

Recovery of gallium and vanadium from gasification fly ash

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Abstract

The Puertollano Integrated Coal Gasification Combined Cycle (IGCC) Power Plant (Spain) fly ash is characterized by a relatively high content of Ga and V, which occurs mainly as Ga₂O₃ and as Ga³⁺ and V³⁺ substituting for Al³⁺ in the Al–Si fly ash glass matrix. Investigations focused on evaluating the potential recovery of Ga and V from these fly ashes. Several NaOH based extraction tests were performed on the IGCC fly ash, at different temperatures, NaOH/fly ash (NaOH/FA) ratios, NaOH concentrations and extraction times. The optimal Ga extraction conditions was determined as 25 °C, NaOH 0.7–1 M, NaOH/FA ratio of 5 L/kg and 6 h, attaining Ga extraction yields of 60–86%, equivalent to 197–275 mg of Ga/kg of fly ash. Re-circulation of leachates increased initial Ga concentrations (25–38 mg/L) to 188–215 mg/L, while reducing both content of impurities and NaOH consumption. Carbonation of concentrated Ga leachate demonstrated that 99% of the bulk Ga content in the leachate precipitates at pH 7.4. At pH 10.5 significant proportions of impurities, mainly Al (91%), co-precipitate while >98% of the bulk Ga remains in solution. A second carbonation of the remaining solution (at pH 7.5) recovers the 98.8% of the bulk Ga. Re-dissolution (at pH 0) of the precipitate increases Ga purity from 7 to 30%, this being a suitable Ga end product for further purification by electrolysis. This method produces higher recovery efficiency than currently applied for Ga on an industrial scale. In contrast, low V extraction yields (<64%) were obtained even when using extreme alkaline extraction conditions, which given the current marked price of this element, limits considerably the feasibility of V recovery from IGCC fly ash. © 2006 Elsevier B.V. All rights reserved.

Keywords: Gallium; Vanadium; Gasification

1. Introduction

Gallium and certain gallium compounds, such as GaAs and GaN, are suitable for the manufacture of high technological optical devices [1–2], such as advanced semiconductors, DVD's, laser diodes and other electronic devices [1–2]. These advanced applications, have created strong interest in the recovery of Ga from a variety of sources. Given the geochemical affinity between Al and Ga, the latter occurs mainly concentrated in bauxites and hosted by diaspore, various aluminosilicates (such as clays), apatite, nepheline and frequently alunite [3]. Ga also has a chalcophile affinity,

and thus, may occur as gallite (CuGaS₂), and is frequently substituted for Zn and Cu in sulphides, mainly in sphalerite (ZnS), germanite (Cu₂₆Fe₄Ge₄S₃₂), and chalcopyrite (CuFeS₂) [1–4]. Given this widely disseminated occurrence of Ga in the earth's crust [2], ore deposits rarely contain >0.1% of Ga, which is usually commercially recovered from bauxites and sphalerite as a by-product of the processing of Al and Zn, respectively [1,2,4]. To a lesser extent Ga is also recovered from industrial Cu processing and technological scrap [4]. The recovery of Ga from bauxite ores is based on the Bayer process, in which Al is extracted by hot alkaline digestion [6], Ga being concentrated in the Bayer liquors up to 0.19 g/L. The recovery methods of Ga from these liquors are based on Al–Ga precipitation by CO₂ and subsequent NaOH re-dissolution [6], on selective Ga extraction using liquid–liquid solvent extraction and ion exchange methods [1,5,7,8] and on employing Hg amalgam with subsequent addition of NaOH [1]. The Ga recovery from acidic solutions produced during Zn processing also involve liquid–liquid solvent extraction [11–12], while other Ga recovery methods from liquors include the use of insoluble amphoteric adsorbents

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[9] or membranes [10]. However, the difficulties associated with isolation Ga from Al always necessitate an electrolysis procedure to obtain high purity Ga end products [1].

