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A feasibility study for a circular approach in oil refining: Metals recovery from hydrodesulphurization catalysts

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ABSTRACT

The paper deals with a profitability analysis developed for a plant that recycles spent hydrodesulphurization (HDS) catalysts. Such catalysts contain molybdenum (Mo), nickel (Ni), and vanadium (V), supported by an alumina (Al_2O_3) carrier. The recycling process is based on a double thermal pre-treatment stage, followed by a series of hydrometallurgical steps that allow recovering Mo and V and a Ni concentrate that need further refining for separation and recovery of the metals.

The economic analysis is based on the discounted cash flow method, and the baseline case analyses show that the net present value (NPV) is 14,877 thousand EUR. The selling price of vanadium pentoxide strongly influences the results. Alternative scenarios are also studied to strengthen the results obtained, considering the sensitivity, scenario and risk analyses. Profitability is confirmed in 87% of the considered scenarios, and in about 81.5%, the NPV of the baseline scenario is achieved. Circular economy models can be realized if products are recovered and if there are technologies that can recover metals. This study confirms that an example of a circular economy is met from the proposed viability analysis, and the economic benefits can be significant.

1. Introduction

Hydrotreating, hydrocracking, reforming, isomerization, alkylation, and fluid catalytic cracking are unit operations using different catalysts to get high-quality products [1–3]. In the oil refining industry, hydrodesulfurization (HDS) catalysts play a vital role in producing low-sulphur fuels and meeting environmental regulations [3,4]. HDS catalysts usually are made of MoS_2, advanced by Ni or Co sulfides supported by porous alumina [4]. In heavy oil or diesel refining by HDS catalysts, a significant amount of transition metals are deposited on the catalyst surface in addition to carbon and sulphur. The accumulation of such elements leads to the deactivation of HDS catalysts. Although the organic deactivation is annihilated by burning off the carbon and sulphur elements, deactivation through transition metal deposition is irreversible, leading the catalyst to the end of its life.

Consequently, about 12,000 to 170,000 tons of spent HDS catalysts are generated worldwide annually [3–6]. This considerable volume of spent catalysts accounts for about 4% of the total refinery solid waste discarded [7–10]. Like most industrial solid wastes, the spent HDS catalysts are classified as hazardous materials that need special care before safe disposal [4,5,11–14].

Meanwhile, a high concentration of strategic metals such as Mo, V, and Ni makes the HDS catalysts a valuable secondary resource for recycling [3,15]. Therefore, recycling spent HDS catalysts has become challenging for a circular approach in refining industries. Thus, a cost-effective and eco-friendly approach is required for recycling [16].

A technical analysis indicates that the recovery processes usually contain pretreatment, leaching, separation, and purification procedures. A pretreatment step is beneficial to improve the leaching efficiency. Such chemical or thermal processes are employed to remove the residual oil, sulphur, and coke deposited on the surface of the catalysts [17–22]. In addition, low-valence sulfides or oxides are converted to high-valence oxides through oxidizing roasting to facilitate subsequent leaching [23–25].

Several leaching strategies are used to bring valuable metals into the solution. Water leaching of a sodium salt-roasted catalyst [21,26], acid leaching [27–31], bioleaching [32–34], and alkali leaching [4,25,35] have been frequently used in research studies.

Water leaching is a simple method with accessible equipment that

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Nomenclature

AMV	Ammonium Metavanadate
BDV	Blow Down Valve
CAPEX	Capital Expenditure
CO	Carbon Monoxide
DCF	Discounted Cash Flow
DFC	Direct Fixed Capital
DPBT	Discounted Payback Time
EAF	Electric Arc Furnace
EPC	Equipment Purchase Cost
H&M	Heat & Material
HDS	Hydrodesulphurization
IRR	Internal Rate of Return
LHV	Low Heating Value
Mo	Molybdenum
MAAs	Magnesium Ammonium Arsenate
MAP	Magnesium Ammonium Phosphate
Ni	Nickel
NPV	Net Present Value
OPEX	Operating Expenditure
P&F	Plate & Frame
p_m	Price of metal
p_{ms}	Percentage of maintenance (refinement)
p_{mr}	Percentage of maintenance (shredding)
p_t	Percentage of tax value
PAC	Powdered Activated Carbon
PCC	Post Combustion Chamber
ppm	part per million
PSV	Pressure Safety Valve
QC	Quality Control
R&D	Research & Development
SCR	Selective Non-Catalytic Reduction
SNCR	Selective Non-Catalytic Reduction
SO_x	Sulphur oxides
TPDC	Total Plant Direct Costs
TPIC	Total Plant Indirect Costs
V	Vanadium
VOC	Volatile Organic Compound
WWTP	Wastewater Treatment Plant

requires no chemical solvents among the different leaching processes. Nevertheless, the pregnant leaching solution contains different elements, including transition metals, sodium salts, and many impurities such as As and P needing special attention in subsequent separation and purification processes [3]. The advantage of acid leaching is the high leaching efficiency, which is obtained by using different organic and inorganic acids [10]. However, wastewater treatment is the major drawback due to the large quantities of acids used during leaching. Bioleaching is an efficient, low-cost, and environmentally friendly process with low energy consumption for recovering metals from spent catalysts. However, it is time-consuming compared to the other techniques [36,37]. Alkali leaching is beneficial for the selective leaching of transition metals from catalysts. Vanadium and molybdenum oxyanions can be dissolved in the alkaline solution, whereas nickel and cobalt oxides are insoluble. It should be noted that alumina dissolution is a possible reaction, especially in concentrated NaOH, which leads to difficulties in the subsequent separation process [25,38,39].

The separation of valuable metals such as Mo, V, Ni, and cobalt from the leaching solution of spent catalysts depends on the previous processing history. Although metals usually exist as cations in acidic solutions, Mo and V are present as oxyanions in alkaline solutions. Accordingly, a suitable method is selected considering the previous procedure and solution properties such as solution pH and ion concentration. Precipitation [40–42], solvent extraction [43–46], adsorption [47], and ion exchange [48–50] are frequently used techniques for separating transition metals from leaching solutions. Some spent catalysts are wet, i.e., containing residual naphtha or other hydrocarbon fractions, in a 5–13% concentration range. Others, instead, are dried and dusty, mostly containing coke and sulphur. Some are based on active metals like Ni-Mo, others on Co-Mo. Few industrial processes are currently available to recycle HDS catalysts, both pyrometallurgical and hydrometallurgical.

