

An environmentally friendly process for the recovery of valuable metals from spent refinery catalysts

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Abstract

The present study dealt with the whole valorization process of exhaust refinery catalysts, including metal extraction by ferric iron leaching and metal recovery by precipitation with sodium hydroxide. In the leaching operation the effects on metal recovery of the concentration and kind of acid, the concentration of catalyst and iron (III) were determined. The best operating conditions were 0.05 mol L⁻¹ sulfuric acid, 40 g L⁻¹ iron (III), 10% catalyst concentration; almost complete extraction of nickel and vanadium, and 50% extraction efficiency of aluminium and less than 20% for molybdenum. Sequential precipitation on the leach liquor showed that it was not possible to separate metals through such an approach and a recovery operation by means of a single-stage precipitation at pH 6.5 would simplify the procedures and give a product with an average content of iron (68%), aluminium (13%), vanadium (11%), nickel (6%) and molybdenum (1%) which would be potentially of interest in the iron alloy market. The environmental sustainability of the process was also assessed by means of life cycle assessment and yielded an estimate that the highest impact was in the category of global warming potential with 0.42 kg carbon dioxide per kg recovered metal.

Keywords

Spent catalyst, ferric iron leaching, metal recovery, life cycle assessment, environmentally friendly process, global warming

Introduction

Refinery catalysts are used in several operations in the petrochemical industry. They can be used in several cycles and regenerated, but beyond a certain point it is more convenient to replace them (Trimm, 2001). Generally refinery catalysts contain metal (Mo, Co, Ni, V) oxides and sulfides, together with residues of sulfur, diesel, and low amount of P and As. Treatments aimed at the recovery of metals from spent catalysts have been the object of several studies both because these metals can be used as secondary raw materials, and in order to reduce the pollution associated to the disposal of this hazardous waste (Marafi and Stanislaus, 2011).

Several treatments can be used for the recovery of metals from catalysts (Marafi and Stanislaus, 2008), mostly based on hydro- and pyro-metallurgical processes (Zeng and Cheng, 2009). In the hydro-metallurgical approach a roasting pre-treatment is carried out in order to oxidize hydrocarbons, carbon and sulfur. The oxidation of metal sulfides improves metal mobilization in the subsequent leaching operation. However, both pyro-metallurgical processes and the roasting pretreatment are highly energy-consuming and produce harmful gases (Ferella et al., 2011; Park et al., 2006; Zeng and Cheng, 2009). More eco-compatible strategies are based on biological processes. In fact, bioleaching strategies aimed at metal leaching from spent petroleum catalysts are based on the acidification of the environment thanks to

the metabolic activity of acidophilic prokaryotes which produce inorganic acids (Gholami et al., 2011; Mishra et al., 2007, 2009, 2010; Pradhan et al., 2009; Szymczycha-Madeja, 2011) and fungi which produce organic acids (Amiri et al., 2011). However, bioleaching presents some technical limitations because of the relatively low process kinetics and toxicity issues. In fact, previous studies have demonstrated that bioleaching could not be effective at the operating conditions typical of full-scale application because the high concentration of the catalyst could be the cause of metal toxicity for the micro-organisms used for metal leaching (Amiri et al., 2011; Beolchini et al., 2010, 2012; Gholami et al., 2011; Santhiya and Ting, 2006). A solution to the environmental limitations of thermal processes and the technical constraints of biological approaches may be represented by ferric iron leaching. In fact, ferric iron acts as an oxidizing agent, mobilizing the

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metals in an aqueous environment without any pretreatment of thermal oxidation. Within the bioleaching process ferric iron is often identified as the main compound involved in the indirect mechanism (Beolchini et al., 2012; Fomchenko and Biryukov, 2009).

Some authors have developed leaching strategies using ferric iron on different matrices: pyrrhotite ore (Beolchini and Vegliò, 1999), silver sulfide (Dutrizac, 1994), chalcopyrite (Córdoba et al., 2008), high-arsenic refractory gold concentrate (Li et al., 2009), wastewater sludge (Bouda et al., 2009) and hydrotreating catalysts (Marafí et al., 1994). Furthermore, the environmental sustainability and the cheapness of the process are favoured by using either biologically produced ferric iron, by means of cyclic regeneration of such iron (Beolchini et al., 2010) or industrial wastewater that contains such element. One of the limits of ferric iron leaching could be the presence of Fe in the precipitates. However if the Fe-metal alloys produced can be marketable the limits of ferric iron leaching are thus bypassed.

