FERRITIC STEELS FOR FRENCH LMFBR STEAM GENERATORS

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Austenitic stainless steels have been widely used in many components of the French LMFBR (Rapsodie, Phenix, SuperPhenix). Up to now, ferritic steels have not been considered for these components, mainly due to their relatively low creep properties. On the other hand, they have some other interesting properties which make them first candidates as materials for steam generators. Other parts can also call upon ferritic alloys, such as support structures and steam piping.

Steam generators require the use of materials which meet the following criteria :

a) mechanical strength at high temperature,

b) stress corrosion resistance in water, steam and sodium, polluted or not by sodia,

c) workability

d) inspectability.

It follows that some ferritic steels are usable when the maximum temperatures in service do not exceed about 530 °C. It is the case of the steam generators of the Phenix plant, where the exchange tubes of the evaporator are made of 2,25 % Cr-1 % Mo steel, stabilized or not by addition of niobium. These ferritic alloys have worked successfully since the first steam production in October 1973.

For the SuperPhenix power plant, an "all austenitic stainless alloy" apparatus has been chosen (exchange tubes made of Alloy 800, grade 1, stainless steel type AISI 316 L for the other parts). However, for the future, ferritic alloys offer potential for use as alternative materials in the evaporators : low alloys steels type 2,25 % Cr-1 % Mo (exchange tubes, tube-sheets, shells), or at higher chromium content type 9 % Cr-2 % Mo NbV (exchange tubes) or 12 % Cr-1 % Mo-V (tube-sheets). Most of these steels have already an industrial background, and are widely used in similar applications : steam generators and superheaters in conventional power stations, and various heat exchangers.

We successively review the various potential applications of these steels with regards to the French LMFBR steam generators, indicating that some points need an effort of clarification, for instance the properties of the heterogeneous ferritic/austenitic weldments.

1 - INTRODUCTION

Austenitic stainless steels have been widely used in many components of the French LMFBR (Rapsodie, Phénix, SuperPhénix). Up to now, ferritic steels have not been considered for these components mainly due to their relatively low creep properties at high temperature. Nevertheless the use of such steels which require good heat exchange properties associated with a high fiability. Other parts can also call upon ferritic alloys, such as support structures and steam piping.

We are going to develop the considerations and the positions that we have adopted now in the perspective of using such steels for making LMFBR steam generators.

A steam generator is an apparatus which has to transform water into steam with appropriate temperature and pressure for its use in the turbine producing electricity. Therefore, the principal function of such a component is to transfer to water the heat produced in the core by an intermediate fluid : the sodium. The very high reactivity of sodium with water makes the steam generators a key component with regard to the good running of the plant.

We recall that in the existing steam generator desings, tubes are used as interface between water (which flows inside) and sodium (which flows outside in the other direction).

2 - CRITERIA SELECTION OF STEAM GENERATOR MATERIALS

The selection of materials for steam generators arise from three different considerations that are :

- First, the S.G. must present the best possible efficiency ; it means a maximum efficiency of the heat exchange and minimum losses of heat.

- Second, they have to present the best possible reliability that is to say working during the longest time without any incident.

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cost which involves a minimum of these materials used, at the lowest cost, associated with a relatively easy fabrication.

These different considerations show that the exchange tube plays the main roll and that the selection of the material of which they are made has to take into account some criteria that we are going to develop here.

- The tubes must present a good mechanical strength consistent with the expected service conditions. By mechanical strength we mean resistance to monotonous stresses (pressure) or cyclic stresses (vibrations, DNB zones, transitory situations, and so on).

- They have to present a good behaviour in normal or accidental surroundings. This aspect deserves a special attention in the case of the LMFBR steam generators which involve two fluids (sodium and water) having a very high mutual reactivity, as we have already mentioned this point.

- They must lead to the construction of the apparatus with the minimum of operating difficulties implying acceptable specific properties (cleanliness, workability, weldability).

- They must be inspectable in service.

- They have to present the least wastage phenomena in case of small leaks.

Apart from these different aspects, concerning the other equipments some thick products can also be used in the S.G. constitution (tube-sheets);this requires a good toughness to avoid the risk of brittle fracture.

When these various criteria are reviewed, no material is found to have the qualities that would make it an obvious choice for steam generators tube bundles.

3 - MATERIAL USED IN THE IN-SERVICE OR IN BUILDING FRENCH LMFBR STEAM GENERATORS

Both austenitic and ferritic steels are actually used in France.

