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Chemical Engineering Journal 84 (2001) 167–171

Chemical Engineering Journal

www.elsevier.com/locate/cej

Study of leaches obtained from the disposal of fly ash from PFBC and AFBC processes

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Abstract

Several works have been carried out in relation to the disposal of residues from conventional coal combustion processes [1,2]. However, these residues are different from those proceeding from fluidised bed combustion systems, mainly due to the sorbent (limestone or dolomite) used to the removal of SO_2 emissions.

In this paper the environmental implications [3] of the disposal of residues from fluidised bed combustion systems are studied. The procedures to evaluate the leaching behaviour of these residues have been done at three levels: shaking, column and lysimeter studies. Comparison between the three methods has been carried out, concluding that the results obtained with columns tests and lysimeter tests are very similar. So, to evaluate the environmental impact of fly ashes, it would not be necessary to do lysimeter tests (which are expensive and need a lot of time) in order to know the behaviour of ashes once they are disposed of.

Keywords: Fluidised bed systems; Lysimeter tests; Leaching

1. Introduction

Coal is the most abundant and widely spread fossil energy resource in the world. For that reason, coal will continue playing and important role in the energy production of the future. However, due to a more exigent environmental legislation, clean coal technologies are being developed, as for example fluidised bed systems, atmospheric and pressurised FBC systems. Large quantities of residues are produced by coal combustion using fluidised systems. During transport, disposal and storage phases these wastes are subject to the effects of rain as a result of which, part of the undesirable components of the ashes may become incorporated in both ground and surface waters. It is important to predict the leaching behaviour of residues to prevent these environmental effects. In this study, a comparison between leaches from ashes produced in different combustion systems (atmospheric circulating FBC, pressurised FBC and conventional pulverised coal combustion) is presented. This study shows the possible environmental effects of disposal ashes, mainly referred to the leaches produced.

The fluidised AFBC and PFBC coal wastes have a high sulphate content [4] and low trace elements concentrations and contain a significant proportion of absorbent (usually limestone) that remains as calcium.

Several methods are foreseen in the legislation to analyse this environmental impact, especially important being leaching tests in the disposal site, by means of columns and lysimeter measurements.

The procedures to evaluate the leaching behaviour of the residues are done in three ways: shaking tests, column tests and lysimeter tests. The shaking tests give information about the maximum achievable leaching, while the lysimeter tests represent more accurately the real conditions which would occur if the sample of solid combustion residues were stored in a disposal site, where it might enter into contact with rainwater.

2. Experimental

2.1. Sources of residues

The solid from the circulating fluidised bed system was generated in a 0.3 MW pilot plant at Ciemat by burning two types of Spanish coals. The ashes were produced in the pressurised fluidised bed proceed through the combustion of a lignite the composition of which is shown in Table 1. Limestone was used as an absorbent in the 80 MW fluidised bed Escatrón plant in Spain. Limestones were using as absorbent of the SO_2 generated during the combustion process.

The combustion of coal in these facilities produced two types of solid combustion wastes, some from overflow of

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1385-8947/01/$ – see front matter
PII: S1385-8947(01)00201-7

Table 1
Characteristics of combustion plants studied[a]

Site (Spain)	Escatrón	Madrid	Madrid
Plant characteristics	Demonstration FBC pressurised bubbling	Pilot FBC atmospheric circulating	Pilot FBC atmospheric circulating
Ashes reference	Ash-1	Ash-2	Ash-3
Coal	(1)	(2)	(1)
Absorbent	(3)	(3)	(3)
Ca/S ratio	1.7–2.0	2	2
Temperature (°C)	840	860	850
Bed ashes (%)	23	21	28
Cyclone ashes (%)	77	79	72

[a] The numbers (1) and (2) represent different Spanish coal types, and number (3) represents limestone.

the bed and others from the particulate control systems. For this study both coal wastes were mixed, obtaining only one sample of leach for testing. Details of the combustion systems are presented in Table 2.

2.2. Chemical composition

The characteristics of the coal used and the type of installation employed in generating the solid combustion wastes have a direct influence on chemical and mineralogical composition of ashes. Data on the chemical composition are presented in Table 3.

The main components of the solids residues from coal combustion in fluidised beds, using limestone as the absorbent of the SO_2, are those arising from the sulphating reaction ($CaSO_4$) and the by-products of this reaction (CaO, $CaCO_3$).