The current crisis in Ukraine, coupled with climate change, has placed relevance on some countries' mistakes in decentralizing their production activities. Besides that, there is also the not-good habit of transferring some of their waste beyond their national borders. These wrong actions negatively affect from an environmental perspective, yet it also generates a socio-economic issue. Disposing of industrial waste incorrectly seriously damages ecosystems but also compromises future opportunities related to employment and the development of the recycling/recovery economy supply chain. Sustainable patterns are even more keenly felt in some sectors that affect the environment, the oil industry indeed being among them, and it is necessary to implement compensatory actions. For instance, refinery processes are intensively dependent on catalysts.

Furthermore, the techno-economic analysis is a crucial part of any process development, which, to the best of our knowledge, needs to be addressed in the reviewed papers. The oil refining industry is involved in the sustainability transition that aims to mitigate the environmental damages [51,52]. The fossil-derived energies are more polluting than renewables; therefore, circular economy practices play a crucial role in mitigating the harms associated with fossil sources [53]. Their goal is not only to mitigate the environmental impact by encouraging recycling practices and reducing landfill use. The recovery of certain materials, particularly metals, is key to identifying possible economic opportunities [54,55]. However, the literature shows that economic analyses applied to circular economy issues in the oil refining industry are lacking [56,57].

Recycling can lead to a circular approach in the oil refining industry, which is the goal of the present study, which proposes a techno-economic analysis of a process for the recovery of Mo, V, and Ni from spent HDS catalysts. This paper considered the hydrometallurgical approach, including a double-stage thermal pre-treatment required to oxidize residual hydrocarbons, coke, and sulphur.

2. Description of process and plant

The process flow-sheet is shown in Fig. 1.

The plant is divided into several sections, listed and described in the sub-paragraphs. The plant's capacity was set at 6000 tons/year in 7/24 continuous operation mode for 300 days/year.

The composition of the catalysts entering the plant is the average of different samples analyzed and treated in the laboratories of an oil&gas company in Dubai (UAE) and collected from two refineries in UAE and Bahrein.

In this study, only wet catalysts were considered; nevertheless, they are usually mixed with dry catalysts containing the same active metals to lower the low heating value (LHV). Most of the data used in the simulations were obtained from experimental campaigns conducted over the years. Each stage was tested at a laboratory scale from thermal pre-treatment to the recovery of Mo and V. Where not available, values from the industrial literature were used to complete the simulations.

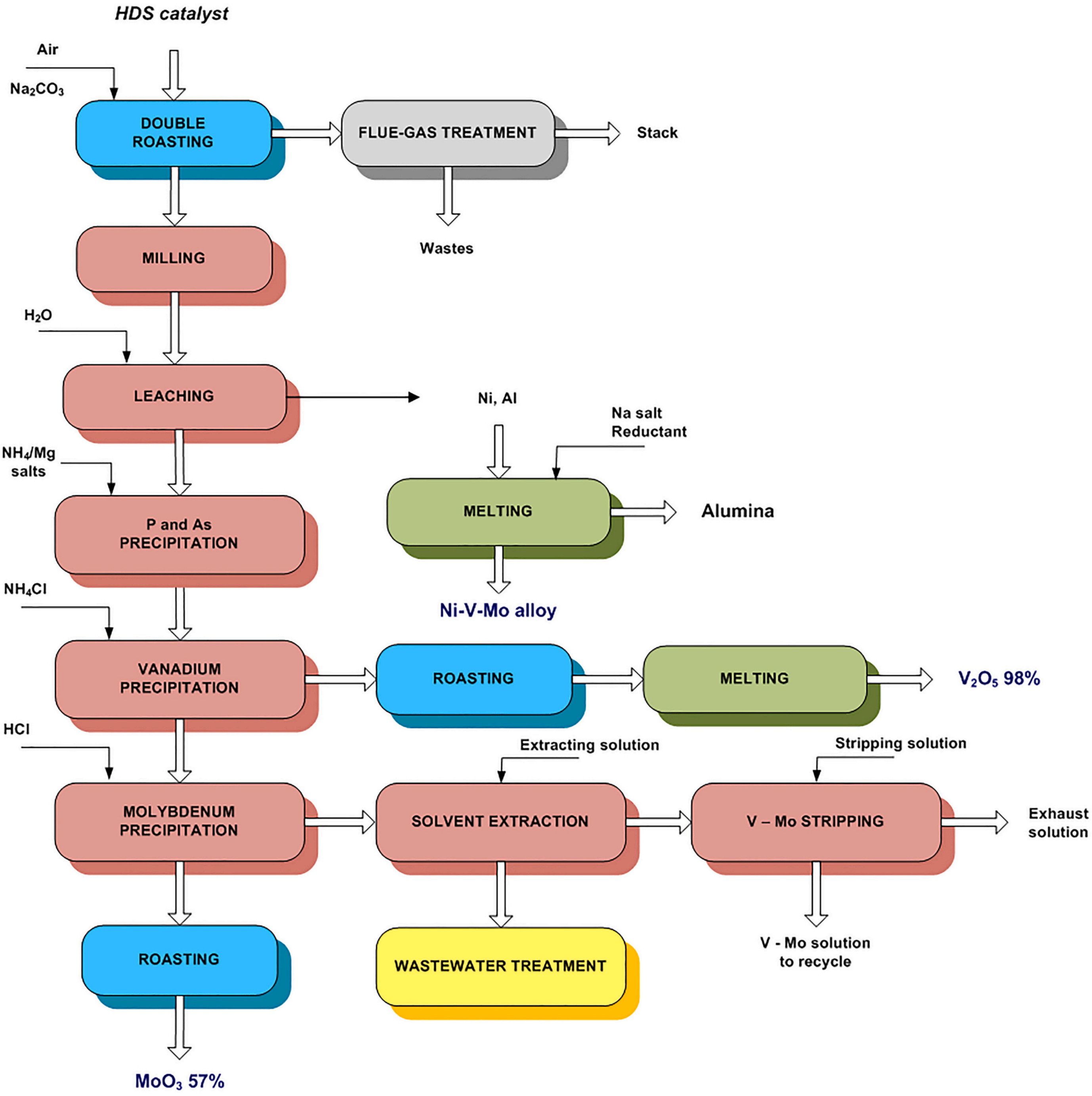

Fig. 1. Flow sheet of the recycling process.

