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RESEARCH ARTICLE

Studying 18-9 stainless steel under the same conditions of oil shale hydropyrolysis and predicting the suitable steel to be used during this reaction.

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Abstract

Hydrogen incinerates in most compounds and element due to its small size, so when it is used in oil shale exploitation, it may react with the elements making up the reactor and the steel enclosure forming the exploitation assembly. In this work we will treat an 18-9 stainless steel under the same hydropyrolysis conditions as the Tarfaya oil shale (Morocco) and predict which elements of the steel will not be affected by hydrogen.The advantage of treating oil shale with hydrogen is that it increases the oil yield compared with pyrolysis, and it also makes these oils lighter, as well as forming numerous hydrides with the mineral matrix, which are also fuels.After treating 18-9 stainless steel and using analytical techniques, we selected the elements iron β and nickel, which do not undergo alteration in the presence of hydrogen. The analytical techniques used in this work are thermogravimetry using the Red-Croft balance**(A.Attaoui :2022)** where we carried out the hydrotreatment, calorimetry (DCA) as an amplified calorimetric differential linked to the balance, morphology carried out by SEM (scanning electron microscope) and which is coupled with dispersive X-rays.

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Introduction:-

In the exploitation of energy materials, whether coal or oil shale, metals and steels undergo a number of alterations depending on the gas used. In this work we focus on the effect of hydrogen during the hydropyrolysis of oil shale on the metals making up an 18-8 stainless steel. Stainless steels are well known and frequently used in the chemical industry. The adjective that describes them emphasizes their main quality of resistance to oxidation, but it is not the only one. They are also very interesting for their mechanical properties, especially at high temperatures. They are the only alloys that can withstand 600 to 1000°C. Their use is limited only by their neutron properties. They are mainly composed of Iron, Chromium (18 to 25%) and Nickel (8 to 20%), all three of which have a tensile strength of several bars. Fortunately, their mechanical properties partly compensate for their absorption capacity by allowing the use of very thin cladding.Thicknesses of 0.05 to 0.06 mm may be sufficiently suitable for enriched uranium (or rather its oxide). Stainless steels are used in water power reactors and sodium-cooled reactors. Their use is generally satisfactory, but several rather alarming incidents have been reported after long irradiations. These observations may give cause for concern, given that these materials are expected to withstand high temperatures (overheating, for example) and prolonged irradiation without failure **(J. Sauterons. Hermann: 1965).**

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1/ Bibliographical Studies

The elements making up stainless steels are generally C, Mn, S, O, Cr, Ni, Mo, Cu and Fe. We have tried to cite a few articles dealing with the thermal behavior of these elements or their combinations as alloys or steels in the presence of hydrogen. The terminal solubility of hydrogen (STH) in alloys is considerably higher at 250°K **(S.H. Lim et al; 1988)** than the STH values in the pure metals that make up these alloys. These authors propose an explanation based on other thermodynamic data for this system and, where these are lacking from their estimates under physically reasonable hypotheses, they assume that the hydrogen atoms, unlike the metal atoms, are in equilibrium between the different phases and that the mixtures of the hydride phases are pseudo-binary.They show that the high STH results from the suppression of the α -α' phase transition in the alloys and the larger deviations from ideal mixing in the hydride phase than in the metal phase. The electromigration and diffusion of hydrogen in alloys containing Ti, Cr, Fe or Mo have been studied. The effective charge number Z* and diffusion coefficient D both decrease with the addition of Ti and Cr, but are only slightly affected by Fe and Mo. A model of hydrogen trapping by the substitutional elements introduced to account for the decrease in D with solute addition cannot adequately explain the decrease in Z* **(H. Hakajima et al:1987).**This decrease in Z* seems to be caused by the change in electronic structure due to the alloying effect. A model for hydrogen trapping by the matrix interface has been suggested **(S.M. Lee and J.Y. Lee:1987)**, in which the high driving force for hydrogen trapping is associated with the lowering of the interfacial free energy. The characteristics of the precipitate/matrix interface on hydrogen trapping are superior to those of semi-coherent carbides. Although the particles are incoherent, this activation energy increases with the size of the precipitated particles. Experimental studies by Haldman and Botty **(R.G. Haldeman and M.C. Botty: 1959**) show that the regeneration of a catalyst and its speed vary with conversion **(Y. Chang and. D.D. Perlmutter: 1987)**.

