

Extraction of valuable metals from amorphous solid wastes

E. David*

National Research Institute of Cryogenics & Isotope Technologies,
P.O.Box 10, Rm.Valcea, Code 240050, Romania

* Corresponding author: E-mail address: david@icsi.ro

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Materials

ABSTRACT

Purpose: This paper undertakes to assess what opportunities exist for the economical recovery of valuable metals from amorphous solid wastes that may be considered as "synthetic ores". Also, this work is an attempt to optimize a leaching process that is the most determinant step of hydrometallurgical process used to extract metals from ores.

Design/methodology/approach: The samples of amorphous material formed from spent industrial catalysts based on Cu, Ni / γ - Al_2O_3 were physically and chemically characterized by atomic absorption spectrometry (AAS) and chemical analysis for to determine the metals content. Then leaching studies were carried out under room temperature, atmospheric pressure and without gas injection in both sulphuric acid with hydrogen peroxide addition and ammoniacal media for to decide which of them would be the best treatment for this kind of waste materials. Also, the dissolution behaviour of Cu, Ni and Al metals was studied in order to assure the best metal recovery conditions in subsequent processes such as solvent extraction, precipitation or cementation techniques.

Findings: The results revealed that addition of hydrogen peroxide to sulphuric acid up to 0.2 M H_2O_2 concentration enhanced leaching of metals remarkably and thereafter remained relatively constant. The highest extraction of metals was found to be 90% Cu, 85% Ni and 80% Al for the following experimental conditions: H_2SO_4 2M, H_2O_2 0.2 M, A 5:1 liquid to solid ratio (L/S). The use of ammoniacal media for leaching allowed the extraction of Cu, Ni and Al but rates of recovery were only about 45 % for Cu, 43 % for Ni and 44 % for Al, much lower than those obtained for sulphuric acid leaching.

Research limitations/implications: The investigated process is suitable for all amorphous solid wastes with significant content in metals such as copper, nickel, aluminium.

Practical implications: Promising directions for adaptation of appropriate and economic separation processes for recovery and recycling of valuable metals from amorphous solid wastes generated in significant amounts from different sectors were identified.

Originality/value: A new route for wastes recycling that will become an unavoidable task not only for recovery the valuable metals and lowering catalysts costs but also for to prevent the environmental pollution.

Keywords: Amorphous materials; Leaching; Copper; Nickel; Aluminium

1. Introduction

Metals play an important part in modern society and historical been linked with industrial development and improved living standards. Society can draw on metal resources from Earth's crust

as well as from metal discarded after use in the economy. Inefficient recovery of metals from the economy increases reliance on primary resources and can impact nature by increasing the dispersions of metals in ecosystems. Spent catalysts from industry and automotive catalytic converters, printed circuit boards of wastes computers, ash resulted from coal combustion

and so one, represent a little part of solide wastes with high content in valuable metals [1-3]. Metals can be recycled nearly indefinitely. Nevertheless, the ability to recover metals economically after use is largely a function of how they are used initially in the economy and their chemical reactivity.

Metals like Ni, Mo, Co, Cr, V, Rh,Pt,Pd,etc., are widely used as catalysts in industry [3]. They are generally supported on porous materials like alumina or silica through precipitation or impregnation processes. After periodical use the catalysts, due to poisoning effect of foreign material and impurities, which deposit on their surface they will become inactive. Only small part of the catalysts could be regenerated in-situ, while the greatest part of them have to be substituted and the spent catalysts will be discarded as waste materials and are classified as hazardous materials for environment [3]. However, such waste materials containing high metal concentrations may be considered as "synthetic ores" since they can serve as secondary raw materials with a consequent reduction in the demand for primary mineral resources [2].

Recycling of spent catalysts became an unavoidable task not only for lowering catalysts costs but also for recovery the valuable metals and reducing their waste to prevent the environmental pollution [2-6]. A variety of processing approaches for recovering metals from wastes has been proposed and most of the literature in this field is patented.

A good way to treat and recycle the metals seems to be achieved by the use of hydrometallurgy process [8-10]. This has a major environmental advantage over conventional smelting since most of the waste products from the process are not produced as air emissions, but rather as solids which can be easily contained. Also the use of hydrometallurgical techniques is becoming more attractive, since the need of high energy requirements or eventual gas collectors and cleaning systems, always necessary in the pyrometallurgical processes, are avoided[4 - 9].