The present study dealt with the whole process of exhaust catalyst valorizations, from metal extraction by ferric iron leaching to metal recovery by sequential precipitation. The environmental sustainability of the process was also assessed by means of a simplified life cycle assessment. Studies in the literature are mostly addressed only to the evaluation of the efficiency of metal recovery. Only a few works deal with the quantification of the environmental impact of the developed processes. Some attempts are represented by the work of some researchers (Idris et al., 2010; Yang et al., 2011) where the authors identify the environmental impact of a process for the recovery of nickel from catalysts used for the palm oil hydrogenation process by metal leaching using sulfuric acid and hydrochloric acid. Nevertheless, the know-how related to the environmental aspects connected to component recovery and disposal of spent catalysts still needs to be improved (Portha et al., 2010; Trimm, 2001). Therefore, the present study was aimed at assessing both the technical and the environmental sustainability of metal (nickel, vanadium, molybdenum) extraction from exhaust catalysts by means of ferric iron leaching in an acid medium. A factorial experiment was implemented investigating the effects on metal recovery of the following factors: (i) the kind of acid; (ii) acid concentration; (iii) the concentration of the catalyst; (iv) the concentration of Fe^{3+} . Laboratory experiments were also aimed at assessing metal precipitation yields and the purity of the precipitates achieved after basification with NaOH at different pH values. The optimized process was finally assessed in terms of its environmental impact according to life cycle assessment.

Materials and methods

Spent refinery catalyst

The catalysts used in this work are those used in the petrochemical industry, in particular during the hydrodesulfurization process for the removal of sulfur from refined petroleum products in the

Lc-Finer processes. Each catalyst is a 5 mm long cylinder in which the active phase is represented by nickel (Ni) and molybdenum (Mo) supported on alumina. The composition in valuable metals of the catalyst is the following (w/w): 4.2% Ni, 4.4% Mo, 9.2% vanadium (V), and 16.0% aluminium (Al). X-ray diffraction analysis (Siemens D-500 diffractometer) revealed the presence of the following mineralogical forms, in order of abundance: Al_2O_3 (aluminium oxide), NiV_2S_4 (nickel vanadium sulfide), Mo_4O_{11} (molybdenum oxide), Ni_3S_4 (polydymite). The aliphatic hydrocarbon content in the spent catalyst was about 5%.

Ferric iron leaching

For ferric iron leaching a factorial plan with four factors was designed (Table 1), and each factor was chosen at two levels in order to understand if the best performance was obtained with high or low concentrations of reagents and catalyst, and which acid should be preferred. The factors were: (i) the acid used for metal leaching (HCl and H_2SO_4); (ii) the concentration of the acids, chosen at two different values (0.5 and 0.05 mol L^{-1}); (iii) the concentration of the catalyst in the flasks (10 and 20%); (iv) the concentration of Fe^{3+} (20 and 40 g L^{-1}), as ferric sulfate. Furthermore, a central point was added, replicated three times, using HNO_3 , an intermediate value of acid molarity (0.3 mol L^{-1}), catalyst (15%) and Fe^{3+} (30 g L^{-1}) concentration. The experiments were carried out in 250 mL flasks with a final volume of 100 mL, incubated at 80 °C with shaking at 200 rpm for 240 min. Liquid samples of the leach liquor were collected at the beginning of the experiments, after 120 min and at the final time (240 min). The specific operating conditions are reported in Table 1.

Metal precipitation

Metals were precipitated from the leach liquor by sequential precipitation using 10 mol L^{-1} NaOH. This basic solution was added to the leach liquor, in order to gradually reach different pH values (1.5, 2.5, 5.5 and 6.5). For each pH, the suspension was filtered and both liquid and solid samples were stored for chemical analysis of metals.

Chemical analyses

Metals (Ni, V, Mo and Al) in the liquid phase were analysed by inductively coupled plasma-atomic spectrometry according to EPA 200.7 (EPA, 2001). For the solid phase, it was previously mineralized by acid digestion (EPA, 2007a, 2007b).

Statistical analysis

In order to test the effects of acid concentration, kind of acid and catalyst concentration on metal extraction yields, a four-way analysis of variance (ANOVA) was carried out using GMAV 5.0 software (University of Sydney, Australia). This program was used in order to assess the statistical significance of the effects in the investigated treatments.

Table 1. Investigated treatments for ferric iron leaching in acid media and metal extraction yields after 4 h leaching at 80 °C.

