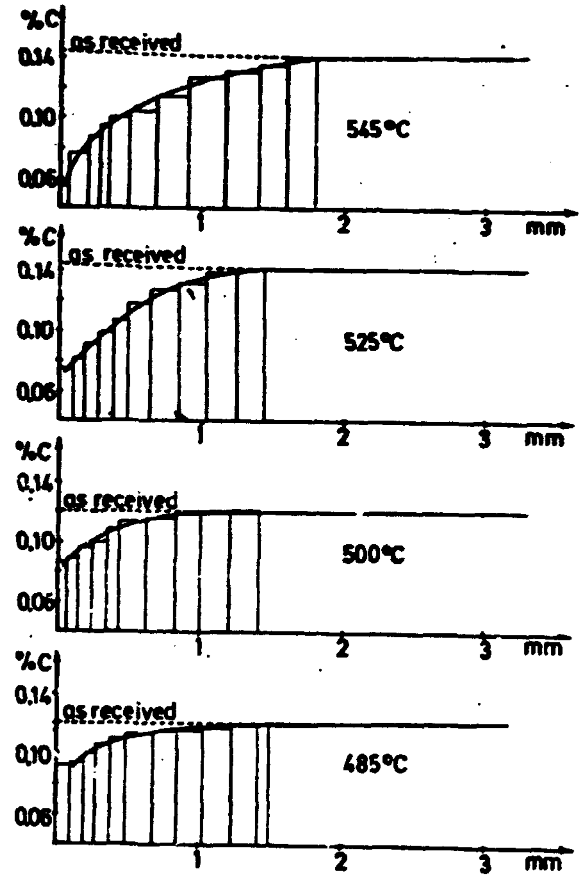

Fig.5. Decarburisation of 2¼Cr1Mo(0.12 -0.14 %C)

2 1/4 Cr - 1 Mo section (simulating an all-ferritic steam generator) has been operated for 25 months. Two types of normalized tempered 2 1/4 Cr - 1 Mo steel were used, one (external tube of the economiser) with a higher carbon content (0,14% - 0,12%) and the other (intermediate tube of the economiser and cooler tube) with a lower carbon content (0,048%).

3.2 - Decarburization of the 2 1/4 Cr 1 Mo steel

Figure 5 shows the decarburization of the high carbon 2 1/4 Cr - 1 Mo steel at 545, 525, 500 and 485° C (chemical analysis).

The carbon losses have been measured by chemical bulk analysis of the samples after test compared with the as received samples.

The carbon losses are :

$4.8 \cdot 10^{-4}$ g.cm^{-2} at 545°C
$1.8 \cdot 10^{-4}$ g.cm^{-2} at 525°C
$1.5 \cdot 10^{-4}$ g.cm^{-2} at 500°C
$1.2 \cdot 10^{-4}$ g.cm^{-2} at 485°C

The decarburization depths are respectively :

1,8 mm, 1,2 mm, 0,7 mm and 0,8 mm.

Figure 6 shows the decarburization of the low carbon 2 1/4 Cr - 1 Mo steel.

The carbon losses are :

$1 \cdot 10^{-4}$ g.cm^{-2} at 545°C
$0.6 \cdot 10^{-4}$ g.cm^{-2} at 525°C
$0.6 \cdot 10^{-4}$ g.cm^{-2} at 500°C
$0.4 \cdot 10^{-4}$ g.cm^{-2} at 485°C

The decarburization depths are respectively :

1,8 mm, 1,6 mm, 1,4 mm and 1,1 mm.

The decarburization depth of the as received tube was 0,7 mm.