3.1. - Phenix plant

For Phenix, the first french LMFBR which produces electricity, a ferritic steel of the type 2,25 % Cr-1 % Mo, stabilized or not by addition of niobium has been chosen for the exchange tube of the evaporators, parts of the steam generators.

This choice founded its justification on the industrial background of this steel for this kind of application at that date, and also by its good corrosion resistance in water (polluted or not). We considered (and we always consider) industrial background as a guarantee against difficulties that cannot always be seem from laboratory work.

Lastly, the mechanical resistance of this steel is sufficient, consistent with the relatively low severity of the nominal service conditions (maximum temperature of sodium : 475 °C, water steam pressure : 190 bars).

three steam generators, each one including an evaporator (exchange tubes made of 2,25 % Cr-1 % Mo steel for the first two and of 2,25 % Cr-1 % Mo-Nb for the third one), a superheater and a reheater (exchange tubes made of austenitic stainless steel type TP 321). Each step has a modular conception.

A simplified plan of this S.G. is shown on the figure 1.

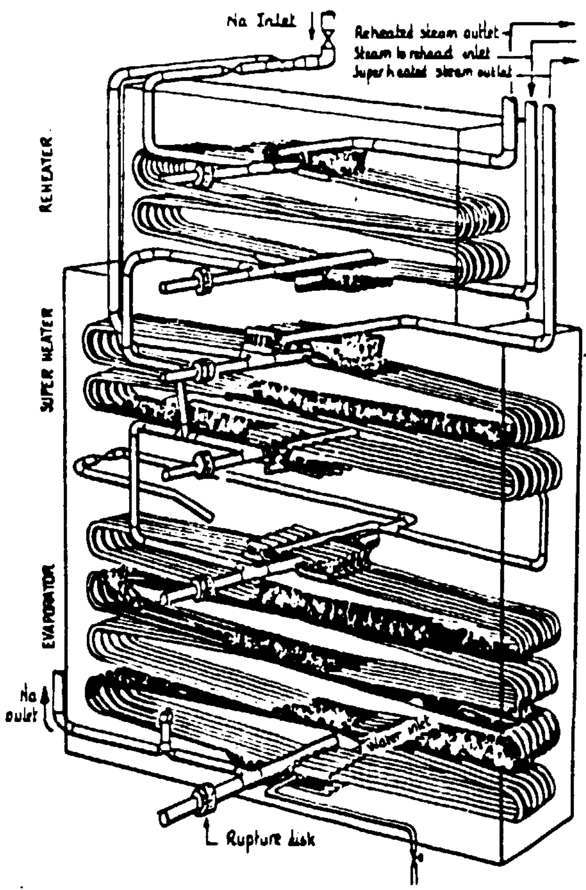

Fig. 1 - Phenix steam generator

Since the first steam production in October 1973, the ferritic alloys have worked successfully for more than 55 000 hours without any incident.

3.2. - SuperPhenix power plant

It was very difficult to extrapolate the steam generator design of Phenix for the equipment of a commercial power plant (1 200 Mwe) without falling into an excessive gigantism of the secondary buildings, which would be hightly detrimental to the economy of this type of reactors.

[illegible] complete change in the design of the steam generators planned to equip SuperPhenix I. In that case, an one-through all austenitic stainless steel apparatus has been developped, with an helicoïdal tube bundle which is hoped to present compatible thermo-hydraulic characteristics with a minimum overall dimensions. (figure 2).

