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POSSIBILITIES OF METALS EXTRACTON FROM SPENT METALLIC AUTOMOTIVE CATALYTIC CONVERTERS BY USING BIOMETALLURGICAL METHOD

MOŻLIWOŚCI WYKORZYSTANIA METOD BIOMETALURGICZNYCH DO EKSTRAKcji METALI ZE ZUŻYTYCH METALOWYCH KATALIZATORÓW SAMOCHODOWYCH

The main task of automotive catalytic converters is reducing the amount of harmful components of exhaust gases. Metallic catalytic converters are an alternative to standard ceramic catalytic converters. Metallic carriers are usually made from FeCrAl steel, which is covered by a layer of Precious Group Metals (PGMs) acting as a catalyst. There are many methods used for recovery of platinum from ceramic carriers in the world, but the issue of platinum and other metals recovery from metallic carriers is poorly described. The article presents results of preliminary experiments of metals biooxidation (Fe, Cr and Al) from spent catalytic converters with metallic carrier, using bacteria of the *Acidithiobacillus* genus.

Keywords: spent catalytic converters, metallic carrier, biometallurgy, *Acidithiobacillus* bacteria

Głównym zadaniem katalizatorów samochodowych jest zmniejszenie ilości szkodliwych składników spalin. Katalizatory na nośniku metalowym są alternatywą dla standardowych katalizatorów na nośniku ceramicznym. Nośniki metalowe najczęściej wykonuje się ze stali FeCrAl, na którą nieniesiona jest warstwa platynowców, pełniących funkcje katalityczne. W pracy przedstawiono wyniki wstępnych prób bioutleniania metali ze zużytych katalizatorów na nośniku metalowym (Fe, Cr, Al), z udziałem bakterii z rodzaju *Acidithiobacillus*.

1. Introduction

An automotive catalytic converter is built mainly of a ceramic (Al_2O_3) or metallic FeCrAl steel carrier with a porous surface into which the elements from Precious Group Metals (PGMs) are deposited. To those elements belong: platinum, palladium and rhodium, which play the catalytic role [1,2]. Currently, the composition of catalytic carrier significantly varies depending the engine displacement and the type of used fuel. The amount of Pt, Pd and Rh in each carrier can range from 1-5 grams for a small car to 12-15 grams for a truck.

About 4 percent of automotive catalytic converters on the market contains a metallic carrier, which is made using corrugated FeCrAl foils, rolled into a spiraling cylinder shape. Such construction allows to increase the contact surface of exhaust gases with the precious metals, which are the catalysts of the reaction and significantly speed up the oxidization of carbon oxides and hydrocarbons and in the same time reduction of nitrogen oxides [3,4]. As a result, the substances appearing at the outlet of the converter, like carbon dioxide, water and nitrogen, are neutral to the environment [4-6].

The typical alloy used for catalytic converter applications is ferritic stainless steel with 17-22% chromium and 4-6%

aluminium. Rare Earth Elements (REE) are also added to FeCrAl alloy in the amount of ~ 0,01%. Common used REE are La, Ce, Pr, Nd, Sm, Gd, Dy, Y, and Er. A metallic carrier is used rather than ceramic one for certain applications to reduce light-off, back-pressure, etc [7]. Catalytic converters with metallic carriers called Metal Substrate Converters (MSC) were originally designed for sport and racing cars where low back pressure and reliability under continuous high load is required. Considering the fact, that the metal heats up much faster than ceramics, metal catalysts rapidly reach „working temperature” and quickly purify exhaust gases. At the same time, they are more resistant to damage caused by thermal shock and high temperature. The advantage of metal supported catalysts is their better thermal conductivity obtained due to high content of platinum [8]. The differences between both type of automotive catalytic converters carriers are shown in Table 1.

