

# PERFORMANCE OF FRESH AND REGENERATED CATALYSTS FOR RESID HYDROTREATMENT

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## Abstract

Coke and metals deposits are known to be the main causes of deactivation of hydrodemetallization (HDM) catalysts when used for Desulfurization of Vacuum Residue (VRDS). This study discusses the relative effects of metals poisoning and coke deposit on initial and steady state activity.

Regeneration of a spent HDM catalyst, unloaded from an industrial VRDS unit, was performed at lab scale under air, and the catalytic performance of the regenerated product studied in pilot plant on various feedstocks. It is shown that, even if the initial HDM activity is somewhat lower for the regenerated catalyst compared to fresh, both materials become equivalent in activity after some time on stream.

Therefore, if an HDM catalyst doesn't reach its maximum metal uptake capacity during the first industrial cycle, it can be re-used for a second run, and reach a higher metal retention, after an off site oxidative regeneration. This is especially true with this specific HDM catalyst developed by IFP, as its unique pore structure (so called "chestnut burr") gives a very high metal retention capacity.

## 1-Introduction

Hydroprocessing catalysts deactivate continuously throughout an operating cycle, essentially because of a progressive coverage of active sites by heavy hydrocarbon molecules called "coke" and contaminants (1-4). Carbon can be removed by regeneration while metals deposition is typically irreversible (3).

Off site regeneration of hydroprocessing catalysts has been widely accepted over the last twenty years by the petroleum refining and petrochemical industry. A majority of units have abandoned the once conventional in-situ technique for a number of reasons including safety and time considerations as well as activity recovery. The high quality achieved by off site regeneration often makes more than one cycle possible, depending on catalyst contamination, severity of operation and unit duty. In addition to this economical incentive for regeneration, more and more stringent environmental regulations for disposal of spent catalysts encourage their re-use. In the case of distillate hydroprocessing, the limit for catalyst re-use often comes

from the activity loss due to metals poisoning. Main contaminants are nickel and vanadium on Vacuum Gas Oil Treatments (FCC pretreaters and hydrocrackers), silicon on coker feeds, arsenic on specific crude oils, as well as sodium in some other cases.

In the case of resid treatments so far, it is not common to regenerate spent catalysts, but rather to recycle them for metals recovery. The first reason is obvious: catalyst at the end of a cycle is heavily loaded with nickel and vanadium, and, activity of regenerated product is assumed to be much lower than that of fresh product. Also the regeneration process is made trickier in this case because of the high coke content as well as the common presence of large quantities of hydrocarbons to be stripped prior to coke burn off. Another concern is the possibility to maintain mechanical strength and average length of the regenerated catalyst particles so that pressure drop created by the catalyst bed remains within acceptable limits.

Nevertheless there is a strong economic incentive to use the catalyst load of a resid unit, or at least part of it twice. Quantities are large and cost saving on fresh material purchase could be important. Moreover higher revenue can be created out of the spent material if its vanadium content is increased. Typically the cost of recycling of a spent distillates hydrotreating catalyst is not compensated for by the value of the metals contained. A spent resid catalyst can get a positive value as soon as its vanadium content exceeds 15 to 20 wt %, depending on metals price. Regeneration and reuse of part of the catalyst bed would lead to a higher vanadium loading thus creating higher value for the spent product.

