consumers is the goal of this study.

CONTRIBUTION TO THE STUDY OF HYDROGEN'S CONTENT IN FERROALLOYS AND ITS INFLUENCE IN THE STEEL'S QUALITY

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INTRODUCTION

The study of hydrogen's solubility in the steel, the problems that come of this property and the ways to combat them, is a constant for all the makers and beneficiaries of use of this material; the mains problems appointed are:

- lost of ductility (01)
- formations of cracks, blisters and pinholes (1,2)
- porosity, superficial defects in metal plates (03)

The addition of Ferroalloys, due to the moment and quantity that are used in the process of steel making , can constitute an important source of hydrogen.

The analysis, quantification, attention and suggestion collected of several researchers allied of reduce this problems in part of producers and consumers is the goal of this study.

HYDROGEN'S SOURCES IN STEEL

SOLUBILITY

The hydrogen's solubility in the iron was studied and showed for several researchers (1,2,4) as figure 01 show.

Verify that the hydrogen's solubility increase with the temperature and it suffers abrupt jumps with the change of solid state to liquid one and also the structural changes of α , γ and δ .

The figure 02 shows that the hydrogen's solubility in the iron is modify by the presence of other elements of alloy (1,4).

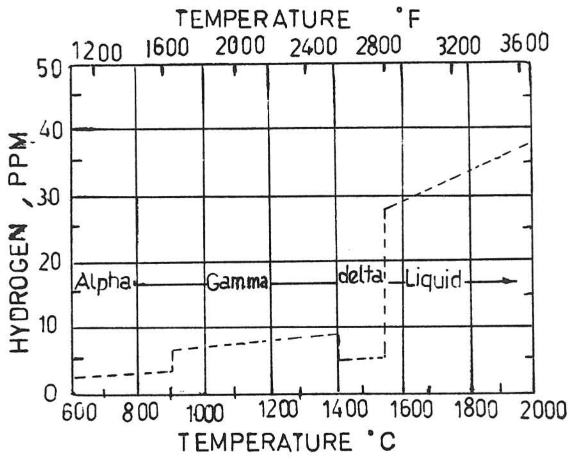

Figure 01 - Temperature effect over the hydrogen's solubility in the iron (2).

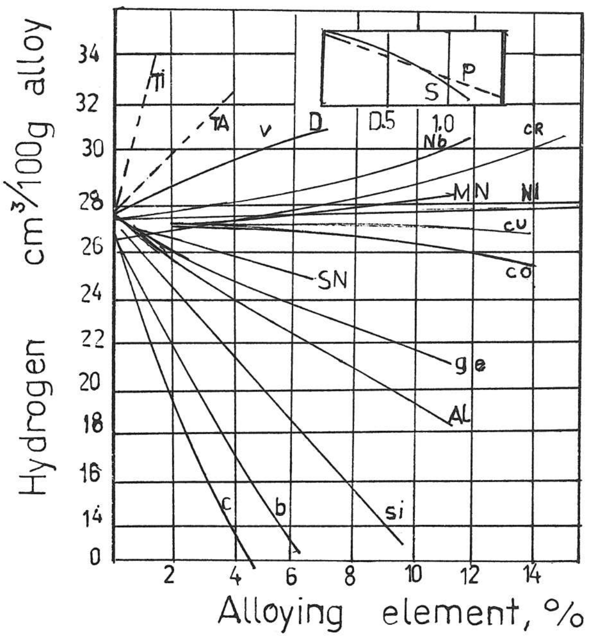

Figura 02 - Solubility of hydrogen in iron-alloying element systems at 1 at and 1600ºC[4].

The principal source of hydrogen present in the elaboration of steels can be listed[2,5]:

- Humidity contained in
  - refractory
  - flux
  - raw-materials
  - ingot mold
  - atmosphere
  - humidity and hydrogen contained in the ferroalloys.

The evolution of the incorporation/removal of hydrogen in several stages of steel fabrication can be accompanied schematicly by the figure 3[2].

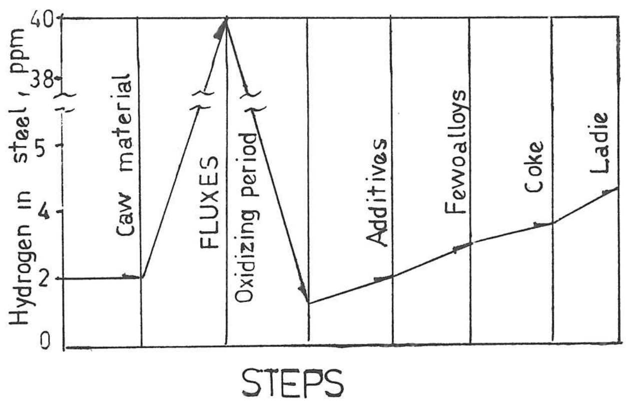

Figura 03 - Introduction/removal of hydrogen in steel for stages[2].