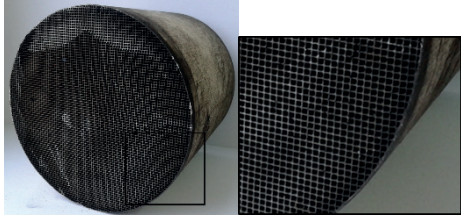
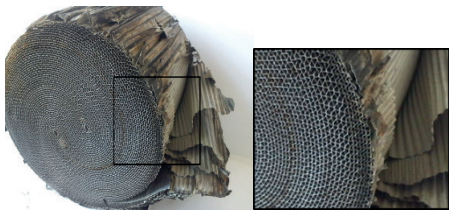
Although there are many methods of treating used catalytic converters with ceramic carrier in pyro- and hydrometallurgical way, there is little literature information on the metals recovery from spent automotive catalysts with metallic carriers. The metallic carrier is grinded by passing it through one or more different types of shredders or hammer

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The differences between both types of automotive catalytic converters carriers [7, 9]

Description	Ceramic carrier	Metallic carrier
Structure	 <p>Honeycomb shape with numerous channels (the most often square cross-section)</p>	 <p>Corrugated FeCrAl foils which are rolled into a spiraling cylinder shape</p>
Examples of materials used in the construction of monolith	Al_2O_3 , $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$; $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$; $\text{MgO}\cdot \text{Al}_2\text{O}_3$; $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2\cdot 3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$; $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot \text{Al}_2\text{O}_3\cdot \text{TiO}_2$; SiO_2 ; SiC ; Si_2N_4 ; B_4C ; ZrO_2 ; $\text{ZrO}_2\cdot \text{MgO}\cdot \text{Al}_2\text{O}_3$	Fe-Cr-Al-(Y) ; Fe ; Fe-Al ; Fe-Cr-Al-Co
Catalytic substance	Pt, Pd, Rh	Pt, Pd, Rh
Additional components improving properties of monolith layer	Different oxides (CeO_2 , NiO or Li_2O) can be added to Al_2O_3 in the direct layer to increase its properties like the resistance to ageing in high temperatures	Rare earth elements are added to FeCrAl alloys to improve the oxidation resistance of alumina at high temperatures by reducing oxidation rates and increasing the scale of adhesion
Balance weight	Steel shell: 2,900 kg Isolation: 1,000 kg Carrier: 0,900 kg Washcoat (with PGMs): 0,160 kg PGM: 0,005 kg Sum: 4,965 kg Material for recycling: 1,065 kg	Steel shell: 1,300 kg Isolation: 0,800 kg Carrier: 1,300 kg Washcoat (with PGMs): 0,155 kg PGM: 0,005 kg Sum: 3,555 kg Material for recycling: 1,460 kg

mills. This step is preceded by separation of various fractions of steel scrap (such as foil-fraction) from the fraction containing precious metals. The Umicore Precious Metals Refining (Maxton USA) - one of the world's largest precious metals recycling facilities - has dedicated and fully automated shredding line to metallic carriers from spent automotive catalysts. This technology allows to achieve a high recovery yield for the washcoat [9, 10]. However, the crushing process can cause a problem - a fine dust (obtained after this process) is rich in precious metals [11].

In addition to classical pyro- and hydrometallurgical methods for spent catalysts processing, attempts of metal extraction involving microorganisms are also undertaken [12, 13]. Most widely discussed works relate to the extraction of metals such as Mo, Co, Al, Ni, V and W from spent petroleum/refiners catalysts [14]. Review of results coming from bioleaching of these metals were extensively presented in the work [14]. There are not many works regarding the possibility of using bacteria in leaching the metals coming from automotive catalytic converters. The one available refers to bioleaching platinum from ceramic catalysts [15], however there is no data on the possibility of extracting metals from metallic converters.

Attempts to extract metals such as Fe, Cr and Al from spent metallic catalyst using bioleaching with mixed culture of *Acidithiobacillus* bacteria were undertaken. The aim of the research was to transfer iron, chromium and aluminium from

a solid phase into solution in the presence of sulfuric acid and Fe^{3+} - product of bacteria metabolism.

2. Experimental method

Waste material. Research was conducted on the waste material in the form of spent Metal Substrate Converters (MSC). The material was cut and subjected to bioleaching experiments in particle size fractions of 2 mm. The metals content in the sample was determined by the atomic adsorption spectrometry (AAS) - Table 1 shows their composition.

