

Occurrence and distribution of valuable metals in fly ash from Puertollano IGCC power plant, Spain

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INTRODUCTION

In 1992 an Integrated Gasification in Combined Cycle (IGCC) plant in Puertollano (Spain) was launched as a THERMIE Targeted Project to demonstrate the feasibility of the European IGCC technology. Now that this plant is running in commercial operation, it proves the use of coal with high efficiency in an environmentally friendly manner. The Puertollano IGCC plant design innovative features focus on two main targets: improved efficiency (45% net, ISO conditions) and reduced emissions. The design concept is arranged at the maximum integration level (specially, the air streams and nitrogen network) and large capacity components (2600 t/day gasifier and 200 MW gas turbine rating) were selected.

Works started at the site in April 1993, and mechanical erection of the Combined Cycle Plant began in June 1994. The first gas turbine operation with natural gas was carried out in April 1996 and in September 1996, the combined cycle 100 hours test was undertaken. The first gasifier firing on design feedstock took place in December 1997, in August 1999 the IGCC 100 hours test was undertaken. Between February and March 2000, ELCOGAS proved the flexibility of the gasification process by carrying out four tests using different coal/coke mixtures (respectively 54/46, 58/42, 42/55 and 39/61 in weight) over 525 operating hours. Until May 2001, 7537 h of operating gasifier have been accumulated. The net electricity production with coal gasification is currently 1379442 MWh and the Gas turbine maximum achieved load on coal gas operation has been 197.6 MW.

The annual production of IGCC by-products from the Puertollano power plant is 12000 tonnes of fly ash and 90000 tonnes of slag. Due to the geochemical peculiarities of the Puertollano coal¹ and to the blend of coal/petroleum coke used as feed fuel, the IGCC fly ash from Puertollano plant is characterized by high contents of valuable elements, such as V, Ni, Ga and Ge. Owing to the high market prices of these elements (441 Euro/kg of Ga, 1000 Euro/kg of Ge, 10 Euro/kg of Ni and 15 Euro/kg of V, see

<http://www.metalprices.com>, ELCOGAS addressed investigations on the evaluation of the possibilities for the extraction of these metals from fly ash. The occurrence and distribution of these metals in IGCC fly ash is totally different from conventional coal fly ash, from which metals have been extracted. Hence, research has to be developed to investigate economically feasible extractive processes specifically for IGCC fly ash.

In this first publication the results on the physical and chemical characterization of the IGCC fly ash, as well as on the occurrence and distribution of valuable metals are presented.

EXPERIMENTAL

Raw gas produced in the gasifier is filtered in two vessels, after cooling down in the waste heat system. In the filter vessels, fly ash is retained through ceramic candle filters, cleaned on-line during filtration, to achieve a minimum dust content in the de-dusted gas. The collected dust falls by gravity into the fly ash cone under 265 °C and is discharged in trucks.

Seven IGCC fly ash samples were collected from the discharge system. The samples were obtained under different operation conditions with a feed fuel made up of a blend of coal and petroleum coke (50:50, see Table 1).

Table 1. Fly ash samples with the indication of the sampling date and the fuel composition.

Sample	Date	coal/coke
21	10 th September 1999	50/50
30	10 th February 2000	54/ 46
66	25 th August 2000	50/50
67	11 th September 1999	50/50
68	16 th September 1999	50/50
69	11 th July 2000	50/50
70	25 th October 2000	50/50

The physical characterization of fly ash included proximate analysis (moisture content and loss ignition determined under 100 and 1050 °C, respectively), as well as the grain size distribution. The grain size distributions of the fly ash were determined by means of a laser light scattering-based particle sizer for grain size determination of powder in suspension, ranging from 0.1 to <600 µm. To this end, an ethanol media with an ultrasound bath prior to the grain size analysis was used.