A mathematical model developed by these authors is based on the interaction between the pore structure of the catalyst and the distribution of coke in the pores.The model shows a large variance and provides a high threshold for coke loading. The fatigue factor for the pore distribution has a maximum respecting the mole fraction of the condensable compound **(S.K. Bhatia: 1989)**.

The ageing mechanism of welded type 308 stainless steel is studied by mechanical tests and by examination of the microstructure. Ageing was carried out at 475°C for 20,000 h. The initial material is austenite with approximately 10% ferrite. After ageing, the duration of the ferrite increases to 100%.

This hardening is accompanied by a significant increase in the ductile-to-brittle transition temperature and a fall in the energy of the upper stage, as measured by Charpy strength tests, and a deterioration in fracture toughness as determined by integral tests. Tensile properties do not change significantly during ageing. Microstructural analysis indicates that the ferrite decomposes spin dally into iron-rich α and chromium-enriched α. In addition, abundant precipitation of α'-rich nickel and silicon G-phase is observed within the ferrite, and $M_{23}C_4$ carbon forms at the austenite/ferrite interface. These effects are similar to those of ageing cast stainless steels **(J.M. Vitek et al: 1991).**Sometimes, a large G-phase or α-precipitates are also observed at the austenite/ferrite interface after ageing longer than 1000h. After comparing changes in mechanical properties with microstructural aspects, it is concluded that both spinodal decomposition and G-phase formation contribute to ferrite hardening. Decomposition leads to embrittlement of the weld as long as the temperature of the ductile-fragile transition rises. The formation of the G phase and the precipitation of the ductile carbide, as shown by the fall in the higher energy and the decrease in fracture toughness. The penetration of hydrogen into metastable austenitic stainless steels was studied between 100 and 400°C using a technique for penetrating hydrogen into these annealed steels. The results are consistent with those found in stable austenitic stainless steels, but after cold deformation, the activation energies of penetration increase in α' while penetration and diffusibility increase exponentially **(S. Xinkui et al: 1989**).Using mainly electro-chemical methods, the chemical potential, diffusion coefficient, partial molar volume and resistivity increment of hydrogen in alloys that have undergone internal oxidation are determined at room temperature. In all sample's hydrogen is trapped at the metal/oxide interfaces formed where irreversible trapping can be distinguished from reversible trapping. In the case of phase boundaries, the orientation and size of oxide precipitates are characterized by electron microscopy and therefore the coverage of phase boundaries by irreversibly bound hydrogen can be calculated. This equivalence and the irreversible nature of the bonding indicate the formation of OH bonds on the phase boundaries.During irreversible trapping, a greater variation in volume is observed than for the dissolution of hydrogen in regular sites. The irreversible component of hydrogen trapping disappears after annealing in the steam of the alloying element **(X.Y. Huang et al: 1991).** As part of research into hydrogen embrittlement of steels, authors **(H.J. Maier et al: 1987**) developed a method for calculating the critical hydrogen concentration leading to crack propagation.The side pre-cracked by fatigue under constant load was exposed to hydrogen using an electrochemical method. They determined

