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RECOVERABLE Pd AND Pt ACCUMULATION IN A $Ca(OH)_2$ BASED CO_2 FILTER OF A HYDROGENATION ORGANIC BYPRODUCT INCINERATION PLANT

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Abstract
Hydrogenation processes are strongly relying on Pd and Pt based catalysts, which are degraded, consumed and discharged during the industrial processes. The mining and beneficiation of these noble metals has increased environmental footprint and increasing costs. Thus, any possibility for recovery, recycling and reuse is an option which must be accurately investigated. In our study we present a case where easily recoverable Pd and Pt bearing waste is generated as a product of incineration gases capture. The hydrated lime based CO_2 capture system produces a $CaCO_3$ matrix containing Fe-oxides aggregated, cemented Pd-Pt accumulations.

***Keywords**: catalysts, recycle, carbon capture*

1. INTRODUCTION

The tar byproduct of an aniline plant reactor must be decomposed by incineration, as the chemically and environmentally most secure method. Variable amount of the applied Pd-Pt-Fe based catalyst will be removed from the reactor together with the tar, as part of the routine operation. The incineration gases – mostly CO_2, with minor residual SO_x and NO_x contribution – and the fly ash product are captured in $Ca(OH)_2$ treated filter bags. As a result Ca-carbonate will be generated, as a matrix of captured product, with variable amounts of Ca-sulphate and the aggregates of the Pd-Pt-Fe system with specific transformations developed during incineration. Thus, the resulting capture waste is a potentially high values secondary raw material [1], requiring a processing route in compliance with the reuse and recycle developments. The first step of such a development is the detailed compositional characterization of the material, presented in this study.

2. EXPERIMENTAL

Samples were prepared by water based separation, magnetic separation and hydrochloric acid dissolution. Crystallographic analysis was carried out by X-ray powder diffraction (XRD, Bruker D8 with Cu-alpha radiation, 40 kV and 40 mA) on air dried specimen. After phase identification, Rietveld refinement was carried out to validate the presence of phases and refine crystallographic data. The chemical structure of components was studies by Fourier-transformed infrared spectroscopy in attenuated total reflection mode (ATR-FTIR). Textural and microchemical characteristics of the material was observed by scanning electron microscopy investigations (scanning electron microscopy with energy dispersive X-ray spectrometry, SEM+EDX) provide a basis for the recycling technology.

3. RESULTS AND DISCUSSION

Crystallographic (Figure 1) and chemical structure (Figure 3) characterization revealed calcite (trigonal $CaCO_3$) as the matrix material, with high amount of residual $Ca(OH)_2$, and sulphates like anhydrite ($CaSO_4$), bassanite ($CaSO_4*0.5H_2O$) gypsum ($CaSO_4*2H_2O$) and cesanite ($Na_7Ca_3(SO_4)_6(OH)*0.8H_2O$).

