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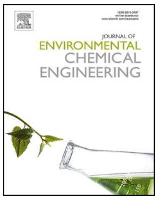

From exhaust to extraction: Evaluating car catalysts waste for a resilient economy

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ABSTRACT

Spent Automotive Catalytic Converters (SACC) are comprised of a support (a honeycomb ceramic structure) coated with a catalytic layer, where Platinum Group Elements (PGE), especially Pt and Pd, facilitate oxidation and reduction reactions to reduce hazardous emissions from car engines. This study provided information about various measurement procedures and principles for characterising SACC, revealing that SACC can release Potentially Toxic Elements (PTE) under environmental conditions. The SACC samples used primarily contain cordierite and moissanite, likely distinguishable upon visual inspection of waste piles. Unlike geological samples, the SACCs samples, considered as a homogeneous matrix, exhibit major elements such as Al, Si, Mg, and Ba, with minor elements including P, Na, Ca, Fe, Ti, Ce, and Zr, posing challenges for geoanalysts and environmental managers. Sequential extraction demonstrated high concentrations of PGE in the residual phase, especially Pt, Pd, and Rh. All other fractions, oxidisable, reducible and exchangeable, showed significant analytical recoveries of PTE such as Zn, Cu, and other trace elements. Watering bulk samples resulted in exceeded reference thresholds, with high Cd, Ni, and Zn, identifying SACC as a potentially hazardous materials. Toxicity tests on three aquatic species (*A. fischeri, R. subcapitata, and D. magna*) indicated both acute and chronic effects, further highlighting the need for proper waste management. The characterisation approach suggested here can help define the most appropriate SACC treatment demonstrating economic profit and ecological benefits.

1. Introduction

Spent Automotive Catalytic Converters (SACCs) pose potential health risks due to their content of Platinum Group Elements (PGE), Rare Earth Elements (REE), and other materials [2,25,41]. These components are crucial for catalytic reactions but can also be environmentally hazardous [24,47,49]. SACCs are unique anthropogenic materials that can contain oxides, particularly ceria and zirconia, used to favour catalytic reactions other than PGE. As per the state-of-the-art particulate filter technology of catalytic converters, cordierite ($Mg_2Al_4Si_5O_{18}$), silicon carbide (SiC), mullite (Al_2SiO_5), aluminium titanate (Al_2TiO_5), and alloy foam are the primary substrates used [16]. In current catalyses, especially Pt and Pd catalyse reduction and oxidation. REE at elevated concentrations are noted mainly because Ce doping controls oxygen excess/deficiency that would affect the conversion of NOx, *n*HC and CO along the substrate structure [34]. During catalyst's normal duty, a similar corrosion effect is on zirconia [36] and, at a low extent, other mineralogical phases. For example, a variation of Ce and Zr concentrations can indicate pollutants dispersal and engine usage.

SACC are anthropogenic materials that are not wasted in the environment due to their high economic value. The composition of SACCs varies depending on the source, and effective management is crucial given the shift towards electric/hybrid vehicles. Indeed, cleaner production chains are wanted not only to recover precious elements, such

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as, Pt and Pd, but also other valuable raw material contained in this waste category, such as REE, Al, Zn, Mn, Fe, Ti, and Zr, among others. In the context of SACCs recycling, existing business-to-business relationships, such as those between catalyst suppliers and oil refineries, facilitate high PGE recovery rates (nearly 100% collection rate). However, data and processing performances of non-centralised recycling paths remain nebulous. These recycling activities are based on aggressive extraction attacks or energy-demanding separation. Nonetheless, their profitability can grow because the economic potential of PGE extraction from SACCs will be up to 1.7 times higher in 2050 than today, according to Liu and Xu [27]. Material characterisation is of tremendous importance also using separation into fractions to explore bulk mineral behaviour for mineral beneficiation in metallurgy, especially when dealing with anthropogenic materials (e.g., [28]).

SACC's honeycomb-shaped structure of ceramics is capable of high resistance to temperature and elemental leaching, while, on top surfaces of the inner structure, a coated layer of catalysing metals can be more susceptible to leaching and environment modifications. Resulting environmental behaviour of SACCs is, therefore, complex, but it can be characterised by different types of tests that allow to classify the waste and conduct quality control for waste management or metallurgic treatment, therefore assessing the associated risk and potential. Important contributions come from Sequential Extraction Procedures (SEP) and other extractions that ground on dividing the total composition into fractions, simulating the impact of natural leaching processes. During geochemical SEP, a material is sequentially leached with different solutions, each selective for a given fraction, to explore the origin, mode of occurrence, biological and physicochemical availability, mobilisation, and transport of metals [33,37]. Bahaloo-Horeh and Mousavi [2] provided an indication for the environmental impact assessment of SACCs based on SEP results. Their SEP practically elucidates how minerals' relative proportion of SACC waste has an impact on elements' availability in the environment. Toxicology testing is another approach that finds tremendous importance in characterising contaminated materials, and most tests performed rely on survival statistics of particularly sensitive organisms. To date, there is no common way to characterise the environmental impact and ecotoxicity of SACCs. Ecotoxicology studies targeting SACC samples are missing in the scientific literature. However, the SACC bulk samples can be divided into fractions to characterise the mineral chemistry and element behaviour also with respect to ecotoxicology.

Considering the lack of environmentally friendly treatment options and a standardised method to classify and collect end-of-life car catalysts, this study aims to characterise SACCs from an Italian company, evaluate their environmental behaviour, and explore elemental recovery and waste management methods through separation into relevant fractions for the mineral chemistry and metallurgy. We considered SACCs as solid contaminated materials and wanted to shed light on chemical content, leachability, and potential toxicity, informing safer management and reuse of such anthropogenic material for a resilient economy. Insights into element behaviour and availability for ecological recycling purposes came from (1) characterising the starting SACC sample and its separates, (2) evaluating elemental fractionation in SACCs through replication of a modified SEP, defining useful indices for environmental protection such as Contamination Factor (CF), Global Contamination Factor (GCF) and Risk Assessment Code (RAC), and (3) assessing the leachability and ecotoxicity of SACC samples, following recognised guidelines for waste classification.

2. Materials and methods

2.1. Samples

A spent automotive catalytic converter (SACC) comprises an outer steel shell and a ceramic monolith coated with the PGE-rich catalytic layer. The SACCs from various car manufacturers used in this study refer to the ceramic support and its catalytic washcoat, already freed from the outer shell, provided by a private company authorised to collect end-of-life car catalysts. The primary sample was divided into subsamples based on colour and size for detailed analysis (Table 1). This differentiation, based on fieldwork concepts of Earth Science allows the evaluation of potential variances in elemental content and exposure risks. Sonication was chosen as a robust separation method to remove loose particles, which can be the main source of PTE and exposure risks. Upon visual inspection, around 600 g sample was carefully quartered to obtain "dark" (D-SACC) and "light" (L-SACC) coloured subsamples (Supplementary information, Fig. A.1). The colourimetric difference can depend on the original colour of the raw materials and ageing, so it can even relate to the amount of unburnt hydrocarbons and sulphur deposited [36]. In parallel, two fractions were separated using a

Table 1
Samples, preparation, and characterisation overview.

Label	Pre-treatment	Experimental	Target
RAW SACC	drying at 50 ± 5 °C, quartering method to get other aliquots	Environmental scanning electron microscopy coupled with energy dispersive spectrometer (E) SEM-EDS	Mineralogy, particle morphology
SONICATED SACC	RAW SACC subjected to sonication	Ditto	Ditto
BULK SACC	RAW SACC subjected to grinding on an agate mill to less than 63 µm particle size	X-ray diffraction XRD, X-ray fluorescence spectrometry XRF, Inductively coupled plasma mass spectrometry ICP-MS, rock magnetic analysis, leaching test, sequential extraction procedure (SEP), percentage of immobile organisms EC50	Mineralogy, Inorganic chemistry with comparison from reference material IMEP−11, magnetic properties, elemental leaching, toxicology
> 2 mm SACC	RAW SACC subjected to sieving on a 2 mm steel sieve, coarse material	XRD, XRF, ICP-MS, rock magnetic analysis, leaching test, percentage of immobile organisms EC50	Ditto
< 2 mm SACC	RAW SACC subjected to sieving on a 2 mm steel sieve, fine material	Ditto	Ditto
D-SACC	RAW SACC subjected to optical separation by colour (handpicking dark-coloured material) and a further quartering step	XRD, Scanning electron microscopy coupled with energy dispersive spectrometer SEM-EDS, XRF, ICP-MS, rock magnetic analysis, leaching test, sequential extraction procedure (SEP), percentage of immobile organisms EC50	Mineralogy, particle morphology, inorganic chemistry, magnetic properties, metal leaching, toxicology
L-SACC	RAW SACC subjected to optical separation by colour (handpicking of light-coloured material) and a further quartering step	Ditto	Ditto

threshold of 2 mm to evaluate coarse (> 2 mm) and fine (< 2 mm) samples of the same material to distinguish relevant grain size fractions (from 0 to −1 of Krumbein phi scale, virtually dividing sand size range from gravel and silt ones).

2.2. Chemical analysis

We employed X-Ray Fluorescence (XRF) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) to determine the elemental concentrations and partially solve challenges tied to matrix correction and interferences during routine analytical determination. XRF was used for total elemental analysis, while ICP-MS provided detailed quantification of PGEs, REEs, and other trace elements. Leaching solutions were analysed using ICP-MS to assess the release of elements under simulated and controlled environmental conditions. Details can be found in Supplementary Information B.