Treatment	Acid concentration (mol L ⁻¹)	Acid	Catalyst (%)	Fe ³⁺ (g L ⁻¹)	Extraction yields (%)			
					Ni	V	Mo	Al
1	1	HCl	10	20	72	69	8	5
2	0.1	HCl	10	20	78	75	12	24
3	0.5	H ₂ SO ₄	10	20	73	73	12	34
4	0.05	H ₂ SO ₄	10	20	73	67	11	33
5	1	HCl	20	20	66	50	4	2
6	0.1	HCl	20	20	69	59	5	2
7	0.5	H ₂ SO ₄	20	20	36	34	6	16
8	0.05	H ₂ SO ₄	20	20	35	34	6	16
9	1	HCl	10	40	73	71	16	29
10	0.1	HCl	10	40	73	71	15	25
11	0.5	H ₂ SO ₄	10	40	99	98	12	50
12	0.05	H ₂ SO ₄	10	40	99	99	14	55
13	1	HCl	20	40	66	61	9	23
14	0.1	HCl	20	40	58	53	8	18
15	0.5	H ₂ SO ₄	20	40	49	47	7	26
16	0.05	H ₂ SO ₄	20	40	50	47	7	27
17	0.3	HNO ₃	15	30	57	16	19	23
18	0.3	HNO ₃	15	30	55	23	20	22
19	0.3	HNO ₃	15	30	53	9	20	20

Life cycle assessment

The software GaBi 4.4 (PE International, Germany) was used for life cycle assessment (LCA), integrated with the EcoInvent database (www.ecoinvent.ch/). The environmental impacts were determined using the methodology CML 2001–Nov. 09 (Guinée et al., 2001a, 2001b). Data were normalized to CML2001 Europe, and then weighted according to CML2001 Experts IKP (Southern Europe).

Results and discussion

Metal leaching

The experimental activity was aimed at assessing the performance of ferric iron leaching in an acid medium for Ni, V and Mo extraction from exhaust catalysts, considered as an alternative sustainable practice to roasting of metal sulfides before the dissolution in acidic medium (Marafi and Stanislaus, 2008). A full factorial plan with four factors was designed in which the effects of different kinds and concentration of acid, catalyst percentage and iron (III) concentration were assessed. In the present study hydrochloric, sulfuric and nitric acid were tested. Sulfuric acid would be preferable both for environmental and economic issues. For example, the production of 1 mol L⁻¹ of the different acids revealed that the impact in the category of global warming potential determined by HCl was 2.1 times higher than H₂SO₄, and the impact determined by HNO₃ was 5.5 times higher than H₂SO₄ (EcoInvent database). Furthermore, among the tested acids, sulfuric acid is the cheapest one whereas nitric acid is the most expensive and hydrochloric acid can form toxic vapours if mixed with oxidizing agents. Nevertheless the complexing ability of chloride and the oxidizing strength of nitrate may result in higher

performance in terms of metal extraction. The leaching experiments were carried out at 10–20% solid concentration, typical of full-scale application. In a previous study by Beolchini et al. (2010) the catalyst concentration was lower (1–2%) as direct bioleaching was the chosen strategy and metal toxicity was supposed to inhibit microbial activity at higher concentrations. Furthermore, different concentrations of iron (III) were evaluated (20–40 g L⁻¹): in perspective of a full-scale application, Fe³⁺ could come from industrial wastewater (i.e. iron-rich sludge or wastewater associated with mine drainage; Hatfield and Pierce (1998), Tay et al. (2003)).

The observed results (Table 1) showed that apart for Mo, the highest efficiencies of metal extraction were observed in sulfuric acid media, with 10% catalyst, in the presence of 40 g L⁻¹ iron (III): 99% for Ni and V, and about 50% for Al. Molybdenum extraction yield was relatively low, with the highest extraction yield (around 20%) in nitric acid media. The high extraction of Ni and V and low extraction of Mo can be easily explained by the speciation of metals as suggested by X-ray diffraction. The highly oxidizing conditions of the experimental systems are ideal for Ni and V, which need sulfide oxidation for dissolution, whereas Mo would need reducing conditions that were not present in the investigated treatments.

Figure 1 gives as an example the temporal profiles of metal extraction yields in sulfuric acid medium in the presence of 20 g L⁻¹ iron (III). Under these operating conditions, the lowest percentage of catalyst (10%) in the experimental systems allowed the highest extraction yield of metals to be reached. For example, after 2 h leaching Ni extraction was 64% with 10% catalyst concentration and 29% with 20% catalyst concentration, at any investigated acid concentration. This trend was observed for all