The main producers of primary Ga are Australia, China, Germany, Japan and Russia while France is the main manufacturer of refined Ga [1], with the final price of this element ranging from 225–450 €/kg (Market Prices, 2003) depending upon purity. Despite the large estimated resources of Ga in bauxites (1 billion kg) and Zn deposits, only a small percentage (40%) is economically recoverable [1–2], so there is considerable interest in evaluating Ga recovery from other significant sources, such as phosphate ores and coal [1–3]. Although the latter typically contains up to 0.10% wt Ga, this element, along with other valuable elements, is concentrated in coal fly ash during coal combustion [13–15] and gasification [16–17]. Such concentration of metal content in fly ash and the potential recovery of these valuable elements, has led to considerable interest in metal extraction methods from coal combustion fly ash [18–20]. Previous studies have proposed fusion [18] and alkaline methods [19] for the recovery of Ga and V from coal combustion fly ash, respectively. Despite this proven suitability of coal fly ash for the extraction of potential metal ore, the most common commercial applications still involve its use in cement and other building materials.

Studies on speciation of valuable elements in the Integrated Coal Gasification Combined Cycle (IGCC) fly ash from Puertollano power plant [16,17,21], have yielded relatively simple and cheap extraction methods. The gasification fly ash is characterised by a relative enrichment in several valuable elements, such as Ge, Ni, Ga, and V, and by the occurrence of fine crystalline sulphides (rather than oxides) for many metals [16–17]. Within the content of these studies, Ge have been shown to occur as water soluble species, generating the possibility of water based extraction methods for this element [21] and allowing for starting the up-scale development of low-cost and environmentally acceptable Ge extraction techniques.

Since Ga occurs in relatively high contents (up to 320 mg/kg) in the Puertollano IGCC fly ash the research has focused on development of feasible extractive process for this element. Much of the Ga occurs as oxide in four-fold coordination, mainly as free oxide but also as Ga oxide substituting for aluminium in aluminium-silicate framework structures. A minor proportion of Ga occurs in sulphides, substituting for Zn in the sphalerite/wurtzite structure [16]. Based on this speciation a NaOH-based extractive process for Ga from the Puertollano IGCC fly ash would appear to be the most appropriate.

Along with the studies on Ga, potential extraction of vanadium from this fly ash was also investigated. Vanadium is commonly recovered from titaniferous magnetite ores and as V_2O_5 from by-products of crude oil, being mainly used to produce high-strength and low-alloy steels [22]. Since 50:50% coal/petcoke blend is gasified in Puertollano IGCC plant, fly ash is predictably enriched in V (up to >6000 mg/kg). Although the main proportion of V (>90%) is in the third valence state into the Al–Si fly ash matrix [17], it may be oxidised to V^{4+} and V^{5+} during NaOH leaching, then extracted as highly soluble vanadates in alkaline media [22–23].

This paper reports on the evaluation of the potential recovery of Ga and V from IGCC Puertollano fly ash using several NaOH-based extraction tests under different temperatures, NaOH concentrations, NaOH-solution/fly ash ratios (NaOH/FA) and extraction times (*t*). Pre-concentration and recovery methods were also investigated.

2. Methodology

2.1. Fly ash samples

Eight IGCC fly ash samples collected under different feed conditions from the Puertollano IGCC power plant (Table 1) were selected for Ga and V extraction tests. These fly ashes mainly differ in grain size and Ca content, with the contents of Ga and V ranging from 149 to 320 mg/kg and from 3302 to 6250 mg/kg, respectively (Table 1). The speciation studies on IGCC fly ash #70 have revealed that a high proportion of Ga (58%) occurs as free oxide, 24% of Ga occurs substituting for Zn in the sphalerite/wurtzite structure, and 18% is found substituting for Al in the Al–Si fly ash matrix. Over 90% of V is in the third valence state in the Al–Si fly ash glass matrix. A similar speciation is also suggested for the other IGCC fly ashes by the correlation of bulk fly ash Ga content with Al ($R^2 = 0.74$), Al–Si-bearing elements, such as Ba (0.75), Cs (0.90), Li (0.78), Rb (0.84), Ti (0.53), and elements associated with sulphides, such as Ge (0.86), Cu (0.63), and Zn (0.64). Furthermore, as show in Fig. 1, except for #129 fly ash, a high R^2 correlation factor (0.72) was obtained among Ga bulk fly ash content and sphalerite X-ray diffraction (XRD) intensity and a negative correlation among Ga bulk fly ash content and Al/sphalerite ratio (0.57). This fact suggests that, except for #129 fly ash, high Ga fly ash content are related to high proportions of Ga in sphalerite structure (rather than wurtzite and Al–Si fly ash matrix). The #129 fly ash shows the highest Ga content but no correlation with sphalerite. Since the lowest sphalerite/wurtzite ratio occurs for this sample (Table 1), a higher occurrence of Ga in wurtzite than in sphalerite is expected.