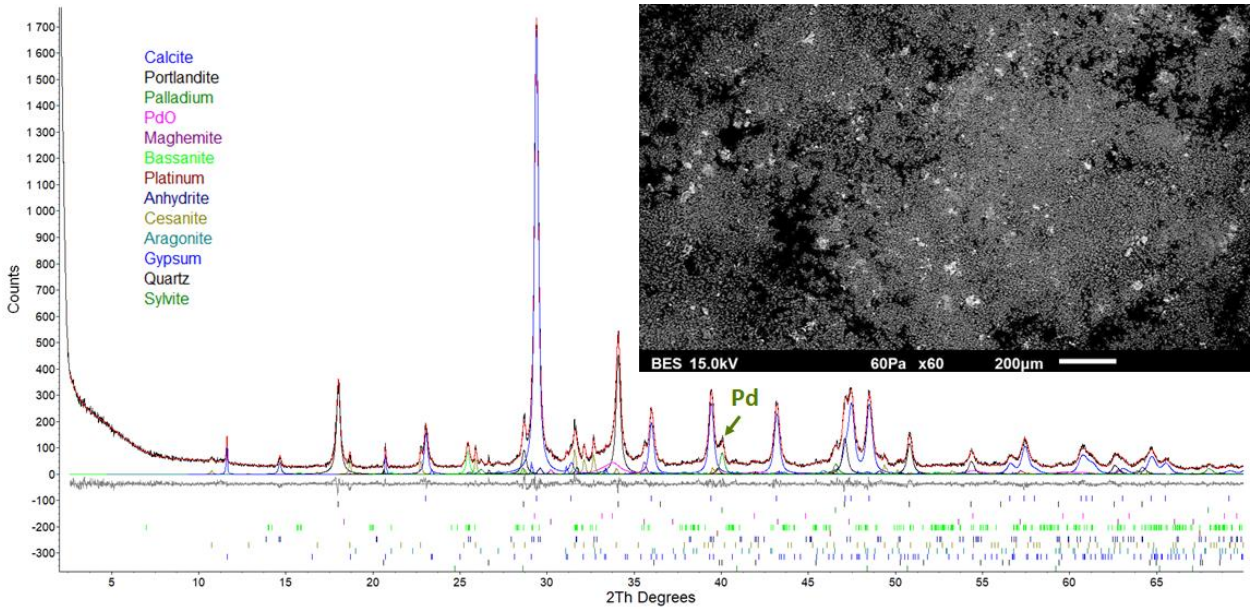

Figure 1. XRD pattern with Rietveld refinement and distribution of Pd-Pt rich fragments (inset, back-scattered electron image)

Minor associated phases are aragonite (orthorhombic $CaCO_3$), quartz (trigonal SiO_2), sylvite (KCl) and maghemite (cubic, gamma-Fe_2O_3).

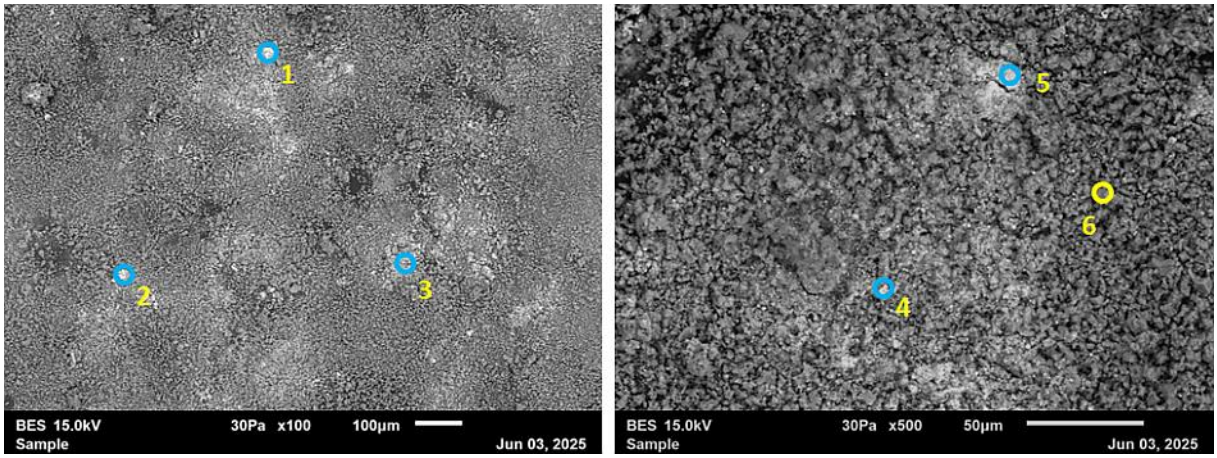

Figure 2. Distribution of high atomic number components in the carbonate matrix, back-scattered electron images, circles mark EDX analysis spots.

These phases provide an insight into the incineration and gas capture reactions and completed with SEM+EDX investigations (Figure 2) provide a basis of metallurgy for recycling technology planning [2]. The high average atomic number spots (numbered spots in Figure 2) in the carbonate matrix show elevated Fe content, with associated rise in Pd and Pt content. Trace amounts Si and Al are related to glass like silicate components revealed by acid leaching of the carbonates. Carbon quantitative data is considered only as indicative, since the powder was mounted on adhesive-

conductive carbon tape. However, its directly proportional variation with Ca content is supporting the observation, that only Ca produces carbonate phases, the calcite and aragonite.

