

SOLUBILIZATION PROCESSING OF ASHES POWER PLANT

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Abstract: The paper presents the attempts of acid and alkaline solubilization of the power plant ashes, using different chemical reagents, at different concentrations. Due to the mineralogical content of these ashes, was elaborated a technological flow for the recovery the iron minerals, resulting an ferrous concentrate containing noble metals. For their recovery from ferrous concentrate, were studied properties of gold, silver and platinum, the conclusion being that these chemical elements can be extracted, in economic conditions, with sodium hypochlorite.

1. Introduction

Hydrometallurgical processing has acquired an important place in mineral technology due to its advantages compared to other methods of recovery of useful mineral substances, such as:

- applicability in case of recovery of ores with low or very low content of useful element;
- applicability in the case of the recovery of "refractory" ores, ie ores which cannot be prepared or are prepared with advantageous technical and economic indicators by ordinary processes;
- the possibility of complex capitalization of raw materials;
- ensuring higher extraction for the useful element;
- obtaining better quality of the finished products than in the usual preparation processes;
- the high degree of selectivity of the hydrometallurgical processing allows the obtaining of monomineral finished products much more frequently than in the case of other preparation methods;
- lower energy, fuel and labor requirements in the ore metal processing circuit;
- the pollution produced by the technologies for obtaining the metal from the ore by hydrometallurgical way is considerably lower than the pollution produced by conventional processes.[1]

Compared to the other advantages listed for hydrometallurgical processing, compared to other methods, it has only one disadvantage: high processing costs that make it available only in cases where other methods of preparation are inefficient. However, the gradual reduction of the contents of mineral substances useful in raw materials, the need to capitalize hard-to-prepare ores but especially the requirements of the industry for increasingly some metals and materials, ensures the application of the hydrometallurgical concentration of materials.

2. Laboratory tests for the extraction of some chemical elements from power plant ash

Inorganic substances from coal, by burning, turn to ash. It contains a number of elements present in large quantities known as major elements or macroelements. They are found in quantities of more than 1% of the mass of ash having a weight that decreases in the order: Si, Al, Fe, Ca, Mg, S, Na, K, Ti, P.

In addition to macroelements whose distribution determines the oxide composition of the ash, in coal are present in small quantities (between 1 ppm and 1%) a number of other elements, known as trace elements, rare elements, minor elements or microelements.

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Table 1 presents the contents in macroelements of the ashes from CET (Thermoelectric Power Station) Paroşeni. [2]

Table 1. The contents of macroelements in ash from CET Paroşeni

Sample		SiO ₂ (%)	Fe ₂ O ₃ (%)	Al ₂ O ₃ (%)	TiO ₂ (%)	CaO (%)	MgO (%)	SO ₃ (%)	Na ₂ O (%)	K ₂ O (%)
Pond Paroseni	I ₁	47,12	8,68	20,08	0,055	6,30	2,50	0,22	0,98	1,87
	I ₂									

Laboratory research was carried out in order to extract some chemical elements from the ash by acid and alkaline leaching.

Alkaline leaching was performed in order to extract aluminum and similar chemical elements in terms of its chemical properties. The leaching rate, expressed by the amount of substance passing into the solution per unit time, depends on a number of parameters such as:

- temperature,
- leaching reagent concentration,
- stirring speed,
- solid particle size,
- leaching time.

The leaching reagent used was sodium hydroxide, at different concentrations, the leaching time was 24 hours, with intermittent stirring at 100 °C - initially to initiate the chemical reaction after which the leaching took place at ambient temperature. The chemical reaction that take place is: [3]



Along with aluminum, the solutions resulting from gray leaching also contain sodium silicate which can be precipitated.



Table 2 shows the weight extractions obtained for different concentrations of sodium hydroxide solution.

Table 2. The weight extractions obtained in the alkaline leaching of ashes from Paroşeni

The solution	The concentration of solution (%)	The weight extraction v(%)
NaOH	5	4,92
NaOH	10	7,32
NaOH	15	5,61
NaOH	20	5,73