Major and trace element concentrations were determined in the fly ash samples by means of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using the sample treatment and analytical conditions determined elsewhere². Silica contents were determined directly by X-Ray Fluorescence (XRF). Fly ash international reference material NBS 1633b was used as a reference sample to check the accuracy of the analytical and digestion methods.

The crystalline phases of the fly ash samples were examined using X-ray powder diffraction with a graphite monochromator, NaI(Tl) detector and Cu K α radiation. Due to

the very fine grain size and to the low content of crystalline phases, a very slow scan (12 s/0.02 °2θ) was applied to obtain enough sensitivity for the detection of the mineral components.

Leaching tests following DIN 38414-S4 recommendations were carried out to determine the solubility of major and trace elements.

A four sequential extraction procedure³ was also applied to investigate the mode of occurrence of selected elements in the fly ash. Attending to the fly ash composition and the extraction steps used, Table 2 summarizes the sequential extraction associations inferred⁴⁻⁶.

Table 2. Modes of occurrence of elements in fly ash as inferred from the sequential extraction procedure used and the fly ash composition.

STEP	REACTIVE	C (M/l)	pH	Phase
1	Acetic acid (CH ₃ COOH)	0.1		exchangeable or soluble
2	Hydroxyl ammonium chloride (NH ₂ OH-HCl)	0.1	2.0 HNO ₃	reducible or bound to Fe-Mn oxides
3	Hydrogen peroxide (H ₂ O ₂) followed by Ammonium acetate(CH ₃ COONH ₄)	8.8 1.0	2.0 HNO ₃	oxidable phases, mainly sulfides
4	Bulk digestion (HNO ₃ :HCl;HF)			residual (bound to silicates)

Finally, several leaching conditions were applied to extract selected metals from the fly ash. Table 3 summarizes the experimental conditions used. The concentrations of the elements of interest in the extraction solutions were determined using the analytical procedures described above.

Table 3. Experimental conditions used for the extraction of selected elements from IGCC fly ash.

	Media	Extractant/fly ash l/kg	t h	T °C
Ge	H ₂ O	2, 5, 10	6, 24	25, 50, 90, 150
V	NaOH (1,2 M)	2, 5, 10	6, 24	25, 50, 90, 150
Ga	NaOH (1,2 M)	2, 5, 10	6, 24	25, 50, 90, 150
Ni	H ₂ O ₂ (0.3-6.6%wt/v)	2, 5, 10	24	25

RESULTS AND DISCUSSION

Fly ash characterization

Moisture and LOI yields of IGCC fly ash were very low, <0.2 and from 2.0 to 3.7 %, respectively. The analysis evidenced two types of sample according to the grain size distribution (Table 4). Fly ashes collected in September 1999 (group 1) have a coarse grain size (median from 32 to 67 μm), whereas the other samples from 2000 (group 2) have a constant fine grain size (median from 2 to 4 μm). The chemical composition of the IGCC fly ashes is summarized in Table 5.

The IGCC fly ash from Puertollano is characterized by a high SiO₂ content (57 to 63 %) and a very high SiO₂/Al₂O₃ wt ratio (3) when compared with conventional pulverized coal

combustion fly ash (PFA). Furthermore, the contents of Pb, V, Zn, Ni, As, Sb, Ge and Ga are very high with respect PFA due to the high contents of Ge, Pb and Zn of the Puertollano coal¹ and to the use of petroleum coke as a feed fuel (Ga, V, Ni). Conversely, the content of Fe, Ca, K, Mg and Na are relatively low. Contents of SiO₂, V, Ni, Co and P are slightly higher in the group 2 (finer fly ash) with respect to the group 1. Conversely, contents of Ca, Zn, Pb, As, Ge, Mn, Sb and Cd are higher in the coarser fly ash.

Table 4. Grains size distribution of IGCC fly ashes (10 and 90 % percentiles and median).