the critical hydrogen concentration by numerically solving the diffusion equation in a stress field. This involved measuring the crack initiation time and the diffusion coefficients of hydrogen solubility using permeability tests. Dilatometric studies on the kinetics of hydrogen attack on carbon steels have shown that the strain rates of these types of steel and (Cr-Mo) steels differ by three or four orders of magnitude.These authors **(T.A. Parthasarathy: 1985)** used a model based on the stress-free growth of methane bubbles to show that the dilatometer results obtained on both types of steel could be explained using a single model. They believe that many grain boundaries undergo cavitation so that bubble growth occurs without stress. Their model predicts a strong variation in strain rate with the density of bubbles growing in the sample. The absence of bubble germination and the low density make the steels much more resistant to hydrogen than carbon steels. They are also using this model to construct cavity growth maps by giving the mechanical mechanisms operating for various hydrogen temperature and pressure conditions.Low strain rate tensile tests and some fatigue tests were carried out at ambient temperature and in air, liquid mercury and hydrogen environments **(C.E. Price and R.G. Norman: 1987**). The hydrogen was produced by an electrolytic method that allowed loading and testing to be started simultaneously. The samples were quenched and tempered to different levels of hardness. Hydrogen embrittlement and mercury embrittlement differ at several points. In hydrogen alone, these authors observed a decrease in strength, a marked sensitivity to the strain rate and an evolution of the cracks from a Trans granular appearance to an intergranular appearance, then to coalescence of the microcavities. In mercury, crack initiation is intergranular. Hydrogen-induced cracking corresponds to plasticity linked to the more rapid penetration of hydrogen.The stationary propagation of an intergranular crack, shielded by dislocations, is controlled by the diffusion of hydrogen at the grain boundaries and at the crack surface **(J. Kameda: 1986).** Numerically, these authors solved the series of second-order differential equations that control the diffusion of hydrogen in the vicinity of the intergranular crack in order to determine the distribution of hydrogen along a crack undergoing stationary displacement. They established the relationship between the stress intensity required for crack propagation and the crack velocity as a function of the diffusivities at the grain boundaries and crack surface and the grain size. While the tendency for hydrogen-induced intergranular crack propagation increases with hydrogen diffusivity, it decreases with increasing crack length and grain size.Iron, a basic element in stainless steels, was studied in the form of single crystals whose surface orientation and tensile axis were chosen so that the rates of hydrogen transport by dislocations could be studied separately as a function of strain rate, lattice hydrogen concentration and temperature. The flow of hydrogen transported by dislocations qualitatively reflected the escape of dislocations from the crystal surface. Quantitatively, the rate of hydrogen transport increased as the strain rate was lowered **(C. Hwang and Bernstein: 1986).** With regard to the morphology of dislocations in iron single crystals during plastic deformation in stage 1 in the presence or absence of hydrogen **(C. Hwang and Bernstein: 1986),** others showed that hydrogen strongly favored the localization tendency of the deformation, especially in the vicinity of spherical inclusions containing hydrogen. The solubility of hydrogen increases with temperature, and there is a clear difference between solubility in α-iron and in γ-iron.It should be noted that the same fact should be observed at the γ-α point at high temperature **(Sieverts and Krum: 1910).** At the melting temperature, the solubility of hydrogen in iron increases sharply. Among the iron hydrides we have FeH_2 and Fe_2H_6**(Weichselgelder :1926)** which have been isolated as a black, powdery precipitate

In general, hydride formation leads to a reduction in the number of active sites on the surface of the solid, since these are engaged in Me-H type bonds. Hydridation results in a reduction in the number of atoms capable of forming hydride, a chemisorption bond **(Palczewska: 1975).**

2/ Experimental part

We will first look at the behavior of 18-9 stainless steel in a thermal hydrogen atmosphere. 18-9 stainless steel, also known as AISI 304 in metalogical nomenclature, has the following composition:

C	Mn	Si	S	O	Cr	Ni	Mo	Cu	Fe
0,042	1,4	0,48	0,004	0,028	17,74	8,8	0,16	0,17	Bases

3/ Absorption of hydrogen by an 18-9 stainless steel

Hydrogen acts almost with the majority of transition metals because of its small size, it enters into insertion in these structures of more or less high compactness and forms hydrides with new bonds. The production of hydrides obviously depends on the physical variables of pressure and temperature. They are identified by X-ray diffraction, generally using a dispersive method, or by morphology. Among the metals transformed into hydrides are iron and chromium, the constituent elements of stainless steels. Photographs (1 and 2) taken using an electron microscope and X-ray dispersive analysis (RXD) coupled with the equipment confirm the formation of these hydrides (Figures 3 and 4).