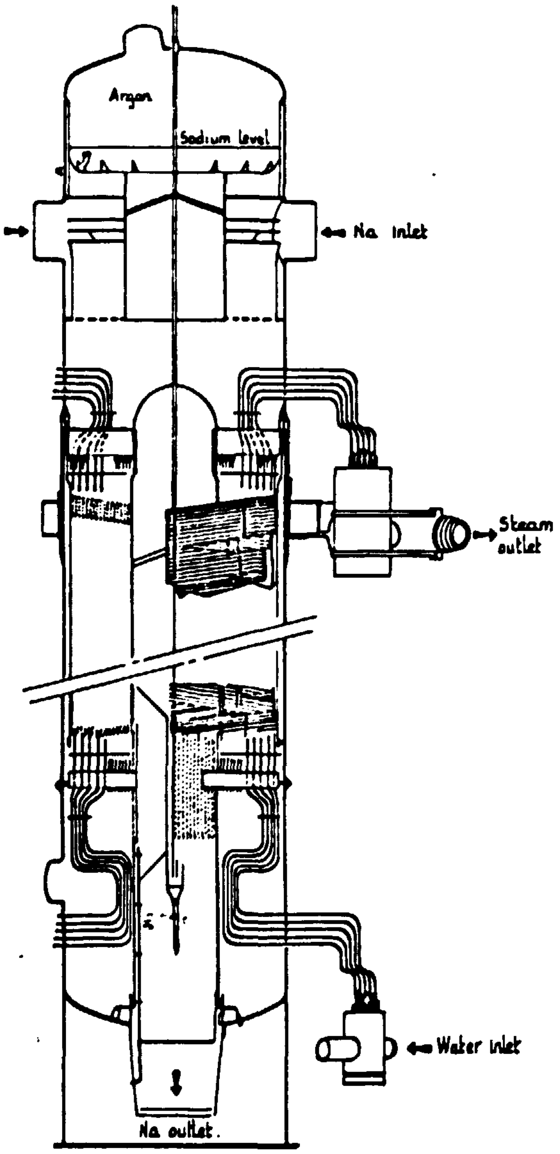

Fig. 2 - SuperPhenix steam generator

The greater severity of the nominal service conditions (maximum temperature of the sodium = 525°C, maximum pressure of the steam = 177 bars) compared with those of Phenix compelled to consider another material for the constitution of the tube bundle, no industrial experience being available on the use of the 2,25 % Cr-1 % Mo steel at sodium temperature in the range 500-550 °C.

[illegible] stainless steel (Ni = 33 % ; Cr = 20 %) has been finally chosen, presenting a better mechanical strength, and a satisfactory behaviour in water, the best among the austenitic stainless steels, concerning particularly its improved resistance to stress corrosion and to wastage by small water leaks.

Fo. steam generators of this type have been built and are presently being connected to the rest of the installation at Creys Malville.

4 - THE FUTURE FERRITIC STEELS FOR FRENCH STEAM GENERATOR

To work at a given temperature the dimensioning of the tubes depends for a great part on the physical and mechanical properties of the materials. At a given level of heat transfer and a given water pressure we are looking for having a minimum thickness of the exchange wall to minimize the primary pressure stresses and the thermal stresses due to the heat flow.

A simple calculation shows that it is interesting to use a material which correspond to a minimal value of the coefficient.

$$\emptyset = \frac{\alpha}{\lambda \sigma^2} \quad \text{where}$$

α is the thermal expansion coefficient,
λ is the thermal conductivity,
σ is the design stress.

Thus it is possible to classify the potential steels for this use, this classification being function of the service temperatures. High temperatures are reserved for austenitic stainless steels whereas ferritic steels are more interesting at low temperatures and even up to about 525 °C. The latter is precisely in the range of temperatures which is considered for the future steam generators. When we also remember that Alloy 800 has certain drawbacks such as its lower thermal conductivity and its higher cost corresponding to a high content of strategical elements, ferritic steels are again been considered for this application.

5 - REVIEW OF THE POTENTIAL FERRITIC STEELS WITH REGARD TO THOSE CRITERIA

The different ferritic steels which are usualy considered for the fabrication of the steam generators, specially the tube bundle, are the following :

- The low alloyed steels, type 2,25 % Cr-1 % Mo, stabilized or not by addition of niobium, and having a bainitic structure.

- The higher chromium alloyed steels, type 9 % Cr-1 % Mo-NbV and having a mixted structure (δ ferrite + martensite).

- The 12 % Cr steels having a martensitic structure.

We are going to review their relative behaviour in connection with the different criteria of use stated above.

[illegible]	[illegible]	[illegible]												
		C	[illegible]	[illegible]	P	S	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	0.10	[illegible]	[illegible]	[illegible]	2.0		0.9					
[illegible]	[illegible]	0.15	0.50	[illegible]	0.03	0.03	2.5		1.1					
[illegible]	[illegible]	[illegible]	0.15	[illegible]	[illegible]	[illegible]	8.0	[illegible]	[illegible]				[illegible]	
[illegible]	[illegible]	0.10	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.0				[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		[illegible]			
[illegible]	[illegible]	0.15	1.00	[illegible]	[illegible]	[illegible]	10.0		1.0		[illegible]			
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]			0.2	[illegible]	
[illegible]	[illegible]	0.15	[illegible]	[illegible]	0.01	[illegible]	[illegible]		[illegible]			[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	19	[illegible]		[illegible]	[illegible]			[illegible]
Alloy 800	[illegible]	[illegible]	1.0	[illegible]	[illegible]	[illegible]	23	[illegible]		[illegible]	[illegible]			[illegible]