Sample	10% Percentile	Median (μm)	90% Percentile
67	2.2	67.0	152.1
21	1.4	27.8	120.4
68	1.3	32.2	133.3
30	1.3	4.3	110.5
66	1.3	4.5	100.0
69	1.4	3.8	65.7
70	1.1	2.1	15.9

Table 5. Range of major and trace element contents in the two groups of IGCC fly ashes.

	Group 1	Group 2		Group 1	Group 2		Group 1	Group 2
	%			mg/kg				
SiO ₂	56.7-57.1	59.5-62.6	Mn	340-356	207-472	Cs	175-195	170-182
Al ₂ O ₃	18.8-19.8	17.7-21.0	Ge	289-313	194-277	Li	182-188	182-197
CaO	5.9-6.5	3.0-3.3	Ga	186-221	149-181	Rb	197-210	191-208
Fe ₂ O ₃	3.8-4.1	3.9-4.8	As	702-833	564-841	Sc	11-12	11-17
K ₂ O	3.3-3.7	3.3-3.6	Sb	590-672	330-633	Se	0-6	2-15
SO ₃	3.1-3.8	2.3-3.9	Cd	23-28	13-21	Sn	55-73	43-73
MgO	0.8-0.9	0.6-0.9	Cu	247-255	242-283	Sr	101-105	94-102
Na ₂ O	0.6	0.5-0.6	Mo	85-108	110-134	Ta	1-3	2-3
P ₂ O ₅	0.3-0.5	0.9-0.5	Co	28-31	32-58	Th	20-22	18-25
TiO ₂	0.5-0.6	0.5-0.6	B	145-162	89-236	U	12	13-14
Zn	0.6-0.7	0.4-0.5	Ba	398-410	356-405	Tl	15-20	12-14
Pb	0.6-0.7	0.3-0.5	Bi	6-10	7-9	W	47-61	58-69
V	0.3-0.4	0.5-0.6	Cr	125-145	129-141	Zr	126-133	130-147
Ni	0.1	0.1-0.2						

The XRD analysis (Figure 1) showed that the major crystalline phases present in the IGCC fly ash are Pb, Zn and Fe sulfides (Galena, sphalerite and wurtzite and pyrrhotite, respectively). Some SEM-EDX analyses were carried out in the fly ash deposited on the heat exchanger tubes that cool down the raw gas from 800°C to 600°C. Metal concentration in these deposits is much higher (> 10 times) than in the current fly ash (discharged in trucks) used in this study. However, we analyzed these deposits to study the form of occurrence. SEM-EDX analysis evidenced the occurrence of Pb, Fe, Zn and Ni-Fe-As sulfides, elemental sulfur and Ge oxides (Figure 2). All these crystalline phases are on the surface of typically rounded fly ash particles, usually with a grain size < 1 μm . The occurrence of sulfides in the fly ash deposits is due to condensation processes from a high H₂S and heavy metal gasification flue gas⁷.

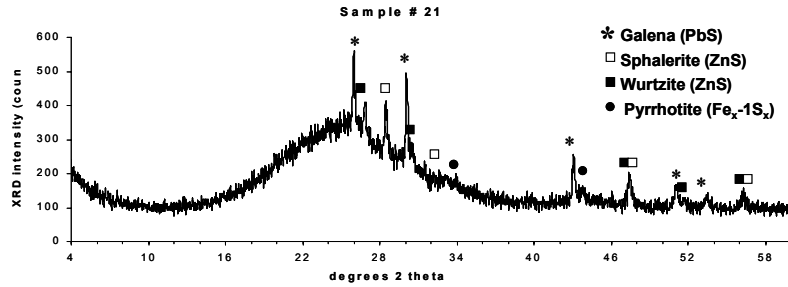


Figure 1. XRD patterns of IGCC fly ash #21.