The most determinant step of a hydrometallurgical process is generally the first, which is the leaching or dissolution of the valuable metals presented in the raw material suffering this short treatment. In many hydrometallurgical processes sulphuric acid has been selected as the cheapest and most effective leachant at temperatures between 40-90°C [6-8].

The main aim of this research work is an attempt to optimize a leaching process to recover copper, nickel and aluminium from spent industrial catalysts under room temperature/atmospheric pressure and without gas injection. Also, the paper is focused on the leaching operation itself as a part of an integrated hydrometallurgical route to recover valuable metals for their recycling.

2. Experimental

The amorphous spent catalyst samples from Romanian petroleum refining industry were used in the form of cylindrical extrudates of approximate diameter 0.3 - 0.4 mm and length of 4-6 mm. They contained residual oil and were washed with hot toluene by Soxhlet process and dried at 110°C before experiments. Samples were ground to fine particle (< 1.0 mm) to improve leaching efficiencies. All reactives employed were pure grade. Leaching tests were carried out in a three-necked, round-

bottom flask equipped with a pH-meter, a magnetic stirrer that was set up to ensure the full suspension of particles and to improve the liquid to solid phase contact.

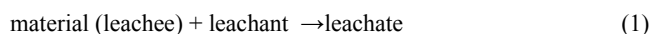
The analysis of components of the starting material were carried out using an atomic absorption spectrometer type Analytic Yena Nova 300 and chemical analysis. Leaching experiments with sulphuric acid (H₂SO₄) with hydrogen peroxide (H₂O₂) addition and ammoniacal solutions that contain ammonium (NH₃) and ammonium carbonate, [(NH₄)₂CO₃], were carried out at room temperature for maximum 20 hrs.

Aqueous solutions were prepared by varying the dissolution of known amounts of reagents H₂SO₄, H₂O₂, NH₃, and (NH₄)₂CO₃ in distilled water. During leaching tests, samples were withdrawn at regular interval of time and after filtration the resulting solution was analysed for metal elements by atomic absorption spectrometry in accord with ASTM D-4793. The reproductibility of the leaching experiments was determined to be of order of ± 1% by repeating selected experiments under identical conditions.

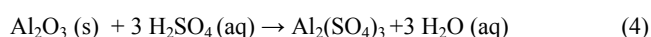
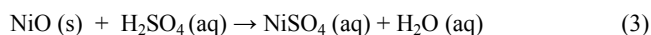
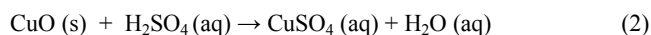
3. Results and discussions

The most important step of a hydrometallurgical process is generally the first, which is leaching i.e. the dissolution of the valuable metal in an aqueous solution. The overall recovery of the metal and the difficulty of separating it from impurity metals are generally governed by the efficiency and selectivity of the leaching process.

Leaching is a method to remove soluble components from a solid matrix. Leaching is described by a very simple process such as is presented in equation (1) :



The solid waste was formed from hydrodesulphurization catalyst (HDS). The main physico- chemical characteristics of solid waste are presented in Table 1. Based on the knowledge of chemical composition and assuming that the main reactions involving CuO, NiO and Al₂O₃ oxides with sulphuric acid and the chemical process describing the dissolution experiment for Cu, Ni and Al given in eqs 2, 3 and 4.



a simple calculation of the stoichiometric amount of H₂SO₄ needed was done . On this basis a ratio of about 1:1 weigh parts of H₂SO₄ dried spent catalyst sample was calculated. This determination was used to estimate the H₂SO₄ consumption and the L/S ratio on the leaching experiments. In the leaching tests the L/S ratio used are presented in Table 2. Chemical analysis of HDS presented in Table 1 confirmed high content of catalyst in metals. With regard to low contents in impurities, their presence was ignored in calculations of the process efficiency .

Table 1. Physico- chemical characteristics of the spent catalyst
Element in dried sample (%)

Density (g cm ⁻³)	0.8					
H ₂ O (%)	0.2					
¹⁾ S _{BET} (m ² g ⁻¹)	82					
Al	Cu	Ni	C	O	Na	S
44.6	12.4	3.2	7.5	24.8	0.18	7.2

¹⁾S_{BET} was determined with BET method

As can be seen in Table 1, the catalyst waste contains high contents of valuable metals such as Al, Cu, Ni and can be considered as an “synthetic ores”. A little content in Na provided from Al₂O₃ that represents catalytic support. The condition adopted for each set of experiments are shown in Table 2, both for sulphuric acid and ammoniacal leachings.