The content of majority compounds, such as SiO_2, Fe_2O_3, Al_2O_3, Na_2O and K_2O, in the solid combustion residues depends on the presence of these components in the mineral matter of the coal used in their generation. This same phenomenon may be observed in the case of the minority elements (Ba, Cr, Ni and V).

The type of installation used in generating the solid residues, AFBC and PFBC, has a direct influence on the mineralogical composition of such residues and on their particle size. When the combustion occurs in a pressurised system, calcite ($CaCO_3$) appears as the main component in the residues generated in addition to anhydrite ($CaSO_4$), while if the system is atmospheric, lime (CaO) is detected instead of calcite. This points to the existence in both systems of different mechanisms in the desulfinization process.

2.3. Leaching tests

Although a chemical waste characterisation can give us an idea about the effectiveness of passing the pollutants through water in order to quantify this phenomena it is necessary to carry out leaching tests [3]. These tests can be classified in two groups, laboratory tests (leaching in shaking batch and leaching in columns) and field-tests [5] (lysimeters and measurements in disposal sites).

Table 2
Chemical analysis of coal

	Coal 1	Coal 2
Proximate analysis		
Moisture (%)	3.7	5.5
Volatile matter (%)	44	33.2
Ash (%)	32.5	29.3
Fixed carbon (%)	23.4	37.5
Elemental analysis		
Carbon (%)	43.8	43.6
Sulphur (%)	8.7	7.5
Nitrogen (%)	0.6	0.5
Hydrogen (%)	3.6	3.3
Oxygen (%)	10.6	15.7
Gross calorific value (kcal/kg)	4513	4382

Table 3
Chemical analysis of coal wastes

	Ash-1	Ash-2	Ash-3
Major elements (wt.%)			
Al_2O_3	4.2	8.7	4.1
CaO	41.0	38.3	41.5
Fe_2O_3	2.4	7.4	1.7
K_2O	0.5	0.3	0.4
MgO	0.6	0.9	0.9
Na_2O	0.5	0.07	0.6
TiO_2	0.06	0.14	0.2
SO_3	19.7	20.1	26.3
SiO_2	12.6	14.2	14.3
Trace elements (ppm)			
As	<1	<1	<1
Ba	98.5	94.0	106.0
Be	1	4	2
Co	4.5	9	4
Cr	24	54	28
Cu	10	18	10
Mn	91	141	86
Mo	<5	<5	<5
Ni	10	26	15
P	248	269	300
Se	<0.15	<0.15	<0.15
V	31	79	38
Zn	60	<10	67

Shaking standardised batch leaching tests [6,7] are used in Spain and many other countries [8] to determine if a residue is hazardous or not hazardous. But that kind of test does not represent the reality as they reveal only the total quantity of an element that can be leached because the test was made in favourable conditions for the leaching. The Spanish legislation governing toxic and hazardous wastes includes two methods of leaching based on agitation: method 1 or EP and method 2 are detailed in Section 2.3.1.

Although shaking tests provide a rapid method to evaluate the leaching characteristics, they produce the least useful results. It is very important to have more representative models of real conditions. To this end, two types of tests can be done, column tests and lysimeter tests. In both cases the liquid percolates through the waste, and the leaches are collected during the test, these are long-term tests. In column and lysimeter tests it is necessary to condition the coal wastes before they are introduced into the lysimeter by adding water to the waste until the appropriate moisture content is reached (preliminary tests are made to determine the quantity of water to obtain the optimum conditioning).

2.3.1. Batch shake leaching tests

Shake tests are the simplest method to evaluate the maximum quantity that can be leached from a residue to obtain a first estimation about the environmental impact of wastes. This test consists of the continuous shaking of the waste with an elution agent, deionized water, working at controlled pH, short times and with a high liquid/solid (L/S) ratio. Two Spanish official methods were employed.

Method 1: the dry waste (100 g), with a particle size not >9.5 mm, was mixed with the liquid (1600 ml of deionized water) with a L/S ratio of 20/1, 24 h at 20–400°C. During the test the pH was adjusted to 5.0 ± 0.2 by addition of 0.5 M acetic acid. After shaking, a liquid–solid separation was made by filtering the solution through 0.45 μm filter and finally the liquid obtained was analysed.