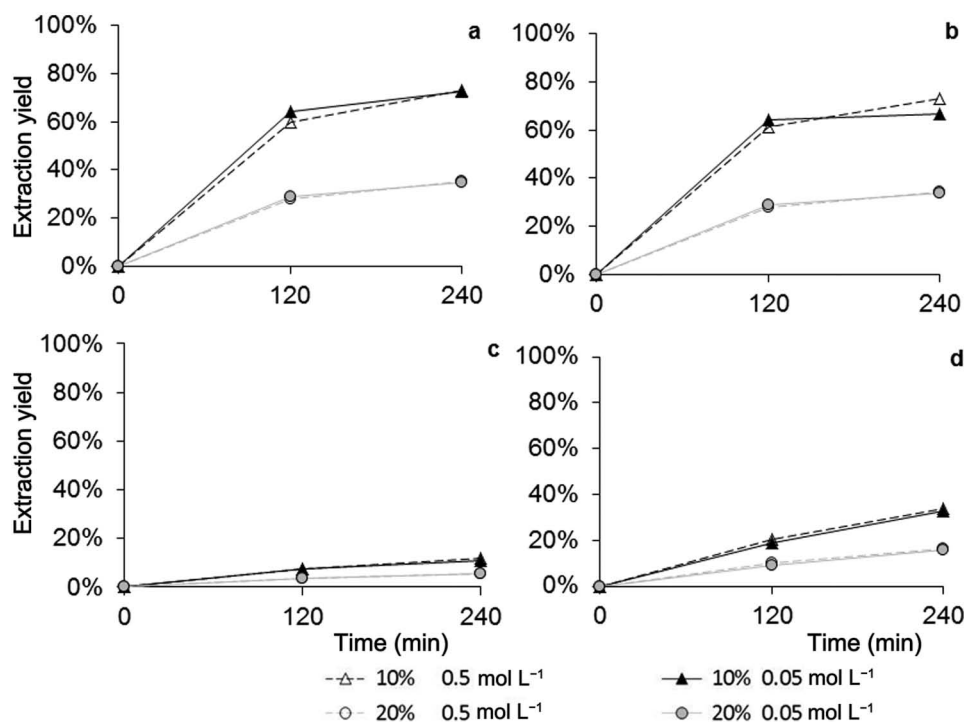
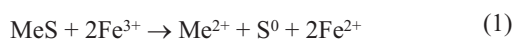


Figure 1. Temporal profiles of metal extraction efficiencies during ferric iron leaching of spent refinery catalyst with sulfuric acid and 20 g L⁻¹ iron (III) (room temperature).

the metals: extraction efficiencies almost doubled with half the solid concentration in the investigated range. This effect of catalyst concentration was significant also with the highest level of ferric iron (temporal profiles not shown, final extraction in Table 1): in any case Ni and V extraction reached the highest value, above 95%, only with 10% solid. This is probably due to the stoichiometry of metal sulfides leaching, which suggests the necessity of even more iron for the highest catalyst concentration (Equation (1)):



In fact according to that stated by the law of chemical equilibrium, the reaction proceeds towards products when the reactants are favoured (excess of metal sulfides and iron). Preliminary tests in the present study confirmed this behaviour, but in order to design an environmentally sustainable process it was decided to use a low amount of Fe (III). Moreover, leaching of metal sulfides can also be favoured by the presence of the acidic environment due to H₂SO₄. The release of metals from the sulfide matrix may also take place according to Equation (2), improving the overall efficiency of metal leaching:



The observed results (Table 1) also provide evidence that there is no need to use other acids and that sulfuric acid, known to be preferable for safety and economic issues, is also the best choice in terms of metal extraction efficiency. In fact it was found that when using sulfuric acid as leaching agent, the extraction

efficiency of Ni and V was almost complete. These data confirm the results of Valverde et al. (2008), which demonstrated that sulfuric acid was better than hydrochloric acid for metal leaching from spent hydrotreatment catalysts. Conversely, the highest value of Mo extraction (about 20%) was observed with nitric acid, but with a significantly low extraction of Ni (about 55%) and V (about 16%).

Furthermore it seems that the lowest acid concentration (0.05 mol L⁻¹) is enough to reach the best performance. Aluminium extraction efficiency was also estimated in all the treatments: in this case process optimization should be aimed at the minimization of Al extraction, since it lowers the quality of the recovered metals. Data in Table 1 show that the highest observed values for Al extraction efficiency were around 50%, for the same treatment that showed the best performance for Ni and V. This aspect has to be taken into account in the downstream processes for metal recovery.