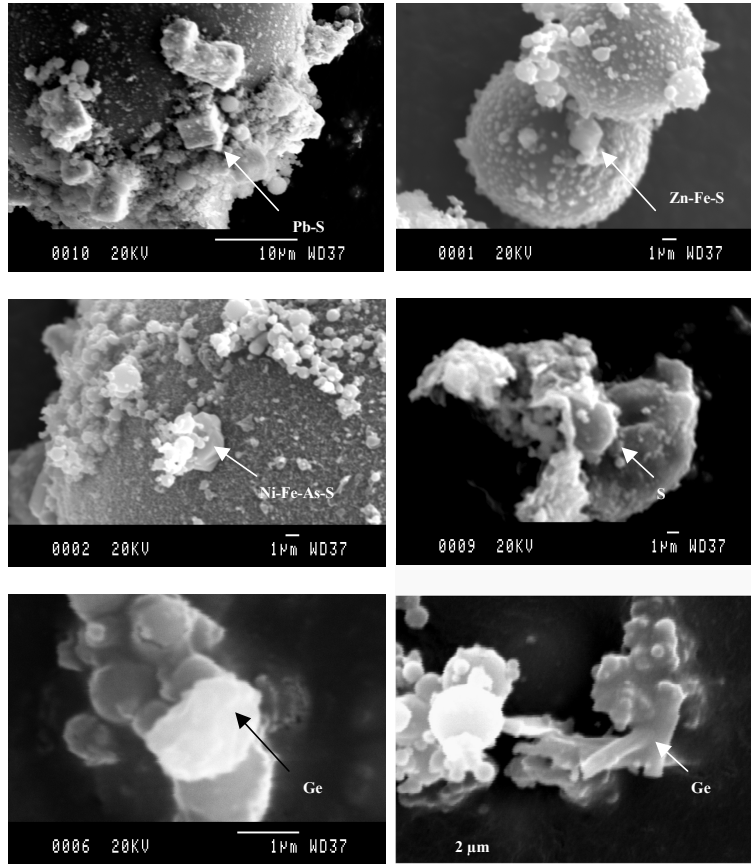


Figure 2. SEM microphotographs, coupled with EDX analysis, showing the occurrence of Pb, Zn-Fe and Ni-Fe-As, elemental sulfur and Ge oxide in the IGCC fly ash.

The water extractable contents (leaching test DIN 38414-S4) of major and trace elements in IGCC fly ash (Table 6) vary widely from >80 % for As and Ge, 10-28 % for Sb, Ni and B, 3 to 2 % for Li, W, P, Co, S, Na, Mg, down to < 0.1 for most of the elements studied. The acidity of the leachates (4.1 to 5.5 pH) and the presence of thiosulfate evidence the presence of acidic species, probably sulfide species. The most interesting result is that Ge occurs in a water soluble species. The highest water soluble Ge species is the hexagonal or the vitreous GeO_2 which have a solubility in water of 4.5 and 5.2 g/l, respectively, under room temperature⁸ and up to 13 g/l under 100 °C. Concerning As, due also to the high solubility, the most probable species occurring in

the fly ash are As_2O_3 (solubility in water under room temperature 37 g/l) or As_2O_5 (1500 g/l). The SEM-EDX analysis evidenced that a proportion of As is also present in Ni-Fe sulfides.

Table 6. Water extractable contents (leaching test DIN 38414-S4) of major and trace elements in IGCC fly ash.

% wt soluble dry basis	
As, Ge	80-92
Sb, Ni, B	10-28
Li, W, P, Co	3-5
S, Na, Mg	1-2
Mo, K, Tl	0.5-1
Ca, Zn, Rb, Sc, Mn, Sr, V, Ba, Cs	0.1-0.2
Al, Fe, Bi, Cd, Cr, Cu, Ga, Pb, Sn, Th, Ti, U, Zr	<0.1

The results of the sequential extraction (Figure 3) for the most interesting metals, (Ge, Ga, V, Zn and As), showed four different modes of occurrence.

