Adsorption of copper cyanide species from tailings pond on flying ash

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ABSTRACT

The objective of this study was to examine the use of flying ash to remove the copper cyanide species from gold mine effluents. In order to discharge them safely with minimum impact to the environment the effluents must be treated in such a way that the legal conditions were attained with the lowest possible cost.

This paper presents the treatment of cyanide solution originating from tailing ponds at the end of detoxification by direct contact with flying ash.

INTRODUCTION

The use of carbon for the adsorption of some substances soluble in water has been widely studied [1],[2],[3]. The success of using it to recover gold from a cyanide complex after a lixiviation process meant a great advance in the adsorption methods. [4],[5].

Adsorption is a phenomenon through which dissolved substances stick to the surface of some solid. This phenomenon takes place because the molecules or ions of the adsorbents attract the dissolved substances holding them in its surface due to the fact that they haven't satisfied all their union forces.

The agents, which influence the adsorption of compounds present in water, are:

1. The type of compound which should be eliminated
2. The compounds which have high molecular weight and low solubility are more easily absorbed
3. The concentration of the compound that should be eliminated
4. The higher the concentration, the bigger the quantity of adsorbent material
5. The presence of organic compounds, which will compete, with the rest of compounds to obtain the available adsorptions places.
6. Water pH, i.e., acid compounds are more easily eliminated at low pH

This work studies the suitability of using adsorption with a coal residue, fly ash, to eliminate metallic cyanide from residual water coming from gold mines which use cyanide lixiviation for extracting gold from ores [6].

Ashes come from burning fossil combustibles. Power plants that burn coal leave out big quantities of ashes into the atmosphere. This by-products coming from burning coal may have more than 70% of alumina, silica, ferric oxide and calcium oxide which makes them be able to be used as adsorbents [7], [8],[9].

Fly ashes are characterised by a fine granulometric distribution and by high quantities of aluminium and silicium in reactive phases [10]. Nowadays, laws in most countries make it compulsory to clean the ashes which are left out by sticking them to filters, so that there is not so much pollution [11],[12].

While some other types of detossification will imply high costs to be put into practice and maintenance, the use of static beds of ashes is an alternative and economic method to destroy residual concentrations of metallic cyanide. Its greatest advantage, apart from its effectivity, is the fact that a by-product, which is generated by power stations, is being used as a raw material for detoxification; thus, the cost of the by-product is very low.

The results obtained in the experiments carried out and which are dealt with below, show the effectivity of ashes in the adsorption of metallic cyanide complex and especially in copper ones. We study the possibility of using them as an alternative method to deal with wastewater, which has been contaminated with copper cyanide, compounds after closing down cyanide lixiviation plants.

Experimental part and results

To test in a laboratory the adequacy of fly ashes coming from a power station to be used as adsorbent material for heavy metals and cyanide compounds, several tests were carried out with wastewater coming from El Valle plant (Asturias-Spain). As a measure method for copper it was used flame atomic adsorption spectrophotometry in the samples at the beginning and once treated. The water samples were taken from those in process in the plant, as well as in the upper and lower drainage in the tailing pond that the Company has in its plant. The fly ashes come from the power station in Soto de la Barca (Asturias).

The analyses carried out to characterise the water through atomic adsorption show similar values for the three sources (Table 1).

The most important difference lies in the values of soluble copper, which varies from values of 3 ppm for the water samples of the lower drainage of the tailing pond, 50-70 ppm for the process water and 100 ppm for the water of the upper drainage. This copper is taking part in a cyanided compound. The destruction of the cyanided complex would leave the metal free, in this case, the copper, which could be eliminated this way by means of precipitation in hydroxide form if the suitable conditions of pH are reached, because the initial pH of the solution is of 8,6.