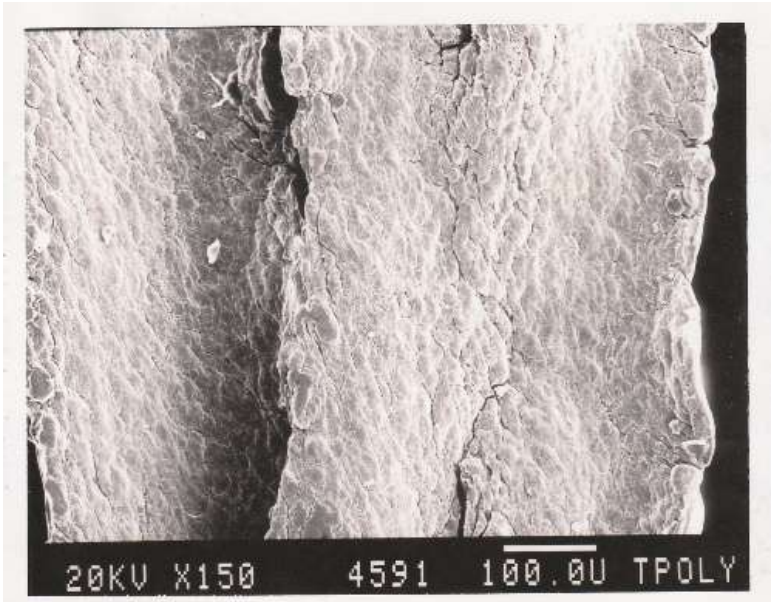

Fig 1: - Raw Stainless steel 18-9.

Fig 2:- Stainless steel 18-9 treated under H_2till 750°C.

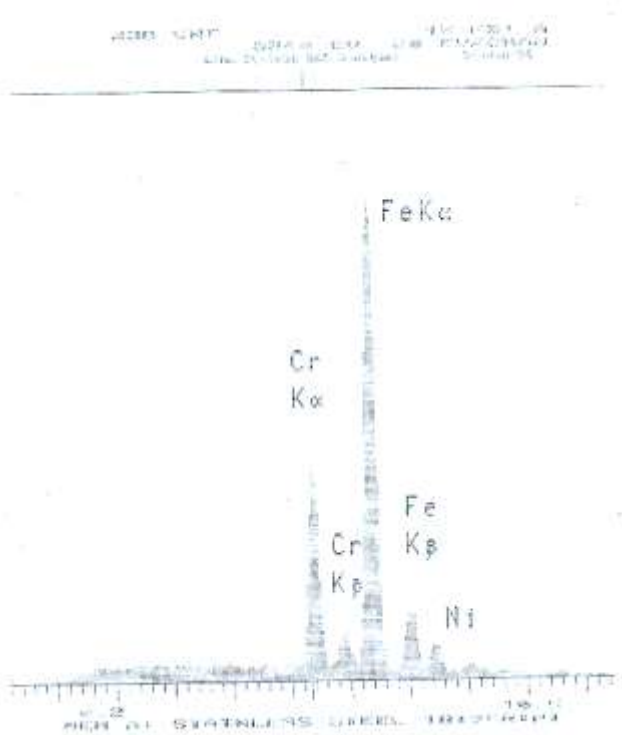

Fig3: - RXD of raw stainless steel 18-9.

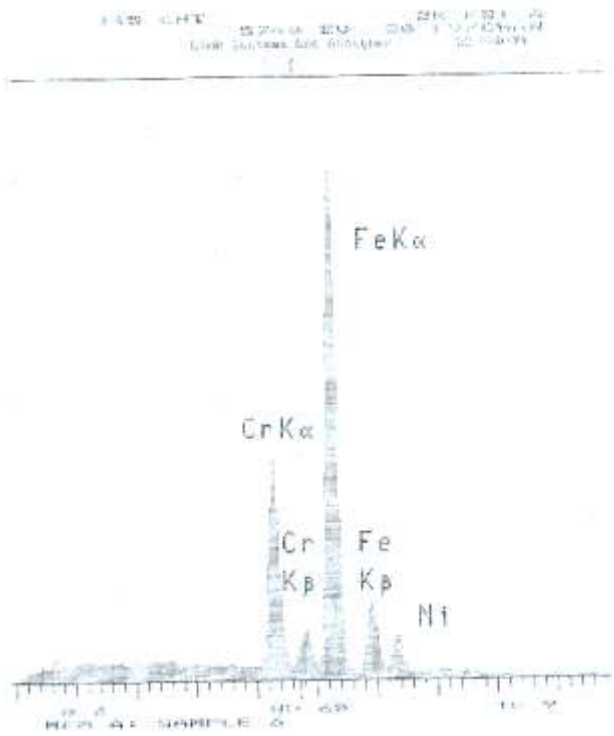

Fig4: -RXD of stainless steel 18-9treated under H_2 till 750°C.