2.1. Roasting of catalysts

The roasting section was simulated by Chemcad® 7 (Chemstation), and the mass balance of all the sections was carried out by Microsoft Excel®.

The roasting of the catalyst can be carried out in a single stage when the required amount of sodium salt, usually Na_2CO_3, is added. A single-stage has some advantages: 1) lower investment, as a sole furnace is needed; 2) smaller flue gas treatment plant, as the SO_2 and the other acidic gases are mainly captured in the furnace and transformed into salts; 3) lower amount of waste generated in the flue gas treatment. The reactions that take place for Mo and V are:

$$2\ MoS_2 + 9\ O_2 + 6\ Na_2CO_3 \rightarrow 2\ Na_2MoO_4 + 4\ Na_2SO_4 + 6\ CO_2 \quad (1)$$

$$V_2S_3 + 7\ O_2 + 4\ Na_2CO_3 \rightarrow 2\ NaVO_3 + 3\ Na_2SO_4 + 4\ CO_2 \quad (2)$$

Hence, each species is directly converted into sodium salt. The great advantage of such a carbonate roasting is that Mo and V are directly converted into the corresponding molybdate and vanadate, which are water-soluble. Hence, they are directly separated from alumina and nickel during the leaching stage. SO_2 is converted into Na_2SO_4, which is water-soluble, so the remaining amount of SO_2 and SO_3 has to be removed from the flue gas in the treatment plant.

In this study, the thermal treatment is carried out in two sequential roasting stages: this choice allows a pregnant cleaner solution, i.e., free of Na_2SO_4, that results in a higher grade of the Mo and V salts precipitated in the downstream stages. That is why it is crucial to use a double roasting stage, although with more disadvantages over the single-stage treatment, and this is the technical solution used for the present study.

Regarding the sulphur oxides (SO_X) reduction, the amount of soda ash (Na_2CO_3) is more or less the same as a single-stage roasting but used entirely in the flue gas treatment. In the first kiln, the metal sulphides are converted into the corresponding oxides, and sulphur is oxidized into SO_2 and partially into SO_3. Coke and hydrocarbons are oxidized into carbon dioxide and water, supposing a conversion yield of 100%. However, the conversion rate is usually lower, and, in addition, many intermediates are formed, like volatile organic compounds (VOCs) and carbon monoxide (CO), especially during the oxidation of the hydrocarbons. Nonetheless, the complete oxidation makes all the calculations easier and releases the entire LHV of the catalyst mixture ($\approx$13,400 kJ/kg). Nickel does not react with carbonate but oxidizes into NiO and partially into Ni_2O_3. The composition of the catalyst subjected to the roasting of compounds like sulphur (sulphide), coke, and residual hydrocarbons is listed in Table 1.

The alumina percentage also includes impurities like iron, magnesium, calcium, manganese (< 0.2–0.3%wt each). The oxidation control is critical to limit the maximum temperature achieved during the treatment and avoid the sintering of catalysts. Once sintered, the leaching of metals would be impossible. The two-stage thermal treatment and the reactions are described in Supplementary Material.

2.2. Flue gas section

The flue gas section heat & material balance (H&M) was carried out by Chemcad® 7 (Chemstation) and Microsoft Excel®. The centralized flue gas plant treats the gas coming from rotary kiln 1 (catalyst oxidation), rotary kiln 2 (roasting with soda ash), rotary kiln 3 (calcination of ammonium metavanadate, AMV), rotary kiln 4 (calcination of molybdic acid), electric arc furnace (EAF) 1 (melting of Ni/alumina solid residue) and EAF 2 (melting of powdered vanadium pentoxide). The plant includes the following stages:

- post-combustion chamber;
- selective non-catalytic reduction (SNCR) of NO_X;
- cooling of the flue gas;
- dry removal of SO_x and other acidic gases;
- wet removal of SO_x.

The flow-sheet of the flue gas section is shown in Supplementary Material.

2.3. Hydrometallurgical section

The material coming from the second kiln is composed of large flakes that need to be milled before leaching as the extraction yield increases with the smaller particle size of the solid. Hence, a ball mill reduces the particle size to <2 mm. The flow sheet of the hydrometallurgical section is shown in Fig. 2.

The leaching phase is divided into three stages in series, where three aliquots of catalysts are leached by the same hot water at 85 °C for 2 h each after filtration. This process arrangement is used to concentrate the metal to recover, i.e., Mo and V. Na_2MoO_4 and $NaVO_3$ are simply dissolved in the water without any chemical reaction. Na_2HPO_4, Na_2HAsO_4, soda ash, and some Na_2SO_4 are also leached during this stage. The unreacted solid, mainly composed of alumina, nickel oxide, and a few parts per million (ppm) of unleached Mo and V salts, is separated from the pregnant solution by a plate and frame filter. The cake is thus washed with fresh water, which is stored and reused for the next leaching cycle. The pregnant solution is contaminated by arsenic and phosphorous salts that have to be removed because they reduce the quality of steel, where Mo and V are added for special alloys. Thus, ammonium vanadate and molybdic acid are recovered by selective precipitation. The details of the operations are described in Supplementary Material.

Table 1
Composition of the catalyst feedstock.

Compound	Flow-rate (kg/h)
MoS_2	41.6
V_2S_3	219.9
NiS	35.7
Coke	116.6
Naphtha	127.4
P	2.5
As	1.5
Al_2O_3	287.5
Total	832.7

2.4. Thermal production of MoO_3, V_2O_5 and Ni-alloy

This section of the recycling plant includes the 3rd rotary kiln, where NH_4VO_3 is decomposed into V_2O_5 and NH_3, and the 4th rotary kiln that performs the thermal decomposition of H_2MoO_4 into molybdenum trioxide $MoO_3$and H_2O. Moreover, the 1st EAF melts the alumina/nickel solid residue from the leaching stage, and the 2nd EAF melts the powdered vanadium pentoxide to get V_2O_5 flakes. The details of the melting furnaces are given in Supplementary Material.