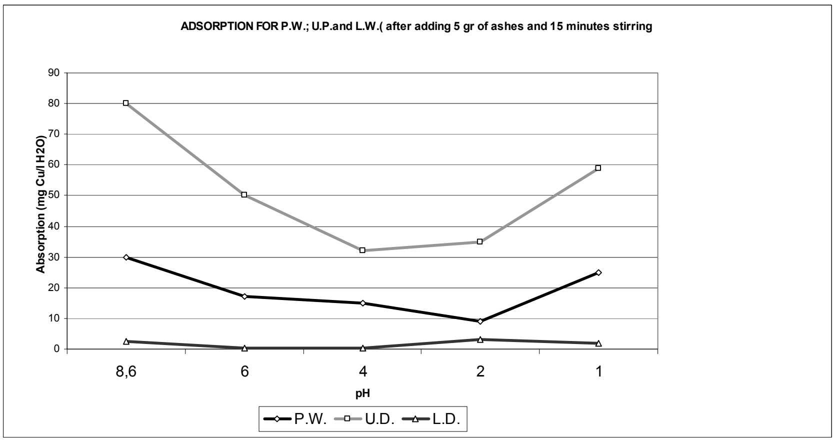
TABLE 1:Analysis of common metals in the water of *W. P., U.D. and L.D.*

Metal	mg/l
Zn	0,10
Cd	0,04
Co	0,20
Na	600
K	26.5
Ca	65
Ni	0,00

Tests were made with samples of 25 ml of water at different pHs and to which different amounts of ashes were added: 1gr., 2gr., and 5grs, alternatively.

To favour adsorption the samples were put under a period of 15 minutes stirring. Once they had been leaked, their copper content in each atomic absorption was measured.

Graphic 1:



In the previous graph the effectiveness of this method is shown. A lowering down in the copper concentration in the solution is reached, coming to a 70% for the upper drainage (corresponding to the higher initial concentration of Cu) with 5 grams of ash and pH 4.

The results of the samples for water process and for the lower drainage of the tailing pond show values lower than 10 ppm Cu. For the upper drainage samples values of 0-0,1 ppm Cu are shown.

Higher periods of stirring: 20,30,40,50 and 60 minutes didn't show better results. In table 2 the results of one of the experiments varied with process water and different stirring periods at pH 8,6 can be seen.

TABLE 2:Analysis of Process Water (55ppm initial) after being treated with 1 gr of ashes and at different stirring periods

Time (minutes)	ppm Cu
0	55
5	43
15	40
30	40
60	40

Later, the influence of temperature over the 25 ml samples with 5 gr. Of ashes and different pHs was studied. In table 3 the results obtained at pH 6 are shown.

TABLE 3:Results of the tests with A.P., D.S. and D.I.,waters with 5 gr of ashes, stirring, pH=6 and different temperatures..

Type of Water (25 ml)	Tª	mg /l of Cu
A.P.	25	21
A.P.	40º	17
A.P.	60º	0,3
A.P.	80º	0,3
D.I.	25	0.3
D.I.	40º	0,3
D.I.	60º	0,3
D.I.	80º	0,3
D.S.	25	50
D.S.	40º	6
D.S.	60º	50
D.S.	80º	49

The results improve the previous ones, but the expenses that would be needed for the necessary installation for the increasing of temperature would not be economically affordable.
Table 4 shows the results obtained at 40 ºC and different pH values.

TABLE 4: Results of tests carried out with A.P., D.S. and D.I., waters with 5 gr of ashes, 15 min of stirring, pH=6, 4,2,1 and 40 ºC.

Type of Water (25 ml)	mg /l of Cu (ini)	mg /l of Cu (fi) pH 6	mg /l of Cu (fi) pH 4	mg /l of Cu (fi) pH 2	mg /l of Cu (fi) pH 1
A.P.	55	17	6	8	24
D.I.	3	0,3	0,3	1,3	3
D.S.	100	6	32	33	33

The data contained in this table come to corroborate the ones shown previously. An improvement in the results with the reduction of pH is observed being higher the improvement in values of pH 6 and pH 4. Increasing the temperature to 40 ºC helps to a better adsorption, but as it has been shown for table 3 results, the expenses for the increase of temperature would not be affordable.
The method was considered from the beginning as an alternative to the problem of a safe closing of treatment plants, so that the option shown was installing static ash beds in continuum that would gather the water of the lower drainage of the tailing pond for its decontamination before sending it to public channels.
In order to verify the adsorption capacity that the ash in a static bed presents, several tests were carried out and their results are shown below.
In a first experiment water volumes of 30 ml each were put through a sample of 5 gr of ashes placed on a filter, measuring the residual copper concentration once filtered. The water that was put through was one coming from the upper drainage with an initial concentration of 70 ppm of Cu and an initial pH of 8,6
In the following graph the results obtained in the 18 tests carried out can be observed. It can be seen how the curve has a slight ascending slope that rises as the volume of water treated increases, clear indication that the ash gets saturated.