TABLE 1
Content of basic metals in analysed MSC sample

Metal	Fe	Cr	Al	Pt
Content, %	57.5	19.7	5.0	0.084

Bacteria. Mixed culture of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* were used. Strain of these bacteria was obtained from the Institute of Geotechnics of Slovak Academy of Science, Kosice. The medium used for bacteria growth was composed of: $(\text{NH}_4)_2\text{SO}_4\cdot 2.0$; $\text{KCl}\cdot 0.1$; $\text{MgSO}_4\cdot 7\text{H}_2\text{O}\cdot 0.25$; $\text{KH}_2\text{PO}_4\cdot 0.5$; $\text{MgSO}_4\cdot 7\text{H}_2\text{O}\cdot 44.2$ (g/dm^3), S_0 . Initial pH of the medium was 1.5 and bacteria were cultured

at 30°C in thermostat. In bioleaching and biorecovery systems high concentration of metal ions may become toxic to bacteria. Therefore adaptation process was conducted. Adaptation of mixed bacteria to heavy metals ions in the medium was carried out over 3 weeks period, with a small dose of waste (<0.1g) added every 2 days.

Bioleaching. Bioleaching experiments were carried out in Erlenmeyer flasks (250 cm³), placed in a thermostat (30°C). Leaching solution in the form of distilled water with addition of 10 M H₂SO₄ (pH 1.5) was used in all biological and chemical experiments. Samples of waste were placed in the leaching systems in the quantity of 2.5g/250 cm³, inoculated with bacteria (30 cm³). The control tests under sterile conditions were conducted parallel, maintaining the same experimental conditions as for biological systems without addition of bacteria. Experiments were carried out in two series of measurements lasting 96 days. Regular measurement of basic parameters were made until 28th day, and the final measurement was conducted on the last 96th day.

Analysis. The changes of Fe, Cr and Al concentration in solutions, the oxidation-reduction potential (ORP) and pH were analysed during experiments. To quantify the amount of Fe, Cr and Al dissolved in the leaching media, 5 cm³ sample was filtered and the filtrate was analyzed by the Atomic Absorption Spectrophotometer AAS (SpectrAA 20 PLUS VARIAN). 1 cm³ solution was also taken to determine the concentration of ferric ion by spectrophotometer (Unicam UV/Vis Spektrometer UV 4).

3. Results and discussion

Bioleaching process was conducted in distilled water acidified by addition of 10 M sulfuric acid with a mixture of bacteria *A. ferrooxidans* and *Athiooxidans* adapted and unadapted to high metals concentration. Process of chemical leaching of iron, chromium and aluminium waste was carried out under identical conditions. The results are shown in Fig. 1 as a dynamic change of the Fe, Cr and Al concentration during leaching, under conditions of initial pH = 1.5.

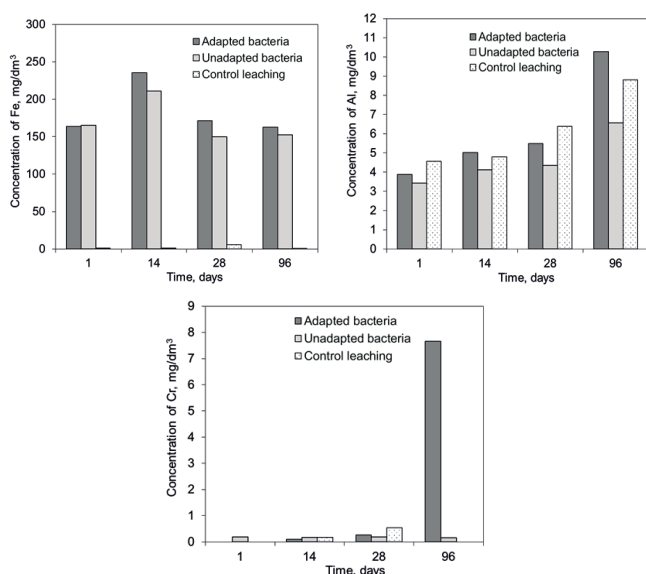
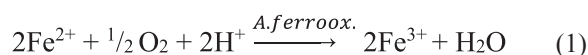