Table 1 - Principal ferritic steels used or considered for the manufacture of fast breeder steam generator tube - Reference heat treatment chemical composition - Comparison with the Alloy 800

5.1. - Environment behaviour

All these steels have a good stress corrosion resistance in a sodium or water media, polluted or not by a little sodia. It is superior to the austenitic candidates. It is a very important advantage that has to be noticed for the ferritic steels. On the other hand, they present the disadvantage to develop a no negligible generalized corrosion when they are in contact with water or steam at high temperatures. Consequently we are obliged to take into account an extra thickness in the design calculations ; moreover, the oxyde film which is formed leads to a perceptible decrease of the thermal performance with the time of service. In that case, a chemical cleaning of the internal surface of the tubes can be considered, in order to give some youth to the apparatus, although this operation is very difficult to do on an industrial scale. Finally, we must note that another consequence of this oxydation is the production of hydrogen wich first after diffusion towards the sodium may form sodium hydride gathering together in the cold traps, and secondly decrease the sensivity of the leak detectors by increasing the background noise.

It appears that further efforts of research have to be engaged, having as a goal :

- First the determination of the extra thickness needed for the calculations without forgetting the consequences of a possible in service scaling of the oxyde layer.

- Second to clarifie and if possible to quantify the modifications of the mechanical properties (particularly fatigue behaviour) induced by the environmental media (polluted or not) and the way to take that into account.

- Third to improve methods and aqueous solutions for cleaning the internal surface of the exchange tubes after a certain time of service.

We have also to notice that the low alloyed steels are susceptible to decarburization by liquid sodium at temperatures higher than about 500 °C, giving a decrease in their mechanical properties. That is why the use of such steels is wilfully limited to this maximal temperature. The more alloyed chromium steels are considered to be no sensitive to this phenomena, this would merit to be verified.

Concerning the mechanical resistance at high temperature, a comparison of the allowable stresses (ASME meaning) of the various considered ferritic materials as a function of the temperature is drawn on the figure 3.

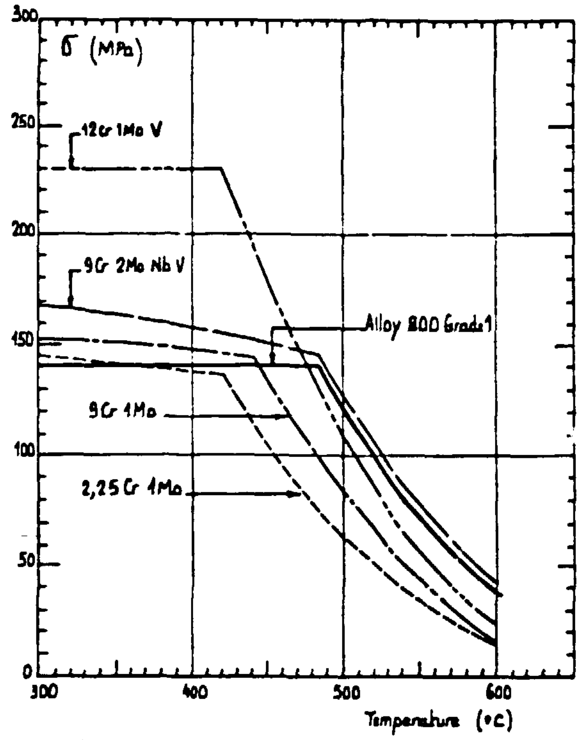

Fig. 3 - Allowable stresses for different ferritic steels for LMFBR steam generator tubes compared with the Alloy 800 ones.

The different curves have been drawn from mechanical characteristic documents which have different degrees of credibility (number of tests, temperatures, times of the creep tests,etc.). However a clear tendancy to better mechanical resistance for a long time with a higher chromium content of the steels can be seen.

For high temperatures, above 520 °C, the allowable stresses of the 2,25 % Cr-1 % Mo and 9 % Cr-1 % Mo steels are too low compared with those of the 9 % Cr2 % Mo-Nb-V and 12 % Cr steels to use them for the constitution of the tube bundle in a steam generator designed with sodium at elevated temperatures (≃ 540 °C).