2.3. Other solid-earth-science methods

Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS) was used for morphological and qualitative chemical analysis. X-Ray Diffraction (XRD) identified major mineral phases, and magnetic analysis provided insights into magnetic properties and mineral composition. Details can be found in Supplementary Information C. Mass-specific magnetic susceptibility (χ), frequency-dependent susceptibility (χ_{FD}), and the mass-specific susceptibility of an induced Anhysteretic Remanent Magnetization (χ_{ARM}) can be evaluated by comparison with other anthropogenic materials (e.g., [14]).

2.4. Leaching

Leaching tests were conducted according to European test method EN 12457–2:2002, under deionised water leaching for 24 hours. We further explored an extended duration of 48 hours to assess another stability point on a longer application time. This approach ensures that the leaching behaviour of potentially metastable minerals occurring into many anthropogenic materials is thoroughly evaluated. At the beginning of the experiments, the chemical parameters of SACCs were pH 5.2 and 50 mV redox potential (Eh). Also, pH-dependent tests was carried out as a material characterisation tool (e.g., [1]) using European test method EN 14997:2015. Sequential Extraction Procedure (SEP) was performed on BULK-SACC, L-SACC, and D-SACC samples to evaluate metals partitioning of samples in specific environmental conditions [33,37]. Replication of a modified, three-step SEP followed the available literature on SACC waste category [2]. Namely, three-step SEP recovers carbonate and exchangeable fraction (*f1*) in step 1, a reducible fraction (*f2*) in step 2, and the oxidisable fraction likely bounded to organic matter and sulphides (*f3*) in step 3. The residue from step 3 represents the fraction of the elements bound to the refractory matrix (*f4*), calculated by difference. Other information can be found in Supplementary Information B.

In the SEP, the extractability percentage is defined according to the following equation:

$$Extractability\% = \frac{C_l \times V_l}{C_t \times V_t} \times 100 \tag{1}$$

where C_l and V_l are leachate's elemental concentration and volume and C_t and V_t are the solid SACCs' elemental concentration and volume, respectively. Contamination Factor (CF), Global Contamination Factor (GCF) and Risk Assessment Code (RAC) helped evaluate the environmental implication derived from SEP, as explained in Table 2.

Table 2
Calculation and classification of CF, GCF, and RAC indexes. In the formulas, f1-4 are the metal content in the different fractions from the SEP.

Index	Formula	Limit value	Classification
CF	$CF = \frac{f1 + f2 + f3}{f4}$	CF < 1	*Low contamination*
		1 < CF < 3	*Moderate contamination*
		3 < CF < 6	*Considerable contamination*
		6 < CF	*High contamination*
GCF	$GCF = \sum CF$	GCF < 8	*Low contamination*
		8 < GCF < 16	*Moderate contamination*
		16 < GCF < 32	*Considerable contamination*
		32 < GCF	*High contamination*
RAC	$RAC = \frac{f1}{total\ metal\ concentration} \times 100\%$	RAC < 1	*No risk*
		1 < RAC < 10	*Low risk*
		10 < RAC < 30	*Medium risk*
		30 < RAC < 50	*High risk*
		50 < RAC	*Very high risk*

2.5. Ecotoxicology

The effect of water leaching on SACCs was evaluated in compliance with the European recommendation (EN 12457–2:2002), so the leachates from test solutions were used to carry out the ecotoxicology experiments according to the procedures described in Tsiridis et al. [45]. Selected toxicity tests used different leachate concentrations after appropriate dilution. Three types of toxicity tests were performed (according to standard methods): luminescence inhibition [18], chronic algal growth inhibition [20], and acute immobilisation tests with *Daphnia magna* [19].Toxicity was expressed as the percentage of immobile organisms. In each kind of test, toxicity was expressed as the percentage of effect on the initial, fixed cell density (ca. 100 cells/ml) and, whenever possible, as EC_{50} along with 95 % confidence limit values. Additional details are in the Supplementary Information D. Finally, the toxicity unit (TU) was calculated as the ratio between the eluate toxicity performance of each test species and the corresponding EC_{50}, according to the formula:

$$TU = \left(\frac{1}{EC_{50}}\right) \times 100 \tag{2}$$

Results of TU were ranked into three main groups using conventional weight scores [26,32] to evaluate the toxicity of the SACC-leachates as follows: no acute toxicity ($TU < 0.4$), slight acute toxicity ($0.4 \leq TU < 1$), and acute toxicity ($1 \leq TU < 10$).

3. Results and discussions

3.1. Chemical composition of SACCs

Table 3 presents the chemical analysis results of SACC samples alongside literature ranges, while Table B.1 in the Supplementary Information provides available measurement results of duplicated solid samples. The bulk sample is rich in Al, Si, Mg, Ce, and Zr, mostly as oxides. The coarse-grained sample differs from the fine-grained one primarily in lower Al, P, Ce, Cr, Sr, Th, and Zn and higher Ba, Ca, K, La, As, Mo, and Zr. Additionally, elements like Pb, V, Ni, and Co are likely more prevalent in the coarse-grained fraction. XRF analysis of dark (D) and light (L) colour-separated fractions reveals notable compositional disparities, with Al, Mg, Ce, and Pb generally higher in L-SACC than D-SACC. The loss on ignition (LOI) values are globally low, likely due to the low content of carbonate minerals. Grain-size and colour separations were used to characterise the sample and inform mineral beneficiation in SACC's hydrometallurgy. Although SACCs are heterogeneous, the prevailing metals showed similarity with the samples used by Bahaloo-

Table 3

Total elemental composition of SACCs by XRF expressed in mg/kg of the element. Representative SACC sample (BULK), optical separates (L, D), and grain size fractions (>2 mm and <2 mm). Relative standard deviation (RSD) is provided on bulk sample as a percentage to confront the variability of literature observations. Literature range from [2,21,42,12,50,11,6,29,40,30,46,36,39,5,17,22]. The loss on ignition (LOI) values and magnetic parameters, such as susceptibility, χ, and susceptibility of ARM, χ_{ARM}, are appended.

	Bulk	%RSD	Optical Separate		Size Separate		Literature range	
	B		*L*	*D*	*>2 mm*	*<2 mm*	*min*	*max*
Al	233300	28	250435	28072	288078	311577	85737	204400
As	21	33	26	5.9	8.8	17		
Ba	5144	27	6230	279	2778	4248	4389	15226
Br	9.4	37	8.9	4.1	4.0	12		
Ca	918	55	677	1119	1740	2445	229	5918
Ce	20900	29	38762	1069	5327	8260	24	64832
Co	12	31	18	790	2.2	1		
Cr	62	35	77	71	68	80		
Cs	241	18	411	115	159	239		
Cu	87	29	153	35	67	73		
Fe	1715	27	1657	1506	2510	2393	1658	10492
Ga	40	29	23	4.9	36	39		
Hf	409	37	451	184	187	429		
K	397	60	482	41	628	1202	66	765
La	503	29	1051	87	1482	2646	1978	28735
Mg	53900	27	53431	1357	40424	31901	271	58400
Mn	90	28	91	75	99	102	15	21840
Mo	68	48	57	36	66	131		
Na	1472	29	1845	145	3328	4686	705	1620
Nb	17	27	8.1	4.0	12	14		
Ni	12	31	12	250	3.9	<1		
P	2343	38	2481	384	3356	3675		
Pb	180	27	327	4.5	53	45		
Rb	25	22	12	11	17	29		
S	<1	35	3000	157	<1	<1		
Sc	8.2	32	4.4	6.4	1	<1		
Si	178400	28	152378	430025	157393	128869	608	149800
Sr	1438	30	56	44	40	71		
Th	235	29	100	90	157	269		
Ti	4759	29	2343	235	2075	1657	378	4196
U	1.1	27	2.5	5.2	<1	<1		
V	115	30	92	127	66	57		
W	306	50	431	6246	<1	<1		
Zn	1030	27	833	120	723	1195	201	4500
Zr	18200	26	17559	7551	7891	17382	44	111786
LOI [%]	0.065	68	0.02	0.004	0.013	0.038		
Mass [g]	8.189		3.479	1.183	5.717	2.864		
χ [10^{-6} m^3/kg]	22.226		31.046	17.759	23.699	10.824		
χ_{ARM} [$10^{-2}A/m$]	46.859		64.616	88.158	42.481	21.726		

Horeh and Mousavi [2]. In particular, the chemical composition of L-SACC is similar, testifying that mineralogical phases are also comparable. Table 3 also reports the susceptibility values, χ and χ_{ARM}, which are relatively low. Low susceptibility typically relates to the prevailing presence of a diamagnetic component such as ceramics, which represents the main support in car catalysts (with low-susceptibility hematite likely being the predominant Fe oxide mineral). Rock magnetic analysis reveals a scarce presence of magnetic minerals. Elevated values of χ and χ_{ARM} may be attributed to Fe particles in the soot. A good correlation of χ values with Fe, Mg, and Ti concentrations can be noted, likely identifying stoichiometric and non-stoichiometric magnetic minerals. There are no references in the literature for comparison, but defining such magnetic parameters can be useful in quickly identifying secondary raw materials usable as industrial magnets or in the semiconductor industry.