The determination of the importance of ferroalloys as source of hydrogen in the steel will depend of quantity of ferroalloy additions, composition, final tolerances and application of products as well as the level of hydrogen present in preceding stages of the addition, because an addition that should dose 1% of the element of alloy through of a ferroalloy that has 100 p.p.m. of hydrogen will cause an increase of 1 p.p.m. in the steel.

To exemplify this limit we show an illustration (fig. 04) of refusal tests by the fault detected in the ultrasonic of a supplier of thick plates[2].

Verify that a divisory of refusal and acceptation fields is a line and not a region, putting the fact of necessity of hard controls in evidence allied to guarantee the quality and the market to the product.

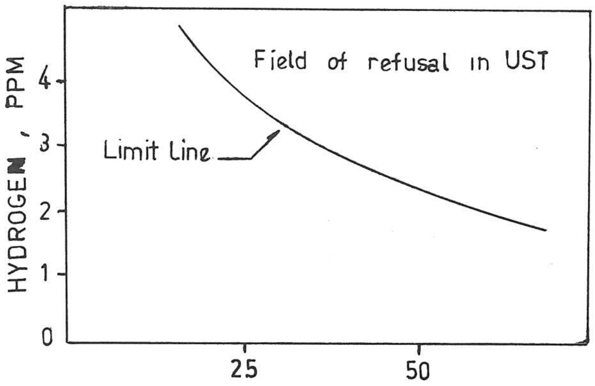

Figura 04 - Refusal field in ultrasonic, for thick plates, in dependence with the content of hydrogen[2].

THE HYDROGEN IN FERROALLOYS:

The presence of hydrogen in ferroalloys has been detected for several authors during along time. The table I show some data [1,2].

The sources usually indicated would be water vapor (charge/atmosphere) and volatiles of reducer exposed in the furnaces.

The solubility of hydrogen in ferroalloys, as in steel, suffers expressive variation, for example:

- in the liquid FeSi75, just out of furnace, were finding values close to 69 p.p.m. and just after the solification, at the same material were finding only 4,5 p.p.m.

Most of the alloys contain hydrogen in excess of the one atmosphere equilibrium values.

TABLE I- EXAMPLE OF HYDROGEN LEVELS IN SEVERAL FERROALLOYS, IN P.P.M.[2].

FeSi45	25 - 45
FeSi75	35 - 90
FeSi A/1	35 - 50
FeSi90	25 - 45
Fesi90 A/1	15 - 35
FeMnAC	115 - 140
FeMnAC	35 - 65
FeMnBC	50
FeSiMn	60
Mn electrolyte	90 - 135
Mn metallic	25
FeCrMC	20 - 45
FeCrBC	20
Cr metallic	04
Cr electrolyte	70
Ca Si	15 - 90

This suggests a subsidiary source of hydrogen which becomes available at lower temperature.

The most obvious sources in a reaction is H_2O, as

$$H_2O + Metal \; — \; Oxide + H_2 \quad (1)$$

This reaction occurs at the metal surface and its extent depends on the amount of surface available, or, materials which sizing is lower, would be more sensitive to the action of hydrogen's absorption. Also the materials electrolyticly produced would have their hydrogen's content increased by the electrolyts.

INFLUENCE OF CLIMATIC FACTORS, STORAGE AND COOLING

Eventhough some works[3] show oposite conclusions, a bigger number [1, 2,4,5,6] informed that the condition of storage is fundamental to keep the ferroalloys with lower contact of hydrogen. The experiences related appoint, for example, that a ferroalloy just made, without water contact, with level of 4 p.p.m. hydrogen in open air, with no rain, can gets level up to 50 p.p.m. during a week. But during a long time and with some rains will cause an elevation of hydrogen's level up to 400 p.p.m.

The figure 05 shows the evolution of hydrogen's content for some alloys subject to eight immersions into the water in a period of 24 days.

Note that the sample with sizing lower (< 10 mm) absorb more quantity of hydrogen. The medium sizing (10 - 30 mm) and finally higher samples (> 31,5 mm) that absorb restrict quantity of hydrogen.

Verify yet that the FeMnAC is more sensitive than the FeSiMn, that is more sensitive than the FeSi75%.