## **2- Hydrodemetallization catalyst characteristics**

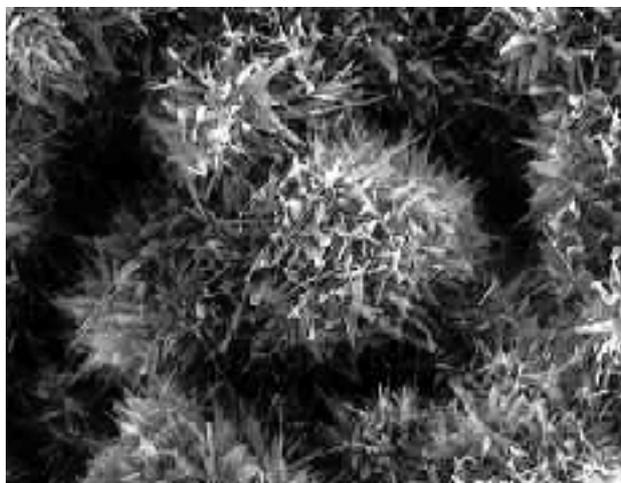
Fixed bed resid upgrading processes typically use an association of several kinds of catalysts, each of them playing a specific and complementary role (1). The first major function to be performed is hydrodemetallization (HDM). Therefore, the HDM catalyst must desegregate large asphaltene molecules and remove as much metals (nickel and vanadium) as possible. IFP has developed a specific HDM catalyst (HMC 841) by optimizing the support pore structure and acidity (2). This catalyst with a “chestnut burr” structure allows a uniform distribution of metals deposited in the grain and therefore a high metal retention capacity is reached. A specific HDS catalyst is placed downstream the HDM catalyst. Its main function is to desulfurize the already deeply demetallized feed as well as to reduce Conradson Carbon (4). Thus, HDS is not the main function of the HDM catalyst.

IFP has developed a Vacuum Resid Desulfurization fixed bed process including permutable swing guard reactors. This system improves the protection of downstream catalysts and increases the unit cycle length. The Hyvahl Process is industrially proven (1). The process scheme includes two swing guard reactors followed by conventional HDM and HDS reactors. The HDM catalyst in the guard reactors may be replaced during unit operation and the total catalyst amount is replaced at the end of a cycle. The HDM catalyst from the normal HDM reactor is usually not saturated with metals at the end of the cycle: it may contain about 20 to 30% of metals when it can tolerate up to 60 % and more. Therefore, the regeneration of this catalyst has been studied with the perspective of re-using it in the guard reactors.

### 3- HDM catalyst Regeneration

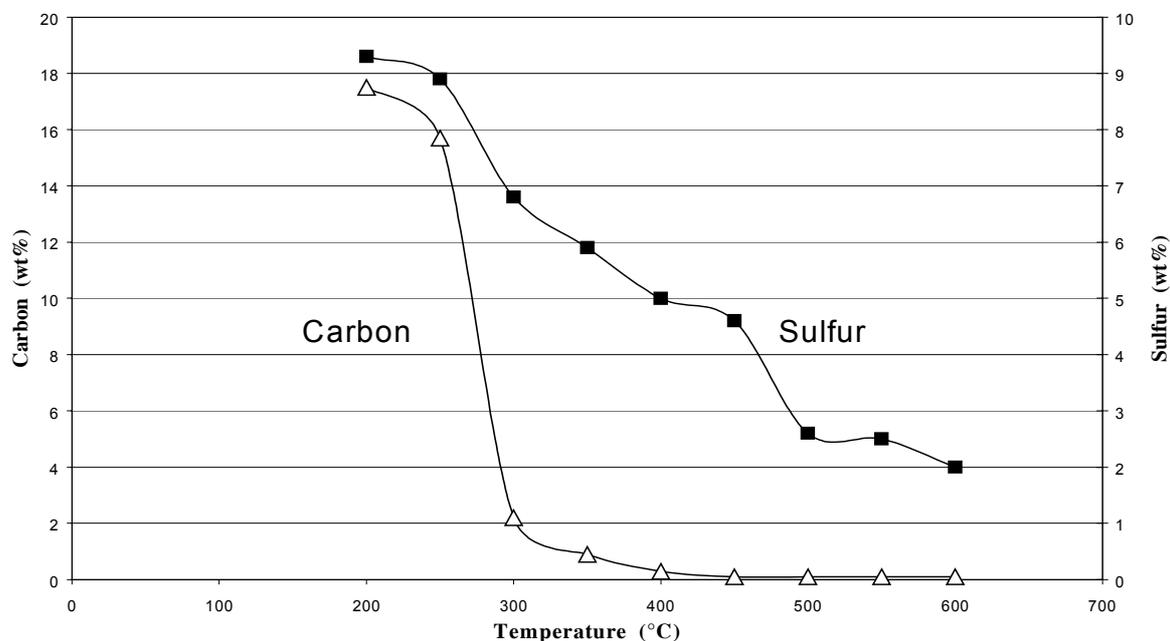
A spent HMC 841 catalyst has been unloaded from an Hyvahl unit at the end of a one-year cycle and its regeneration studied by Eurecat. Metals deposit on the spent catalyst varies from 18 to 23 wt %, with an average at 21 wt % (expressed as weight of metal nickel + vanadium on the fresh catalyst basis), which is not yet the saturation level for this type of high capacity HDM catalyst. On the other hand, carbon content is rather high: around 30 wt % on the catalyst as such and 18 % of hard coke after stripping at 200°C.