Method 2: 100 g of dry waste with a particle size not larger than 4 mm was treated successively with deionized water and acetic acid, maintaining the same conditions as in method 1. The test finishes when the lixiviate reached 4.5 ± 0.1 of pH value.

2.3.2. Continuous tests

Continuous tests can be made in columns or lysimeters. In both cases, before beginning the test, the ashes need a previous stage in order to arrange the solid wastes for the following phase. The ashes were treated with deionized water until reaching the adequate moisture content (defined previously in the laboratory test). It was considered that the ashes were well prepared when the fine particles were balled, forming little spheres. It is necessary to obtain a homogenous bed and facilitate the passage of liquid through the bed.

The ashes from Escatrón were compacted to 50% of the maximum compacting that it is possible to reach, in order to decreases the volume of wastes. Tests with ashes compacted and without compacting were carried out when there was enough quantity of sample with the purpose of comparing the results obtained (Table 5).

2.3.3. Column tests

The column tests represent more accurately the real situation although in this type of test the conditions when a waste is situated in a disposal site are not totally simulated. These tests were made in PVC columns of 160 mm diameter and 1000 mm height. The liquid percolates upward through the column and samples are taken at the exit of the column during the tests.

The irrigation flow was 4 cm^3/h, this is 5 or 6 times higher than the rain regimen from the driest zone where the installations studied are located (Escatrón).

In this type of test it is necessary to know the composition of the first percolate as this will contain higher concentrations than the rest. The only problem of this type of test is that on some occasions the permeability decreases so dramatically during the test that no flow of leachate is produced.

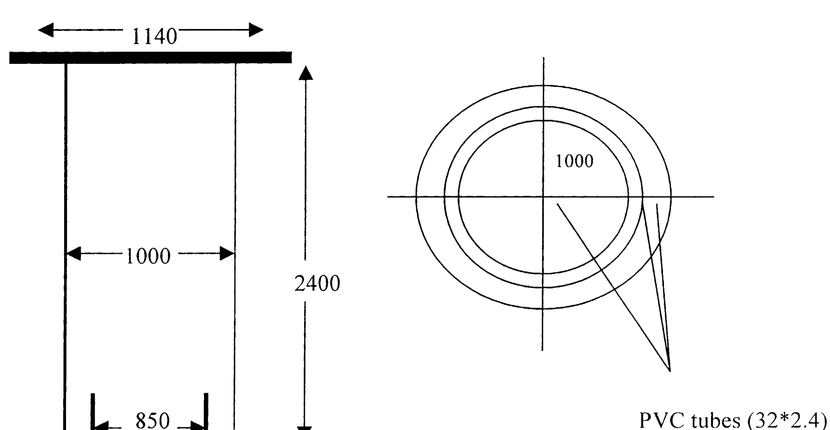

Fig. 1. Lysimeters (size in mm).

2.3.4. Lysimeter tests

Lysimeter tests represent the exact conditions when a residue is disposed of. In this case the liquid percolates down-flow through the lysimeter and samples are taken at the exit of the column during the tests, so that natural rain conditions are simulated.

The lysimeter scheme is presented in Fig. 1. It consists in a cylindrical tank of 1000 mm diameter and 2400 mm height and has three pipes with 32 mm diameter and 80 mm height. Two of them are situated in the back end for the lixiviate drain adjacent to the central and peripheral areas and the other one is situated in the area for spillage.

When the ashes were conditioned these were placed in the lysimeters on top of a layer of broken-stone (15 cm). The length of time for this test was 10 months. During this time a watering of 60 l was made each week. The total volume supplied to each lysimeter was equivalent to the rain fallen during 10 years, considering the recorded rain flow in this area (400 l/m^2 per year). No special problems with the watering of the lysimeters were experienced in the test.

2.4. Comparison between tile leaching tests

Using the ashes obtained from the two combustion systems, three types of leaching tests have been carried out and the characteristics of the test are presented in Table 4.

The principal components of the leaches content obtained for each of the ashes tested, in shaking tests, columns and lysimeters are shown in Table 5.