The chemical composition of minor and trace elements in SACCs reveals inherent incompatibility, evident from the chondrite-normalised REE plot (Supplementary Information, Figure B.1). The heavy REE (HREE) in SACCs tend to increase, and the light REE (LREE) have an irregular trend, and this trend does not recall geogenic samples. The observed increase in HREE can be due to the origin of raw materials, e.g., for the Zr production from zircon mineral, which typically shows HREE enriched patterns. The peak in Ce mostly contributed at identifying SACC as anthropogenic, since Ce oxide has been added to the matrix, and, if low purity ceria was added, the LREE are also enriched, in particular La. The sum of REE plus Sc and Y ($\sum$REY) ranges 1–3.8 g/100 g in SACCs samples, with the far most abundant Ce (2.4 g/100 g on average) followed by La. Eu showed a positive anomaly likely due to the high Ba content. D-SACC showed lowest Ba and no positive Eu anomaly. While the Eu anomaly can be an isobaric interference related to Ba, ceria impurities can be a reason for overall LREE enrichment and Tb anomaly in REE chondrite-normalised pattern of Figure B.1. Although of lower importance compared to LREE, Ce and La, such an impurity can translate in a Tb grade of about 10 kg/t in SACC waste category. From a geochemical perspective, these irregular trends highlight that, if SACC are exposed to environmental weathering, elements leached from SACC can superimpose geogenic provenance signals of elements in the environment. Therefore, the anthropogenic signals of SACCs should be regarded carefully to minimise the potential environmental impact when SACCs are produced and managed. In parallel, the variable presence of elemental impurities influences the recovery efficiency of wanted resources during SACC recycling with current processing methods. Fig. 1 illustrates a plot of logarithmic concentrations of selected elements normalised to the average upper continental crust, providing insights into the environmental and economic significance of SACCs. In other words, Fig. 1 overviews elemental abundances in SACCs, including optical separates, compared to a typical geogenic value, highlighting their relevance as an economic resource or source of PTE contamination. Negative and positive values signify depletion and enrichment relative

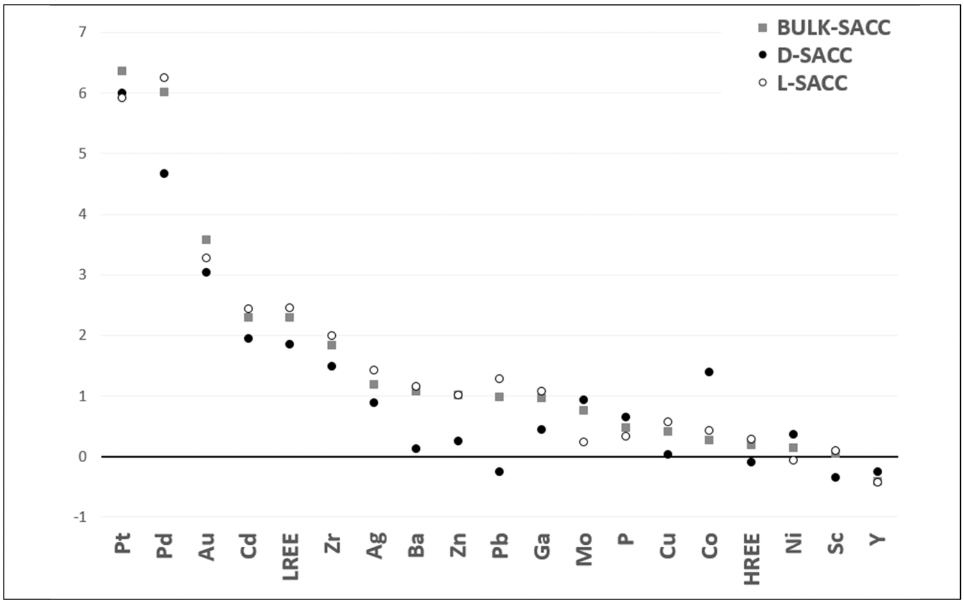

Fig. 1. Enrichment compared to the Earth's crust of a selection of elements and the corresponding SACC samples (Bulk, D, and L). In the y-axis, the enrichment factor is calculated using Upper Continental Crust-normalised and log-transformed ICP-MS concentration data.

to the crust, respectively, with variations spanning one order of magnitude per scale unit on the ordinate. Positive values underscore the anthropic contribution compared to an average geogenic sample. Several elements, including precious elements such as Pt and Pd, are enriched by up to six orders of magnitude, categorising SACCs as "precious waste" for urban mining [13,43]. Notably, SACCs contain Pt and Pd up to 1700 mg/kg, while typical PGE ores have a total content of less than 10 mg/kg. PTE such as Cd, Ba, Zn, Pb, and others are relatively high in the bulk samples and separated subsamples (Table 3, Fig. 1).

3.2. *Morphology and mineralogy of SACCs*

According to the XRD analysis, the raw SACC and its sonicated counterpart exhibit a cordierite matrix (Fig. 2), with the diffraction pattern of cordierite ($Mg_2Si_5Al_4O_{18}$) dominating as a major mineralogical phase. The raw SACC sample after sonication maintains a clear diffraction pattern of cordierite, but a few weak peaks suggest the presence of a zeolite like ZMS-5. Zeolite coatings, applied via methods such as slurry deposition followed by thermal stabilisation or direct hydrothermal synthesis, are commonly used for the selective catalytic reduction of NOx from automobile exhaust [48]. Cordierite emerges as the predominant ceramic substrate, likely due to variations in the composition of different end-of-life catalytic converters. Other ceramic substrates may also be present as minor phases in the XRD analysis, but bulk SACC likely leaches metals according to the chemical behaviour of predominant cordierites coupled to structures of the catalytic wash-coat.

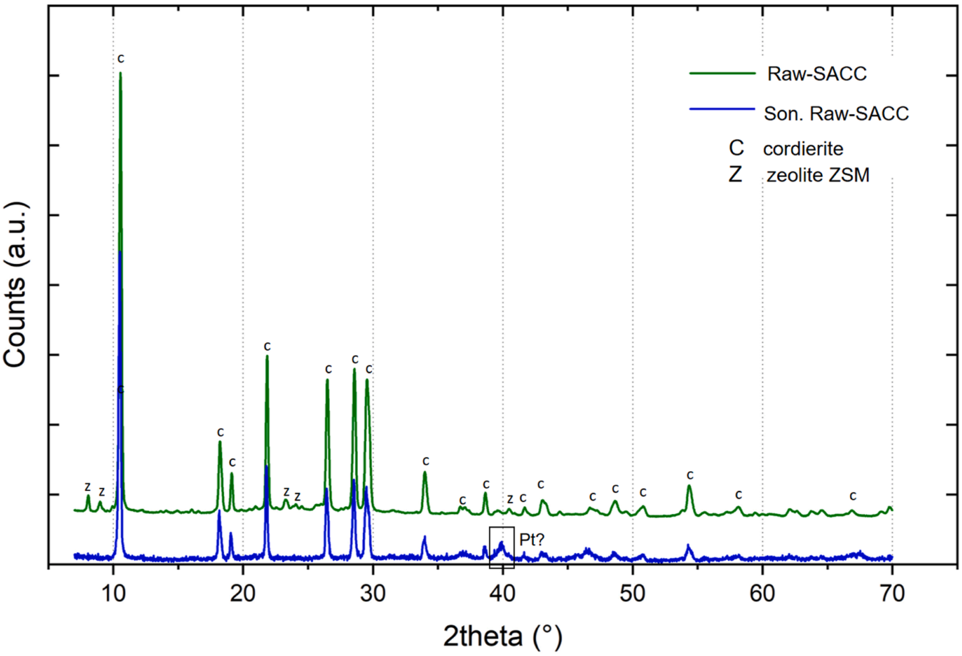

Fig. 2. XRD analysis Raw-SACC (green line) vs Raw-SACC after sonication (blue line). C, cordierite, and Z, zeolite are the main minerals identified by Open Crystallography Database search-matching procedures; some PGE-bearing minerals can be present (Pt?).

Notably, peaks of low intensity around 40° 2Θ indicate the presence of Pt metal, particularly evident in the sonicated sample. The sonication freed the raw samples from small particle aggregation and other surface adhesions that can constitute a noise (e.g., peaks' overlap and broadening) in the diffractograms of XRD analysis. Therefore, the Pt- and other PGE-minerals are recognisable, within the analytical resolution, compared to the non-sonicated SACC. At the same time, it can be said that sonication suites a mineral beneficiation strategy. A marker in Fig. 2 highlights this clustering of peaks, confirming a high PGE content. The mineralogical analysis reveals various phases characterising the matrix of SACCs, with differences in trace minerals possibly attributed to the presence of different catalytic layers and substrates in the collected waste. In the Supplementary Information, Figures C.1 C.2, and C.3 report the raw XRD patterns of D-SACC and L-SACC and their SEM analysis for comparison. Detecting major and other minerals can contribute to correct resource assessment in industrial minerals recycling. However, it remains to be seen if SACC mineralogical assemblages can enhance current SACC processing and recovery.

The microscopic observation reveals almost entirely cavity-filled honeycomb structures without sonication (Fig. 3, Figure C.3). Elements like O, Si, Al, Mg, and Ca are easily detected as major elements on EDS spectra (Figure C.2). Ce and Zr can be detectable, especially in the sonicated sample. Some areas of the untreated sample show loadings of Fe and Zn as loose phase particles (see SEM micrographs and their EDS analysis in Figure C.3 and Table C.1, respectively), likely tied to the fuel impurities rather than to the ceramic support or the catalytic wash-coat. Indeed, Fe and Zn can be present as metallic elements or, most likely, their oxides in the hollow part of the honeycomb structure where particles, including soot, agglomerate. Loose grains or clumping of loose grains can contain Pt, but the readable peak is below the instrumental error. Phases with high Pt concentrations are found in the honeycomb support walls (washcoat inheritance) more frequently in the sonicated samples than in the raw ones. This suggests that a relatively simple action like removing the soot and minor aggregates improves metal selection toward better Pt recovery. From an environmental perspective, handling SACC after minimal cleaning can decrease the inhalation risk of small particles containing PTE.