3.1 : Specificity of the hydrides formed

As we saw in the previous paragraphs, dispersive X-rays make it possible to quantitatively clarify conversions of basic elements, in this case stainless steels. The measurements obtained before and after hydrotreatment are generally proportional to the actual concentrations of these components. We will establish the values of the dispersive X-ray

peaks (Fig 3 and Fig 4) of the constituent elements of 18-9 stainless steel before and after reaction, as well as the percentages of elements both before and after reaction, as follows:

Table2:-Percentage of chemical elements rawstainless steel and hydrotreated till 750°C.

Composition	Raw stainless steel	Stainless steelhydrotreatedtill 750°C
Feα (cm)	15,75	16,3
Feα (%)	57,5	56,6
Feβ (cm)	2,2	2,5
Feβ (%)	8,0	8,7
Crα(cm)	6,8	7,1
Crα(%)	24,8	24,7
Crβ(cm)	1,6	1,5
Crβ (%)	5,8	5,2
Ni(cm)	1,15	1,4
Ni (%)	4,2	4,9

The dimension values in the table are relative to an A4 page of the record, while the figure is a collapsez copy

We will establish the ratio of the percentages of the elements making up the stainless steel after and before reaction

Table 3:-Rapport ofpercentage chemical elements hydrotreated till 750°C of stainless steel and raw stainless steel.

Feα	Feβ	Crα	Crβ	Ni
0,984	1,088	0,996	0,897	1,167

If we exclude the elements that are increasing, insofar as we have a decrease in the others, this is because the values are relatively proportional to the concentrations. We observe a significant decrease for Feα, Crβ and Crαwhich undergo hydridations, so we have an alteration during the reaction of the stainless-steel constituents in the orderCrβ(0,897) Feα(0,984) then Crα (0996).**As for Ni and Feβ**, we note an inhibition to alteration due to hydrogen under temperature.

Hydriding does not change the electronic structure of the elements; it only affects the lattice, whose parameter changes with the H- concentration. We will translate these hydridation phenomena more easily for some elements than others because of their structural differences. Chromium Crβelectrolytic, which has a compact hexagonal structure, undergoes the most hydriding, followed by iron Feα and chromium Crα.

4/ Calorimetric study of the hydrotreatment of the five samples in the presence of 18-9 stainless steel.

Amplified differential scanning calorimetry is the analytical technique used in this section. Small-weight filaments of 18-9 stainless steel were introduced into the six oil shale samples. The mass fractions were 3.3%, 5.7% and 6.7%. The contents were then hydrotreated in a non-isothermal Red-Croft balance (21°C/min to 750°C). The two figures show the two SEM photos of the Z3 experiment before and after the reaction;

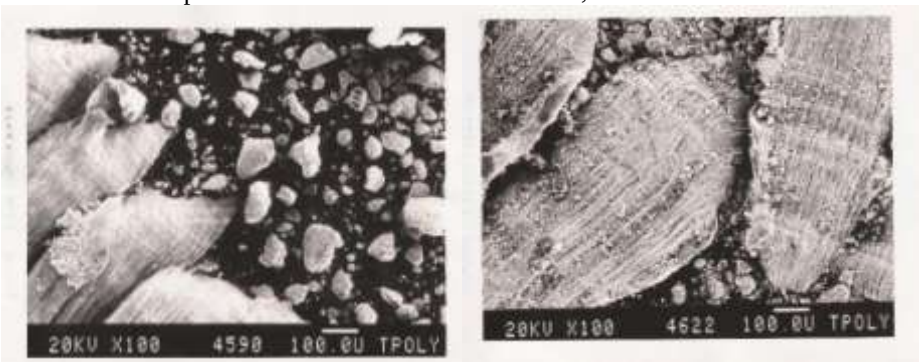

Fig 5: - Z3 and stainless steel befor reaction **Fig 6:-** Z3 and stainless steel after reaction.

