Germanium and Gallium Extraction from Gasification Fly Ash: Optimisation for Up-scaling a Recovery Process

Fátima Arroyo[2]; Oriol Font[1]; Constantino Fernández-Pereira[2]; Xavier Querol[1]; Josep María Chimenos[3]; Hubert Zeegers[4]

[1]IDAEA-CSIC (Institute of Environmental Assessment and Water Research Spanish Research Council) and IJA-CSIC (Institute of Earth Sciences, “Jaume Almera”).

[2]AICIA (Chemical and Environmental Engineering Department of the University of Seville, Technical Engineering School, Camino de los Descubrimientos s/n, Seville (Spain), 41092)

[3]University of Barcelona, Department of Materials Science and Metallurgical Engineering

[4]War Eagle Mining Company

KEYWORDS: Germanium, Gallium, Fly ash, Integrated Gasification with Combined Cycle (IGCC)

ABSTRACT

Germanium and gallium occur as water soluble Ge (hexagonal-GeO_2 and GeS_2) and Ga oxide species in relatively high contents in the Puertollano Integrated Gasification with Combined Cycle (IGCC) fly ash. Both the speciation and contents of Ge and Ga in this co-gasification (50:50 coal/pet-coke) fly ash, allowed starting research for developing water (Ge) and alkaline (Ga) extraction methods. In view of the relatively high Ge and Ga extraction yields obtained in these early extraction tests, the research was currently directed towards the optimisation of the extraction procedure by investigating the extraction (simultaneous if possible) of both elements to obtain high extraction yields regardless of the fly ash and operational conditions of the IGCC plant. A number of extraction tests were carried out using different extractants (H_2O, NaOH, HCl, H_2SO_4, H_2O_2, $Ca(OH)_2$, $NaHCO_3$, $H_2C_2O_4$ and $C_6H_6O_2$), to cover a wide range of extraction conditions (acid, alkaline, complexant, reducing and oxidising), on a number of IGCC fly ash samples from the Puertollano IGCC plant produced under different conditions. The results revealed that relatively high Ge extraction yields (up to 83 % after 2 h leaching period) may be achieved using a weak acid solution. Gallium yielded up to 70 and 64 % extraction after a 24 h leaching period using a weak acid and alkaline solution, respectively. The variability obtained in the Ge extraction yield among different fly ash samples is lower than that obtained by water extraction. These major findings increased feasibility for a potential up-scaling of the extraction process of these elements and allowed to start research of subsequent enrichment and separation methods in a small scale pilot plant.

INTRODUCTION

Germanium and gallium occur in relatively high contents in the fly ash produced in the Puertollano (Spain) Integrated Gasification with Combined cycle (IGCC) power plant

(ELCOGAS plant). Highly water soluble Ge species (hexagonal-GeO_2, Ge sulphides) and Ga phases (either as free Ga oxide and Ga in the Al-Si fly ash matrix) are the prevalent species of these valuable elements in the Puertollano IGCC fly ash[1-3]. Both speciation and the relatively high contents of valuable metals in this gasification fly ash justified to start research on evaluating the potential feasibility of an extraction and recovery process for Ge and Ga from this gasification fly ash. Based on the Ge and Ga speciation in the Puertollano IGCC fly ash, a sequential extraction procedure based on a starting water leaching step for the extraction of Ge and subsequent alkaline leaching (NaOH-based extractant) of the resulting solid residue for the extraction of Ga, was designed. After extraction, subsequent enrichment of the Ge and Ga leachates and precipitation methods were investigated to evaluate the efficiency of the process and the purity of the Ge and Ga end-products. Enrichment by re-circulating the extracted solution, by activated carbon[4-5] and by solvent extraction[6-7] was tested for Ge. This valuable element was precipitated as GeS_2 by sulphiding the enriched solutions or as organic complex by adding pyrocatechol (CAT) and cetyltrimethylammonium bromide (CTAB) to the enriched solutions, and subsequently roasted[8]. The Ga content in the leachates was enriched by re-circulating the extracted solution and subsequently precipitated by carbonating the enriched alkaline solution[3].