The solid residues produced from Ge extraction with water, performed at 25 and 90 °C, water/fly ash (W/FA) ratio of 2, 5, and 10 L/kg and 6, 12, and 24 h on Puertollano IGCC fly ash, were used as a starting material for the Ga and V extraction tests. Since the preliminary water leaching did not noticeably altered the major fly ash characteristics, and neither Ga nor V were leached in substantial amounts (<0.01% bulk fly ash content), this solid residue may be considered as an IGCC fly ash (Fig. 2). The lower XRD intensity of galena and wurtzite in the XRD patterns of the solid residue produced from Ge extraction with water at 90 °C and W/FA = 5 L/kg, suggests a partial dissolution of these sulphides with respect to that of initial fly ash (Fig. 2).

2.2. Extraction and recovery of Ga and V

The recovery process for Ga and V from the IGCC Puertollano fly ash was devised as follows: (a) extractive process from IGCC fly ash, (b) pre-concentration in the leachates, and (c) precipitation tests.

Table 1
Main physical and chemical characteristics of eight Puertollano IGCC fly ash types selected for this study

	Fly ash							
	#21	#67	#68	#30	#66	#69	#70	#129
Feed conditions								
Coal/coke	50/50	50/50	50/50	54/46	50/50	50/50	50/50	50/50
Limestone dose (%)	3.9	4.1	3.9	2.3	2.3	n.d.	2.6	2.4
Grain size (μm)								
P10	1.4	2.2	1.3	1.3	1.3	1.4	1.1	1.4
P50	27.8	67	32.2	4.3	4.5	3.8	2.1	3.7
P90	120.4	152.1	133.3	110.5	100	65.7	15.9	26.3
BET SA(m^2/g)	8	9	8	8	10	5	4	7
Porosity (cm^3/g)	0.1	0.1	0.1	0.03	0.1	0.03	0.03	0.04
LOI (%)	4	7	6	6	11	4	3	5
Major (%)								
C	6	6	5	6	10	4	2	4
Al_2O_3	19	19	20	19	19	21	18	24
CaO	6.4	6.5	5.9	3.0	3.3	3.3	3.2	3.6
Fe_2O_3	3.8	4.0	4.1	3.9	4.4	4.6	4.8	4.3
K_2O	3.3	3.6	3.7	3.3	3.3	3.4	3.6	3.8
MgO	0.8	0.9	0.8	0.6	0.7	0.7	0.9	0.6
Na_2O	0.6	0.6	0.6	0.5	0.6	0.6	0.6	0.6
P_2O_5	0.4	0.4	0.5	0.4	0.5	0.5	0.4	0.5
SiO_2	57	57	57	62	59	60	63	55
SO_3	3.1	3.8	3.3	2.8	3.9	2.3	2.6	2.7
TiO_2	0.5	0.6	0.6	0.5	0.5	0.6	0.6	0.6
Trace (mg/kg)								
Ba	398	399	410	384	387	405	356	433
Bi	6	8	10	7	8	9	7	5
Co	31	31	28	58	41	35	32	53
Cs	175	187	195	182	174	170	175	249
Cu	247	252	255	271	283	242	275	392
Ga	186	197	221	155	175	181	149	320
Ge	289	292	313	277	244	235	194	420
Mo	85	99	108	123	134	110	121	135
Sb	592	590	672	633	513	467	330	381
Th	20	22	21	25	18	21	20	22
U	12	12	12	16	14	14	13	6
V	3302	3896	4249	5458	5791	5037	4589	6256
W	47	54	61	60	58	69	61	80
Zn	6508	5675	6878	3922	5004	4304	3961	7230
Sphalerite/wurtzite ratio	–	1.4	3.6	2.0	1.3	1.7	1.4	1.2