The diffraction patterns obtained for L-SACC and D-SACC (Fig. 4) reveal distinct ceramic substrates: cordierite is the predominant diffraction pattern in L-SACC, while D-SACC primarily consists of moissanite (SiC), another common substrate used in automotive catalysts [16]. Both samples, especially L-SACC, exhibit peaks of Ce oxide, along with small peaks possibly attributed to sphalerite (ZnS) in D-SACC and hematite (Fe_2O_3) in L-SACC. In the SEM/EDS analysis of powdered sample stubs, distinct morphology and composition are observed for D-SACC and L-SACC samples (Figure C.4 of Supplementary Information). L-SACC displays flattened morphologies with fractures and irregular shapes such as needles, angular grains, and loose particles, often characterised by high brightness. In contrast, D-SACC exhibits irregularly rounded morphologies with occasional Ce-rich particles. Brightness differences readily distinguish acicular forms and loose grains, primarily containing Al and Si in L-SACC, while irregular, angular forms may be rich in Fe, Pt, and Ce. Rare bright particles rich in Ti may appear needle-shaped or irregular. It is hypothesised that the primary catalytic support in the sampled stockpile is cordierite, followed by aluminium silicates and silicon carbides.

3.3. Leaching assessment of SACCs

The impact of water washing on SACCs was assessed to understand their environmental behaviour when exposed to rainwater, aligning with European recommendation EN 12457–2. Even though this waste is generally handled with care and not left in the environment mainly due to economic reasons, mishandling SACC waste can lead to groundwater and soil contamination. Water washing with deionised water effectively removes easily soluble salts, occasionally enhancing leaching efficiency during metallurgical extraction by eliminating water-soluble salt impurities. Due to their water solubility, this process can eliminate chlorides, amphoteric metals, and alkali earth metal salts. In SACC samples' leaching test, elements like Ca, Mg, K, Na, Ba, and Sr are readily dissolved, with Ca, Ba, and K almost completely dissolved. According to standard leaching tests (24 h watering at ambient temperature, Table 4),

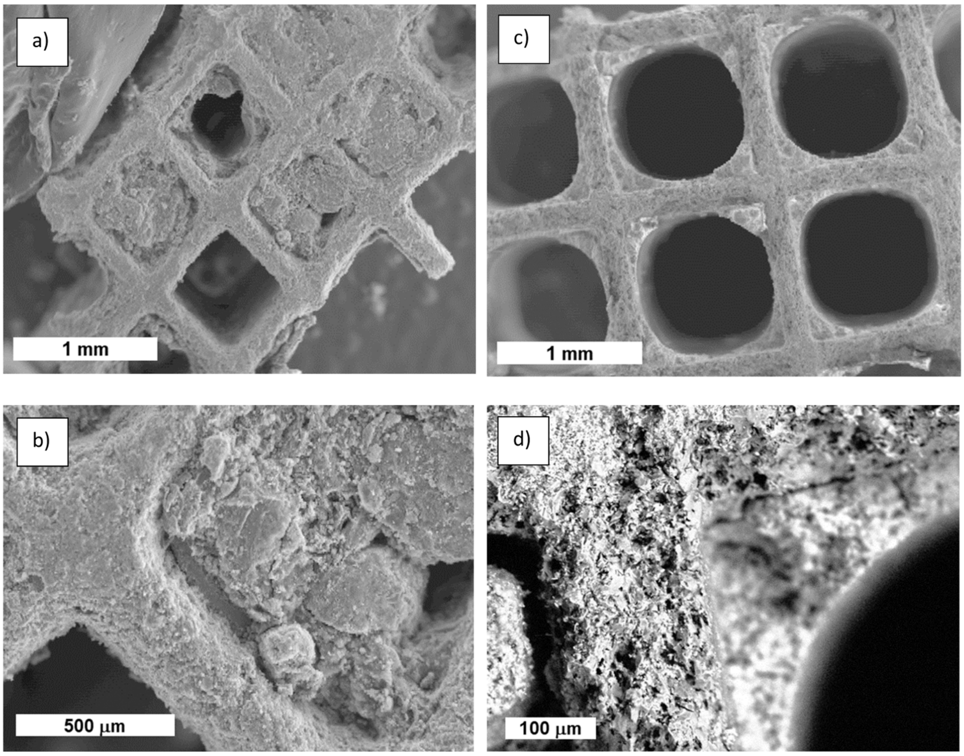

Fig. 3. SEM images of raw SACC (a, b) and its sonicated counterpart (c, d). Jeol 6400 operating conditions were 20 kV and 1.2 mA current and 1 mm beam diameter.

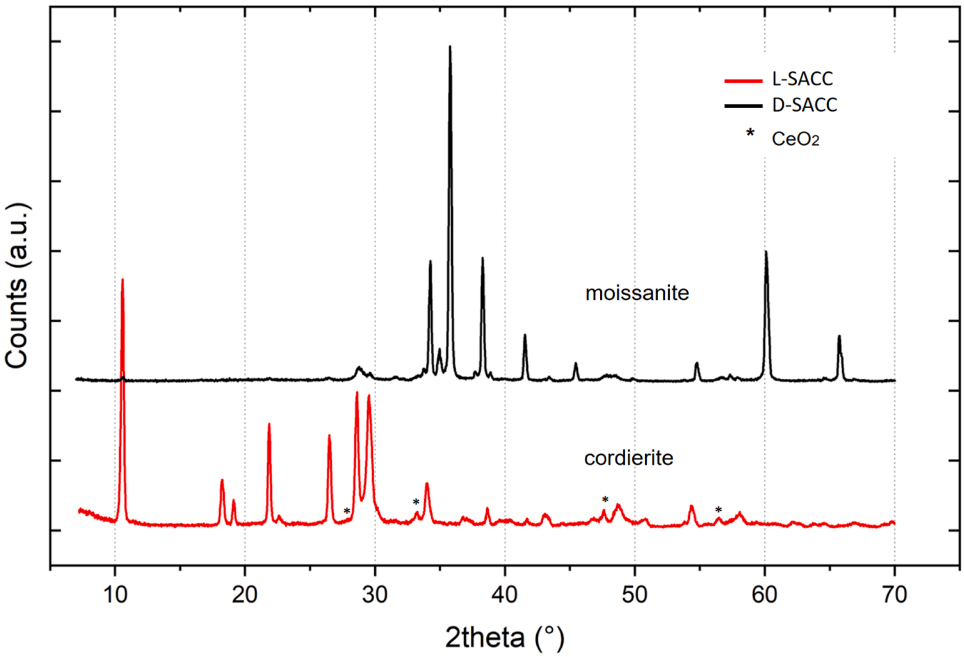

Fig. 4. XRD analysis of L-SACC (red line) vs D-SACC (black line). Cordierite and moissanite are the main minerals identified by Open Crystallography Database search-matching procedures in L-SACC and D-SACC, respectively. The position of CeO_2 diffraction lines is marked with an asterisk.

Table 4
Leaching test after 24 and 48 hours compared with the regulatory thresholds of Italian decree 186/2006 [15] in the standard test of 24 hours. Chemical concentrations are expressed in ug L-1; DL is the detection limit calculated based on calibration blanks; bdl means below the detection limit; underlined values exceed the regulatory limit.

Determinant	DL	After 24 h	After 48 h	Regulatory threshold
As	0.34	bdl	bdl	50
Ba	0.27	433	787	1000
Cd	0.59	7.6	51.6	5
Cr	0.16	7	15	50
Co	0.16	2.8	9.6	250
Cu	0.61	19	33	50
Pb	0.80	2.8	6.4	50
Ni	0.38	87	197	10
Se	0.45	0.6	1.9	10
V	6.83	0.16	37	250
Zn	2.34	2740	5159	3000
pH	-	5.2	5.2	5.5 – 12.0

Cd and Ni concentrations exceed regulatory thresholds, and the pH falls slightly below the limit range (e.g. for Italian reference see [15]), so SACC must be regarded as a potentially contaminated material and follow appropriate treatments. In 24 hours, the pH did not vary substantially from the standard conditions. Leaching continues after 24 hours, with significant dissolution of Zn and Cd observed (Table 4; after 48 h), so SACC ageing should be limited. The water solubility of representative SACCs for selected analytes is provided in Table B.2.

The leachate analysis over time provided insights into the leaching behaviour of elements in L-SACC and D-SACC samples, with concentrations measured after 24 and 48 hours (Fig. 5). Al, Mg, Pb, Zn, and many REEs initially exhibited higher solubility in L-SACC, with slight peaks at 6 h and 24 h. However, a significant decrease was observed in L-SACC from 6 hours onwards, while leaching from D-SACC generally increased over time. Notably, Al and Mg had higher initial concentrations in L-SACC than D-SACC. Conversely, Al and REE leaching from D-SACC showed an increasing trend from 20 hours until the end of the experiment. Regarding PGEs, Pd concentration in the leachate was low and peaked at 4 hours, while Pt solubility appeared higher in D-SACC leaching. The leaching trends of L-SACC were similar to bulk SACC, indicating the presence of similar minerals. However, exceptions were noted for Pt, La, and Gd, whose solubility in D-SACC increased after 24 hours, resembling bulk SACC of the standard leaching experiments at 24 hours (CC in Fig. 5).

The pH-dependent leaching is used to evaluate metal solubility across various pH values tested. In acidic conditions promoted by HCl, the leaching efficiency of Pt and Pd is significant, as corroborated elsewhere [24], due to the formation of hexachloro complexes. Fig. 6 shows pH-dependent leaching of BULK-SACC where most elements exhibit higher leaching at acidic pH values, notably Al, Mg, Pb, Zn, and Pt, while Pd begins to solubilise at a pH of 3. Al, Zn, Pb, and Pt demonstrate increased mobility at low pH values and minimal mobilisation at alkaline or circumneutral conditions. Both Al and Pt exhibit high concentrations at extremely high and low pH set points, indicating an amphoteric behaviour, which is apparent for Al only, forming aluminate with water at 9 pH. Additionally, Mg, Zn, Pb, and many REEs display a similar trend with high solubility at pH levels below six, followed by a slight increase and subsequent decrease as pH increases, forming insoluble hydroxides. Furthermore, Fig. 6 underscores the significant mobility of Mg, Zn, and Pb across each pH interval. The Acid and Base Neutralization Capacity (ACN and BNC) determinations are presented as Supplementary Information (Fig. B.2). Endmembers ACN3 and BNC9 are used throughout the tests because they are considered industrially relevant conditions for SACC treatment to determine the acid or base demand. Acid and base demand equals 1.6 mmol H^+g^{-1} (using HCl) and 1.05 mmol OH^-g^{-1} (using KOH), respectively.