The above Ge and Ga recovery procedures allowed the production of up to 90-93 % purity of hexagonal-GeO_2 end-product and concentrations of 8 % for the Ga end-product the purity being much higher than that of the Ge and Ga end-products obtained by current industrial recovery processes for these elements[9-10]. The total Ge recovery from IGCC fly ash yielded 50-62 %, enabling a theoretical production of 3500 kg of GeO_2/year with the current annual production of fly ash in the Puertollano IGCC power plant (over 12,000 tonnes). The final potential recovery yield obtained for Ga attained 132-152 mg Ga/kg fly ash, this being equivalent to 1582-1821 kg of 8 % purity Ga/year given the current annual production of the Puertollano IGCC plant.

These promising results promoted research for the up-scaling of the recovery process. To this end, the optimization of a number of parameters of the Ge and Ga recovery process is required. Potential limitations for the immediate process industrial application are the relatively wide variability of the water Ge extraction yields for the fly ash produced in different operational conditions of the IGCC plant and the commercial use of the extracted fly ash.

The most important operational parameter controlling the Ge extraction yields is the limestone dosage. In the Puertollano IGCC plant limestone is added to a coal/pet-coke feed fuel blend as a fluxing agent. The comparison of Ge extraction yields obtained for 13 IGCC fly ash samples in the same extraction conditions (25^{o}C, water/fly ash ratio of 10 L/kg and 24 h leaching period) revealed that generally Ge yielded a lower extraction percentage (40-50 %) at high limestone dosages (4 %) than reached (53-91 %) when those are reduced down to 2 %[1,11]. Other operational conditions apart from limestone dosage are also controlling water Ge extraction yields since fly ash produced with over 2 % limestone resulted in the lowest Ge extraction yield (22 %)[11]. Most probably the occurrence of water soluble Ge species and /or that of other elements controlling the Ge extraction are modified by different operational conditions. The Ga extraction yields for different Puertollano IGCC fly ash samples are not as irregular as those of Ge, suggesting the mode of occurrence of Ga is less sensitive to changes in the operational conditions.

In view of those antecedents, the research was then focused on finding an extractant for Ge and/or Ga from IGCC fly ash, ensuring high and regular Ge and/or Ga extraction yields regardless of the operational conditions of the IGCC plant. To this end, different extraction tests were carried out using several common extractants covering a wide range of extraction conditions (acid, alkaline, complexant, reducing and oxidising) on a number of historical and new IGCC fly ash samples from the Puertollano IGCC plant produced under different operational conditions.

EXPERIMENTAL

Samples

For the optimization of the Ge and Ga extraction from IGCC fly ash, 4 historical (aged) and 4 new IGCC fly ash samples from the Puertollano IGCC plant (Table 1) were selected. The historical IGCC fly ashes cover the operational period 2000-2005 of the ELCOGAS plant and were produced under different operational conditions (mainly different limestone dosages, Table 1). The new IGCC fly ash samples were collected in the Puertollano IGCC plant from June to September 2008, a period in which the plant operated under relatively steady conditions.

The Ge and Ga contents in the Puertollano historical and new fly ash samples were determined by inductively coupled plasma mass spectrometry (ICP-MS). A special two-step sample digestion method for the analysis of potentially volatile elements devised by Querol et al.[12] was used to dissolve the solid samples prior to digestion.

As shown in Table 1, unlike Ge and Ga contents and water Ge extractable yields (Table 1) among the historical IGCC fly ash samples probably result as a consequence of a different mode of occurrence due to different operational conditions. The Ge and Ga contents in the historical Puertollano IGCC fly ash samples selected in this study are representative of the range of Ge and Ga concentrations and water Ge extraction yields found in this fly ash[11]. The Ge and Ga contents of the new fly ash samples are also in the range determined for these elements in this gasification fly ash. Regarding their variability, the Ge and Ga contents in fly ash collected within a single monthly operational period (FA#15, #16 and #17) show small differences (40 and 60 mg/kg differences between highest and lowest values for Ge and Ga, respectively, Table 1), but increasing differences up to 94 and 72 mg/kg for Ge and Ga, respectively, are observed in the case of longer sampling periods (2-3 months) (FA#18). Since the IGCC plant operated under relatively steady conditions during the sampling period and the mean life of the feed coal stockpile of the ELCOGAS plant is around 2-3 months, it may be thought that the Ge and Ga content in the feed coal is controlling the contents of these elements in the IGCC fly ash over other operational parameters. The trace element content in the Puertollano feed coal was found to be the major factor controlling the Ge and Ga content in 13 Puertollano IGCC fly ash samples produced from 1999 to 2005[11].