A statistical analysis of the achieved data was performed for a better understanding and process optimization, considering as response the metal extraction efficiencies. Figure 2 shows as an example the ANOVA results for Ni, in which the effect of main factors and interactions are shown together with the significance limit ($p < 0.05$). It can be observed that the main significant factors are catalyst concentration (negative effect) and iron (III) (positive effect), as previously observed. Furthermore a significant negative effect of the interaction BC (acid-catalyst) is also evident in Figure 2, which is not easily recognizable from data in Table 1. This means that the negative effect of catalyst concentration becomes not significant if hydrochloric acid is used instead of sulfuric acid. Similarly Figure 2 also shows a significant positive effect of the interaction BD (acid-iron): the positive effect of iron (III)

concentration is significant only with sulfuric acid and not with hydrochloric acid. These aspects may be associated to the complexing action of chloride ion toward dissolved Ni ions, which favours the extraction process. This assumption can be confirmed by previous studies involving spent catalysts. In one of them the authors recovered Ni as nickel sulfide with 99% yield using sulfuric acid (Al-Mansi and Abdel Monem, 2002). In another one the researchers recovered Ni as nickel oxide using hydrochloric acid, with lower yields (73%; Chaudhary et al. (1993)). Finally, data observed for V extraction efficiency were similar and not significant effects were observed for Mo (data not shown).

In conclusion, this experimental study allowed the operating conditions for ferric iron leaching to be defined: 0.05 mol L⁻¹ sulfuric acid, 40 g L⁻¹ iron (III), 10% catalyst concentration. Under these conditions, almost complete Ni and V extraction efficiencies are expected, with 50% Al and less than 20% Mo.

Metal recovery

Metals were separated from the leach liquor by sequential precipitation with 10 mol L⁻¹ NaOH. The pH values (1.5, 2.5, 5.5,

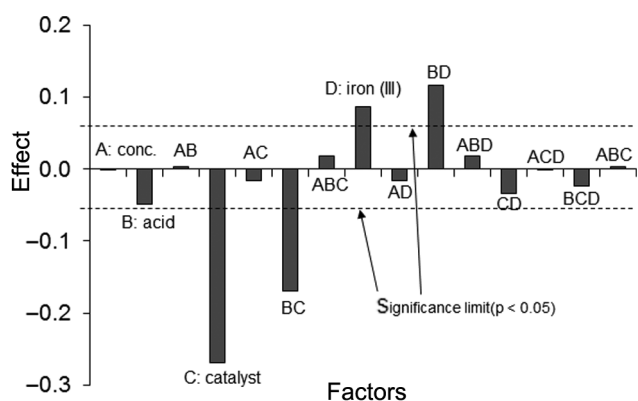


Figure 2. Effect of main factors and interactions on nickel extraction efficiency during ferric iron leaching in acid media (experimental plan and responses in Table 1; A, molarity; B, acid; C, catalyst concentration; D, iron concentration).

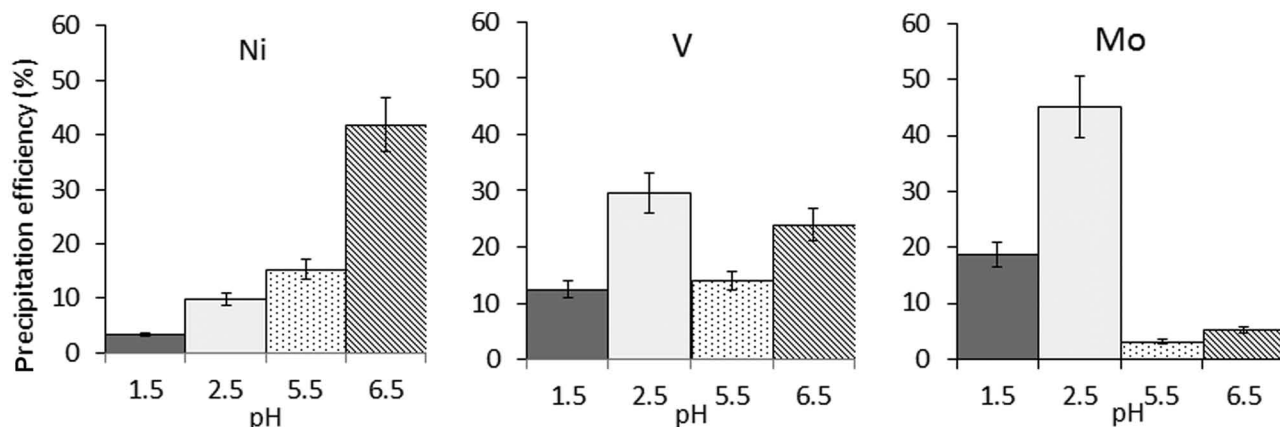


Figure 3. Precipitation efficiency of Ni, V and Mo for different pH during sequential precipitation with sodium hydroxide (room temperature).