Regeneration has been studied at laboratory scale by following carbon and sulfur removal at various temperatures. Experiments are performed in ventilated muffle furnace using 50g of product dispersed as a monolayer on a plate in order to avoid any hot spots. A two-step heating is applied, quick up to 300°C, then at 10°C/min to the final temperature where it stays 4 hours. Carbon and sulfur are analyzed using a LECO CS300, based on sample combustion and infrared detection of carbon and sulfur dioxides.



Electron microscope picture of HMC841 catalyst evidencing the 'chestnut burr' structure.

Figure 1 shows the carbon and sulfur removal curves at temperatures between 200°C and 600°C. Carbon curve is rather steep between 250 and 300°C while Sulfur is eliminated gradually all along the temperature range. Compared to results previously obtained on distillate hydroprocessing catalysts (5), these results may look surprising.



**Figure 1** : Carbon and sulfur content of the spent HDM catalyst as a function of regeneration temperature at laboratory scale

Carbon elimination on distillate hydroprocessing catalysts is typically obtained between 350°C and 400°C in the same conditions, whereas it is observed at a temperature inferior to 100°C for this HDM catalyst. This is despite the fact that the carbon content is here much higher than for typical distillate applications. Two complementary reasons may be proposed. First, the very open structure of this support probably makes the oxygen diffusion easier than for a conventional alumina or zeolite catalyst. Secondly the very low combustion temperature may be due to a catalytic effect of Vanadium oxide, which is known for its catalytic properties in oxidation.

Sulfur elimination curve of a typical sulfided CoMo/NiMo catalyst shows two steps: around 2/3 of the sulfur content is oxidized at 200°C whereas the other 1/3 needs temperatures of 400°C to 600°C to be totally eliminated. This last part is believed to be due the decomposition of sulfate adsorbed on the alumina support and formed previously during the sulfide oxidation step. The trend is different here, as sulfur elimination is regular over the whole temperature range without being complete. Again here the Vanadium species are assumed to play a predominant role as oxidizing agent of Sulfur dioxide to trioxide. Sulfates formation is thus favored to the detriment of the gas phase elimination of SO<sub>2</sub>. Later these sulfates require high temperatures of decomposition and are even not totally removed at 600°C.

Eurecat has prepared a one-liter sample at pilot scale for further catalytic testing by IFP.

## 4- Regenerated catalyst performance

### 4-1 Characterization

As mentioned above, the first criterion of reusability for an application in a resid hydrotreater is the physical integrity of the product. This HMC841 catalyst has the specificity to be rather solid as illustrated by its high Bulk Crush Strength (BCS) value of 1.8 MegaPascal, probably due to its spherical form. The regenerated material has a similar value of 1.7 MPa.

Surface Area is a good tool to assess the quality of regenerated catalyst for distillate applications. For a safe reuse, a regenerated catalyst typically needs to have a Surface Area of more than 75-80 % of fresh, although this rule of thumb has some exceptions. In this case, the results are totally out of this picture as Surface Area recovery is only 30 %. At first glance, the catalyst would not be reusable. Another interesting feature is the Porous Volume measured by Mercury Porosimetry. Here also recovery is on the low side with only 50 % of the original value.