Germanium and gallium extraction tests

To achieve a high and regular Ge and/or Ga extractable yield, regardless of the operational conditions of the IGCC plant, 8 extractants were selected: H_2O, NaOH, HCl, H_2SO_4, H_2O_2, lime, oxalic acid ($H_2C_2O_4$) and catechol ($C_6H_6O_2$)). These extractants cover a wide spectrum of extraction conditions: acid, alkaline, oxidising and complexant conditions. As it is well known, Ge forms stable complexes with some organic reagents, so it was evaluated if the formation of some of the aforementioned complexes accelerated the leaching or improved the extraction yield.

Based on the conditions prompted by the extraction and recovery process for Ge[1,11] and Ga[11], the extraction conditions were fixed at 50^{o}C, 5 L/kg, from a 2 to 24 h leaching period. The concentration of the extractant solutions are summarised in Table 2.

These extraction tests were applied to the historical IGCC fly ash samples. The results of the extraction tests allowed the selection of the optimal extractant (s) for Ge and/or Ga. Extraction tests with the optimal extractant were subsequently applied to the new IGCC fly ash to check results and start research on optimisation of the whole recovery process for Ge and/or Ga.

Table 1. Production date, limestone dosage (%), coal/pet-coke ratio, Ge and Ga content (mg/kg) and water Ge extraction yields[2] (%) in the historical and new fly ash samples selected for Ge and Ga extraction tests.

	Fly ash	Date	Limestone	Coal/pet-coke	Ge content	Ga content	water Ge extraction yields
historical	FA#2	11/09/1999	4.1	50:50	347	284	51
	FA#7	24/10/2000	2.6	50:50	244	221	83
	FA#10	--/11/2002	2.2	50:50	356	296	55
	FA#13	20/10/2005	2.5	50:50	319	299	22
new	FA#15	03/06/2008	2.7	50:50	235	275	-
	FA#16	30/06/2008	2.8	50:50	268	284	-
	FA#17	02/07/2008	2.8	50:50	228	223	-
	FA#18	19/09/2008	2.4	50:50	174	212	-

Table 2. Experiments for Ge and Ga extraction from fly ash.

Reagents	H_2SO_4	HCl	H_2O	CaO	H_2O_2	$NaHCO_3$	NaOH	$C_6H_6O_2$	$H_2C_2O_4$
Molarity (M)	0.1- 0.5	0.1- 0.5	-	0.5-1%	0.1-0.5	0.1	0.1-0.5	0.1	0.1

RESULTS

Extraction of Ge and Ga from historical IGCC fly ash samples

Extraction with water

The historical Puertollano IGCC fly ash samples were produced during the operational period 1999-2005. Consequently these fly ashes must be aged. Due to the occurrence of fine condensed and reduced species and a high proportion of Al-Si glassy matrix (97 %) in the Puertollano IGCC fly ash[1], the major effects of aging most probably are the conversion of sulphide/arsenide to sulphate/arsenate species and a slight and partial crystallization of the Al-Si glassy fly ash matrix. Due to the very low occurrence of oxide species, carbonation may be of lower significance than sulphatation. The aging of fly ash may affect the mode of occurrence and consequently the extractable yields of valuable elements from this fly ash. In view of this, the effect of the aging of the historical IGCC fly ash samples produced in the ELCOGAS plant was tested by applying the EN 12457-2 water leaching test. According to this European regulation the leaching test was carried out in a closed system with a water / fly ash ratio of 10 L/kg, during 24 hours at room temperature (25^oC).

Previous studies carried out on the leachability of metals from Puertollano IGCC fly ash[2] revealed that Ge, As, Sb and Ni are the elements with highest extractable levels. The comparison between the results obtained from the early leaching tests (when fly ash was produced) and the leaching test carried out after storage of fly ash during several years (2-5 years) has been made. The extractable potential of Ge is reduced by a factor from 1.3 to 1.6, that of As from 2.1 to 2.8, Sb from 1.4 to 3.3 and that of Ni from 1.3 to 2.2, evidencing that aging of the IGCC fly ash reduces the mobility of Ge and other soluble elements in the ash. The causes of this are currently being investigated.