and 6.5) were fixed in accordance to the predictions obtained with the software MEDUSA (Puigdomenech, 2009). Metal recovery was tested on the real leach liquor of the treatment characterized by the presence of 0.05 mol L⁻¹ H₂SO₄, 10% catalyst and 40 g L⁻¹ Fe³⁺, where high extraction efficiency of metals were observed (see 'Metal leaching' above). Figure 3 shows the precipitation efficiencies of Ni, V and Mo at several pH values. It seems that the best pH for metal precipitation are: 6.5 for Ni (40%) and 2.5 for V (30%) and Mo (around 50% precipitation yield). Nevertheless it is evident that all metals precipitate to a certain extent, for all the experimented pH values. Indeed, Figure 4 shows the composition of the four solid precipitates and confirms that the selective separation of the extracted metals was not feasible by means of sequential precipitation. All precipitates contain iron (around 15%), Al (in the range 2–5%), V (5% at low pH, 2–3% at pH 5.5–6.5), Ni (1–2%). Very low Mo content was observed (less than 1%) in the two precipitates at pH 1.5 and 2.5, and it was not significant in the other solids. The observed results suggest that a metal recovery operation by means of a single-stage precipitation at pH 6.5 would simplify the procedures and give a product with an average content of Fe (68%), Al (13%), V (11%), Ni (6%), Mo (1%) marketable for companies that use them as feeds for a final purification. The extraction process developed herein was indeed a compromise between metal extraction yield and environmental sustainability. Other processes laterally connected to the principal aim of this work (i.e. the investigation of the technical and the environmental sustainability of the process of Ni, V and Mo extraction) could be considered in other investigations, such as ion exchange in order to further optimize metal recovery from the liquid solution, or purification steps to wastewater before dumping.

Environmental impact assessment

This section of the manuscript deals with the environmental impact assessment of the ferric iron leaching process for Ni and V extraction from exhaust catalyst and production of a

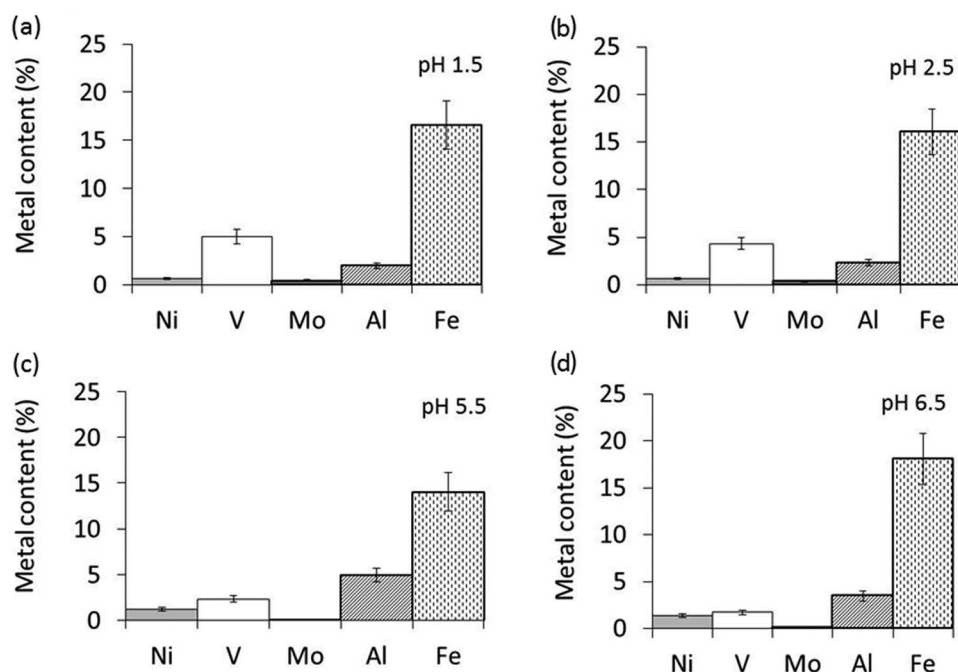


Figure 4. Metal content in the solid precipitated at different pH during sequential precipitation with sodium hydroxide (room temperature).

metal mixture applicable in the sector of iron alloys, as developed through the previously reported experimental study. The environmental impact was quantified by means of life cycle assessment. In particular, such analysis was aimed at the first estimation of the process impacts in the main impact categories according to the University of Leiden - Institute of Environmental Sciences (CML) approach. The functional unit chosen was 10 000 t exhaust catalyst, the average capacity of a full-scale plant, which corresponds to about 5000 t metal product (1600 t Ni, V, Mo, Al from the catalyst plus 3400 t Fe). Figure 5 shows the system boundary of the processes, with the exhaust catalyst as input material. The first operation is ferric iron leaching in sulfuric acid medium, followed by recovery of metals from the leach liquor by a single-stage precipitation with sodium hydroxide. The analysis was also aimed at the identification of the most critical step of the process and at a comparison with primary production processes. Inventory analysis was performed considering as a basis the results previously reported in the experimental section. For the production processes of energy and raw materials, the GaBi 4.4 software integrated with EcoInvent database v.2.2 was used. When not available, production processes of chemicals (e.g. ferric sulfate) were considered (Ullmann, 1997) and built inside the software GaBi. The specific impact categories selected were the following: global warming, abiotic depletion, acidification, eutrophication, photochemical ozone creation, ozone layer depletion, and the relative characterization models were those developed by the Center of Environmental Sciences of Leiden University (CML), in The Netherlands, implemented inside the software GaBi. Table 2 shows the estimated impacts in the six selected categories for the ferric iron