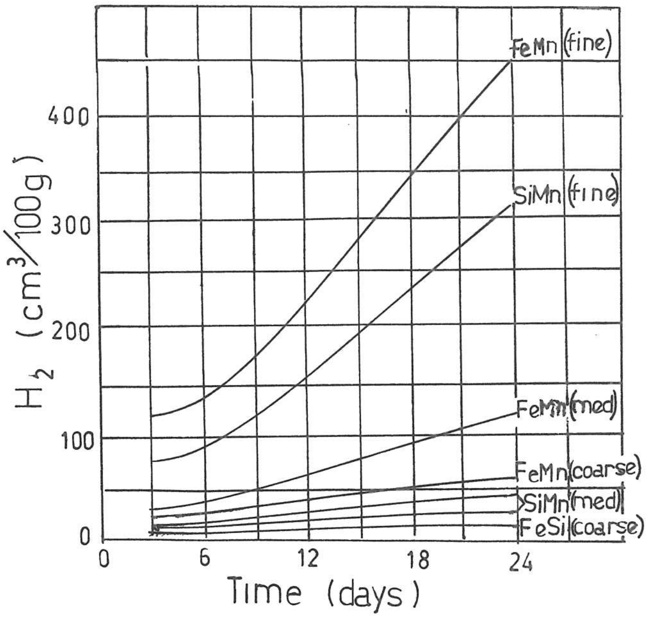

Figura 05 - Residual of H_2 after 8 immersions in water[1].

The usage of cooling the ferroalloys with water, after the ingot mold, shoud be extinguished allied to avoid the elevation of its level of contained hydrogen.

During the transportation of the products to the consumers it's important to keep the ferroalloys protected of rainings during the way.

ALTERNATIVE TO THE REDUTION OF HYDROGEN LEVELS IN FERROALLOYS.

The alternatives that aim to reduce the hydrogen levels in the ferroalloys that will be used can be divided in two categories:

- Initiative in the Producer:

. To avoid the cooling or any alloy contact with water during the fabrication's process.

. The benefaction (crushing, classification and storages) must be indoors, protected of rains.

. The material's transportation, must be made covered in a canvas, doesn't caring what kind of transportation in use (trucks, carriage, etc...)

- Initiative in the Consumer:

. Storage indoors;

. If necessary proceed to a preheating of the material before its application. This preheating will be more effective if there is the necessity of prevent the oxygen and nitrogen (vaccum heating). There are related[1,2,3] of experiences that confirm redutions up to 90% initial hydrogen's content when the material is preheating to 600ºC during 2 hours (figure 06).

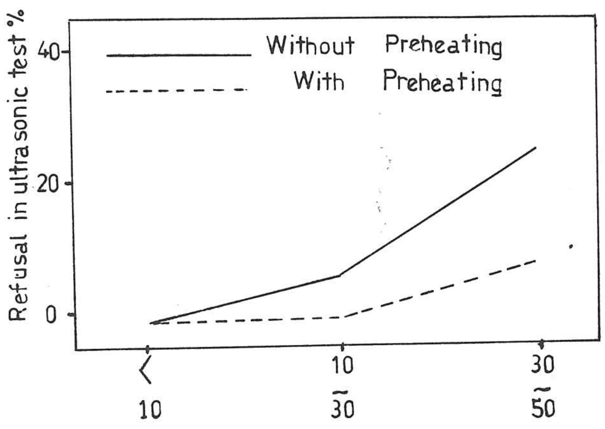

Figure 06 - Influence of preheating over the percentage of refuse in ultrasonic test.

To combat the hydrogen's level in steel the most viable process are the bubbling with inert gases or a vaccum treatment of the liquid metal, as figure 07, but the costs with those processes aren't accessible for all kinds of produtions.

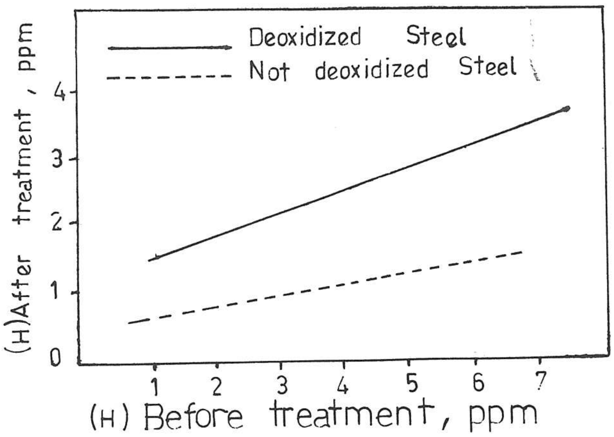

Fig. 07 - Effect of vaccum treatment on hydrogen's content of steel.