The Ge extraction yields at 50^oC, 5L/kg, ranged from 25 to 68 % among the historical and aged IGCC fly ash samples selected (Table 3). As a consequence of the aforementioned aging effect on IGCC fly ash samples, the Ge extraction yields obtained with FA#2 and FA#7 are lower than those achieved in earlier leaching tests (fresh fly ash, in Figure 1). Conversely, Ge yielded higher extraction percentages in aged than in fresh FA#10. Nevertheless, the Ge extraction yields obtained for this fly ash is relatively close in both extraction tests. As Figure 1 shows, with the exception of FA#7, the Ge extraction yields are very similar after a 6 or 24h extraction period between fresh and aged (historical) IGCC fly ashes. These differences may be attributed to the different composition and aging among the IGCC fly ash samples.

Table 3 Germanium extraction yields (%) obtained with magnetic stirring, at 50^{o}C, water/fly ash ratio of 5 L/kg and 6-12-24 h extraction period, for historical and aged fly ash.

Extraction time (h)	2	6	24
FA#2	25	27	32
FA#7	42	39	56
FA#10	45	50	68
FA#13	25	30	29

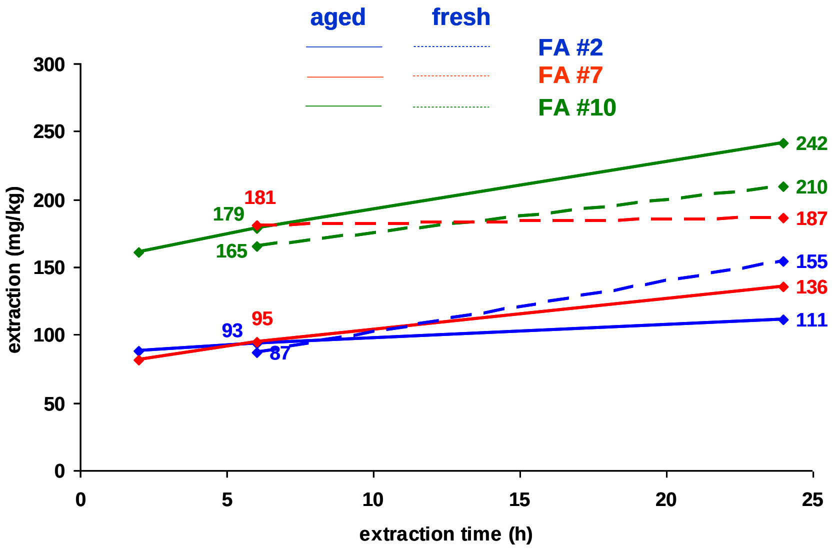

Figure 1. Comparison between the Ge extraction yields (mg/kg) obtained for fresh and aged FA#2, FA#7 and FA#10 fly ases with magnetic stirring, at 50^{o}C, water/fly ash ratio of 5 L/kg and 6-24 h extraction period.

Extraction in acid conditions

Extraction tests in acid conditions revealed different Ge and Ga extractable yields when H_2SO_4 or HCl were used. The extraction with H_2SO_4 yielded relatively high Ge extraction percentages (49 to 82 %, Table 4) while, low Ge extraction yields (<50 %) were obtained using HCl as extractant regardless the IGCC fly ash sample and extraction conditions.

Similarly, Ga reached relatively high extraction yields (35-71 % with 0.5 M H_2SO_4) while low extraction yields were reached by 0.1M H_2SO_4 (<21 %, Table 4) and 0.1-0.5 M HCl (<30 %).

The highest Ge extraction yields (80-82 %) were reached with 0.1 M H_2SO_4 after 24 hours for low Ca fly ash. The high Ca fly ash (FA#2) also yielded high Ge extraction (63 %, table

4) at the above conditions. The leaching tests also gave acceptable Ge yields (67-74 %) after a leaching period of 6 hours (Table 4).