According to the SEP analysis summarised in Fig. 7, there are notable differences between binding fractions. Cations like Pb, Pd, Pt, Ce, and La exhibit the highest leaching from L-SACC, particularly in the presence of hydroxylamine hydrochloride (step 2#). Conversely, Al and Mg display a higher leaching rate from D-SACC in step 2#, while Pt, Zn, and some REE are effectively extracted with acetic acid (step 1#). Additionally, oxidising conditions are required to leach approximately an additional 15 % of the Zn present. The low mobilisation of Al in L-SACC confirms the presence of refractory ceramic phases as the primary representative of SACCs support type, where elements related to the residual fraction are likely in aluminosilicates. The extractability percentage of Ca in the

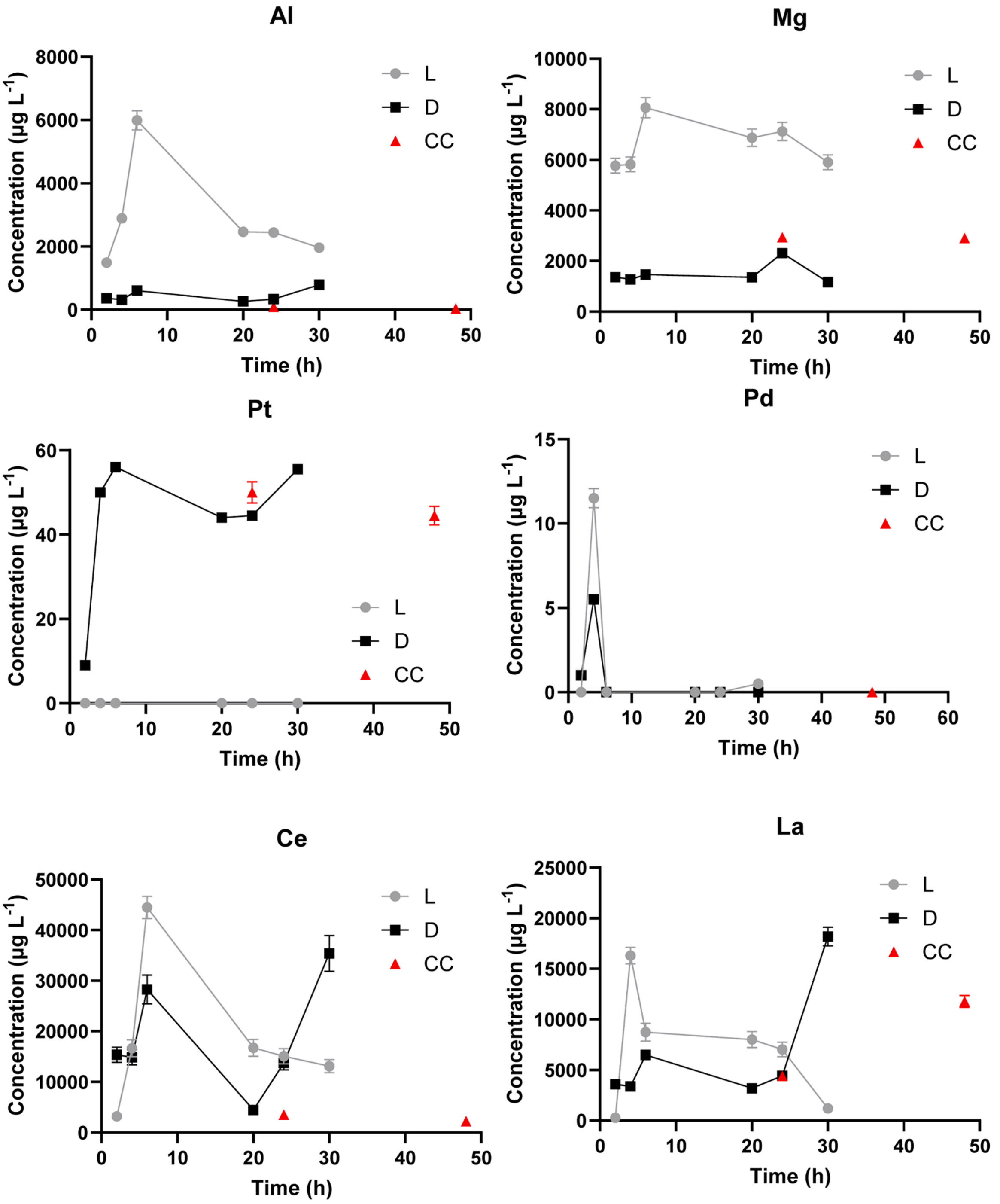

Fig. 5. Time-dependent leaching test of D-SACC and L-SACC samples, with elemental concentration in µg L^{-1}. The leaching of the BULK-SACC after 24 and 48 h is reported as a reference (CC, see Supplementary Tab. B.2).

exchangeable fraction decreases from approximately 75 % in bulk-SACC to nearly zero in D-SACC, where Ca partitions mainly in a stable residual fraction or in the reducible fraction. We infer that the exchangeable fraction may overlap with the reducible one. While most ions of concern leached almost completely after the acid-soluble step (3#), the influence of the redox potential may be minimal in subsequent steps. Although some similarities exist when using the same SEP on SACCs [2], the results of the SEP can be misleading, emphasising the need to define a standardised procedure for this waste. Using another reagent, such as NaOCl, can provide stronger oxidising conditions (with relatively less H$^+$) in f2 to improve overall results.

However, elements in the residual fraction show minimal mobilisation under typical environmental conditions, and the difference in mobilisation is mainly tied to the monolithic ceramics used as the raw material. Generally, SEP results can be crucial considering that the type of substrate can significantly impact metallurgical processes or minimise environmental impacts. As their lifecycle ends, often shortened by stringent regulations, SACCs are collected separately and undergo specific treatments for Pt-Pd recovery, particularly in regions prioritising economic gains over potential environmental risks. The calculated CF, GCF, and RAC (%) values for several elements are reported in Table B.3. Most elements showed CF < 1, indicating low or no contamination. However, Ca, Ba, Cd, Cr, and La may pose a higher degree of contamination. The GCF value suggests that B-SACC is the riskiest material

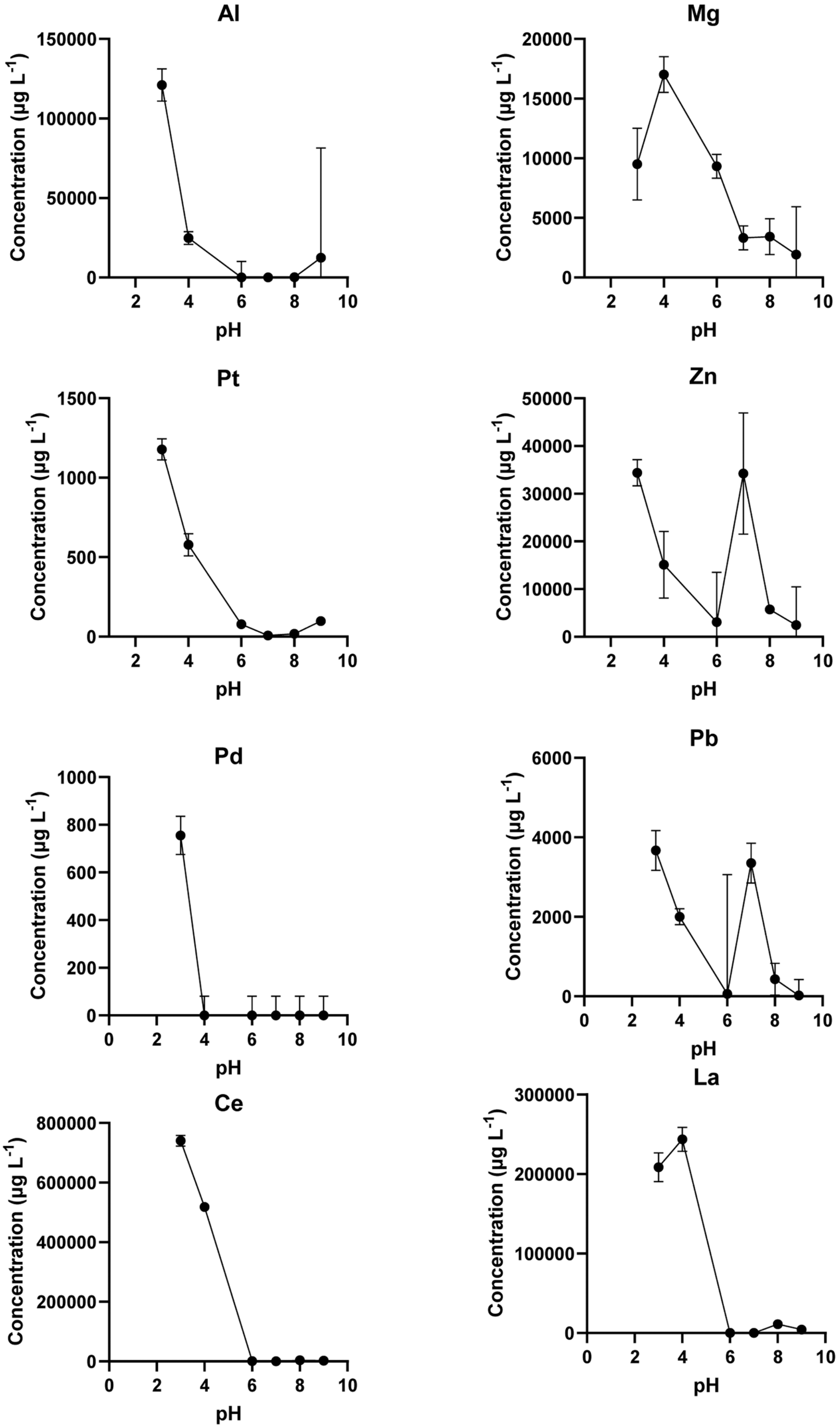

Fig. 6. pH-dependent leaching test on B-SACC samples, with elemental concentration in μg L^{-1}.

compared to the optical separate samples (D-SACC and L-SACC), indicating that mixing different technology types of car catalysts results in a higher degree of contamination. According to the RAC percentages (Table B.3), releases of Ca, Cd, Nd, and Zn in B-SACC, La, Nd, Sm, and Zn in D-SACC, and Cu, Ni, and Zn in L-SACC, are very likely hazardous to any environmental matrix.