leaching process. The impacts were normalized and weighted, with the aim of comparing the results obtained in each impact category and understand what was the most critical for the environment. Normalization was carried out according to all European Union (EU25+3, CML2001 – Dec. 07) and weighting was referred to Southern Europe (CML2001 – Dec. 07, Experts IKP). Figure 6 shows the results of the performed elaborations. It can be observed that the highest impact was in the category of global warming potential: this means that any environmental optimization should be finalized at the minimization of carbon dioxide emissions as the main purpose. An estimation of 0.42 kg carbon dioxide per kg recovered metals was performed, that is, really lower than impacts of primary production processes (EcoInvent database). The estimation was obtained by dividing the carbon dioxide emissions calculated with the software GaBi by the mass of recovered metals. Primary production processes which produce high purity metals were compared with the process used in the present study that produced a metal mixture from end of life catalyst, to suggest that this latter process would give a significant saving for the environment in terms of carbon dioxide emissions. The economic relevance of catalyst recycling is also important, as the mean lifetime of the catalyst is 1–2 years and the quantity of catalyst that is disposed of has been estimated to be 150 000 t year⁻¹ (Dufresne, 2007)

Furthermore, as reported in Figure 7, the most critical step of the process was metal precipitation which made a contribution of around 68% to global warming potential due to the production process of sodium hydroxide. Further work may be aimed at finding an alternative precipitation agent, with a lower impact in the global warming potential category.