It may be concluded that moderately high and similar Ge extraction yields (67-74%) may be achieved for IGCC fly ash produced at different operational conditions with a relatively weak H_2SO_4 solution (0.1 M) and low extraction periods (6 h). Similar to Ge, but not simultaneous with Ge extraction, high Ga extraction yields (71 %) among IGCC fly ash samples were observed with H_2SO_4 0.5 M.

The extraction of Ge and Ga also produce relatively high levels of impurities (Ni and Zn among others) and may be the main limitation for the use of this extractant for subsequent enrichment and purification steps.

HCl does not seem to be a suitable extractant for the Ge and/or Ga from the historical and aged IGCC fly ash, yielding very low extraction yields. However the extraction with HCl should be checked with fresh IGCC fly ash samples, before considering rejection of this reagent as a potential extractant for Ge and Ga, since relatively high and simultaneous Ge and Ga extraction yields (77 and 40 %, respectively) were obtained with fresh FA#7 using 0.1 M HCl at 25^{o}C, 5 L/kg and 6 h leaching period.

Table 4. Ge extraction yields (%) in H_2SO_4 extraction tests

	0.1M H_2SO_4			0.5M H_2SO_4		
	2h	6h	24h	2h	6h	24h
FA#2	-	-	63	-	-	-
FA#7	50	67	80	49	66	73
FA#10	48	70	82	42	55	50
FA#13	68	74	82	64	60	61

Extraction in alkaline conditions

The extraction of Ge and Ga using alkaline extractants, generally resulted in low yields. The extraction of Ge yielded <15 %, < 20 % and <50 % using lime, Na bicarbonate and NaOH, respectively regardless of the IGCC fly ash and extraction conditions. Similarly the extraction of Ga yielded <40, <20 % and <64 % using lime, Na bicarbonate and NaOH, respectively.

The low Ga extraction yields reached with NaOH are most probably due to the formation of Na-Al-Si and Ga zeolitic gel due to the extraction temperature selected (50^{o}C) as reported in previous studies[3]. In those studies an extraction temperature of 25^{o}C was selected for obtaining high Ga yields. Also, the aging of fly ash may reduce the extractable contents of this valuable element and it should be checked on fresh fly ash.

Table 5. Ge extraction yield (%) in NaOH extraction tests

	0.1M NaOH			0.5M NaOH		
	2h	6h	24h	2h	6h	24h
FA#2	-	-	-	-	-	-
FA#7	17	16	13	32	33	33
FA#10	15	14	9	22	23	20
FA#13	30	21	6	51	49	51

Extraction in oxidising conditions

The results carried out using hydrogen peroxide as extracting agent show that Ge and Ga extraction yields are very similar to those obtained using pure water.

Extraction with complexing agents
As shown in Table 6, the use of a complexing agent, such as catechol or oxalix acid, as an extractant accelerated the leaching of Ge, reaching relatively high and regular Ge extraction yields in the IGCC fly ash produced in different operational conditions. The Ge extraction yielded from 53 to 83 % in only a 2 h leaching period using oxalic acid and from 30-60 % and 33 to 65 % in 2 and 6 h period respectively, using catechol.

Gallium yielded extremely low values using the above complexing agents.

Apart from the fast, regular and relatively high Ge extraction, oxalic acid is highly selective for this valuable element and the leachates are characterized by low levels of impurities.

In view of these results, the use of a low concentrated oxalic acid aqueous solution seems to be highly appropriate for the extraction of Ge from IGCC fly ash.

It should be noted that the Ge extractions yields reached with oxalic acid after a 2 h leaching period are comparable to those obtained with water on the fresh historical fly ash samples used in this study by applying the EN 12457-2 leaching test[1,11]. However, the most important differences are the increase of the Ge extraction yield from 22 % (using water) up to 65 % (using oxalic acid) on FA#13, the reduction of the extraction period from 24 to 2 hours and the higher selectivity for Ge achieved after using oxalic acid.

Table 6. Ge extraction yields (%) using extraction with catechol and oxalic acid.