From the perspective of environmental protection, recovery process based on capture, enrichment, and final separation by electrodeposition

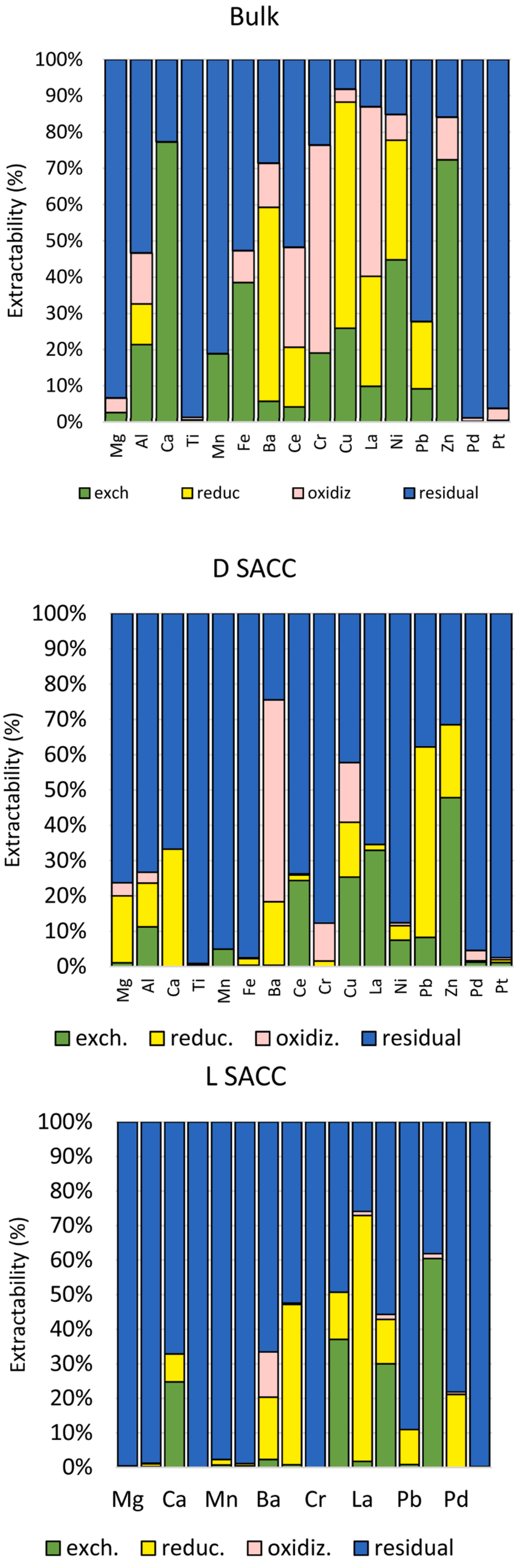

Fig. 7. SEP elements distribution of a) bulk-SACC, b) D-SACC, and c) L-SACC. Exch means exchangeable, reduc means reducible, oxidiz means oxidisable.

is the best way to extract PGE from SACC [27]. Existing research on SACC management and recovery may be enhanced by new biotechnological solutions [21], where fervour is on developing advanced biological processes in new hybrid SACC treatment to make, for instance, actions like oxidisation ecologically.

3.4. Ecotoxicology testing

To evaluate the potential risks associated with managing SACCs, ecotoxicity tests were conducted on appropriate leaching extracts from the five samples BULK, L, D, < 2 mm, and > 2 mm -SACC.

Fig. 8 summarises toxicity data of SACC leachates on three organisms, *A. fischeri*, *R. subcapitata*, and *D. magna,* selected to represent three trophic levels in line with EU Directive 2008/98/EC [10]. The results show that the toxicity of undiluted SACC leachates on *A. fischeri* and *D. magna* was higher than that on *R. subcapitata*. The undiluted B-SACC leachate had the highest toxicity, which resulted in 100 % toxicity for *A. fischeri* and *D. magna*. The undiluted leachates from D-SACC and L-SACC samples also showed relatively high toxicity. Specifically, the D-SACC leachate resulted in 67.54 % and 50.5 % toxicity for *A. fischeri* and *R. subcapitata*, respectively, while the L-SACC leachate showed 47.64 % and 53.34 % toxicity for *A. fischeri* and *R. subcapitata*, respectively. The leachate from fine-sized SACC (< 2 mm) exhibited significant toxicity on *R. subcapitata* only, whereas that from the coarse-sized SACC (>2 mm) had low toxicity on all three organisms. This suggests that monolithic materials, such as the coarse-sized SACC, may pose less risk to the environment and living organisms than their fine-sized counterparts. Based on the results, EC_{50} values could only be calculated for the Bulk, D, and L samples, as the < 2 mm and > 2 mm fractions of SACC showed insignificant toxicity to any of the tested species.

The leachate from bulk samples (B-SACC) had the lowest EC_{50} value of 33.4 % on *R. subcapitata*, while 94.9 % and 89.7 % for D-SACC and L-SACC leachates, respectively. Similarly, for *D. magna*, the B-SACC leachate showed the lowest EC_{50} value of 21.7 %, while the D-SACC and L-SACC leachates had higher EC_{50} values of 91.28 % and >100 %, respectively. For *A. fischeri*, the B-SACC leachate had the lowest EC_{50} value of 18.0 %, followed by D-SACC ($EC_{50} = 42.9$ %) and L-SACC (EC_{50} = 80.34 %) leachates.

A. fischeri showed the lowest EC_{50} values, indicating a higher sensitivity to the SACC eluates than the other two species. *D. magna* also showed relatively low EC_{50} values, indicating moderate sensitivity. *R. subcapitata* had the highest EC_{50} values, suggesting it was the least

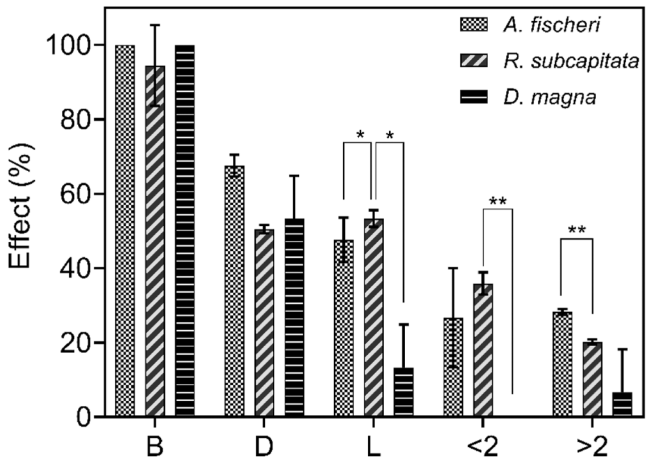

Fig. 8. Toxicity assessment of SACC leachate data across three organisms: A. fischeri (exposure duration: 0.5 hours), D. magna (24 hours), and R. subcapitata (72 hours). Asterisks denote statistically significant differences in toxicity as determined by Tukey's post-hoc test, with $p < 0.05$ indicating a significant difference (*), and $p < 0.01$ indicating a highly significant difference (**).

sensitive species to the eluates among the tested organisms. The TU approach further supported the results of the ecotoxicity tests, confirming that SACC leachates can show acute toxicity and adverse effects on aquatic biota (Table 5).

The observed variability in toxicity among the tested species can be attributed to the differences in the chemical speciation of PTE in the powders, which affects their bioavailability. As a result, the uptake of these elements may differ among biological species, leading to varying degrees of toxicity. A direct correlation was observed between the elemental concentrations in the leachates and the toxic effects on each test organism. Statistical analyses on toxicity experimental data, in particular, a principal component analysis (Supplementary Information D) found that elements like Cd, Cr, Cu, Li, Pb, and Zn were correlated to microorganisms' toxicity, with Zn contributing the most. The toxic synergy of these elements has been frequently observed [7], but predicting their effects is complex and depends on a wide range of parameters (e.g., [4]). For example, most Cu-Zn ratios displayed synergistic effects, as demonstrated in studies where the presence of Cu significantly enhanced the toxicity of Zn [31]. This is likely due to altered speciation and bioavailability in the presence of these metals, which can lead to increased oxidative stress in target organisms [9]. The same statistics confirmed that harmful effects should not be attributed to one specific element but are likely influenced by the combined effects of various PTE [38]. Factors such as pH and conductivity can significantly influence leachate ecotoxicity [8]. For example, the 1:1 combination of Cu and Zn concentrations often resulted in different effects compared to other ratios. Previous studies have also demonstrated that the simultaneous availability of Zn and Cd can enhance toxic effects, as seen on algal cell growth [3]. Supposedly, the sensitivity of the bacteria is attributed to the overarching presence of Zn in the SACC leachate (Table 4). Zn may have facilitated the uptake of Pb in *D. magna* [23], which has been shown to disrupt Na^+ and Ca^{2+} homeostasis [35]. Previous studies showed similar results on *A. fischeri* [44]. Pt and Pd played a role eventually in SACC toxicity. All tested species seem correlating with PGE such as Pt (Figure D.1). It would be helpful to determine the "no observable adverse effect level" (NOAEL) concentrations to establish a threshold leaching value and appropriate handling procedures for these materials. Given the complexity of elemental interactions and their environmental effects, further studies are needed to determine the "no observable adverse effect level" (NOAEL) concentrations of these PTEs in SACC leachates. Additionally, expanding the range of tested species and improving test representativeness will be crucial, considering the heterogeneity of anthropogenic materials like SACCs.