The following table shows the different temperatures of the DCA peaks in this study.

Table 4: - Temperatures of pick DCA for carbonate decomposition under hydrogen.

Sample	Z, 3,3% stainless steel T(C°) pick DCA for carbonate decomposition	Z, 5,3% stainless steel T(°C) pick DCA for carbonate decomposition	Z, 6,7% stainless steel T(°C) pick DCA for carbonate decomposition	T (°C) pick DCA alone sample (H_2)
Z0	708	704	692	701
Z1	687	688	693	692
Z2	710	686	693	689
Z3	678	671	672	668
Z4	678	676	679	677

As we calculated in the previous chapters, the average temperature difference, with or without stainless steel, of the DCA peaks of the carbonate's decomposition $\sum\Delta T/\sum i$ is of the order of 2.3°C, which is a positive value and the energy absorbed in the form of heat is 1.43 J/g (with Cp=0 ;62j/g°K). Thermal hydrotreatment of oil shale in the presence of 18-9 stainless steel therefore involves a loss of energy.

6/ Conversion rate of oil shale in the presence of 18-9 steel.

The same tests as above were used for the thermogravimetric (Red-Croft) study of the five shale samples fitted with the 0.033 mass fraction of 18-9 stainless steel. Figure 7 shows Δm/mo = f(T) for this non-isothermal hydrotreatment without stainless steel, while figures 8, 9, 10, 11 and 12 show Δm/mo = f(T) for this non-isothermal hydrotreatment with stainless steel.

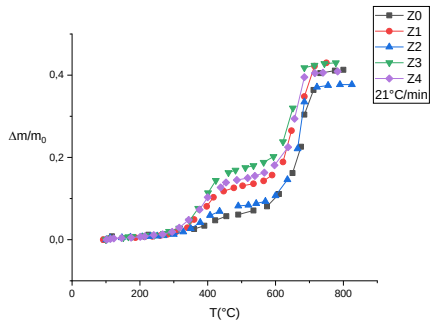

Fig 7: - Thermograms of different layers under hydrogenhydrogen with 0,033 stainless steel