TESTS MADE WITH THE PRODUCED MATERIAL IN THE C.C.P.M.

Planing of the Tests

The tests developed in the alloys produced by C.C.P.M.

1st Test - Estimate of the Influence of Storage's Conditions.

Methodology. It was chose the sizing 20 - 50mm, taking three samples of each material:

- Sample 1 - Determination of the initial hydrogen's content.
- Sample 2 - Sample subject to storage indoors for 20 days.
- Sample 3 - Sample subject to storage outdoors, included rains, for 20 days.

Those values permit also the comparison between the materials as higher or lower, capacity of hydrogen's absorption.

2nd Test - Estimate of the Capacity of Hydrogen's Absorption by Immersion (30 days under water)

TABLE II - CHEMISTRY ANALYSIS OF ALLOYS

	Mn (%)	Si (%)	Fe (%)	C (%)	P (%)	Ca (%)	Al (%)
FeMnAC	75,5	0,10	16,4	6,9	0,30	-	-
FeSiMn	65,5	16,8	15,0	1,8	0,23	-	-
FeSi75	0,07	76,7	21,13	0,02	0,02	0,70	0,32

Methodology: Starting to samples under water for 30 days, tried to get dated about the absorption of H_2.

The material, after the immersion was dried to 105ºC for 6 hours.

3rd Test - Estimate of the Influence of the Sizing as the Capacity of Hydrogen's Absorption.

Methodology. It was chose the sizing 50 - 100 mm to the comparation of the anterior material (20 - 50 mm).

The material chose was the FeSi75.

RESULTS OF THE TESTS (TABLE III)

The results should consider:

- Medium temperature in the period:19.7 ºC;
- Medium relative air's humidity: 72 %;
- Pluviometric precipitation : 15 mm;

ANALYSIS OF THE RESULTS

By the analysis of table III verify that, as the storage's conditions as the initial's content, the material that more absorved the hydrogen was FeMnAC (206%) followed by FeSiMn (81%) and FeSi75 (35%), however the biggest absolute's content were find in FeSi75 alloys.

The figure 8 shows, graphicly, the evolutions of hydrogen's level for these materials.

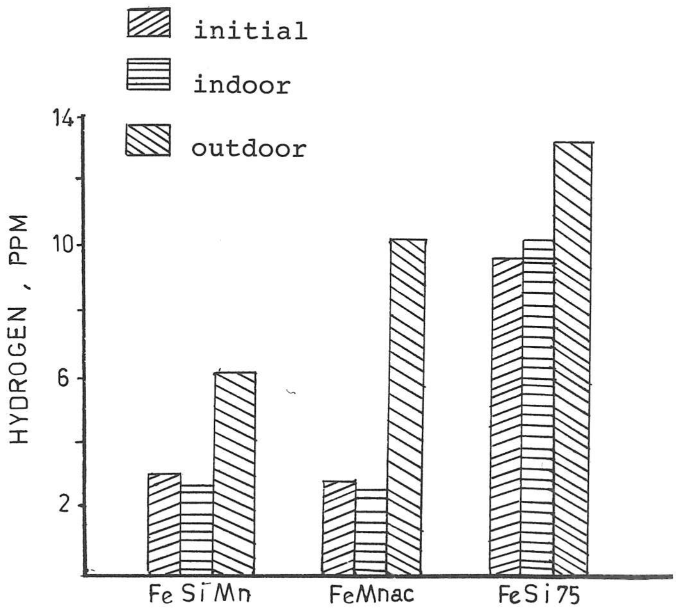

Figura 08 - Evolution of hydrogen's level related to the storage's conditions.

TABLE III - RESULTS OF THE TESTS

Nº	MATERIAL	STORAGE'S CONDITION	EXPOSITION CONDITION	HYDROGEN'S LEVEL P.P. M. IN WEIGHT	P.S.
01	FeMnAC	initial	-	3,3	
02	FeMnAC	indoor	air humidity	2,7	
03	FeMnAC	outdoor	air and rains humidity	10,1	
04	FeSiMn	initial	-	3,2	
05	FeSiMn	indoor	air humidity	2,8	
06	FeSiMn	outdoor	air and rains humidity	5,8	
07	FeSi75	initial	-	9,5	
08	FeSi75	indoor	air humidity	9,8	
09	FeSi75	outdoor	air and rains humidity	12,8	
10	FeSi75	outdoor	air and rains humidity	13,2	Size: 50-100mm
11	FeMnAC	-	under water	12,1	
12	FeSiMn	-	under water	6,3	
13	FeSi75	-	under water	15,9	

Note that the indoor samples show practicly the same hydrogen's level than the initial samples.