Finally the quality of the active phase has been also looked at using the simple test of Toluene hydrogenation under hydrogen pressure. Hydrogenation activity is only 18 % of fresh. So here also the performance of the regenerated product seems very low. So, except for mechanical strength, which remains high, the other three parameters of Surface Area, Pore Volume and active phase quality have been strongly affected by metals contamination. Nevertheless, it was decided to check the catalyst performance in actual conditions.

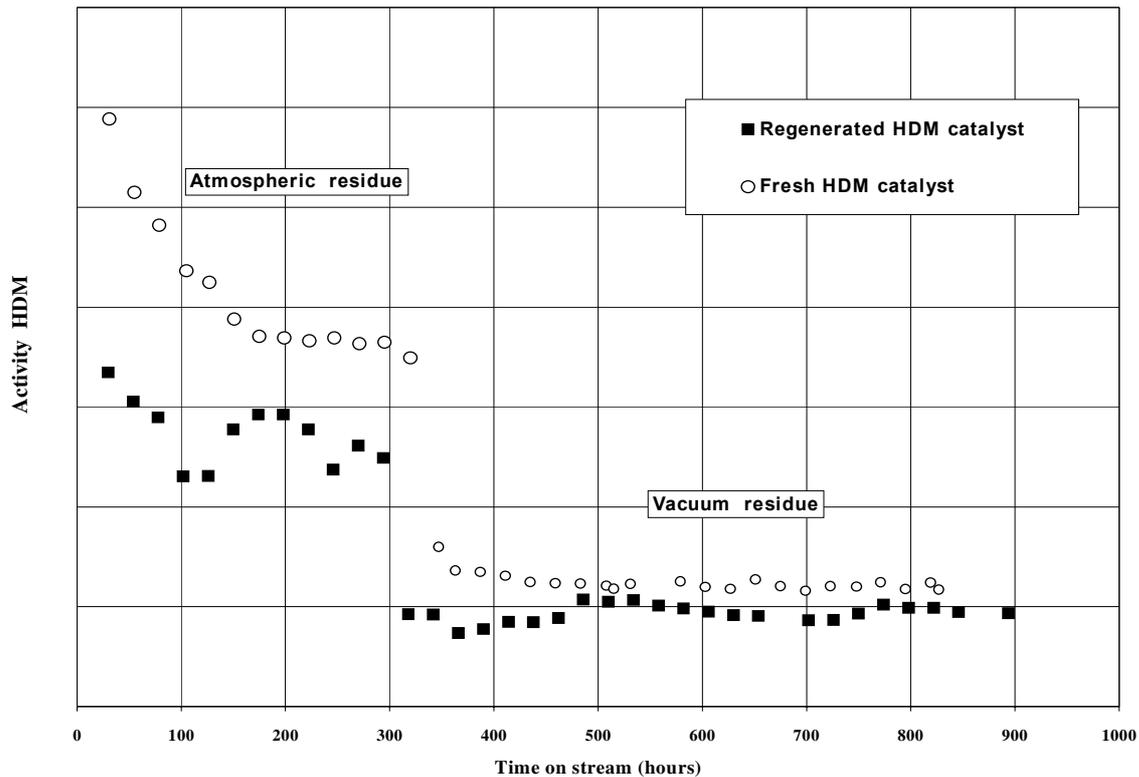


Pilot plant unit for resid hydroprocessing with a reactor capacity of 1 litre.

## 4-2 Activity for HDM and HDS

The regenerated HMC 841 catalyst has been tested in a pilot unit equipped with a one-liter reactor working in isothermal configuration. Feedstock is first an Arabian Light Atmospheric Residue and then an Arabian Light Vacuum Residue. In the second part of the test, the capacity for metals retention is determined on Boscan crude. The same test was also performed with a fresh catalyst.