4. Conclusions

An appropriate treatment for Spent Automotive Catalytic Converters (SACC) will eventually depend on socio-economic pathways by decision-makers, and comparative and reference data are necessary to address the recycling of PGE, REE, and secondary raw materials from SACC waste category. This study characterised SACC samples, also using their separate fractions, to explore elemental composition, behaviour in the environment, and ecotoxicology.

Table 5

EC_{50} values and confidence intervals (95 % CI) for Bulk-, D-, and L-SACC leachates, assessed across different organisms. Toxic Unit (TU) scores indicate the level of toxicity, categorized as follows: no acute toxicity ($TU < 0.4$), slight acute toxicity ($0.4 \le TU < 1$), and acute toxicity ($1 \le TU < 10$).

Organism	Sample	TU	EC_{50} (95 % CI)	Toxicity
A. fischeri	**Bulk**	5.5	18.0 (17.2–18.9)	**Acute toxicity**
	D	2.3	42.9 (32.4–59.7)	**Acute toxicity**
	L	1.2	80.3 (61.9–92.3)	**Acute toxicity**
R. subcapitata	**Bulk**	2.9	33.4 (24.8–44.9)	**Acute toxicity**
	D	1.0	94.9 (87.1–105.0)	**Acute toxicity**
	L	1.11	89.7(80.6–102.2	**Acute toxicity**
D. magna	**Bulk**	4.5	21.8 (20.1–23.46)	**Acute toxicity**
	D	1.1	91.3 (79.9–105.8)	**Acute toxicity**
	L	< 0.4	>100	No Acute toxicity

- SACC contain valuable Platinum Group Elements (PGE) like Pt and Pd, and Rare Earth Elements (REE), especially Ce, making them important for urban mining compared to other secondary sources. SACCs represent a significant source of REE and PGE (up to 27 $g \cdot kg^{-1}$ and 5 $g \cdot kg^{-1}$, respectively). In tested batch conditions, colour separation can distinguish moissanite-rich and cordierite-rich SACCs and the size separation can enrich elemental fractions in the solid sample (Al, P, Ce, Cr, Sr, Th, and Zn in fine-grained samples and Ba, Ca, K, La, As, Mo, and Zr in coarse-grained ones).
- Elemental mobility tests under simulated conditions confirmed that SACC can release Potentially Toxic Elements (PTE), such as Ba, Cd, Cu, Pb, Pt, Mo, REE, and Zn, at high concentrations to be hazardous to any environmental matrix. Elemental leaching trends between grain size and colour separation were similar, according to the presence of similar minerals in the separated samples. The results of a sequential extraction procedure (SEP) on SACC indicated that hardly soluble phases may hinder the total recovery of valuable elements such as Mg, Mn, Ce, and Pd, other than Pt. Also, SEP suggested that the bulk sample is the riskiest material compared to separate fractions, pointing to rapid separation/treatments to prevent contaminant releases.
- The waste heterogeneity and variability in the leaching and concentration of PTE complicated the assessment of SACCs' toxicity potential. All SACC samples exhibited high toxicity to three significant species of aquatic microbiota: *A. fischeri, R. subcapitata, and D. magna*. However, causes and mechanisms of toxicity should be clarified to assess such materials' eco-compatibility. NOAEL (No Observable Adverse Effect Level) is suggested as a decision-making tool.

The significant mobilization of toxic elements under various conditions is concerning, especially considering the projected increase in SACC quantities and the current treatment options. Multi-angle observations from a use-case basis employing sequential extraction, leaching, and toxicity tests can contribute to the discovery of appropriate test environments for new technology, such as biotechnologies, thus providing room to advance knowledge and industrial transfer incrementally. Optimising the recycling route through such studies is crucial as soon as these material flows can be identified and sampled to prevent irresponsible waste disposal, resource depletion, and adverse environmental and health impacts.

CRediT authorship contribution statement

L. Vitale: Writing – review & editing. **L. Vigliotti:** Writing – review & editing, Methodology. **T. C. Meisel:** Writing – review & editing, Project administration, Methodology. **L. Mantovani:** Writing – review & editing, Project administration, Methodology. **I. Vassura:** Writing – review & editing, Methodology. **A. Siciliano:** Writing – review & editing, Methodology. **Valerio Funari:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization. **H. I. Gomes:** Writing – review & editing, Project administration. **E. Dinelli:** Writing – review & editing, Project administration, Methodology.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Valerio Funari reports financial support was provided by CON IL SUD Foundation. Helena I. Gomes reports financial support was provided by The Royal Society. Valerio Funari reports financial support was provided

by The Royal Society. Valerio Funari reports financial support was provided by Government of Italy Ministry of University and Research. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Acknowledgment of potential conflicts

The authors declare the absence of any potential conflict of interest that may have appeared to affect the neutrality of this manuscript.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2024.114883.

Data availability

Data will be made available on request.

References

[1] H. Ai, K.A. Clavier, B.E. Watts, S.A. Gale, T.G. Townsend, The efficacy of pH-dependent leaching tests to provide a reasonable estimate of post-carbonation leaching, J. Hazard. Mater. 373 (2019) 204–211, https://doi.org/10.1016/j.jhazmat.2019.03.089.

[2] N. Bahaloo-Horeh, S.M. Mousavi, Comprehensive characterization and environmental risk assessment of end-of-life automotive catalytic converters to arrange a sustainable roadmap for future recycling practices, J. Hazard. Mater. 400 (2020) 123186, https://doi.org/10.1016/j.jhazmat.2020.123186.

[3] A. Báscik-Remisiewicz, E. Tomaszewska, K. Labuda, Z. Tukaj, The effect of Zn and Mn on the toxicity of Cd to the green microalga Desmodesmus armatus cultured at ambient and elevated (2%) CO2 concentrations, Pol. J. Environ. Stud. 18 (2009).

[4] A. Cesaro, A. Marra, V. Belgiorno, A. Siciliano, M. Guida, Chemical characterization and toxicity assessment for the sustainable management of end of life cathode ray tubes, J. Mater. Cycles Waste Manag. 20 (2018) 1188–1198.

[5] J. Chen, K. Huang, A new technique for extraction of platinum group metals by pressure cyanidation, Hydrometallurgy 82 (2006) 164–171.

[6] A. Chen, S. Wang, L. Zhang, J. Peng, Optimization of the microwave roasting extraction of palladium and rhodium from spent automobile catalysts using response surface analysis, Int. J. Miner. Process. 143 (2015) 18–24.

[7] S.J. Cobbina, Y. Chen, Z. Zhou, Low concentration toxic metal mixture interactions: effects on essential and non-essential metals in brain, liver, and kidneys of mice on sub-chronic exposure, Chemosphere 132 (2015) 79–86, https://doi.org/10.1016/j.chemosphere.2015.03.013.

[8] A.X. Corrêa, R.C. Testolin, M.M. Torres, S. Cotelle, J.J. Schwartz, M. Millet, C. M. Radetski, Ecotoxicity assessment of particulate matter emitted from heavy-duty diesel-powered vehicles: influence of leaching conditions, Environ. Sci. Pollut. Res. 24 (2017) 9399–9406.

[9] D. de Paiva Magalhães, M.R. da Costa Marques, D.F. Baptista, D.F. Buss, Metal bioavailability and toxicity in freshwaters, Environ. Chem. Lett. 13 (1) (2015) 69–87.

[10] Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives, Official Journal of the European Union OJ L 312/3, 22.11.2008, 3–26EN 12457-2:2002. Characterisation of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 2: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction).

[11] V.V. Eskina, O.A. Dalnova, D.G. Filatova, V.B. Baranovskaya, Y.A. Karpov, Separation and preconcentration of platinum-group metals from spent autocatalysts solutions using a hetero-polymeric S, N-containing sorbent and determination by high-resolution continuum source graphite furnace atomic absorption spectrometry, Talanta 159 (2016) 103–110.

[12] M.L. Firmansyah, F. Kubota, M. Goto, Selective recovery of platinum group metals from spent automotive catalysts by leaching and solvent extraction, J. Chem. Eng. Jpn. 52 (2019) 835–842.

[13] A. Fornalczyk, M. Saternus, Vapour treatment method against other pyro-and hydrometallurgical processes applied to recover platinum form used auto catalytic converters, Acta Metall. Sin. 26 (2013) 247–256.

[14] V. Funari, L. Mantovani, L. Vigliotti, E. Dinelli, M. Tribaudino, Understanding room-temperature magnetic properties of anthropogenic ashes from municipal solid waste incineration to assess potential impacts and resources, J. Clean. Prod. 262 (2020) 121209, https://doi.org/10.1016/j.jclepro.2020.121209.