The capacity of hydrogen's absorption to the materials under water can also be analyzed in the table III.

The figure 09 shows schematicly the results.

Verify again that related to the initial tenors, the biggest capacity of absorption was showed by FeMnAC (266%) followed by FeSiMn (97%) and then FeSi75 (67%).

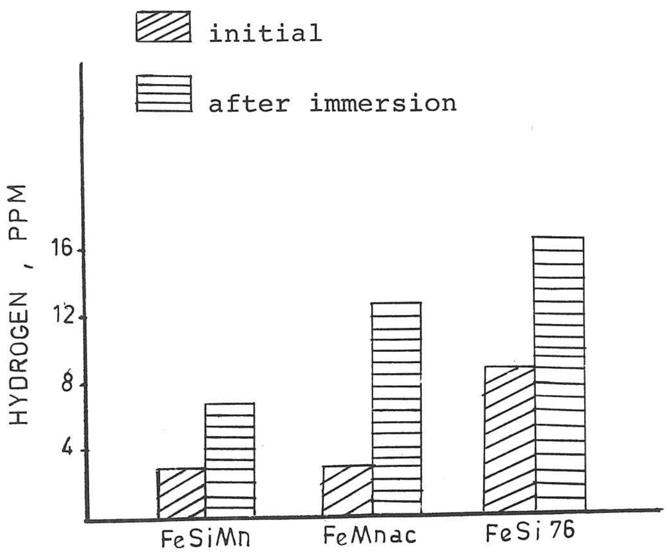

Figure 09 - Capacity of hydrogen's absorption under water (30 days).

The analysis of table III shows that the hydrogen's level presented in the immersion's test are 20% to 25% bigger to FeMnAC and FeSi75 and 10% to FeSiMn than the results of samples that stay outdoors subject to rains.

The influence of sizing was also showed in table III and represented in figure 10.

It isn't note the sensitive diference of hydrogen's absorption, in the test's condition, to the ranges of 20 - 50 and 50 - 100 mm.

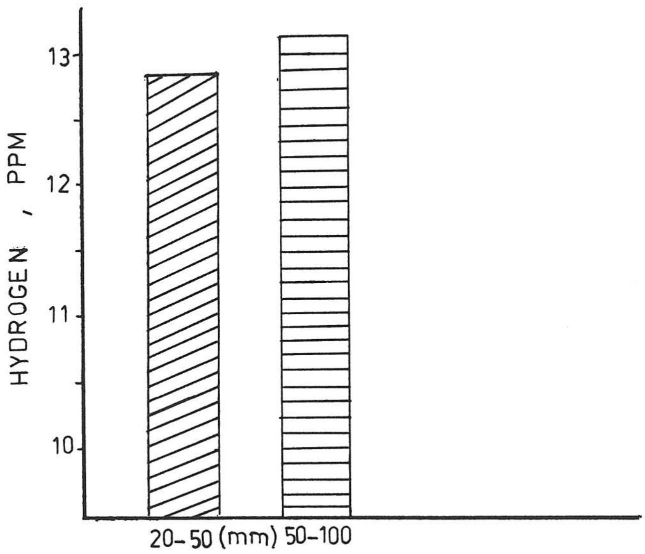

Figure 10 - Influence of sizing on hydrogen's absorption.

CONCLUSIONS AND SUGGESTIONS

Synthesizeing what was showed we can related the group of conclusions and suggestion as followed:

- The ferroalloys are supplying sources of hydrogen to the steel, however the importance of this source is conditioned to the quantity of the material to be added to the steel, as well as the hydrogen's content of them; to the residual level specified to the steel and also the hydrogen's levels present before the addition.
- The hydrogen's levels showed in the tests realized with the alloys produced by C.C.P.M. are a lot more inferior than the ones in the bibliography.
- Each kind of alloy has a diferent capacity of absorption of hydrogen and the study showed that FeMnAC has more capacity than FeSi75 followed by FeSi Mn.
- There is hydrogen's absorption during the storage outdoors, mainly during the rain's seasons.
- Didn't note, to the case of FeSi75, large variation in hydrogen's absorption to the ranges of 20 - 50 mm and 50 - 100 mm.
- The initial level of hydrogen is bigger to the alloy FeSi75, however there isn't significative diference between FeMnAC and FeSiMn.
- The hydrogen's absorption under water shows more critic to FeSi75 and Fe MnAC related to the material storaged outdoor.
- There are initiatives to be taken as producer and consumer(storage indoor , attention during the transportation)

allied to avoid the increase of hydrogen's level in ferroalloys and for consequence, in the steel.

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