2.5. Wastewater treatment

All the waste streams, i.e., wash water and spent solutions, coming from all the other sections of the recycling plant, are stored in a tank; downstream of it, there is the wastewater treatment equipment. The aim is to produce treated water that can be reused in the recycling plant. Water consumption is huge, so it is crucial to reuse water and limit the pumping from the groundwater table [58]. A small drain may be possible, but this depends on the recyclable amount of water. Since the waste streams are mixed, a partial neutralization occurs because of alkaline and acidic solutions.

Nevertheless, the reactor is used for the neutralization up to a pH of 7.5–8. The neutralization causes the precipitation of metal hydroxides separated from the liquid by a P&F filter. NaOH 50% is used as a precipitation agent. The sludges are stored in a sheltered area, before final disposal. The filtered solution is sent to the wastewater treatment plant (WWTP) of the industrial district site to remove organic compounds and make the water quality useful for reuse. A technological approach that optimizes the mix of substances used can reduce the impact of water on processes [59–61], and a WTTP is one solution that can achieve circularity [62].

2.6. Economic method

An accurate estimation of investment and operating costs was carried out using the H&M balance of the 6000 tons/year plant. The economic analysis was developed according to Peters et al. [63].

In addition, the identified estimates were matched with literature and then with experts from recycling plants. It has to be pointed out that the analysis was developed for refineries and petrochemical companies that own the spent HDS catalysts. Other companies can also invest in recycling, but the HDS catalysts must be found and collected from the market. When the metal prices are relatively low, the petrochemical companies need to pay to dispose of their catalysts because of the treatment costs; instead, in periods like the current one, when the prices are very high, petrochemical companies sell the catalysts on the market. Hence, the purchase of spent catalysts represents an additional and significant annual operating cost that must be considered when performing the profitability analysis of the recycling plant.

The Discounted Cash Flow (DCF) method is widely used in the literature and project evaluation related to circular economy models

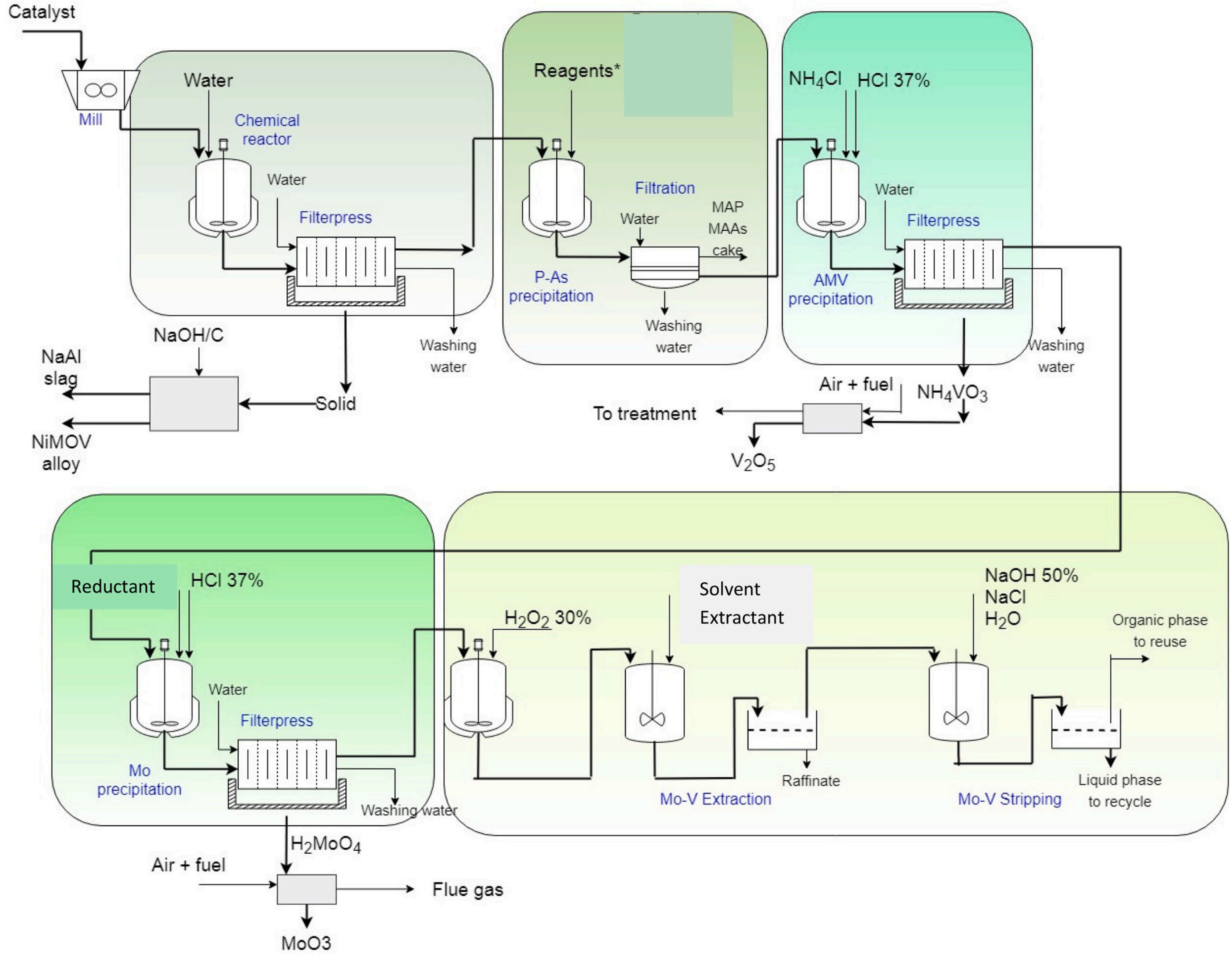

Fig. 2. Flow sheet of the hydrometallurgical section.

because it has the advantage of considering all the cash flows of a project and assessing the value of money over time. The significant limitation of these analyses is that it is based on estimates that the values can assume. Hence, it is necessary to provide alternative scenarios in which the variables are made to change [64,65]. The indicators used for this analysis are the Net Present Value (NPV) which measures the amount of profit achieved by the implementation of the project; the Profitability Index (PI), which measures the wealth gained per unit of investment; the Discounted Payback Time (DPBT) which quantifies how long it takes for the project to return from the initial investment cost and the Internal Rate of Return (IRR) which measures the economic return of the project. In this way, we offer a comprehensive set of indicators suitable for assessing the cost-effectiveness of this project.