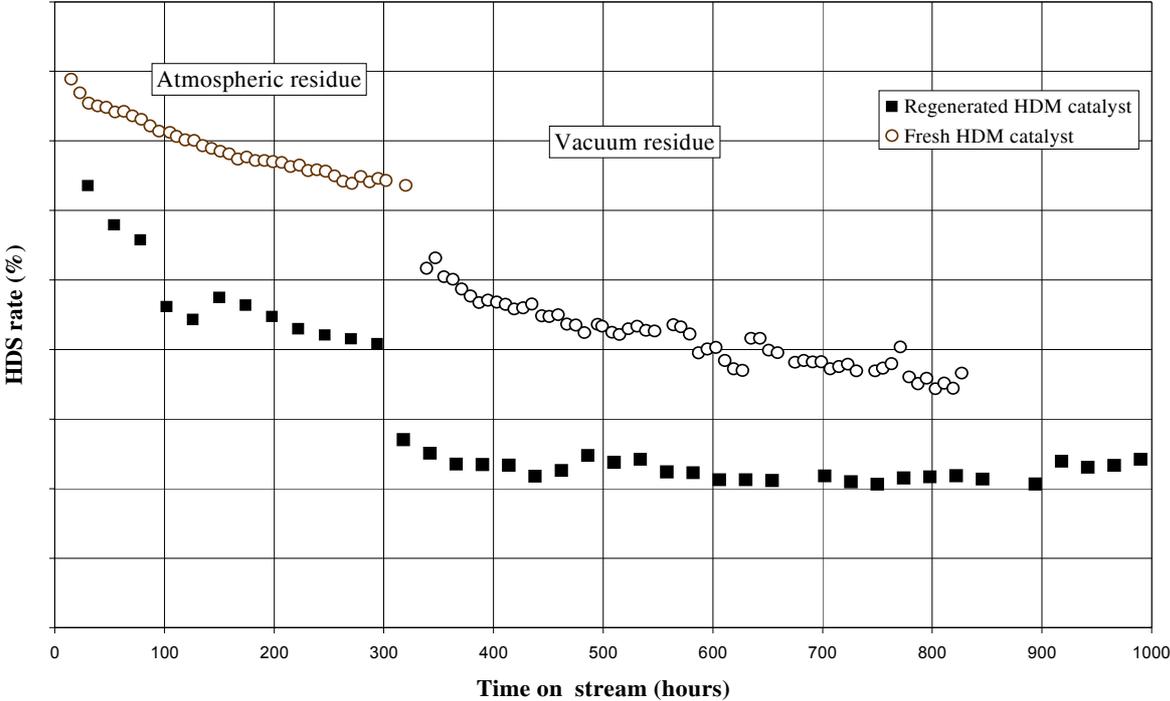
Figure 2 shows the hydrodemetallization (HDM) activities of fresh and regenerated catalysts plotted versus time on stream. During the first hours, the regenerated catalyst is much less active than fresh. This activity deficit is clearly due to metals poisoning of the regenerated product. However the fresh catalyst activity decreases rapidly during the first hours on stream, whereas this deactivation is less severe for the regenerated catalyst. This deficit of HDM activity for the regenerated catalyst is also observed after the switch to vacuum residue, but after some time on stream, activity difference becomes very low.