Table 1. EDX measurements marked on the BES images in Fig 2 (non-standardized weight percents)

	P	Fe	K	O	C	Na	Mg	Al	Si	S	Cl	Ca	Pd	Pt
1	0,29	19,25	0,14	36,79	10,54	2,77	0,47	0,12	0,77	2,62	0,37	8,85	14,27	2,76
2	0,11	15,07	0,16	38,65	13,85	1,2	0,37	0,06	0,81	2,65	0,45	17,93	7,46	1,21
3	0	1,66	0,11	48,18	14,73	0,67	0,35	0,05	0,16	1,39	0,44	30,97	1,23	0,06
4	0,28	20,7	0,2	34,96	10,62	2,65	0,4	0,14	0,76	2,54	0,36	8,27	14,99	3,12
5	0,37	19,53	0,23	29,6	8,92	1,84	0,91	0,07	0,96	3,22	0,52	9,94	21,2	2,69
6	0,12	25,63	0,33	24,77	12,13	1,19	0,46	0,09	0,75	4,41	0,42	17,3	11,25	1,15

Chemical structure investigations (Figure 3) support the presence of S in the sulphate minerals found by XRD, the Mg incorporation in calcite crystal lattice and presence of reactive portlandite. Upon water immersion and subsequent drying, the portlandite OH-band is eliminated, transformed into carbonate phase. However, it was observed during this rehydration process, that pH rises to 10-11 and if ultrasonic stirring is applied, the dispersion of the metal-rich particles will increase.

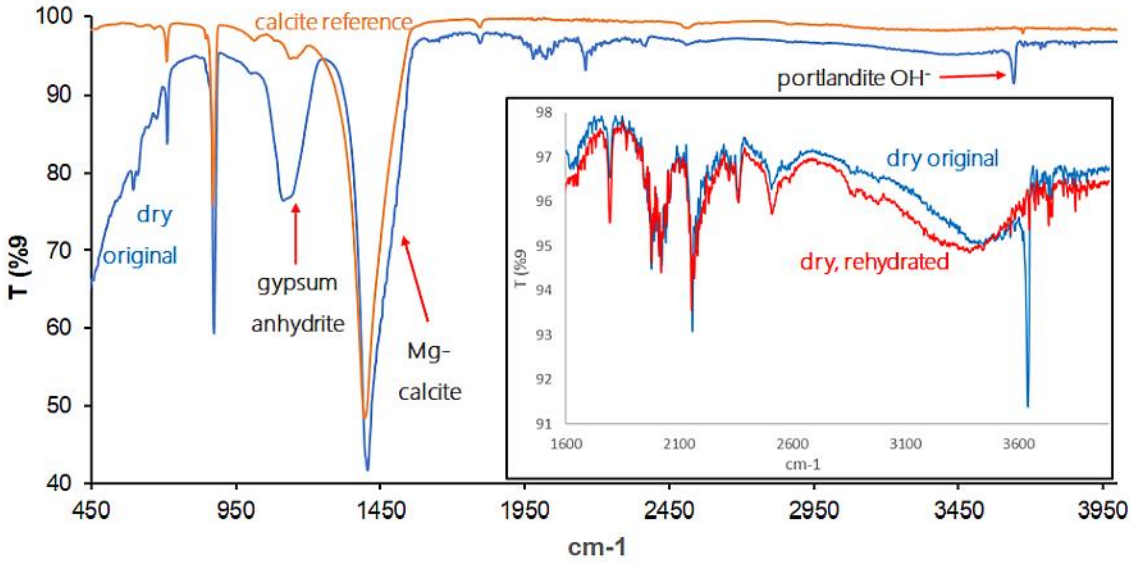

Figure 3. ATR-FTIR spectra of original filter product sample, calcite reference and rehydrated product (red spectra, inset).