The plant has an estimated useful life of 10 years, a construction time of 1 year, and an opportunity cost of capital quantified at 5%. Capital received from third parties is considered, with a 5-year loan and an interest rate of 3%. The materials/products obtained in the sales phase and those used in the operational phase, adding both the cost of workers and utilities, will not be subjected to an inflation rate because we prefer a prudent scenario. Revenues are larger than operating costs, and under the effect of inflation, cash inflows tend to grow more than cash outflows. The plant is considered to be built in a Middle East country: the level of taxation is set at 25%. The following sections analyze the investment costs, operating costs, and revenues.

2.6.1. *Capital expenditure*

Several items were determined to have a reasonable quantification of

Table 2
Evaluation of CAPEX.

Item		Cost (EUR)
Mainequipment		10,860,000
Auxiliary and unlisted equipment	7%	760,200
Drums/big bags for packaging		86,005
Laboratory equipment		300,000
Equipment Purchase Cost		12,006,205
Installation	40%	4,802,482
Piping	7%	840,434
Instrumentation	8%	960,496
Insulation	3%	360,186
Commissioning + Spare parts (2-years)	5%	600,310
Electricals	7%	840,434
Buildings	25%	3,001,551
Yard improvement	5%	600,310
Total Plant Direct Cost (TPDC)		24,012,410
Engineering, Procurement, Construction	10%	2,401,241
Construction & supervision	12%	2,881,489
Contingencies	1%	240,124
Total Plant Indirect Costs (TPIC)		5,522,854
Direct Fixed Capital (before correttive coefficient)		29,535,265
Direct Fixed Capital (DFC)		35,442,318

the total capital expenditure (CAPEX), listed in Table 2.

The main equipment item considers all the main equipment like furnaces, kilns, grinders, reactors, pumps, storage tanks, columns, compressors and fans, P&F filters, etc.; the capacity and the characteristics of the main equipment were determined by SuperPro Designer® software package.

Auxiliaries include smaller equipment like conveyor belts, dosing pumps, forklifts, and intermediate tanks. A laboratory is also required to carry out some tests for process control and optimization purposes and quality control of the products. Drums and big bags are also needed to package the final products. The sum of these items represents the Equipment Purchase Cost (EPC). Installation of equipment, piping, instrumentation, etc., was calculated as a percentage of EPC [63]. The sum of the items above is the Total Plant Direct Cost (TPDC). Engineering, construction, and contingencies (Total Plant Indirect Costs) were added to the TPDC, giving the Direct Fixed Capital (DFC) nearly 35,442,318 EUR. This cost includes a correction coefficient, estimated at 20%, which considers the increase in costs related to the period of the conflict in Ukraine. The capital investment is subdivided into five equal amounts, equal to 8,693,603 EUR/year, and interests vary from 1,043,232 EUR/year (during the year zero) to 260,808 EUR/year (during the fourth year).

2.6.2. Operating expenditure

The annual operating costs associated with the operation of the plant are indicated in Table 3.

The expenses associated with the maintenance and repairs (2,126,539 EUR/year) and assurance (177,212 EUR/year) are calculated in function of the main equipment. Specific conversion factors are used in the function of CAPEX, which are equal to 6% and 0.5% for maintenance and assurance, respectively. In addition, the same approach is proposed for facility-dependent costs. The total cost is 850,616 EUR/year using a specific conversion factor of 3% more than CAPEX.

Consumables include filters, oil, and grease, membranes, graphite electrodes, and laboratory consumables. This item is fixed equal to 222,000 EUR/year.

Utilities consider electric energy and methane needed to heat the kilns. The plant consumes around 24 million kWh/year and considering the contemporary factors of the equipment, a 6 MW electric substation is required. The unit cost of electricity is assumed to be 0.145 EUR/kWh, according to Statista, considering a price range that varies by 40%. The total cost of electric energy is 3,472,407 EUR/year. The total required methane amounts to 838,210 Nm^3/year, for a total expense of 301,755 EUR/year. In this case, an average value of 0.36 EUR/Nm^3 is considered, evaluating the range from 0.30 to 0.42 EUR/Nm^3.

Labour includes gross wages for a plant manager, a logistic manager, one technical director, and two office workers. One laboratory analyst, four maintenance workers, and 24 skilled workers are necessary to run the plant continuously and cover the 24/7 shifts; one safety consultant and one commercial consultant complete the teams. The total amount of labor cost is 919,320 EUR/year. Royalties are due as the process is a proprietary technology of an external company. This item is fixed equal to 240,000 EUR/year.

The detailed operating costs due to raw materials and waste streams are reported in the Supplementary Material. In particular, the main costs are due to Na_2CO_3 (695,520 EUR/year), HCl 37% (461,736 EUR/year), NaOH (294,019 EUR/year), extractant (210,000 EUR/year) and NH_4Cl (130,291 EUR/year). The total value associated with raw materials equals 2,293,174 EUR/year. Again, the correction coefficient introduced for CAPEX was considered. It is worth noting that this coefficient increased all operating costs (only utilities are an exception). Instead, the main items among waste disposal costs are due to Na_2SO_4 from flue gas treatment (280,800 EUR/year) and alumina slag (244,800 EUR/year). The total value associated with the Waste Disposal Cost amounts to 574,200 EUR/year without considering the correction efficiency. Finally, further operating costs considered are Laboratory (48,000 EUR/year), Miscellaneous (30,000 EUR/year), and Transportation (18,000 EUR/year).

Table 3
Evaluation of OPEX.