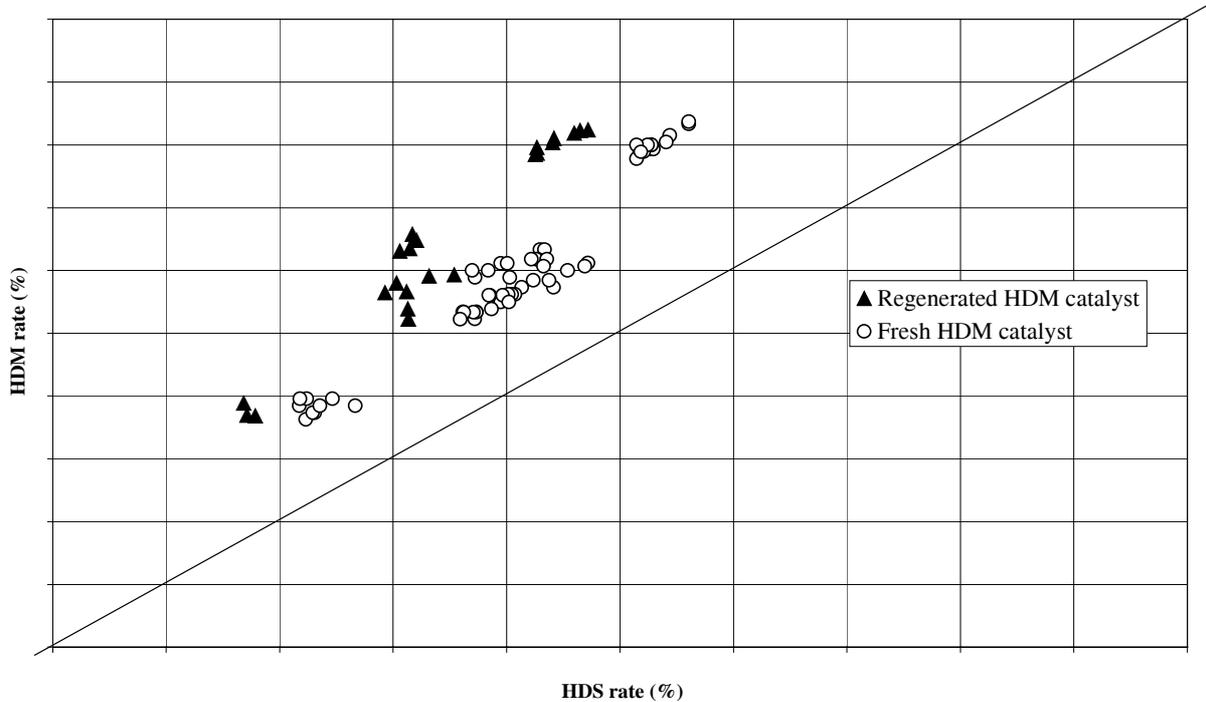
**Figure 2 :** Hydrodemetallization activity versus time on stream for fresh and regenerated catalysts

For the HDS function (Figure 3), the great gap between the two catalysts is mainly due to the initial metal deposit on the regenerated catalyst. It is known that nickel and vanadium sulfides strongly inhibit HDS reactions, whereas they do have some HDM activity. So this can explain why the balance between HDM and HDS selectivity of the regenerated catalyst is in favor of

HDM (Figure 4). Moreover, deactivation of the HDS function due to coke and metals deposits appears higher for the fresh catalyst, whereas the regenerated catalyst reaches certain stability more rapidly.



