INTRODUCTION

What is a catalyst? What is it used for?

By definition, catalyst is an element in a chemical reaction that participates in the reaction but is not used up. In the case of the BASHYCAT project and for the petrochemical industry in general, the catalyst takes the form of small elements similar to granules (there are different shapes and colours, depending on their composition) known as “hydrotreatment catalysts”. These catalysts are composed of an aluminium or silica base on which metal oxides are deposited, e.g.

- molybdenum and nickel oxide, known as nickel-molybdenum catalysts (NiMo),
- molybdenum and cobalt oxide, known as cobalt-molybdenum catalysts (CoMo),
- tungsten and nickel oxide, known as nickel-tungsten catalysts (NiW).

They participate in several chemical reactions, making it possible to transform the crude oil into petrol or diesel that can be used in our vehicles.

Among the reactions involving hydrotreatment catalysts we have:

- Desulphurisation reactions (extraction of the sulphur contained in the crude oil)
- Deoxygenation reactions (extraction of the carbon contained in the crude oil)
- Denitritation reactions (elimination of the nitrogen compounds contained in the crude oil)
- Hydrocracking reactions (splitting the large carbon molecules in the crude oil into smaller ones)
- Demetallisation reactions (removal of metals such as vanadium, nickel and arsenic contained in the crude oil).

The quantity of used catalysts is increasing from year to year. It is therefore important to consider solutions for recycling them that are compatible with environmental protection and saving natural resources.

What solution is there for used catalysts?

European directive No. 2001/81/CE dated 23 October 2001 restricts the emissions of pollutants such as sulphur dioxide, nitrogen oxides, etc. into the atmosphere. Consequently, levels of sulphur in petrols and diesel should not exceed 10ppm as from 2019.

The result of this directive is a significant increase in the amount of used catalysts, which will be used in greater numbers by oil companies to achieve the threshold fixed by the European Commission.

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The hydrocracking catalysts are placed in columns known as refining columns. The crude oil extracted from the ground passes through these columns and is thus cleaned of all the harmful elements. If these elements were not removed before using the petrol in our cars for example, they would be released in the exhaust gases and would pollute the atmosphere.

When the crude oil goes through the refining column, the catalysts therefore capture:

- the sulphur, avoiding sulphur dioxide (SO2) emissions
- the carbon, avoiding carbon dioxide (CO2) emissions
- the nitrogen compounds, avoiding nitrogen oxide (NOX) emissions
- the metals, thus avoiding the emission of fine metal particles.

What is a used catalyst?

What quantities are obtained per year in Europe?

As the catalyst is used, it wears out and can no longer extract all the harmful elements. This is known as a used catalyst. The used catalysts therefore contain the elements they are composed of (alumina, sometimes silica, molybdenum, nickel and phosphorus) and the harmful elements captured during the refining process (sulphur, carbon, hydrogen, nickel, vanadium, arsenic, etc.). In Europe, 25,000 tonnes of used NiMo catalysts polluted with high levels of vanadium and 1,000 tonnes of used NiW catalysts are produced each year.

A European Directive aiming to increase the volumes of used catalysts...
### Methodology

The project is centred around several actions:

1. **The regeneration of used catalysts**: This is carried out in a technical furnace, which restores the catalyst’s original properties.
2. **Roasting**: This is the first stage in recycling used catalysts during which the sulphur is removed. The sulphur is captured by a system of fume filtration and is transformed into sodium sulphate powder.
3. **Hydrometallurgy**:
   - A first sub-stage during which the catalysts are plunged into a bath allowing certain metals they contain to go into solution. After this operation, the leaching liquor is treated.
   - A second sub-stage allows the leaching liquor to be purified of substances such as phosphorus or arsenic.
   - Finally, the third sub-stage allows the metals to be purified of substances such as phosphorus or arsenic.

### Pyrometallurgy, this stage can be:

- **Calcination (dehydration of the mud concentrated in metals)**
- **Fusion (melting of the residual solids to separate the mineral content (called slag) and the metal content (metal ingots)**: Several raw materials are obtained as a result of these thermal treatments: metal concentrates (including calcium molybdate or calcium tungstate or vanadium oxide depending on their composition), slag and metal ingots (e.g. iron alloys of nickel-molybdenum).

3,900 tonnes of used catalysts were sourced during the project. The industrial feasibility of regenerating NiMo catalysts polluted with vanadium and NiW has been proved. Over 16% of the tonnage was regenerated during the project and the remainder was recycled. A complete used catalyst recycling channel is in place: new raw materials (patents registered No. EU 06794235.9 and 04.356204.0) have been produced and marketed, allowing the metals recovered by the process, such as molybdenum, tungsten, vanadium and nickel, to be sold, thus saving our natural resources: catalyst recycling was carried out in compliance with the environmental standards for clean gas emissions applicable to centres for the incineration of dangerous waste, thanks to the innovative treatment patent No.EU 04.356204.0 of the fumes and recycling of the resulting by-products. This gas treatment plant is certified by the French inspection authorities.

### THE RESULTS OF BASHYCAT...

#### What happens to the used catalysts thanks to the Bashycat project?

The used catalysts are:

- Either regenerated or they then have a second life in a refinery
- Or recycled, then they are transformed into new raw materials.

Below is a diagram showing the life-cycle of used catalysts treated during the BASHYCAT project:

#### THE ENVIRONMENTAL RESULTS...

Through the various processes implemented on an industrial scale, the Bashycat project can be a viable, clean, long-standing alternative:

- to scraping used catalysts. Scraping poses considerable environmental problems (high leaching levels of the metals contained in the catalysts. These elements can enter the food chain by ground water infiltration and can then be a danger to humans).
- to exportation to countries that do not apply our social and environmental standards.

Numerous harmful effects are associated with used catalysts:

- Nickel, molybdenum, vanadium and tungsten in the form of sulphur compounds are extremely toxic to humans (carcinogenic, mutagenic and affecting reproduction) and the environment (highly mobile) if they get into the food chain or nature.
- If the sulphur is not captured, it can cause acid rain or salt waste to contaminate surface and underground water.
- The heavy and light hydrocarbons can affect the air, the water and the soil if they are not treated.
- The toxicology of poisonous elements such as arsenic, selenium or fluoride in low concentration is well-known.

All the new products manufactured and marketed in the context of the Bashycat project are substitute for metals that are mostly imported into Europe and are often of strategic importance for our economies and our industries:

- Nickel comes from Asia or the Americas for the manufacture of stainless steels.
- Molybdenum is imported from Asia to manufacture stainless steels and for the chemical industry.
- Vanadium is imported from Africa for special steels and pigmentation.
- Tungsten is imported from China to manufacture cutting tools.

These metals are used in sectors with high added value: the automotive industry, the electronics industry, the pharmaceutical industry, the construction industry, the energy industry...

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#### CONCLUSION

The Bashycat project demonstrates that eco-industry is not just a concept but an industrial reality!