Item	Cost (EUR/year)
Raw Materials	2,293,174
Labor-Dependent	919,320
Maintenance & Insurance	2,764,501
Laboratory/QC/R&D	48,000
Consumables	222,000
Waste Treatment/Disposal	689,040
Utilities (electric energy + methane)	3,774,162
Transportation	18,000
Miscellaneous	30,000
Running Royalties	240,000
Facility-Dependent Cost	850,616
Annual Operating Costs	11,848,812

2.6.3. Revenues

The main revenues of the plant (Table 4) are commercial grade vanadium pentoxide and molybdenum trioxide. Furthermore, the metal alloy in the EAF 1 represents an additional revenue. This fraction is not of commercial-grade, so it must be sold to metal and steelmaking plants for further refining.

As far as the first two products are concerned (V_2O_5 98% min and MoO_3 57% min), a purity level in output equal to 90% is considered. Instead, for the other item (NiVMo alloy - 72/25/3%), the level of purity is considered in the intermediate phase with a value of 40%, as it will have to be processed further. This purity should it be reached in its maximum value, could be read as a lower price recognized to recycled material. The effect on the economic model is the same.

Metal prices are based on of appropriate reference sites [66,67,68], and both a minimum and a maximum value were identified for each. The following values were chosen:

- for metal V_2O_5 98% min, an average value of 6.5 USD/lb. considering the range from 4 to 9 USD/lb.
- for metal MoO_3 57% min, an average value of 8.5 USD/lb. considering the range from 5.5 to 11.5 USD/lb.
- for NiVMo alloy - 72/25/3%, an average value of 5.0 USD/lb. considering the range from 2.5 to 7.5 USD/lb.

For conversion factors, 1 USD = 0.95 EUR and 1 lb. = 0.4536 kg were considered. It is necessary to underline that correction coefficients are not considered regarding revenues because recent values are assessed.

3. Results

Results are proposed for baseline (Section 3.1) and alternative (Section 3.2) scenarios. The goal is to provide robustness to the results and to assess which variables are critical.

Table 4
Products obtained from the recycling plant.

Products	Annual production (tons/year)	Selling price (EUR/ton)	Annual revenues (EUR/year)
V_2O_5 98% min	1272	12,252	15,587,464
MoO_3 57% min	239	16,022	3,829,857
Ni/V/Mo alloy (72/25/3%wt)	227	4189	950,000
		TOTAL	20,367,321

3.1. Baseline scenario

The results of this economic model highlight how the circular economy model can be achieved because recycling of materials, with spin-offs of waste that is recovered and not disposed of properly, allows for economic opportunities. Fig. 3 shows some decidedly interesting results.

The NPV of the plant is 14.9 million EUR as a result of ten years of operation, in which revenues are very significant compared to operating costs (20,367 thousand EUR vs. 11,849 thousand EUR during the first year of operation). The DPBT is equal to 7 years, also determined by the deferment over five years of the initial investment, which is not substantial compared to the operating costs and the annual wealth obtained from the recovery of metals. Certainly, the cut-off period of recycling projects may have smaller values than 7 years. However, the results obtained in this paper also depend on the conservative choices made in which costs were considered increased due to the historical period of conflict. It should also be pointed out that these results can be achieved if the plant works at its full capacity; this condition is achieved if products are collected and ready to be fed back into a production cycle. Moreover, the other economic indicators also confirm economic profitability since the PI is 0.34. Therefore, for each EUR invested, there is a return of one-third of one EUR, and the IRR, equal to 18%, is higher than the opportunity cost of capital. The IRR can be calculated in this project as there are no traps for its calculation, and the value is very high due to the delta generated between revenue and operating cost compared to the value of investment costs.

Let's proceed to evaluate the decomposition of the cash flows. As far as discounted cash inflows are concerned, around three quarters are associated with grade vanadium pentoxide (76.5%), followed by molybdenum trioxide with 18.8% - Table 5. As far as discounted cash outflows are concerned, operating costs account for 68% compared with 32% associated with investment costs - Table 6. Among these costs, a decisive role is associated with utilities, particularly, the cost of electricity (29%). The period of the energy crisis is reflected in this result. However, the additional investment could reduce this result, which could concern the installation of a renewable plant [69]. The second most relevant variable is maintenance (21.5%), as recycling plants require thorough cleaning to maintain the purity level of recovered materials. Next, as the third variable weighing most heavily on costs, are raw materials (19%). Labor-dependent (7.9%), Waste treatment/Disposal (5.9%), and Facility-Dependent Cost (5.8%) represent significant shares of OPEX.

Table 5
Distribution of discounted cash inflows.

Items (Costs)	Percentage
V_2O_5 98%min	76.5%
MoO_3 57% min	18.8%
NiVMo alloy - 72/25/3%	4.7%

Table 6
Distribution of discounted cash outflows.

Items (Costs)	Percentage
Investment cost	36%
Operative cost	64%
Items (Operative costs)	Percentage
Raw Materials	20%
Labor-Dependent	8%
Maintenance & Insurance	24%
Laboratory/QC/R&D*	0.4%
Consumables	2%
Waste Treatment/Disposal	6%
Utilities (electric energy + methane)	32%
Transportation	0.2%
Miscellaneous	0.3%
Running Royalties	2%
Facility-Dependent Cost	6%

* QC: Quality control; R&D: Research & Development.

3.2. Alternative scenarios

Alternative scenarios are proposed in multiple case studies. A single variable can vary within the sensitivity analysis (Section 3.2.1). As for the scenario analysis (Section 3.2.2), more variables were varied, and finally, in the risk analysis (Section 3.2.3), more values were changed by associating a probability distribution. All the analyses were considered as a function of the NPV as output.