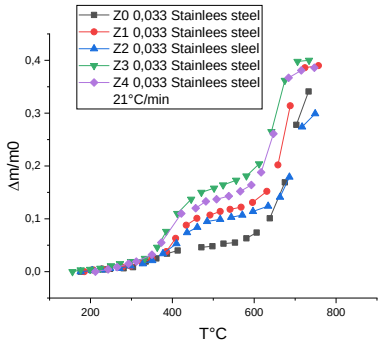

Fig 8: - Thermograms of different layers under

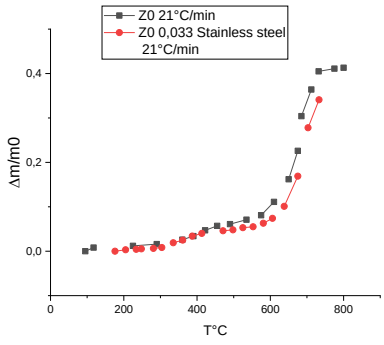

Fig 9:- Thermograms of Z0 layer under hydrogen with 0,033 stainless steel

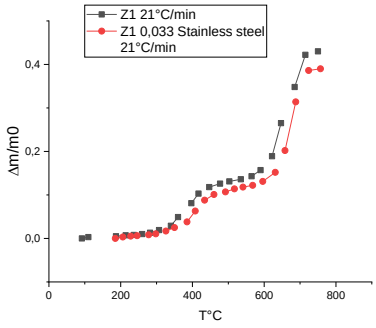

Fig 10:- Thermograms of Z1 layer under hydrogen with 0,033 stainless steel

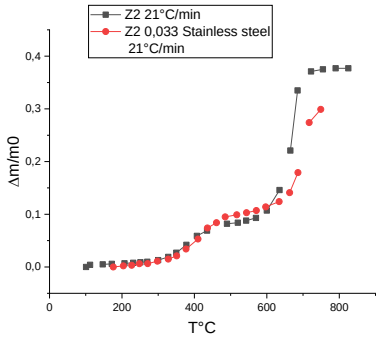

Fig 11:- Thermograms of Z2 layer under hydrogen with 0,033 stainless steel

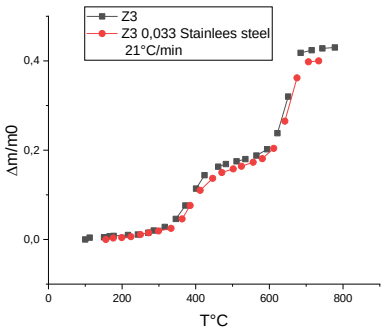

Fig 12:- Thermograms of Z3 layer under hydrogen with 0,033 stainless steel

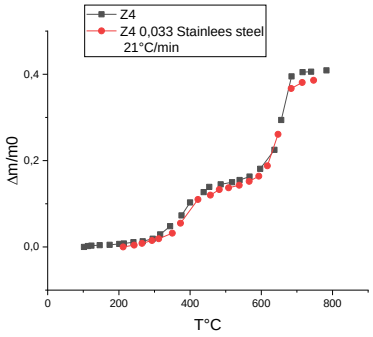

Fig 13:- Thermograms of Z4 layer underhydrogen with 0,033 stainless steel.

A clear decrease in the conversion rate can be observed for both oils and carbonates. In the case of oils, this decrease is remarkable for samples Z0, Z1, Z3 and Z4. As for the carbonates, the decrease is greater for samples Z0, Z1 and Z2.

Conclusion:-

Exploiting oil shale for hydrotreatment requires the use of metals, whether alloys or steels, for the development of reactors and accessories for a given exploitation process. Hydrogen, which is the basic reactant, is a small molecule that can be easily incorporated into metals, and is likely to deteriorate after several uses. Examples include the Hytort process, which was designed to operate according to the "Hydroretorting" test using a flow of hydrogen, and pyrolysis, which was designed to operate according to the Fisher test. It should be noted that during the Fisher test 42% of the aliphatic carbon in oil shale will form aromatic carbon **(P.A. Lunch and J.C. Janta et al: 1984)**. The Hycrude cooperation, which had applied the "Hytort" process to compare shales from the east and west of the United States, has recently extended this work to most of the world's deposits **(R.B. Tippin et al: 1984).**

In this work we tested 18-9 stainless steel under our hydrotreating conditions, with a pressure equal to 1 atmosphere. Several analytical techniques were used:

The thermogravimetric study (Red-Croft) of the five shale samples provided with the 0.033 mass fraction of 18-9 stainless steel showed us a decrease in the conversion rate, which is clearly observed for both the oils and the carbonates. As far as the oils are concerned, this decrease is remarkable for samples Z0, Z1, Z3 and Z4. As for the carbonates, the decrease is greater for samples Z0, Z1 and Z2.

The calorimetric study (DCA) shows that the average temperature difference, with or without stainless steel, of the DCA peaks of the decomposition of $\sum\Delta T/\sum i$ carbonates is of the order of 2.3°C, which is a positive value and the energy absorbed in the form of heat is 1.43 J/g (with Cp=0,62j/g°K). Thermal hydrotreatment of oil shale in the presence of 18-9 stainless steel therefore involves a loss of energy.

For the dispersive X-ray analysis, we established the ratio of the percentages of the elements constituting the stainless steel after and before reaction.

Feα	Feβ	Crα	Crβ	Ni
0,984	1,088	0,996	0,897	1,167

If we exclude the elements that undergo increases, insofar as we have a decrease in the others, this is because the values are relatively proportional to the concentrations. We observe a significant decrease for Feα, Crβ and Crαwhich undergo hydridations, so we have an alteration during the reaction of the stainless-steel constituents in the orderCrβ(0,897) Feα(0,984) then Crα(0,996).

As for Ni and Feβ, we note an inhibition to alteration due to hydrogen under temperature. We therefore confirm that the alloy most resistant to such treatment using hydrogen will be based on Nickel and Iron β.

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