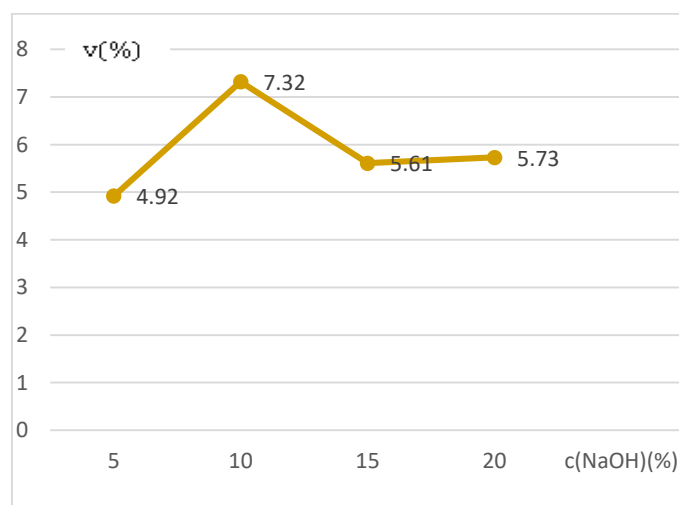


Fig.1. The variation of weight extraction with the solution concentration $v=f(c_{NaOH})$

It is found from the presented data that the highest extractions by weight were obtained in the case of using NaOH solutions - 10% concentration. These values of the extractions are small if we take into account the fact that the share of aluminates and silicates in the ashes of Paroşeni is over 70%, therefore the alkaline leaching proved to be inefficient for these ashes.

Acid leaching was performed in order to verify the possibilities of hydrometallurgical recovery of ash.

In order to choose the optimal leaching reagent and the corresponding concentration, several sets of tests were performed, with different reagents, at different concentrations, the results of which are presented in table 3. Acid leaching was performed cold, by intermittent stirring, at a leaching time of 2 hours.

From the data presented in table 3 it is observed that the highest extraction by weight was obtained by using as a leaching agent nitric acid - concentration 15%, 15.38%.

Table 4 shows the weight extractions obtained for titanium, this element not being of economic interest due to the very small values of the extractions.

Table 3. The weight extractions obtained to the acid leaching of the ashes from Paroşeni

The leaching solution	Solution concentration c(%)	Weight extraction v(%)	The leaching solution	Solution concentration c(%)	Weight extraction v(%)
HCl	5	11,87	HNO ₃	20	11,11
HCl	10	11,95	H ₂ SO ₄	5	8,07
HCl	15	11,64	H ₂ SO ₄	10	9,50
HCl	20	11,26	H ₂ SO ₄	15	7,55
HNO ₃	5	11,87	H ₂ SO ₄	20	7,53
HNO ₃	10	14,72	HCl:HClO ₄	1:1	11,51
HNO ₃	15	15,38			

Table 4. The weight extractions obtained to the acid leaching of titanium

The leaching solution	Solution concentration c(%)	Ti weight extraction v(%)
HCl	5	0,021
	10	0,027
	15	0,048
	20	0,046
HNO ₃	5	0,021
	10	0,141
	15	0,293
	20	0,269
H ₂ SO ₄	5	-
	10	-
	15	-
	20	-
HCl+HClO ₄	1:1	0,085

3. Extraction of noble metals from ash

Taking into account the fact that the share of iron minerals represented by magnetite, hematite, including those resulting from the burning of pyrite in the ashes of Paroşeni is about 10%, the concentration tests were oriented towards magnetic separation. The concentration of ash in the magnetic field results in a magnetic product, a non-magnetic and sterile product [4]. Chemical analyzes were performed on these products in order to determine the content of precious metals [5].

Table 5. The metal contents of products from magnetic separation

Product	Weight extraction [%]	Contents			
		Fe[%]	Au[g/t]	Ag[g/t]	Pt[g/t]
Magnetic product (P.M)	5,92	55,31	1,00	42,16	0,376
Non-magnetic product (P.N)	1,14	20,19	0,03	8,37	0,05
Waste	92,94	5,11	0,16	10,76	0,0053
Feeding	100	8,26	0,209	12,15	0,072

From the data presented in table 5 it is observed that in the tailings the contents of precious metals are quite high. The explanation consists in the fact that the tailings contain iron oxides, therefore implicitly precious metals of micron dimensions, trapped in a ceramic clay binder. In order to recover the chemicals in this product, a very advanced grinding should be carried out.

The concentration of platinum and gold in iron compounds - oxides and hydroxides (magnetite, hematite, limonite) is due to the fact that these chemical elements have a strong siderophilic character. Silver is strongly calcophilic, so it is contained in sulfides. The state of iron oxides of sulfides is also achieved by the direct

combustion of coals which usually contain pyritic iron sulfides. In conclusion, the concentration of ferrous compounds also determines the concentration of these valuable elements [6].