	Catechol			Oxalic acid		
	2h	6h	24h	2h	6h	24h
FA#2	-	-	51	53	-	7
FA#7	58	64	58	83	56	13
FA#10	59	65	50	76	79	18
FA#13	29	33	34	65	34	10

Extraction of Ge and Ga from new IGCC fly ash samples
Extraction of Ga and Ge from Puertollano IGCC new fly ash samples using water, oxalic and sulphuric acid were selected because of the relatively high and regular Ge or /Ga extraction yields.

The results of the Ge extraction with water at 50^{o}C, 5 L/kg carried out on new fly ash are in the range of 70-90 % in some cases, as expected for the mode of occurrence of Ge and other elements in the fresh IGCC fly ash.

The results obtained with oxalic and sulphuric acids also confirm the good results previously obtained with historical IGCC fly ashes.

CONCLUSIONS

The results of the extraction tests carried out on IGCC fly ash samples revealed that relatively high and regular (regardless of the operational conditions of the power plant) Ge extraction yields may be achieved using oxalic acid (53-83 %) in only a 2 h leaching period and 67 or 74 % after a 6 or 24 h leaching period respectively, using sulphuric acid. Although the water extractable yields are relatively irregular among fly ash produced under different operational conditions and are reduced by aging, the fresh IGCC fly ash samples can in some cases reach high yields (70-80 %).

The advantages and weaknesses of each extractant for the extraction of Ge and Ga from IGCC fly ash may be summarised as follows:

a) Oxalic acid: fast and relatively high and regular Ge extraction yields with a high selectivity for Ge.
b) Sulphuric acid: high and regular Ge extraction yields but needs longer leaching periods and has a low selectivity for Ge. Gallium may be extracted simultaneously with Ge but in very low proportions (<18 %)
c) Water: Relatively high and selective Ge extraction yields but considerably irregular among different fly ashes.

The extraction of Ga from IGCC fly ash is not as feasible as that of Ge, since relatively high yields may be achieved, 71 and 64 % using H_2SO_4 and NaOH, respectively, but after large extraction periods (24 h) producing high levels of impurities.

The different chemical behaviour between the Ge and Ga species in the IGCC fly ash resulted in different optimal extraction conditions, making difficult the simultaneous extraction of both valuable elements. The results also suggest that the aging of IGCC fly ash results in reducing the Ga extraction when HCl or NaOH are used. Research is being focused to corroborate the potential suitability of these reagents for extracting Ga from this gasification fly ash. Currently germanium extraction tests using oxalic acid are being developed at a small scale pilot plant.

REFERENCES

[1] O. Font, X. Querol, A. López-Soler, J.M. Chimenos, A.I. Fernández, S. Burgos, F. García Peña. Fuel 84 (2005) 1384-1392.
[2] O. Font, X. Querol, F. Plana, P. Coca, S. Burgos, F García Peña. Fuel 85 (2006) 2229-2242.
[3] O. Font, X. Querol, R. Juan, R. Casado, C. R. Ruiz, A. López-Soler, P. Coca, F. García Peña. Journal of Hazardous Materials, 139, 3, 31 (2007), 413-423.
[4] J.P, Marco, D. Cazorla, A. Linares. Patent ES 2257181 A1.
[5] J.P, Marco-Lozar, D. Cazorla-Amorós, A. Linares-Solano. Carbon 45 (2007), 2519-2528.
[6] F. Arroyo, C. Fernández-Pereira, X. Querol, O. Font, P. Coca, J.M. Chimenos, A.I. Fernández. Patent WO/2008/003808.
[7] F. Arroyo, C. Fernandez-Pereira. Ind. Eng. Chem. Res. 47 (2008) 3186-3191.
[8] F. Arroyo, O. Font, C. Fernández-Pereira, X. Querol, R. Juan, C. Ruiz, P. Coca. (2009) Journal of Hazardous Materials. In press.
[9] K.J. Bayer (1888). Process for obtaining alumina. Patent nº 382, 505.
[10] Asturiana de Zinc. Ge recovery process. Personal communication.

[11] O. Font. Trace elements in Integrated Gasification Combined Cycle Fly ash: extraction of potentially valuable elements. (2007) PhD Dissertation. Universitat Politècnica de Catalunya.
[12] X. Querol, J.L. Fernández-Turiel, A. López-Soler. Fuel 74 (1995) 331-343.