Table 2. Sulphuric acid and ammoniacal leaching conditions adopted in the different experimental tests

Reagent and L/S ratio used	Test number					
	1	2	3	4	5	6
L/S	5:1	10:1	20:1	5:1	10:1	20:1
H ₂ SO ₄ (M)	1	1	1	2	2	2
H ₂ O ₂ (M)	0.2	0.2	0.2	0.2	0.2	0.2
pH	1.4	1.4	1.4	1.2	1.2	1.2
NH ₃ (M)	0	0.5	1.0	1.5	2.0	2.5
(NH ₄) ₂ CO ₃ (M)	1	1	0	1	1.5	2
pH	8.5	9.6	11.2	9.6	9.75	9.84

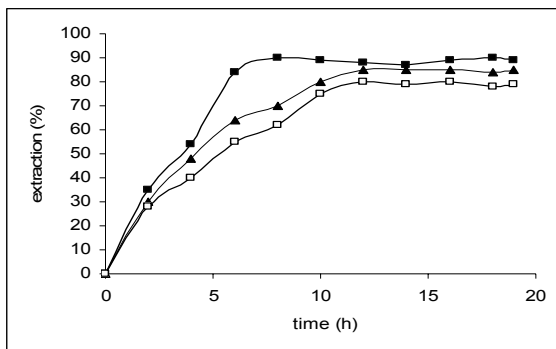


Fig. 1. Influence of leaching time on metal extraction (Test 4, Leaching conditions: t_{max}=20 hrs; stirring speed= 250 rpm; H₂SO₄ concentration: 2M, H₂O₂ concentration 0.2M, L/S = 5/1; Symbols represent individual metals: ■-Cu, □-Ni, ▲-Al)

Leaching with the H₂SO₄ solution was carried out at room temperature over a period of time of maximum 20 hrs. The progression of the dissolution process on the various metals over time with H₂SO₄ leaching solution shown that the best results were obtained in the condition of test 4. These results are presented in Fig.1.

The optimal conditions for H₂SO₄ leaching were found to be a solution 2M and L/S ratio of 5:1 which achieved 90% recovery of Cu within 8 hrs, while Ni and Al were 85% and 80 respectively in 12 hrs (see Figure 1 and Table 2 and 3).

Regarding the ammoniacal leaching, the comparison of the results obtained on test 1 and 3 (Table 3) leads to the conclusion that the presence of ammonium carbonate has a stronger influence than ammonia in the metal ion dissolution.

Table 3. Effect of different leachant conditions in the leaching for Cu, Ni, Al in different media

Leaching test	Leached metal (%)					
	Cu		Ni		Al	
	I	II	I	II	I	II
1	82	32	78	11	65	26
2	85	28	79	23	73	19
3	88	21	81	6	77	9
4	90	45	85	31	80	44
5	77	39	83	40	79	41
6	76	37	80	43	76	36

I-Tests {1-6} achieved with H₂SO₄ and H₂O₂ solution (see Table 2)
II-Tests {1-6} achieved with NH₃ and (NH₄)₂CO₃ solution, (see Table 2)

However it can be considered that the presence and the combined effect of both reagents (ammonia and ammonium carbonate) are fundamental to an effective dissolution of the metal ion elements.

The addition of ammonium ions increases the rate of solution in ammonia up until a certain ammonia-ammonium ratio is reached, where further addition has not effect. For the conditions tested sulphuric acid proved to be an efficient leaching medium for the Cu, Ni and Al metals present in catalyst wastes, although with a quite low selectivity, whereas the inverse situation occurred when ammoniacal media was used instead.

The effect of stirring speed on the metal leaching efficiency from the spent catalyst was investigated in solution containing 2M H₂SO₄ in the range of speed from 100 to 600 rpm.