Fig. 1. The concentration of iron, chromium and aluminium obtained in the biological and chemical leaching

The concentration of iron in biological samples with adapted and unadapted bacteria remained at a comparable level (Fig. 1). The maximum concentration of iron leached in this way was found at 14th day and was about 235 mg/dm³ and 211 mg/dm³ with adapted and unadapted bacteria, respectively. The results of the control leaching experiments were significantly lower (0.63 – 1.2 mg/dm³). After reaching maximum concentration of Fe total (Fe_{total}) in biological tests (14th day) within the next few days there was its decline. This relationship is reflected in the course of pH and Fe³⁺ concentrations changes. The initial increase in pH (Fig. 2) can be attributed to the oxidation of Fe²⁺ to Fe³⁺ as a result of bacterial oxidation (Eq. 1) which is accompanied by the consumption of acid and process of waste dissolution [16-20]:



The initial concentration of Fe³⁺ was maintained at about 91.5 mg/dm³, which contributed to the Fe_{total} leaching. Together with the observed decrease in the concentration of Fe³⁺ (on 20th day of bioleaching) and parallel decline in pH, a process of slowing down dissolution with a downward trend of Fe_{total} concentration in the solution was observed. Fe³⁺ was not detected in the chemical leaching tests (control experiments). This indicates that the oxidation of Fe from waste is mainly affected by a biological process.

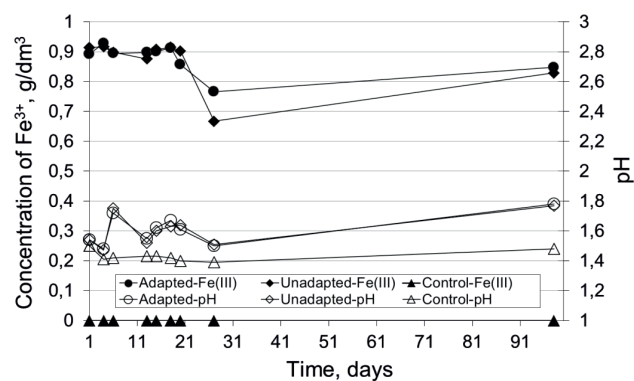


Fig. 2. Changes in pH and Fe³⁺ during biological and chemical leaching

An increasing trend of aluminium concentration during the leaching process was observed. A comparable degree of Al transition to solution in biological and control samples was achieved, 10.28 mg/dm³ and 8.8 mg/dm³ on 96 days, respectively. Minimal effect of bacterial oxidation on aluminium extraction was found. The main role in leaching process plays the pH and chemical mechanism of oxidation. Increasing pH (Fig. 2) favours extraction of aluminium, both in chemical and biological tests. Low dissolution of Al (32%) observed Ilyas et al. [21] during leaching metals in column with acidophilic heterotrops. These results indicated that dissolution of aluminium was contributed to both acid leaching and bioleaching.

In case of chromium the lowest value of metal concentration in the solution during the biological and chemical leaching was obtained. Concentration of this metal in tests with unadapted bacteria remained at the level of 0.17 mg/dm³. Increase in chromium transition to the solution was observed on 96th day for the sample with adapted bacteria (7.66 mg/dm³). This behaviour indicates activation of further adaptation process by bacteria, dependent not only on the concentration of metal but also on the cumulative contact time.

4. Conclusion

On the basis of Fe bioleaching from spent metallic catalyst converter it was found that the extraction of iron involving adapted and unadapted bacteria proceeds similarly, but bacteria plays a crucial role in this process. On the contrary, in the case of aluminium only slightly more metal (by 20%) was obtained by the bacterial activity in comparison with the control leaching test where only chemical leaching took place. Clearly better results were achieved for chromium, where process efficiency using adapted bacteria has grown along with a contact time. Finally, it can be concluded that in the metals oxidation, which affect the degree of their transition into solution, takes part both biological oxidation process (especially for Fe and Cr) as well as chemical oxidation (in the case of Al).

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