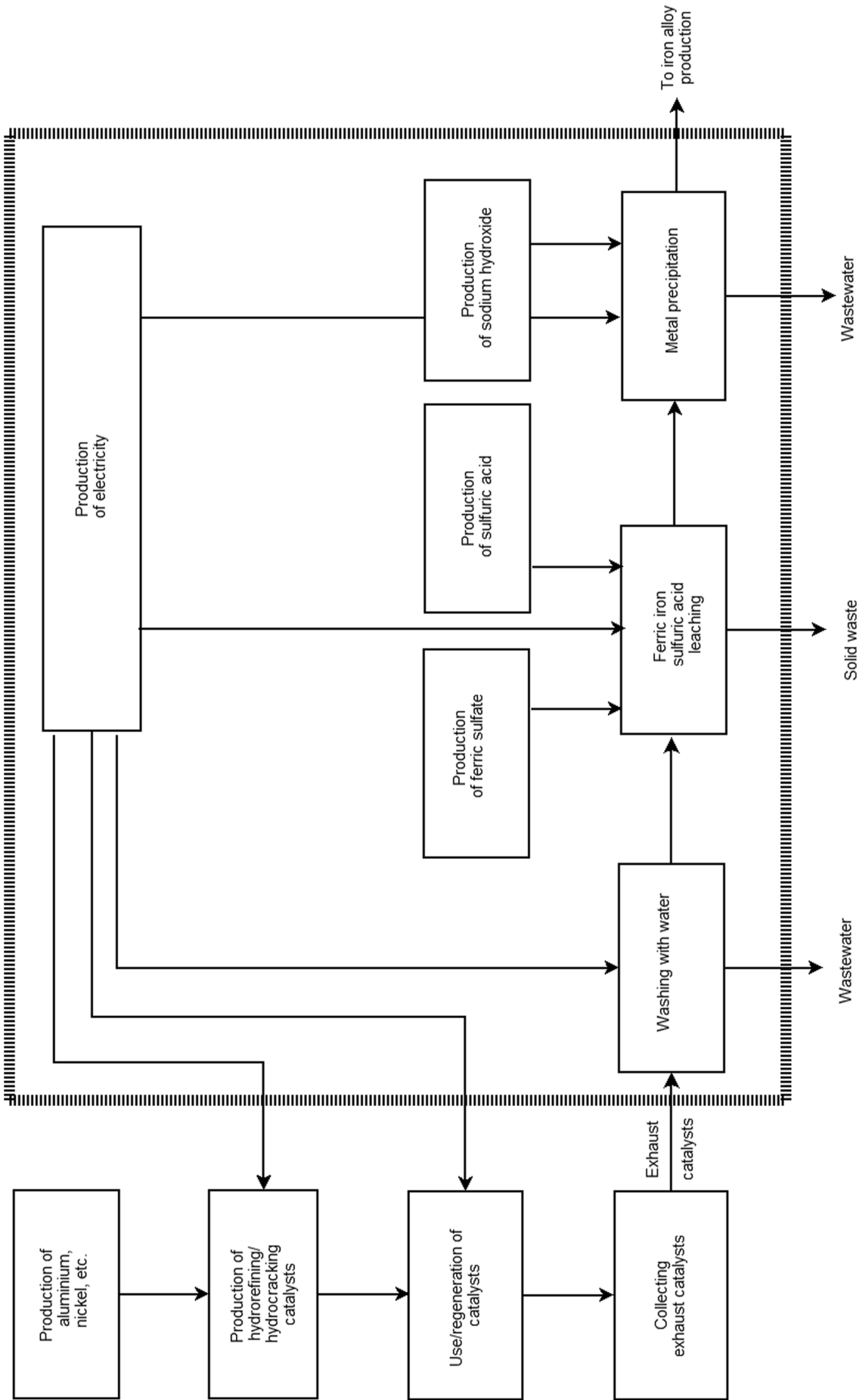


Figure 5. System boundaries for the life cycle analysis applied to ferric iron leaching in acid media. Processes addressed to purification of wastewater and management of solid waste were not included in the system boundaries.

Table 2. Estimated impacts in the selected environmental categories for ferric iron leaching in acid media (CML2001 – Nov. 09): functional unit 100 000 t end of life catalyst.

Impact category	Value	Unit
Abiotic depletion	19	t Sb-equiv.
Acidification potential	16	t SO ₂ -equiv.
Eutrophication potential	580	kg phosphate-equiv.
Freshwater aquatic ecotoxicity potential	10	t DCB-equiv.
Global warming potential	2100	t CO ₂ -equiv.
Human toxicity potential	66	t DCB-equiv.
Marine aquatic ecotoxicity potential	2.0 × 10 ⁵	t DCB-equiv.
Ozone layer depletion potential	6.2 × 10 ⁻²	kg R11-equiv.
Photochemical ozone creation potential	1	t ethene-equiv.
Terrestrial ecotoxicity potential	7	t DCB-equiv.

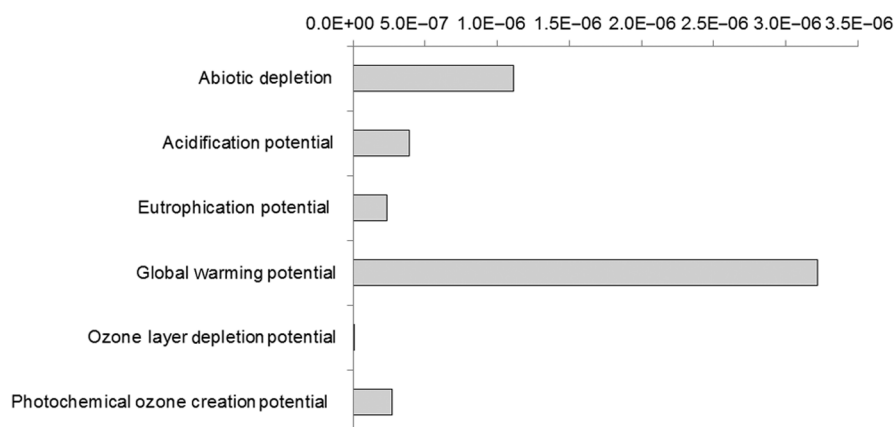


Figure 6. Relative environmental impacts of the ferric iron leaching in acid media, referred to Southern Europe territory (normalization to CML2001 Europe, weighting to CML2001 Experts IKP, Southern Europe): functional unit 100 000 t end of life catalyst.

Global Warming: 0.42 kg CO₂ kg⁻¹ metal

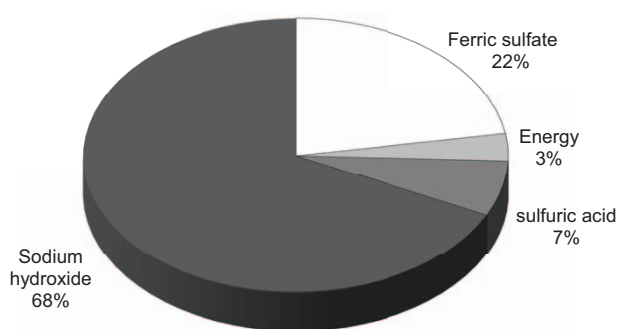


Figure 7. Main contributions in global warming potential of ferric iron leaching in acid media.

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