[15] Gazzetta Ufficiale, R.I., 2006. Decreto Legislativo 3 aprile 2006, n. 152. Norme in materia ambientale. G. U. n. 88 del 14 aprile 2006 - Supplemento Ordinario n. 96 (In Italian).

[16] B. Guan, R. Zhan, H. Lin, Z. Huang, Review of the state-of-the-art of exhaust particulate filter technology in internal combustion engines, J. Environ. Manag. 154 (2015) 225–258, https://doi.org/10.1016/j.jenvman.2015.02.027.

[17] S. Harjanto, Y. Cao, A. Shibayama, I. Naitoh, T. Nanami, K. Kasahara, Y. Okumura, K. Liu, T. Fujita, Leaching of Pt, Pd and Rh from automotive catalyst residue in various chloride based solutions, Mater. Trans. 47 (2006) 129–135.

[18] ISO 11348-3:2007 Water quality — Determination of the inhibitory effect of water samples on the light emission of Vibrio fischeri (Luminescent bacteria test) — Part 3: Method using freeze-dried bacteria.

[19] ISO 6341:2012 Water quality — Determination of the inhibition of the mobility of Daphnia magna Straus (Cladocera, Crustacea) — Acute toxicity test.

[20] ISO 8692:2012 Water quality — Fresh water algal growth inhibition test with unicellular green algae.

[21] S. Karim, Y.-P. Ting, Ultrasound-assisted nitric acid pretreatment for enhanced biorecovery of platinum group metals from spent automotive catalyst, J. Clean. Prod. (2020) 120199.

[22] C.-H. Kim, S.I. Woo, S.H. Jeon, Recovery of platinum-group metals from recycled automotive catalytic converters by carbochlorination, Ind. Eng. Chem. Res. 39 (2000) 1185–1192.

[23] I. Komjarova, R. Blust, Multi-metal interactions between Cd, Cu, Ni, Pb and Zn in water flea Daphnia magna, a stable isotope experiment, Aquat. Toxicol. 90 (2008) 138–144, https://doi.org/10.1016/j. aquatox.2008.08.007.

[24] O. Lanaridi, A.R. Sahoo, A. Limbeck, S. Naghdi, D. Eder, E. Eitenberger, Z. Csendes, M. Schnürch, K. Bica-Schröder, Toward the recovery of platinum group metals from a spent automotive catalyst with supported ionic liquid phases, ACS Sustain. Chem. Eng. 2021 9 (1) (2021) 375–386, https://doi.org/10.1021/acssuschemeng.0c07384.

[25] A. Liati, P. Dimopoulos Eggenschwiler, Characterization of particulate matter deposited in diesel particulate filters: visual and analytical approach in macro-, micro- and nano-scales, Combust. Flame 157 (9) (2010) 1658–1670, https://doi.org/10.1016/j.combustflame.2010.02.015.

[26] G. Libralato, A.V. Ghirardini, A. Francesco, How toxic is toxic? A proposal for wastewater toxicity hazard assessment, Ecotoxicol. Environ. Saf. 73 (2010) 1602–1611, https://doi. org/10.1016/j.ecoenv.2010.03.00750.

[27] Y. Liu, Z. Xu, Potential prediction and coupling relationship revealing for recovery of platinum group metals from spent auto-exhaust catalysts based on machine learning, J. Environ. Manag. 365 (2024) 121533, https://doi.org/10.1016/j.jenvman.2024.121533.

[28] L. Mantovani, C. De Matteis, M. Tribaudino, T. Boschetti, V. Funari, E. Dinelli, S. Toller, P. Pelagatti, Grain size and mineralogical constraints on leaching in the bottom ashes from municipal solid waste incineration: a comparison of five plants in northern Italy, Front. Environ. Sci. 11 (May) (2023) 1–15, https://doi.org/10.3389/fenvs.2023.1179272.

[29] M.H. Morcali, S. Akman, O. Yucel, Determination of the optimum NiS fire assay parameters for Pt, Pd, and Rh in automotive exhaust catalytic converters, Chem. Eng. Commun. 202 (2015) 1145–1154.

[30] C.A. Nogueira, A.P. Paiva, P.C. Oliveira, M.C. Costa, A.M.R. Da Costa, Oxidative leaching process with cupric ion in hydrochloric acid media for recovery of Pd and Rh from spent catalytic converters, J. Hazard. Mater. 278 (2014) 82–90.

[31] M.O. Obiakor, C.D. Ezeonyejiaku, Copper–zinc coergisms and metal toxicity at predefined ratio concentrations: Predictions based on synergistic ratio model, Ecotoxicol. Environ. Saf. 117 (2015) 149–154.

[32] G. Persoone, B. Marsalek, I. Blinova, A practical and user-friendly toxicity classification system with microbiotests for natural waters and wastewaters, Environ. Toxicol. 18 (2003) 395–402, https://doi.org/10.1002/tox.10141.

[33] G. Rauret, J.F. López-Sánchez, A. Sahuquillo, R. Rubio, C. Davidson, A. Ure, P. Quevauviller, Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials, J. Environ. Monit. 1 (1999) 57–61, https://doi.org/10.1039/a807854h.

[34] Reif, K., 2015. Gasoline Engine Management. In Gasoline Engine Management. https://doi.org/10.1007/978-3-658-03964-6.

[35] J.T. Rogers, M. Patel, K.M. Gilmour, C.M. Wood, Mechanisms behind Pb-induced disruption of $Na+$ and $Cl-$ balance in rainbow trout (Oncorhynchus mykiss), Am. J. Physiol. Regul. Integr. Comp. Physiol. 289 (2005) R463–R472, https://doi.org/10.1152/ajpregu.00362.2004.

[36] R. Rumpold, J. Antrekowitsch, Recycling of platinum group metals from automotive catalysts by an acidic leaching process, South. Afr. Inst. Min. Metall. Platin 695 (2012) 695–713.

[37] A. Sahuquillo, J.F. López-Sánchez, R. Rubio, G. Rauret, R.P. Thomas, C.M. Davison, A.M. Ure, Use of a certified reference material for extractable trace metals to assess sources of uncertainty in the BCR three-stage sequential extraction procedure,

Anal. Chim. Acta 382 (3) (1999) 317–327, https://doi.org/10.1016/S0003-2670(98)00754-5.
[38] S. Satyro, M. Race, F. Di Natale, Simultaneous removal of heavy metals from field-polluted soils and treatment of soil washing effluents through combined adsorption and artificial sunlight-driven photocatalytic processes, Chem. Eng. J. 283 (2016) 1484–1493, https://doi.org/10.1016/j.cej.2015.08.039.
[39] O. Šebek, M. Mihaljevič, L. Strnad, V. Ettler, J. Ježek, R. Štědrý, P. Drahota, L. Ackerman, V. Adamec, Dissolution kinetics of Pd and Pt from automobile catalysts by naturally occurring complexing agents, J. Hazard. Mater. 198 (2011) 331–339.
[40] D. Shin, J. Park, J. Jeong, B. Kim, A biological cyanide production and accumulation system and the recovery of platinum-group metals from spent automotive catalysts by biogenic cyanide, Hydrometallurgy 158 (2015) 10–18.
[41] P. Solaimani, A. Saffari, C. Sioutas, S.C. Bondy, A. Campbell, Exposure to ambient ultrafine particulate matter alters the expression of genes in primary human neurons, NeuroToxicology 58 (2017) 50–57, https://doi.org/10.1016/j.neuro.2016.11.001.
[42] J. Spooren, T.A. Atia, Combined microwave assisted roasting and leaching to recover platinum group metals from spent automotive catalysts, Miner. Eng. 146 (2020) 106153.
[43] Z. Sun, Y. Xiao, H. Agterhuis, J. Sietsma, Y. Yang, Recycling of metals from urban mines - a strategic evaluation, J. Clean. Prod. 112 (2016) 2977–2987, https://doi.org/10.1016/j.jclepro.2015.10.116.
[44] V. Tsiridis, M. Petala, P. Samaras, Interactive toxic effects of heavy metals and humic acids on Vibrio fischeri, Ecotoxicol. Environ. Saf. 63 (2005) 158–167, https://doi.org/10.1016/j. ecoenv.2005.04.005 59.
[45] V. Tsiridis, P. Samaras, A. Kungolos, G.P. Sakellaropoulos, Application of leaching tests for toxicity evaluation of coal fly ash, Environ. Toxicol. (2006), https://doi.org/10.1002/tox.20187.
[46] A.K. Upadhyay, J. Lee, E. Kim, M. Kim, B. Kim, V. Kumar, Leaching of platinum group metals (PGMs) from spent automotive catalyst using electro-generated chlorine in HCl solution, J. Chem. Technol. Biotechnol. 88 (2013) 1991–1999.
[47] Q. Wang, M.A. De Luchi, D. Sperling, Emission impacts of electric vehicles, J. Air Waste Manag. Assoc. 40 (9) (1990) 1275–1284, https://doi.org/10.1080/10473289.1990.10466782.
[48] T. Wang, S. Yang, K. Sun, X. Fang, Preparation of Pt/beta zeolite–Al2O3/cordierite monolith for automobile exhaust purification, Ceram. Int. 37 (2) (2011) 621–626.
[49] J. Zhang, J. Richter, C. Kaczmarek, Catalysts for post euro 6 plug-in hybrid electric vehicles, 2020, SAE Int. J. Adv. Curr. Prac. Mobil. 2 (6) (2020) 3151–3163, https://doi.org/10.4271/2020-01-0354.
[50] Z. Zhao, Z. Qiu, J. Yang, B. Ma, Z. Li, S. Lu, Y. Xu, L. Cao, W. Zhang, Recovery of rare earth element cerium from spent automotive exhaust catalysts using a novel method, Waste Biomass-.-. Valoriz. (2019) 1–10.