3.2.1. Sensitivity analysis

A complete sensitivity analysis requires varying the individual variables and showing which affects NPV the most. In this paper, the following variables are varied (Table 7):

- both pessimistic (minimum metals price) and optimistic (maximum metals price) scenario are considered for the revenue variables. The values are chosen according to Section 2.6.3. In addition, the scenario in which the purity level of all metals (or price recognized to

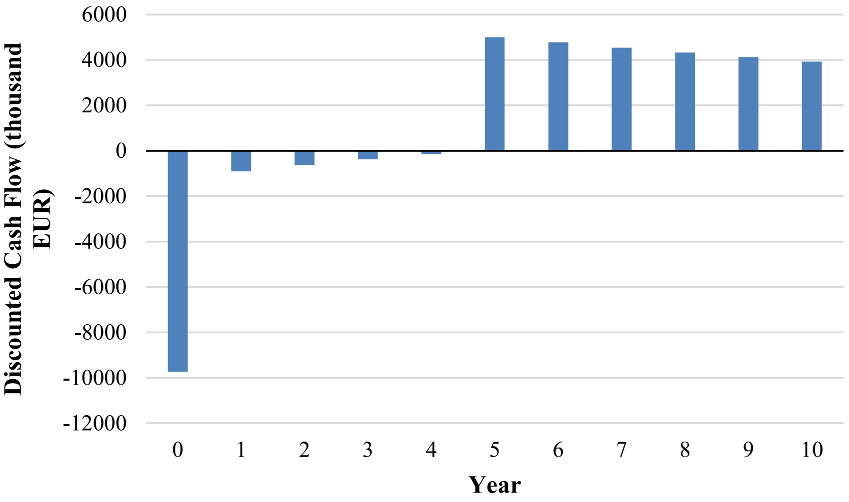

Fig. 3. Economic results (NPV) in the baseline scenario.

Table 7
Economic results (NPV) in the sensitivity analysis. All data are reported in thousand EUR.

Variable	Value
$V2O_5$ 98%min price min	-25,157
$V2O_5$ 98%min price max	50,113
MoO_3 57% min price min	5851
MoO_3 57% min price max	23,222
NiVMo alloy - 72/25/3% price min	11,705
NiVMo alloy - 72/25/3% price max	17,979
Purity level/Recycled price recognition −10%	−1116
Waste disposal cost +20%	13,824
Waste disposal cost −20%	15,931
Labor-Dependent +20%	13,472
Labor-Dependent −20%	16,273
Maintenance & Insurance 20%	11,469
Maintenance & Insurance −20%	18,200
Raw Materials +20%	11,371
Raw Materials −20%	18,281
Electric energy cost +20%	5396
Electric energy cost −20%	25,507
Facility-Dependent Cost +20%	13,741
Facility-Dependent Cost −20%	16,013
Investment cost +20%	3199
Investment cost −20%	25,115
Taxes 40%	10,571
Discount rate 3%	20,119
Discount rate 7%	12,543

recycle metals) is reduced by 10% is also studied. The analysis is conducted for all three items;

- as far as cost variables are concerned, in this case, both pessimistic and optimistic scenarios are considered, and the baseline value is made +/− 20%, respectively. The analysis is conducted for the variables that have the greatest impact on costs: waste disposal cost, labor-dependent, maintenance, raw materials, facility-dependent cost, electric energy cost, and investment cost;
- as far as the other variables are concerned, the discount rate (cost opportunity of capital) is varied by +/− 2%, and the percentage weight of taxes is assumed to equal 40%.

The results confirm the plant's profitability, which is verified in almost all scenarios. The most significant variation is achieved with the minimum price of grade vanadium pentoxide equal to 4.0 USD/lb. In this case, the NPV is negative, equaling −25,157 thousand EUR. In a specular manner, with the maximum price of this metal (9.0 USD/lb), NPV equals 50,113 thousand EUR. The other scenario in which NPV is negative occurs if the recycled price recognition or metal purity is 10% lower for all three products (−1116 thousand EUR). The other most significant variations occur for investment costs since it is true that they are less significant than operating costs. Still, in percentage terms, they are the ones that affect the most as a single variable among the costs and also influence the value of some of the investment costs (e.g., maintenance, assurance). Their percentage weight is greater than that of electricity costs. The NPV is 3199 thousand EUR and 5396 thousand EUR in the two relatively pessimistic scenarios. Returning to examine the revenues, it shows that the second metal recovered, molybdenum trioxide, still affects the result. Its minimum price of 5.5 USD/lb. determines an NPV of 5851 thousand EUR. This analysis allowed us to photograph alternative scenarios in which a single variable varies. The greatest variations occur for the variables that most affect costs and revenues. The investor's benefit is knowing the bottom line if any of these phenomena occur.

3.2.2. Scenario analysis

The scenario analysis is evaluated initially for revenue components that more significantly affect output than cost components. These results highlight how these plants that support resource circularity rely significantly on metal selling prices. In addition, the current crisis and unavailability of some raw materials inevitably push up the price of these products. In this way, the circular process can re-introduce materials that would be difficult to find in the production cycle. The results are shown in Table 8, and it is worth noting that in the optimistic scenario, in which the maximum prices of metals are considered, NPV is 60,692 thousand EUR. However, in the pessimistic scenario, in which the minimum prices of metals are considered, the NPV decreases significantly and is reduced to −37,356 thousand EUR. Second, we look at a scenario analysis concerning only the major cost components (investment, electricity, maintenance, raw materials). Again, we consider scenarios where all four variables vary by +/− 20%. The results are less significant than those recorded for revenues: −15,014 thousand EUR and 37,598 thousand EUR in the pessimistic and optimistic scenarios, respectively.

All the scenarios proposed for the sensitivity and scenario analysis can occur because they relate to real variations in the variables. However, no probability of the occurrence of such variations has been identified.

Given the results obtained in the baseline scenario, the DPBT was found to be non-low; it was decided at this stage to consider an alternative scenario in which investment costs are spread over 10 years, and interest is thus paid for the same time duration. To measure the actual difference, a change in the interest on the debt is not considered. Fig. 4 proposes the new results that offer an improvement in all indicators: NPV of 17,635 thousand EUR, PI 0.41, IRR 46%, and DPBT of 3 years.

3.2.3. Risk analysis

The Monte Carlo method is used to evaluate the risk analysis of a project in which the cumulative distribution function related to stochastic variables is applied. The method is applied to 1000 runs of NPV values under varying economic conditions [70]. We consider the following Excel function for the variables subject to variation:=NORM.INV(RAND(mean,standard_dev). The variables considered are the three metals selling prices, waste disposal costs, maintenance & repair, raw materials, electricity energy costs, labor costs, and facility-dependent costs. The mean is defined according to input data, while the standard deviation is calculated according to the range. All choices are defined using the same approach proposed in the sensitivity analysis. Fig. 5 proposes the results in terms of NPV for several runs.