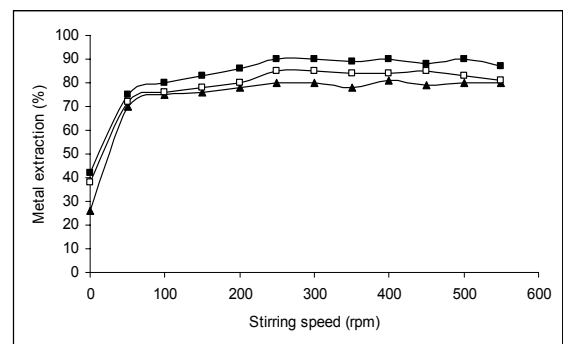


Fig. 2. Effect of stirring speed on metal extraction, extraction time of 12 hrs, in solution containing 2M H₂SO₄ with 0.2 M H₂O₂ addition. Symbols represent individual metals: ■-Cu, □-Ni, ▲-Al)

The results presented in Figure 2 show that the leaching of copper, nickel and aluminium was almost independently of the stirring speed. This indicates that the diffusion of the reactants

from the solution towards the surface of a catalyst particle and the products away from the surface of the particle was fast and hence did not control the leaching rate within the range of the stirring speeds tested. All subsequent experiments were carried out at a stirring speed of 250 rpm to assure the invariance of this parameter.

Hydrogen peroxide added to H_2SO_4 solution was used to help the dissolution of Cu, Ni and Al metals from the spent catalyst. The influence of H_2O_2 concentration on the leaching of copper, nickel and aluminium from spent catalyst was determined by varying the initial concentration of H_2O_2 from 0.05 to 0.3 M in 2M H_2SO_4 solution.

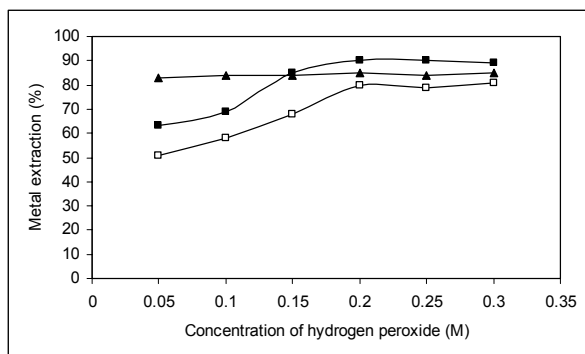


Fig. 3. Effect of H_2O_2 concentration on metal extraction efficiency during 12 hrs leaching in H_2SO_4 2M. (Symbols represent individual metals: ■-Cu, □-Ni, ▲-Al)

Figure 3 shows summarized metals extraction after 12 hrs leaching. Generally, the extraction of Cu, Ni and Al was gradually increased up to 0.2 M H_2O_2 concentration and then remained constant. The extraction of Al was practically not affected by the concentration of H_2O_2 within the whole range. The highest extraction of metals was observed in 2 M H_2SO_4 solution with 0.2 M H_2O_2 during 12 hrs leaching. For the sulphuric acid leaching the comparison of results obtained from the tests performed by utilising the same acid concentration, i.e. {1,2,3} or {4,5,6} groups (see Tables 2 and 3) shows that no significant variations were observed on the dissolution of the valuable metals with the increase in the L/S ratio. This trend might indicate that equilibrium leaching conditions were reached even by using the lower L/S ratio. This is an advantage on the process cost. In the ammoniacal leaching experiments the L/S ratio was kept at values indicated in Table 2, for tests. The pH control in all these experiments was of fundamental importance. From analysis of data presented in Table 2 and 3, the dissolution of Cu, Ni and Al in ammoniacal solution was higher for average pH values closer to pH 10.

4. Conclusions

The leaching tests performed have shown that the efficiency of sulphuric acid with hydrogen peroxide addition towards several metallic elements such as Cu, Ni and Al contained in industrial spent catalysts is much higher than that observed by using ammonia/ammonium carbonate. The metals dissolution by H_2SO_4

is almost complete while leached levels reached upon by ammoniacal solutions are only half of those registered in acidic media, even after 20 hrs. Amongst all the leaching experiments carried out with H_2SO_4 conditions followed for test 4 the H_2SO_4 2M, H_2O_2 0.2 M, 5:1 L/S ratio have assured the most favourable economical situation. The test allowed the effective treatment of a higher amount of spent catalysts with the lowest sulphuric acid consumption and the maximum recovery for the desired valuable metals was achieved. The highest extraction of metals was found to be 90% Cu, 85% Ni and 80% Al. The use of ammoniacal media for leaching allowed the extraction of Cu, Ni and Al but rates of recovery were only about 45 % for Cu, 43 % for Ni and 44 % for Al, much lower than those obtained for sulphuric acid leaching.

From leach solution copper could be then recover by cementation or extraction processes, nickel and aluminium by precipitation technique.

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