2.2.1. Ga and V extraction process

A number of NaOH-based extraction tests were performed in order to optimise the Ga and V extraction conditions from Puertollano IGCC fly ash. Tests were carried out applying a

wide range of temperature (25, 50, 75, 90, 120, and 150 °C), NaOH concentration (0.1, 0.5, 0.7, 1, 2, and 3 M), NaOH/FA ratio (2, 3, 5, and 10 L/kg) and extraction times (3, 6, 9, and 24 h). To reduce the economic costs that would suppose the use

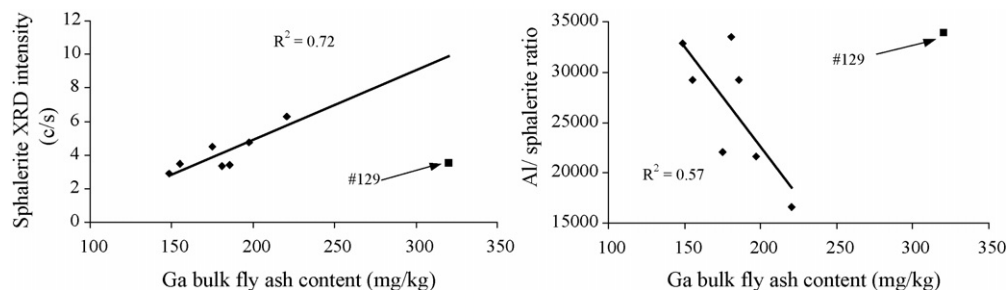


Fig. 1. Cross correlation plots among sphalerite XRD intensity and bulk Ga content, as well as Al/sphalerite and bulk Ga content, in eight Puertollano IGCC fly ash samples.

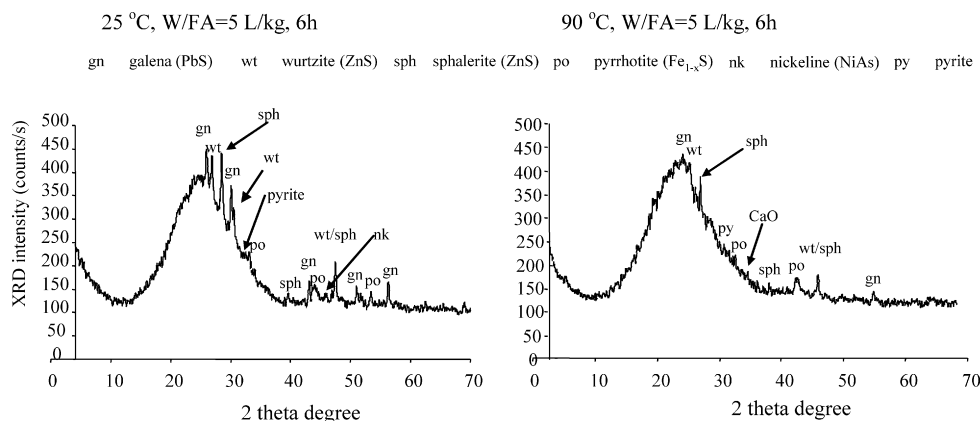


Fig. 2. XRD spectra obtained for the solid residues arising from the Ge extraction with water at 25 °C, W/FA ratio of 5 L/kg and 6 h (left) and at 90 °C, W/FA ratio of 5 L/kg and 6 h (right).

of high extraction times, $t > 9$ h were not tested for temperatures > 25 °C. Similarly, given the high costs that would result from high NaOH/FA ratios and high temperatures, NaOH/FA ratios > 5 L/kg were not applied for temperatures > 90 °C. For the Ga and V extraction tests PVC vessels of 50 mL capacity with continuous mechanical stirring were used for tests at room temperature, and a closed heated system in 60 mL Saville PFA reactors with continuous magnetic stirring on hot plates for the tests at 50 and 90 °C. The use of close extraction systems would minimize the possible oxidation of sulphides by oxygen from the air during the extraction process. The reactors were immersed in a water bath for better control and a homogeneous application of temperature. For the tests at 150 °C, a Parr 2L 4843 autoclave reactor with continuous stirring by mechanical agitation, temperature and pressure controls was used.