- Ge is mainly associated to the soluble phase (70%) and only a 30% is present in the residual phase, confirming the occurrence of an hexagonal or vitreous Ge dioxide.
- Zn, Ni and As mainly occur as soluble (from 35 to 50%) and reducible and oxidable species (35-60%). The acidity of the leaching steps for both oxidable and reducible phases probably accounts for the dissolution of the very fine Zn and Ni sulfides observed by SEM-EDX and XRD
- Ga is mainly bound to oxides (55 %) with minor proportions attached to the oxidable (25%) and aluminium silicate (20%) fractions.
- V is mainly bound to the oxides in the aluminium-silicate matrix (85 %).

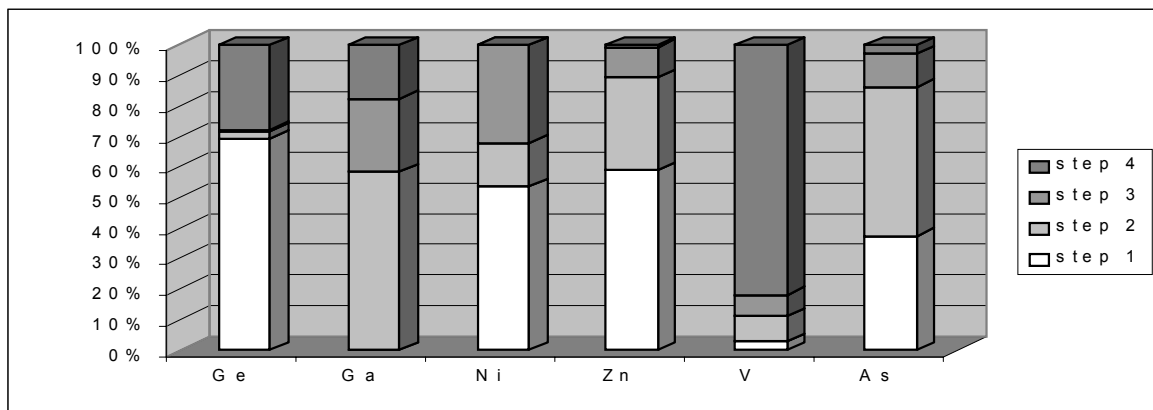


Figure 3. Modes of occurrence of Ge, Ga, Ni, Zn, V and As in IGCC fly ash as deduced from the sequential extraction tests. Step1: soluble species, step 2: reducible species, step 3: oxidable species, step 4: oxides in the residual fraction.

Nickel

Based on the significant sulfide association of Ni obtained from SEM-EDX analysis and the sequential extraction study and the low efficiency of water leaching tests (see Table 7), an oxidizing media was used to extract this metal from the fly ash.

Table 8 shows high extraction yields (from 59 % to 80 %) for Ni by means of H₂O₂ leaching. The extraction yields increase as a function of the H₂O₂ concentration and the extractant/FA ratio. Thus, the highest extraction rate (78-80 %) is reached under room temperature, an extractant/FA rate of 10 l/kg, and 0.66 to 3.3 % wt/v H₂O₂.

High extraction yields are also obtained for Ge (59 to 78 %) but lower than those obtained with water. Conversely, As and Sb contents in the leaching solutions are very low (>1% and from 3 to 5 % respectively).

Table 8 Ni, Ge, As, Sb extraction yields, using group 2 fly ashes and hydrogen peroxide, as a function of % wt H₂O₂ and extractant/FA (l/kg). Values in % wt extracted with respect to bulk fly ash content.

T=25°C												
t=24 h	Ni			Ge			As			Sb		
% H ₂ O ₂ wt/v	0.66	1.98	3.3	0.66	1.98	3.3	0.66	1.98	3.3	0.66	1.98	3.3
5 l/kg	59	69	78	13	47	57	<1	<1	<1	3	3	4
10 l/kg	78	79	80	48	68	78	<1	<1	<1	5	4	4

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