It appears that, from this point of view, if we wish to preserve for the futur LMFBR the same hydraulic characteristics as those of SuperPhenix 1, only 9 % Cr-2 % Mo-Nb-V or 12 % Cr steels remain potential canditates for their use as exchanger tubes. In this respect we can note that the curve related to the Alloy 800 (grade 1), material used for the SuperPhenix 1 steam generator tube bundle, is very close to that corresponding to the 9 % Cr-2 % Mo-Nb-V steel.

[illegible] again, in [illegible] to lead to the constitution of strong documents allowing a better classification of the steels following this criteria.

It can also be pointed out that the expected long term creep ductility of these steels is not very dramatic. That is shown on the figure 4 for the 9 % Cr-2 % Mo-Nb-V steel for which the total creep elongation is not expected to fall down below 5 % in the temperature range 500 °C-650 °C. That anticipates no notch effect for this type of material.

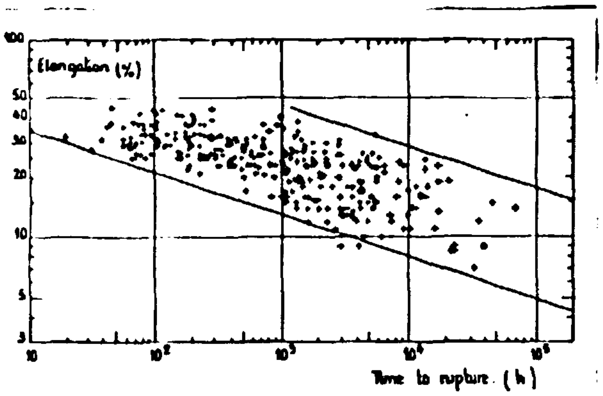

Fig. 4 - 9 Cr 2 Mo-Nb-V ferritic steel : creep ductility in the temperature range 500 °C-650 °C.

Others mechanical characteristics that we have to consider are fatigue and creep-fatigue, particularly at high temperatures. As a matter of fact, the exchange tubes are subject in service to cyclic sollicitations due to thermal fluctuations owing to the excellent thermal conductivity of the sodium used as heat transfert fluid. Those cyclic sollicitations can be in the plastic field (due to the thermal transient operating situations, as starting/stopping situations for instance) or in the vibration field (due to the DNB fluctuations). Therefore it is of importance to know very well the response of the materials to these different sollicitations. Now, only a few high temperature data concerning these ferritic steels are available, excepted for the 2 1/4% Cr-1% Mo alloy which is a little more completed. Therefore we have here again to carry out a very significant effort in this way to obtain the necessary results to be able to achieve acceptable computations.

Finally, concerning the toughness of thick products, if these are necessary as tube sheets in some S.G. designs, it can be seen on the figure 5 that the alloys with a mixte structure (δ ferrite + tempered martensite) clearly show less suitable Charpy V transition curves than the single phase ones ; consequently, this bad mechanical property makes them unacceptable to form thick plates keeping back pressure. From this point of view, the impact properties of the other considered steels seems acceptable to us for a such application. In that case, the connections of the tubes with the tube-sheets need some arrangements concerning the technical procedures just as the demonstration of their behaviour in service.

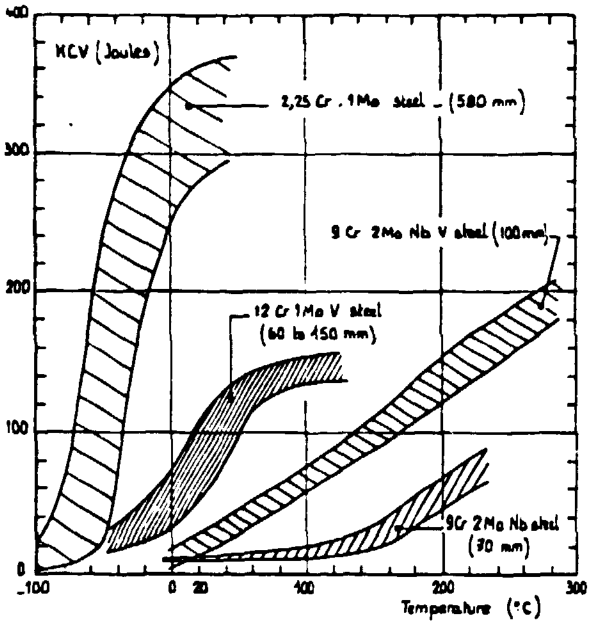

Fig. 5 - Impact transition curves for 4 different ferritic steels in thick products.