The residual but reactive $Ca(OH)_2$ indicates that carbonatation reactions create a semi-continuous shell which hinders CO_2 capture, while aragonite is the product of fast carbonate crystallization – these two processes might be interrelated, and their relevance in the subject is not determined. The sulfate phases are mostly present as individual grains or aggregates of several micrometers. The most important relation is found between maghemite and the Pd and/or Pt phases. Due to the size of these phases their metallic, oxide or mixed nature cannot be determined, thus an assumption is made that PdO observed by XRD coexists with Pd and is a host for Pt.

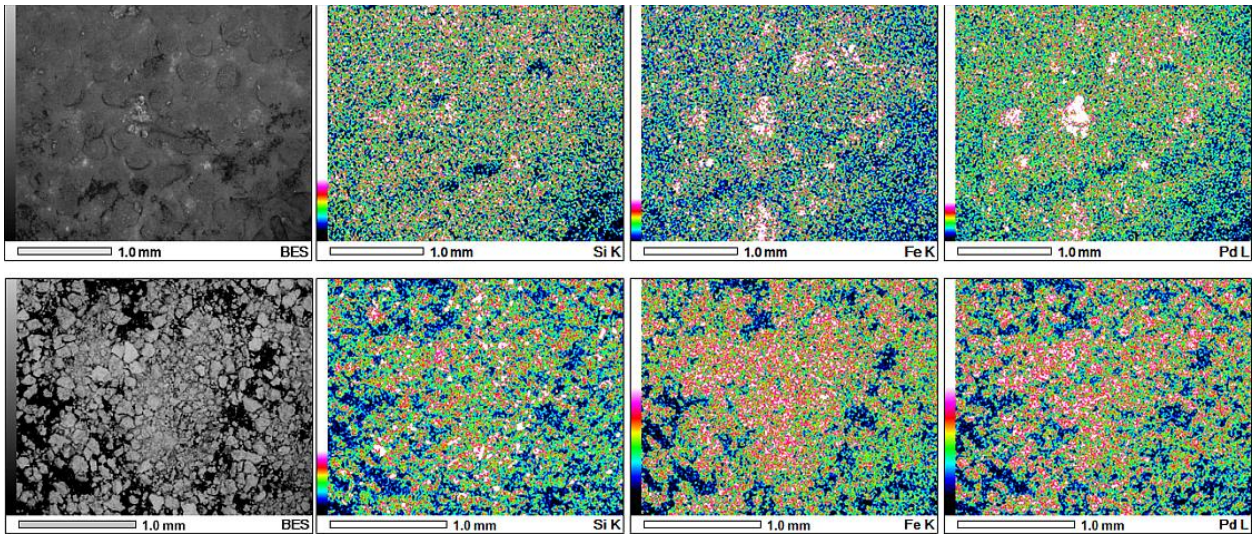

Figure 4. Effect of HCl treatment on elements enrichment, upper row the original sample, lower raw the acid insoluble residue (colors mark concentration increase towards white)

These phases occur in a wide size range, the larger are aggregates of tens of millimeters, built up by smaller irregular units, strongly associated to the Fe-oxide (Figure 4). Since only maghemite was identified by XRD, it is assumed but not assured, that other Fe-oxide phases, nor amorphous oxides are present.

4. CONCLUSIONS

Preliminary test results show, that Fe-oxide cements the Pd-Pt phases, since their concentration is possible by magnetic separation. Also, the residual $Ca(OH)_2$ can be utilized as a useful component, in water immersed dispersing tests it was evidenced, that Fe-oxide cemented aggregates are liberated from the carbonate matrix as a result of pH swing and carbonate dissolution-reprecipitation.

The cubic Fe_2O_3 is a useful component for enrichment/separation of metal bearing aggregates with several physical methods, however the catalysts metals are only partially contained in the oxidic aggregates.

The nature of the gas filtration products opens the possibility of chemical, physical or metallurgical processing for noble metal recovery, the most probable solution being the combination of the above, based on the preliminary experiments.

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