**Figure 3 :** Hydrodesulfurization rate versus time on stream for fresh and regenerated catalysts



**Figure 4 :** Selectivity HDM/HDS of fresh and regenerated catalysts

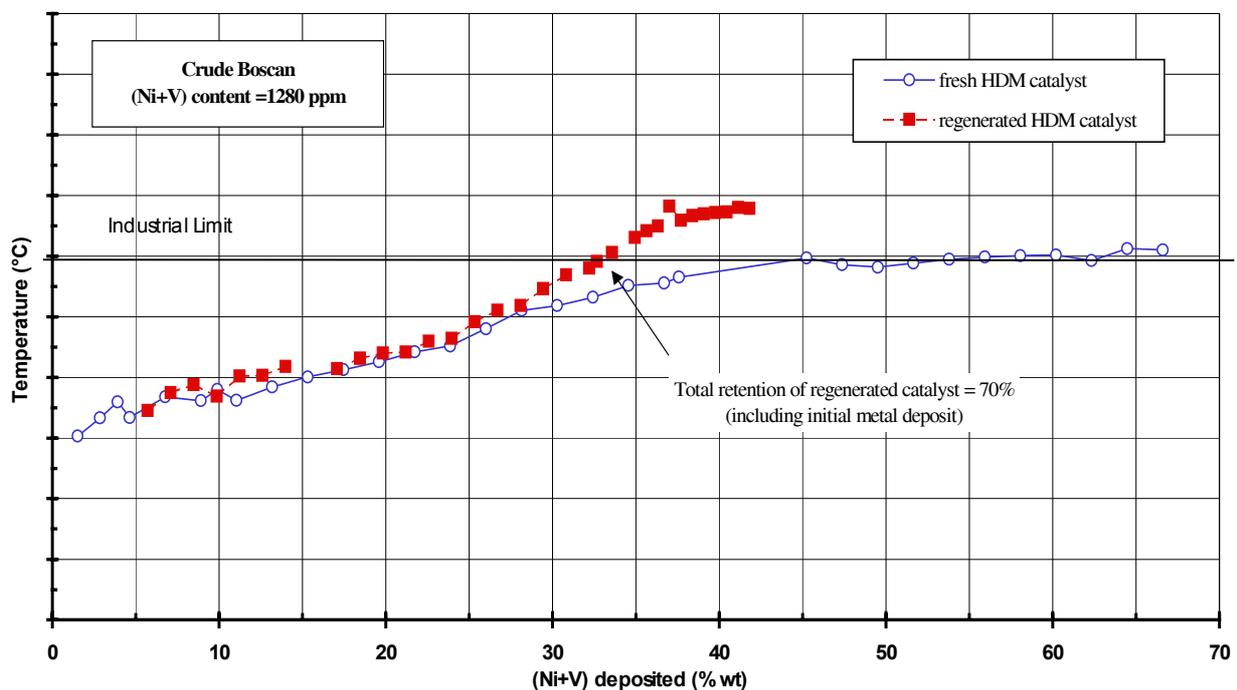
So, after some time on stream, the HDM activities of the regenerated and the fresh catalyst become equivalent with the HDS level remaining slightly lower. This result validates the idea of re-using the HDM catalyst in the permutable reactors, where the main purpose is HDM, provided that metals retention capacity of this regenerated catalyst is sufficient.

#### 4-2 Metals retention capacity

The IFP HDM catalyst with its unique pore structure shows a very high retention capacity that can be as high as 100 % expressed in Ni+V content based on fresh catalyst. The used catalyst unloaded from the Hyvahl unit had a metals content of only 21.6 % wt. Since oxidative regeneration shows interesting results, it was necessary to check that the regenerated HDM catalyst could still offer a high retention capacity.

This property has been followed in the second part of pilot test performed with Boscan crude. This heavy feedstock with its high metal concentration (1280 ppm of Ni+V) allows rapid accumulation of an important quantity of metals on the catalyst.

Figure 5 shows the reactor temperature necessary to maintain a given HDM performance of 70 % versus the metals deposit. Temperature profiles for fresh and regenerated catalysts are very similar.



**Figure 5 :** Normalized Temperature for obtaining 70% HDM at constant LHSV (x axis is the weight of Ni+V deposit per weight of loaded catalyst x 100)

These results demonstrate that both catalysts are able to maintain a high and constant HDM rate and to reach the same retention level, by operating at a temperature below the industrial limit. For regenerated catalyst, the 35 % metal deposited is reported to the weight of loaded catalyst. In consequence, we have to correct this value by two factors: first the weight ratio of loaded catalyst versus fresh catalyst and secondly the initial metal deposit. So, for the regenerated catalyst, the total metal retention, including the initial metal deposit, reaches 70 % weight of the fresh catalyst.

## 5- Conclusion

Regeneration at lab scale of the HYVAHL HDM catalyst shows, as expected, a low recovery of Surface area, Pore Volume and Hydrogenation activity, but high mechanical strength. However, regenerated catalyst performance for resid hydrotreatment is outstanding: initially lower than fresh for hydrodemetallization, and then equivalent or even better for high metals loading; and still slightly lower for hydrodesulfurization.

This indicates that the use of a regenerated HDM catalyst in the swing reactor of an Hyvahl unit would allow to typically double its metals content compared to the first cycle. In other words it would allow to fully profiting from this very innovative “chestnut burr” structure allowing high metals uptake without significant porosity blockage.

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