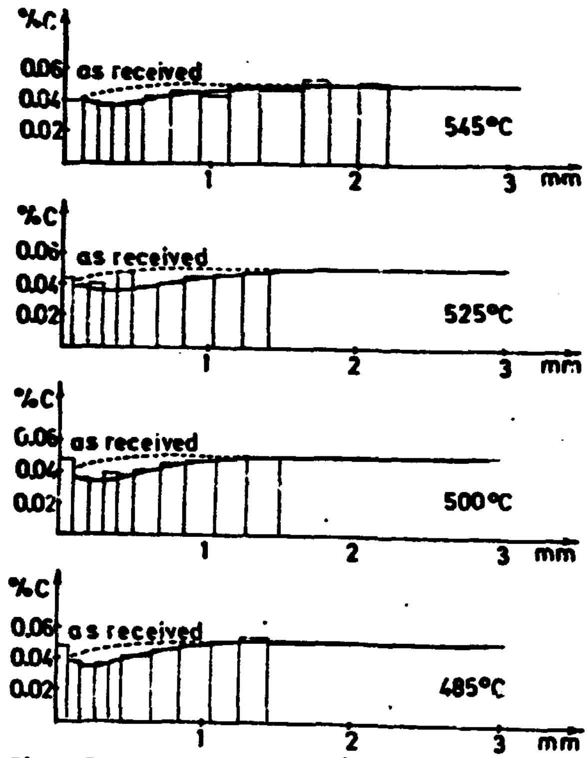

Fig.6. Decarburisation of 2 1/4 Cr 1 Mo (0.048 %C)

Examinations reveal a significant decarburization of the steel with the higher carbon content at 545°C. In contrast, the low carbon steel is only slightly decarburized. For the two types of steel the extent of the decarburization is decreasing with the temperature. Assuming that decarburization is a phenomenon dependent on $\sqrt{t}$, rate constants for the decarburization process have been calculated as :

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$c = 1.8 \cdot 10^{-8}\ g.cm^{-2}.s^{-1/2}$ at 500°C
$c = 1.5 \cdot 10^{-8}\ g.cm^{-2}.s^{-1/2}$ at 485°C

for the high carbon 2 1/4 Cr - 1 Mo steel.

For the low carbon 2 1/4 Cr - 1 Mo steel the calculated rate constants are :

$c = 1.3 \cdot 10^{-8}\ g.cm^{-2}.s^{-1/2}$ at 545°C
$c = 0.8 \cdot 10^{-8}\ g.cm^{-2}.s^{-1/2}$ at 525°C and 500°C
$c = 0.5 \cdot 10^{-8}\ g.cm^{-2}.s^{-1/2}$ at 485°C

Analysis of available decarburization data was performed by ARMIJO (1). He has calculated the corresponding decarburization rate constants and he has plotted these values as a function of 1/T. Nearly all values are contained between two lines. Figure 7 shows the two lines of ARMIJO and the values of the rate constants calculated from our results. It can be seen from this plot that the values of these rate constants are comparable to those obtained elsewhere, in tests where the thermohydraulic conditions have often been widely different (i.e. both static and isothermal dynamic experiments.) It appears therefore that decarburization is not sensitive to the thermohydraulic conditions, at least in the range investigated in those experiments.

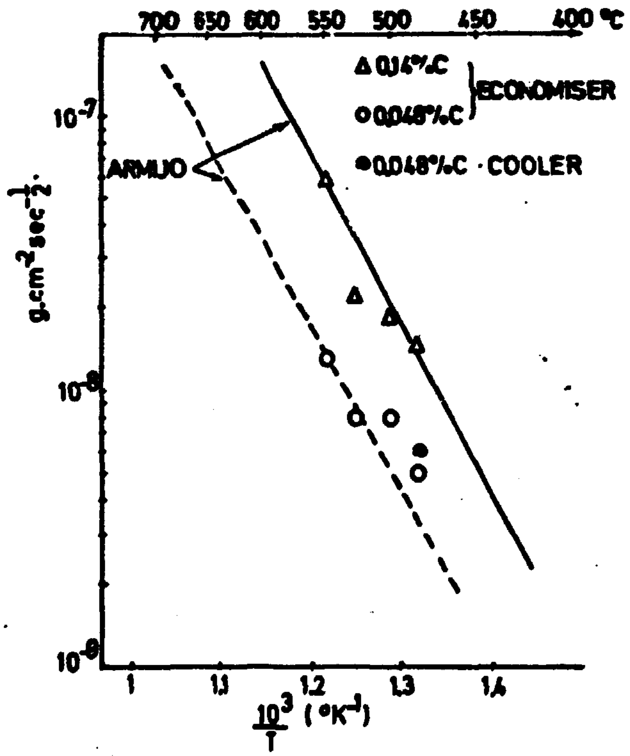

Fig.7. Decarburisation rate constants

REMARKS

1) For a given sodium activity, the rate constants as calculated above may depend on the bulk carbon content of the materials and on the metallurgical structure. For the specimens studied, it can be seen that, at the various temperatures, the ratios between the rate constants corresponding to the higher and to the lower carbon materials are roughly equal to the ratio between the carbon contents. This result could be expected as it has been pointed out above that the metallurgical structure of the various specimens are of the same type. Other tests carried out by

EDF in an isothermal loop (530°C) confirm, on an other hand, the strong influence of the structure on the decarburization kinetics at a given bulk carbon content.