The results proposed in this analysis confirm that the plant's profitability is not always verified. The most negative scenarios for the investor could be those in which minimum metal prices are verified, which, together with other very unfavourable economic conditions, could push to an economic result of −84.678 thousand EUR. A diametrically opposite situation where all variables are assumed in a favourable scenario may drive an economic impact of 190,823 thousand EUR.

This analysis, compared to the previous one, introduced probabilities to the events that could happen, and the major information it provides us with is the profitability of these plants. The NPV is positive in 87.5% of the scenarios analyzed. Moreover, in about 81% of the assumed case studies, it achieves profitability at least equal to that found in the baseline case. This set of results proposed for the alternative scenarios allows us to observe that many case studies are analyzed from a DCF-based economic reference model and consider the randomness of all the main critical variables.

Table 8
Economic results (NPV) in the scenario analysis. All data are reported in thousand EUR.

Scenario	Value
Prices Revenues, min	−37,356
Prices Revenues, max	60,692
Main Costs, min	37,598
Main Costs, max	−15,014

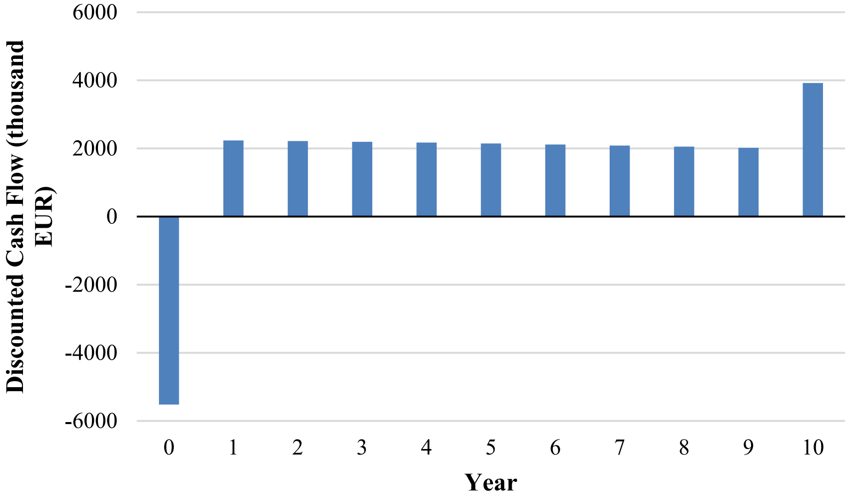

Fig. 4. Economic results (NPV) in the scenario analysis with investment distributed in 10 years.

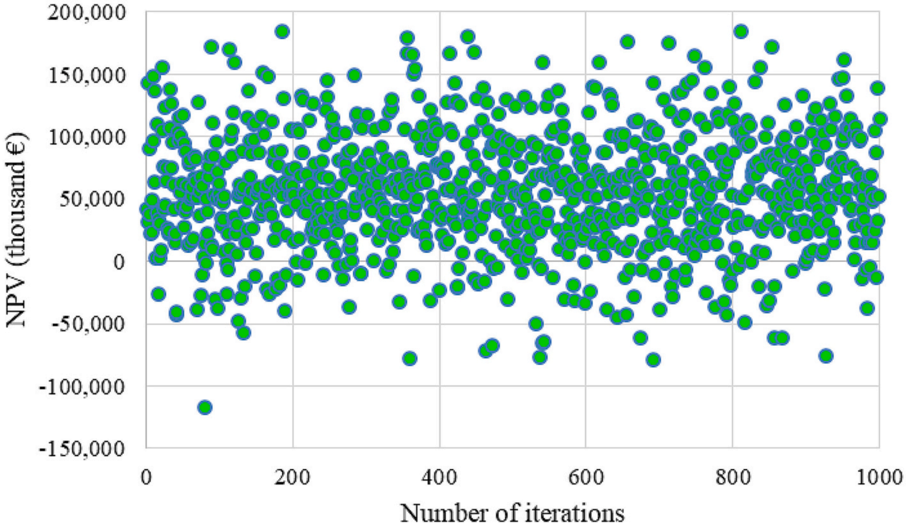

Fig. 5. Economic results (NPV) in the risk analysis.

4. Conclusions

Refineries represent some sort of secondary mines, similar to the parallel concept of urban mining. Several waste types, particularly catalysts, contain valuable metals at a greater concentration than those in the primary ores, even ten- or hundred-fold more. This paper demonstrates that their extraction and refining are more economical than primary ore processing, making recycling an attractive investment. Hence, the circular economy model can be successfully applied to the oil refining sector, as the economic indexes are robust and outstanding, even in international geopolitical unruliness.

The recycling process was simulated using laboratory and industrial literature results over the past years. The relevant plant, with a capacity of 6000 tons/year of spent HDS catalysts, can produce 1272 tons/year of V_2O_5 98%wt, 239 tons/year of MoO_3 57%wt (both commercial grade), and 227 tons/year of Ni/V/Mo alloy with an approximate composition of 72/25/3%wt, respectively.

Once the technical feasibility of the plant, which can give value to these wastes, is verified, it needs to be demonstrated whether the case study is an example of the circular economy. The results suggest some salient aspects:

- the waste should be collected and properly treated;
- the plants should keep the purity of the recovered metals to a maximum;
- the selling price of the recycled metals shall be close to that of the original items.

The change in metal prices influences the bottom line more significantly than costs. In particular, the prices of molybdenum trioxide and vanadium pentoxide have a crucial influence on the results. The baseline and several alternative scenarios are analyzed to give robustness to the proposed values. Conspicuously, in 89% of the scenarios, the NPV is positive, and the following results are achieved in case of an investment spread over 5 years: NPV of 14,877 thousand EUR, PI 0.34, IRR 18%, and DPBT of 7 years. In the case of a 10-year scenario, the following values are obtained: NPV of 17,635 thousand EUR, PI 0.41, IRR 46%, and DPBT of 3 years.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.susmat.2023.e00634.

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