Table 4
Characteristics of the different leaching test[a]

Test type	Sample weight (kg)	Ratio L/S	Time
Shaking method 1	0.1	20/1	1 day
Shaking method 2	0.1	100/1	5 days
Column	10.6–21.2	2.1/1	10 months
Lysimeter	1180–1950	1.6/1	10 months

[a] L/S: liquid/solid.

The values referred to the solubilization of majority elements in the shaking test are much higher than the watering tests (columns and lysimeters) detaching the calcium and sulphate values. This effect is less clear for sodium and potassium because in these elements the values are closer and sometimes these are reversed.

In method 2 the solubilization of compounds is much higher than method 1, due to fact that in method 2 the ratio L/S, the duration of test and the quantity of acetic acid are increased.

In columns and lysimeters the abilities to wash out pollutants are similar so it is sufficient to use columns tests in order to foresee the behaviour of these wastes in a disposal site. Column tests need less time and cost.

On the other hand, the compacting of the ashes has produced no effect over the solubilization of compounds, the effect is principally, that the permeability and the volume in the disposal site decrease.

The minor elements are not detected in the leaches or have very low concentrations and can be considered without environmental impact.

Table 5
Leaching of components in the different type of tests[a]

Wastes coal	Leaching of components (%)					
	Shaking tests		Column tests		Lysimeter tests	
	Method 1	Method 2	NC	C	NC	C
Ash-1 (Escatrón)						
pH			9.5	9.5	9.5	9.5
Ca	19.1	79.5	0.36	0.25	0.18	0.17
K	1.2	8.6	10.2	9.8	12.4	11.2
Na	2.2	8	3.44	3.25	1.7	1.74
SO_4	13.7	52.8	3.37	2.64	1.82	1.56
Ash-2 (Ciemat)						
pH			12		12	
Ca	21.1	76.7	0.15		0.09	
K	1	7.1	9.91		13.8	
Na	38.6	100	15.5		18.1	
$SO_4^{=}$	9.6	51	0.84		0.79	
Ash-3 (Ciemat)						
pH			13		13	
Ca	20.2	68.6	0.23		0.34	
K	2	8.5	9.65		22.7	
Na	6.4	<32	18.6		18.6	
$SO_4^{=}$	6.7	35.2	0.5		0.65	

[a] NC: no compacted; C: compacted.

2.5. Toxicity of leaches

Taking into account the fact that solid combustion residues are a relatively new material, no legislation currently governes them, as a result of which the legislation applicable to toxic and hazardous wastes is used for the toxicity study. This law indicates that in order to determine the toxicity or a given waste, bio-tests are to be performed, among others.

As regards the toxicity of solid fluidised combustion wastes, it may be considered that according to the bio-tests, these wastes can not be considered hazardous, since the results of these tests show values far from those indicating toxicity. The only toxicity shown by the leachates obtained from the different leaching tests consists of their high alkalinity and sulphate content. In any case, given the small flows of leachates and the fact that they will be diluted to a large extent when they are introduced into public systems or river basins, the contamination that they might cause can not be considered a problem.

3. Conclusions

The main conclusions obtained in this work have been classified in two groups.

Tests are necessary in order to establish the toxicity of the ashes. In order to study the toxicity of the leaches from coal wastes in a disposal site it is necessary to carry out the shaking test, initially. If the leachates are not toxic, it is not necessary to do more tests because shaking tests represent the best leaching conditions and generate the highest quantity of leachates.

If the leachates are toxic, it advisable to perform column tests because the results in these tests are more approximate to find out what can occur in the disposal site. Field-tests are not obligatory because they provide the same results as column test and they are more expensive and need more time.

The toxicity of ashes produced from different types of combustion processes. Their high pH and their high contents in calcium sulphate characterise the leachates obtained in all tests. The other soluble elements present in the ashes (Na, K) are found in very low concentrations and these values will decrease when the test advances.

The high sulphate concentrations and the high pH in the leaches indicate that these ashes should be considered as toxic residues according to the European legislation, but not toxic if the Spanish legislation is applied.

The minority components of ashes, such as heavy metals are present at very low levels, below the detection limit of the analytical techniques. This is due to a very high pH in the majority of the cases. At this high pH the metals in the ash are precipitated (except the amphoteric elements, Al, Zn, Cr, etc.).

The effect of compacting leads only to a reduction in permeability and in the volume in the disposal site and no effect are detected on the solubilization of the components.

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