2) Extrapolating from the above results it can be deduced that after twenty years of operation at 545°C, the mean carbon content of the high carbon 2 1/4 Cr - 1 Mo steel (0.14%) should be 0,09%, and the one of the low carbon 2 1/4 Cr - 1 Mo steel (0.043%) should be 0.036%.

3.3 - Carburization of the 316 L steel

The 316 L steel is observed to have been carburized. Figure 8 shows the carburization of the 316 L steel at 550, 500, 463 and 410°C. The carbon gain per surface area appears independant of temperature between 400 and 550° C : 8.10^{-5} $g.cm^{-2}$. But the carbon content at the surface is higher for the lower temperatures. Extrapolating from this result, it can be deduced that, after twenty years of operation, the carbon gain of the 316 L steel should be 2.4 . 10^{-4} $g.cm^{-2}$.

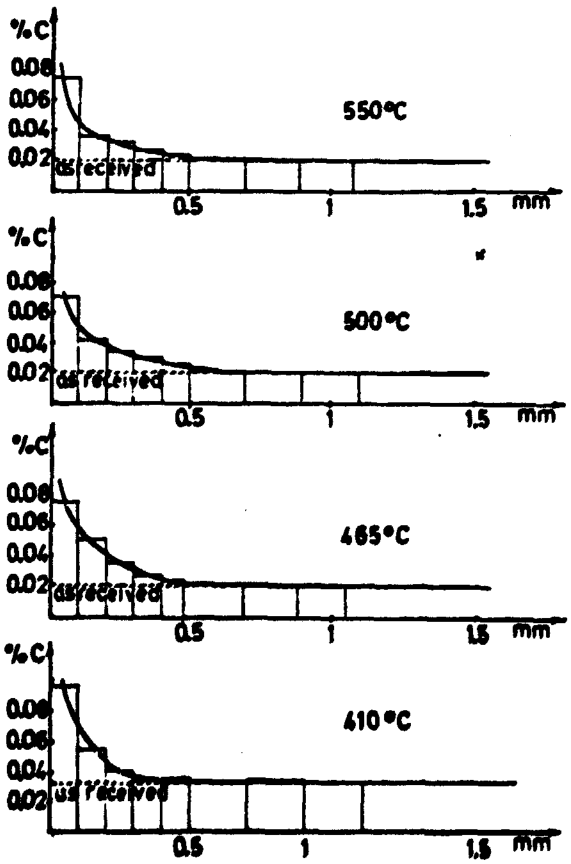

Fig.8. Carburisation of 316 L

4 - CONCLUSION

It can be concluded from the various tests which were carried out that the carbon transfer between the 2 1/4 Cr - 1 Mo steel (350°C - 475°C) and austenitic steels 316 L (350°C - 550°C) and 321 H (475°C - 550°C) is practically negligible in the operating conditions of PHENIX steam generator (CARNACIER A and ICARE loops).

Study of the loop CARNACIER B2 has demonstrated the importance of temperature and initial carbon concentration for materials of the same metallurgical structure. It can also be concluded that the kinetics of decarburization are practically insensitive to thermohydraulic conditions in the range investigated.

Again, at CEN FONTENAY (CEA) /2/, a study made with a dynamic isothermal circuit has confirmed that the carbon losses are functions of $\sqrt{t}$ and that the application of the classic diffusion laws to the results leads to an apparent diffusion coefficient which is 500 to 1000 times lower than the diffusion coefficient applicable to carbon in α-iron. The rate constants of decarburization also are in good agreement with those obtained elsewhere in the other tests.

These results allow to conclude that the use of 2 1/4 Cr - 1 Mo steel does not raise any difficulties up to 500°C, but at 550°C, the 2 1/4 Cr - 1 Mo steel may not be used. Tests currently in progress on CARNACIER and ICARE loops with 2 1/4 Cr - 1 Mo superheaters up to 530°C should provide information as to the maximal temperature at which this material could be used in a sodium heated steam generator without leading to a harmful carburization of the 316 L steel of the IHX and to a significant reduction in tensile strength and stress-rupture life of the ferritic steel.

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