In order to be able to propose technologies for extracting noble metals from coal ash, it is necessary to study certain chemical properties of them.

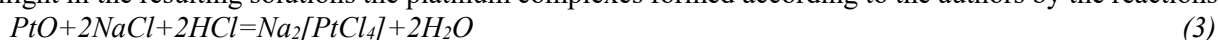
Because these chemicals are associated with iron oxides, it is not possible to use conventional processes such as cyanide for gold and silver, leaching with royal water for platinum as this would involve excessive consumption of reagents.

3.1. Properties of noble metals

Platinum

Platinum is one of the most reactive platinum metals. It dissolves easily in royal water and even in hydrochloric acid in the presence of air. The other acids do not attack platinum. Platinum is sensitive to the action of hydrochloric acid in the presence of oxygen due to its complexation by the Cl^- ion.

By treating the oxidized platinum surfaces with hydrochloric acid, Anson and Lingone managed to highlight in the resulting solutions the platinum complexes formed according to the authors by the reactions:



This is an indication in favor of the existence of stoichiometric oxides of PtO and PtO₂.

Breiter and Weininger demonstrated that the respective ions can be formed on the basis of corrosion reactions according to a scheme that does not involve the presence of phase oxides based on local reactions, the cathodic process being:



and the anodic one:



respectively:



Regarding the nature of the Pt-O system formed, there are the following more significant concepts:

- During the oxidation of platinum, the chemisorption of oxygen species takes place, until the formation of a monomolecular layer. This process can be followed by a process of rearrangement of atoms.
- Formation of a monomolecular layer of adsorbed oxygen, the excess oxygen entering the deeper layers of the network.
- Chemisorption of species with oxygen up to the ratio Pt: O = 1: 1, the excess forming a phase oxide (combination).
- Phase oxides are formed in all potential domains. It is assumed that the formation of the film is controlled by the chemisorption of oxygen species, the oxidation of the surface gradually advancing [7]:



This oxidation process can be followed by:

- rearranging the chemisorbed species to form a more compact species;
- incorporation of surface oxygen atoms into the platinum network:



- the formation of a phase oxide:



The oxide film formed is not soluble contributing to the increase of the chemical resistance of platinum by passivation. In the presence of chloride ions, platinum oxides are dissolved by complexation according to reactions (3) and (4).

In conclusion, the platinum surface can be oxidized with nitric acid, hydrogen peroxide, potassium permanganate, etc., and the oxide film can be removed by complexing with the help of the chloride ion, thus reaching the total dissolution of the metal.

Gold

Gold is nobler than platinum, but only in the absence of complexing ions. In their absence (cyan chloride) they corrode easily.

Gold oxidizes more easily in an alkaline environment than in an acidic environment, which can be easily dissolved in the presence of complexing agents.

Silver

Silver is a metal much less noble than gold and platinum dissolving easily in nitric acid, royal water, etc.

3.2. Extraction of platinum from ash

The control of the chlorinating dissolution process of noble metals requires a good knowledge of the kinetics of this process. Taking into account the large volume of chemical analyzes that should be performed to determine the optimal leaching conditions for gold, silver, platinum, the research focused mainly on platinum recovery.

Attempts to extract platinum using sodium hypochlorite were performed on the products resulting from the magnetic separation [8].

In order to determine the optimal leaching time, several leaching tests were performed, at different times, on the magnetic product (table 6).

Table 6. The influence of leaching time in platinum extraction

Leaching time (h)	Final Pt content b(ppm)	Pt Recovery m(%)
1	-	-
2	0,336	10,5
4	0,283	24,6
8	0,039	89,5
24	0,0086	97,7

Figures 2 and 3 show the variation of the metal extraction and the platinum content of the leached product, depending on the leaching time.