We have to notice that the thickness of the products is an important factor of the variability of this property, the thick products being less tough than the thin ones for a given base metal (figure 6).

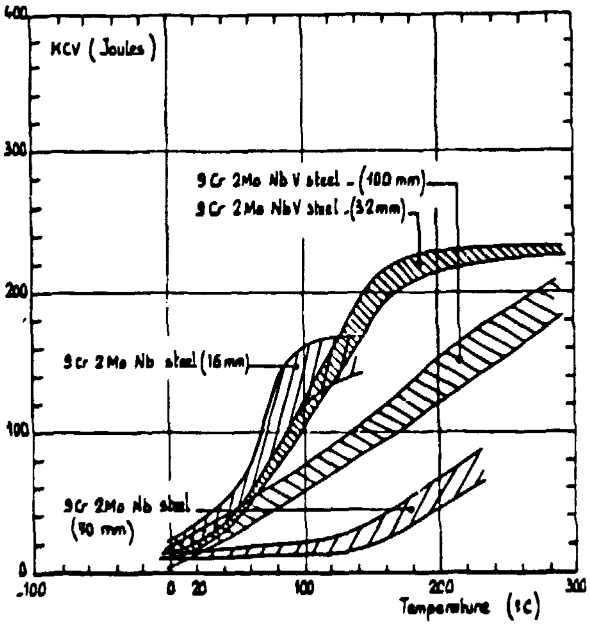

Fig. 6 - Comparison of impact transition curves for 2 ferritic steels with different thickness.

More of these ferritic steels are widely used in similar applications. It is particularly true for the 2,25 % Cr-1 % Mo and 9 % Cr-1 % Mo steels which constitute the tube bundle of steam generators equipping reactors operating already in many countries.

The 9 % Cr-1 % Mo-Nb-V alloy have been used for superheaters operating at temperatures of about 600 °C in EDF conventional power stations. Some incidents have affected these tubes which have no important consequences when thinking of this same alloy in the LMFBR steam generators.

If all these steels are relatively easy to transform in tubes corresponding to nuclear standards (on certain conditions of operation), which can be easily bent, their welding is more critical in comparison with the austenitic steels ; this is due to the precautions that have to be taken and essentially because heat treatments are often necessary to prevent hydrogen cracking. We note that higher the chromium content, more important are the problems of weldability of the steels. Here again, an important mass of Research and Development is needed to first specify the welding procedures and second to qualify the mechanical behaviour of these weldmants associated with the parent metals ones.

We have also to point out for all ferritic alloy steam generators the problem of the jonction of this apparatus to the sodium pipings which are generally made of austenitic stainless steels. So the heterogeneous ferritic/austenitic steels weldments need a particular attention with regard to the justification of their mechanical behaviour because of the different thermal expansion coefficients of the two steels.

5.4. - Inspectability

The inspectability of the steam generator tubes sets the problem of knowing the kind of imperfections that we want to detect : measurable variations of the wall thickness or located defects (cracks). For the first ones, two methods are developed using ultrasonics or eddy currents. This last one forms the subject of studies in the C.E.A. laboratories.

Concerning the second ones, its seems that presently there is no method that could solve the problem.

In fact, the situation can be summarized by saying that if for this point of view, all the ferritic steels are equivalent, a lot of efforts is required to reach a level of inspectability equal to that of the austenitic stainless steel tubes.

6 - CONCLUSION

We have tried to show how the ferritic steels take an important place in our preoccupations for their use in the french LMFBR steam generators.

If we decide, for the future fast breeder reactors, to maintain similar thermohydraulic conditions to the SuperPhenix ones, our choice for the constitution of the steam generator tube bundle in ferritic steels is limited to the alloys type 9 % Cr-1 % Mo-Nb-V or 12 % Cr, with a preference for the first one, principally because our good industrial background knowledge.

On the other hand, it is absolutely out of question to select this alloy for thick plates if such a use is necessary. This field is now still open with the goal to use a material showing the best compromise between a sufficient mechanical resistance and an acceptable toughness at room temperature.

In any case, the final selection of the materials will be possible only after a lot of R and D works, which we have shown the necessity, will be achieved to obtain sufficient results filling out the documents and allowing to justify the in-service behaviour of the apparatus.

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