GRAPHIC 2:

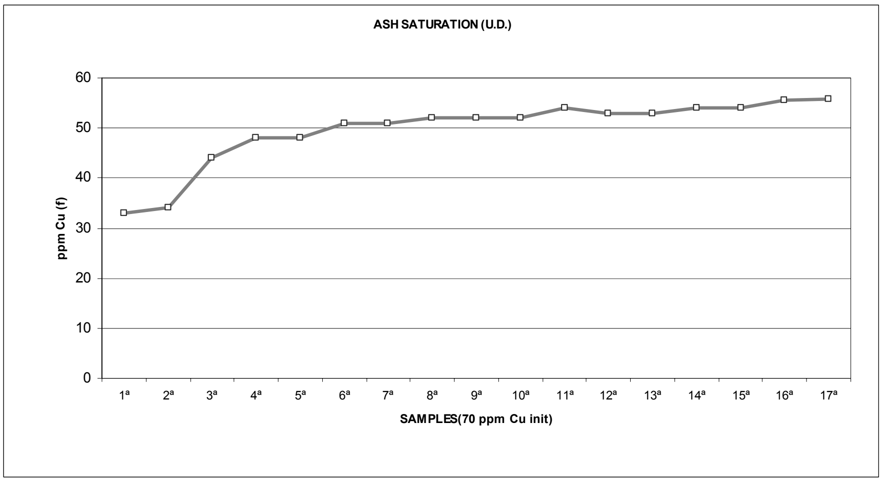
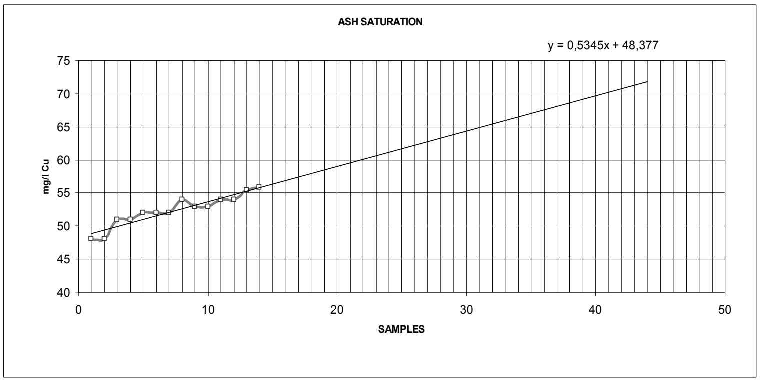


TABLE 7:

ml of water treated	510
ppm Cu initial	1.190
ppm Cu collected per gr. of ash	83,12

With the previous data and observing the ascending tendency of the graphic, an extrapolation of the results was carried out, calculating thus the necessary quantity of water needed to reach the total saturation of the ash.

GRAPHIC 3:



From the grap, taking as a final saturation value that for which the analyzed residual copper in the water sample, once treated, coincides with the initial concentration (70 ppm), it can be deduced that it would be needed to pass 1,2 litres of water with an initial concentration of 70 ppm of Cu to be able to saturate the 5gr. of ash completely.

As a solution to the mine problem: due to the fact that the water precipitates Cu naturally as it passes through the beds underneath this work has been centred in the lower drainage water because it would be the most suitable place for setting up the installation as a prolongation of the containment tailing pond.

Therefore, the water to be treated will have as a maximum value of concentration 3 ppm of Cu. The new tests were made with volumes of 60 ml of water on 10 gr, of ash.

GRAPHIC 4

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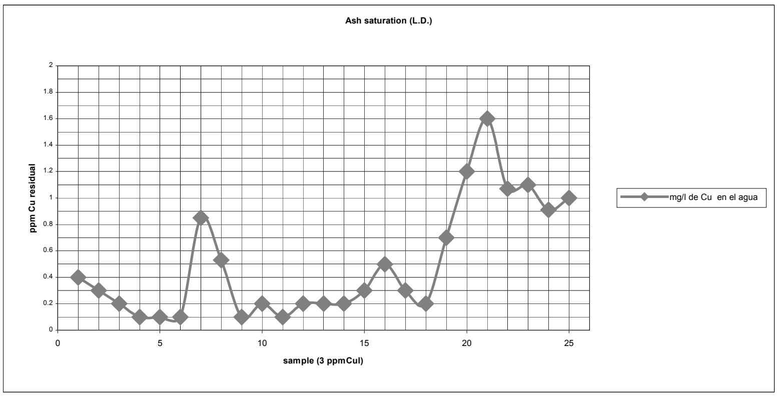