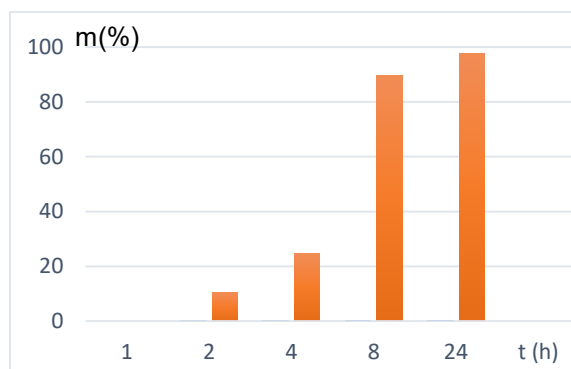


Fig. 2. Variation $m=f(t)$

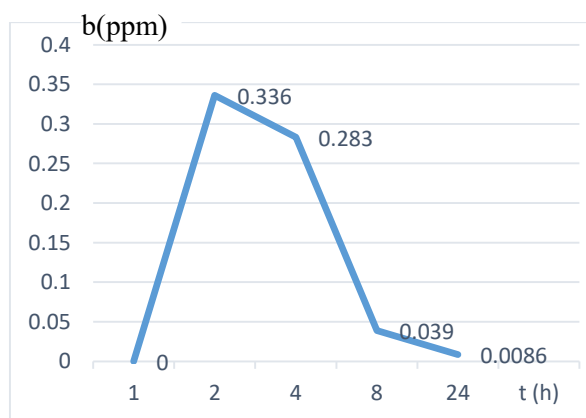


Fig. 3. Variation $b=f(t)$

It is observed that the highest metal extraction, respectively the lowest platinum content in the leached product was obtained for a leaching time of 24 hours of 97.7% and 0.0086 ppm Pt. In order to recover the gold and silver from the magnetic product, the leaching was also performed with industrial sodium hypochlorite, 10% concentration, at a leaching time of 24 hours and intermittent stirring.

After the leaching time expired, the solution was acidified with hydrochloric acid, the solution was removed to remove chlorine, after which the cementation with pure spectral iron took place. The cement was filtered and treated with nitric acid to destroy the unreacted iron and implicitly the silver. In table 7, the metal extractions obtained after leaching gold, silver and platinum are presented.

As a result of the products obtained (metal extractions of more than 85%) it is considered that the leaching with sodium hypochlorite following the magnetic concentration is effective. It should be noted that leaching with this reagent in the industrial phase requires the same facilities as for cyanide.

Table 7. Metal extractions obtained to the gold, silver and platinum leaching

Product	Weight extraction [%]	Content Fe [%]	Metal recovery [%]			
			Au	Ag	Pt	Fe
Feeding	100,0	8,26	100,0	100,0	100,0	100,0
Magnetic concentrate	5,92	55,31	90,85	85,45	97,7	39,64
Nonmagnetic concentrate	1,14	20,19	8,84	12,65	8,82	2,79
Waste	92,94	5,11	0,31	1,90	1,33	57,57

4. Conclusions

The capitalization of thermal power plant ash is a major problem of interest due to its technical and economic implications. Except that in some cases increasing the size of these dumps limits their service life and are sources of environmental pollution, they can be sources of particularly valuable raw materials.

The aim of this paper was to highlight these secondary resources of raw materials - existing in the ash ponds from thermal power plants that use energy oils from the Jiu Valley - likely to be used efficiently after processing by conventional and / or unconventional technologies.

The chemical analyzes highlighted the existence in the ashes of Paroșeni of some microelements such as: Cu, Pb, Zn, Co, Mo, Cr, V, Ti, Mn, Cd, Au, Ag, Pt, U [9]. Although the contents of the chemical elements present in the ashes taken from the Paroșeni tailings ponds are smaller than the minimally exploitable ones worldwide, exploiting the advantage that these ashes do not require operating costs but exclusively preparation, adapted to their specific characteristics.

The mineralogical analyzes performed on the ashes of Paroșeni revealed minerals such as: hematite magnetite, pyrite, dolomite calcite, kaolinite, quartz, complex artificial silicates, etc. Taking into account these properties, the concentration method applied was magnetic concentration.

The products resulting from the application of this technological scheme are:

- a magnetic product containing precious metals which, due to its iron content of 55.31%, can be used as such in the steel industry and for the recovery of precious metals. The share of this product represents 5.92% of the gray mass;

- a non-magnetic product with a weight of 1.14%;

- tailings usable in the construction materials industry whose share represents 92.94% of the gray mass.

Attempts for acid and alkaline solubilization of power plant ash aimed to obtain acceptable weight extractions, resulting in acid leaching with nitric acid concentration 15%, 15.38%.

Attempts to extract platinum using sodium hypochlorite were performed on the products resulting from the magnetic separation, the highest metal extraction, respectively the lowest platinum content in the leached product was obtained for a leaching time of 24 hours of 97.7% and 0.0086 ppm Pt.

In order to recover the gold and silver from the magnetic product, the leaching was also performed with industrial sodium hypochlorite, 10% concentration, at a leaching time of 24 hours.

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