From the data collected in graph 4 and, as in the case of the water from the upper drainage, the necessary calculations were carried out to value the amount of water necessary for the saturation of the ash. In this case, and since we want to send the water to the river, the value taken for the saturation of the ash was that in which the value of the residual copper is of 0,5 ppm. Thus, it was obtained that for the water of the lower drainage, much less contaminated in copper, 282 kg of ash would be necessary to treat the 33,840 dairy litres of water and to be able to send them to a public channel with a totally safe copper concentration. Making the pertinent calculations this would mean an annual expense of 103 tn of ash (taking as a basis the data of the volumes for the lower drainage given by the Company (Table 8), the calculations were made from the average value of the volume of the drainage which is 23,5 l/min; this is, 33,840 l/ a day)

It is necessary to emphasize that the results obtained are affected by the small concentration of copper present since different cations (like calcium) dissolved in the water are attracted by the ash with greater force than that with which the copper is attracted [13], giving this as result the smaller adsorption of this element by the ash and the peaks present in the graph.

TABLE 8:
Volume of lower drainage 30/11/02 -18/10/2002

Date	Volume (l/min)
25/01/2002	24,01
01/02/2002	26,4
08/02/2002	24
15/02/2002	25,64
22/02/2002	21,42
01/03/2002	24,9
11/03/2002	24
16/04/2002	23,6
03/05/2002	24,5
13/05/2002	21,4
24/05/2002	23,8
17/06/2002	22,5
02/07/2002	30,6
19/07/2002	22,4
24/07/2002	22,5
08/08/2002	22,68
20/08/2002	21,47
01/10/2002	10,9
18/10/2002	29,8

Finally, filters similar to the ones that could be used in the plant were built in the laboratory. To carry this out, the data exposed in the specialized bibliography were taken as a basis [14].

The bibliographical references recommend the use of filters with two layers for a filtration of the characteristics wished [15][16]. To obtain the maximum yield from this type of two-layer-filters, they must be made with 1/3 of sand and 2/3 of anthracite ash or any other material lighter than sand.

The option tested in laboratory with sand of different granulometries and ash from the bottom reached the wanted results. It was used with alternative layers of ash and sand of varying granulometria to give the filter enough permeability to allow the volume of filtering to agree with the one needed.

For the case of the installation in plant, once reached the saturation of the ash, it would be changed. The mixture of sand and ash could be used to stuff roads or, once separated; the sand could be used in new filters. The ash could be put under a washing process with water slightly acidulated passing copper to a solution. A later cementation or scraping would allow the recovery of the copper.

The ash, once free from copper would not be able to be used for the cleaning of water because in its new conditions it would attack the cyanide like an acid, with the consequent undesirable loosening of hydrocyanic.

CONCLUSIONS

After the study of the results obtained during the tests made, we can conclude that the adsorption of cyanided complexes of copper on ashes that come from a Power station turns out to be an effective and economical method of detoxification.

The elimination of copper cyanide from water is very effective in values of pH between 4 and 6 but it would imply a high risk because of the loosening of hydrocyanic gas.

Stirring the samples treated with ash as much as heating them with ash, improve the results obtained but, they would be very expensive for putting into operation and maintenance.

Although the adsorption is much more effective with high copper concentrations, it would be adequate to design a plant with static filters of ash for the water of the lower drainage it would be put after this drainage, and would allow the safe closing of the plant as the filters would not need to be changed for several years.

The plant would consist of several two-layer filters through which the lower drainage water would pass in a continuum before sending it to a public chanel. At the end of the last filter, an analyzer of copper would be placed in continuum which would indicate us the saturation of the ash that had been reached.

Then, the ash would be changed rebombing the water to the upper part of the tailing pond, installing bombs and an intermediate deposit which already exists In the mine, through treat the water again.

The ash would be transported, sand and ash altogether, without being separated being able to be used in road building [17].

In the case of a recovery of the copper retained by the ash, the solution would be a washing with water slightly acidulated so that the copper would pass to a solution to undergo later a cementation over scrap iron.

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