The content of major and trace elements were determined by means of inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS), respectively. To detect possible changes in the solid residues arising from the Ga and V extraction tests with NaOH, those were dried at 60 °C over 48 h and the mineralogical composition determined by XRD. Due to the very fine grain size and to the low content of crystalline phases, a very slow scan (0.025° $2\theta/5$ s) was applied to obtain enough sensitivity for the detection of the mineral components.

2.2.2. Pre-concentration tests

In order to investigate the feasibility of the re-circulation process to concentrate Ga, the leachate obtained at 25 °C, 0.7 M, 5 L/kg, and 6 h was selected. Under these extraction conditions relatively high Ga extraction yields are obtained using relatively low NaOH consumption and low extraction time. These experiments were based on a first extraction step with the subsequent filtration of the leaching solution. A second step was based on the extraction of a non leached fly ash amount using the leachates obtained during the previous extraction step. This process was repeated up to 13 times.

2.2.3. Precipitation from the leachates

The Ga precipitation tests from pre-concentrated Ga leachates were carried out by carbonation attained by bubbling the solution with CO₂. The main objective of these tests was to evaluate the efficiency and selectivity of this process for Ga precipitation from the solution as a function of pH. Furthermore, a selective acid precipitation of Ga was evaluated as a method to increase Ga purity by previous acid re-dissolution of the precipitate obtained by carbonation. For these tests intermediate concentrated Ga leachates, (78–102 mg/L) were selected for the Ga precipitation tests. These Ga leachates were obtained by applying 2–3 re-circulation steps, at 25 °C, 0.7 M NaOH, NaOH/FA ratio of 5 L/kg and 6 h on the solid residue arising from the water Ge extraction on fly ash #129.

Two different Ga precipitation tests were carried out:

- To investigate the precipitation of Ga as a function of pH, the leachate containing 78 mg/L of Ga was bubbled with 6.9 Ln of pure CO₂, for 35 min, equivalent to a CO₂ flow of 198 mL/min. During this process, the starting pH (13.5) was decreased to 7.4 after 37 min. Nine aliquots of the remaining solution were sampled under successively decreasing values of pH (11.5, 11, 10.5, 10, 9.5, 9, 8.5, 8, 7.4). The content of major and trace elements were analysed by ICP-AES and ICP-MS, respectively.
- To obtain a Ga precipitated for subsequent selective acid Ga precipitation, a single precipitation process was performed by bubbling 350 mL of the concentrated leachate containing 102 mg/L of Ga, with 270 mL/min of pure CO₂ for 23 min, to decrease pH down to 7.4. Prior the subsequent selective Ga precipitation, the precipitate obtained by carbonation was re-dissolved in acidic (HCl 0.1N, pH 1). This attempt to segregate Ga from impurities in the re-dissolved solutions increasing pH of the acidic extract, was based on the theoretically different precipitation pH range of Ga and impurities under acidic conditions. So, considering the solubility products of Ga(OH)₃ and Al(OH)₃, Ga starts to precipitate at pH 2.9 at 1.2×10^{-3} M while Al starts precipitation when pH reached 3.9 at 1.58×10^{-3} M.

3. Results and discussion

3.1. Gallium recovery process

3.1.1. Gallium extraction

To check the feasibility of NaOH as an extractant for Ga from IGCC fly ash, a number of Ga extraction tests were carried out fixing extraction conditions at NaOH 1 M, 25 °C and NaOH/FA ratio at 10 L/kg but varying the extraction time (6, 12, and 24 h). These tests were performed on the solid residues arising from the Ge extraction with water at 25 °C, W/FA ratio of 5 L/kg and 6, 12, and 24 h on eight Puertollano IGCC fly ash samples.

The results of these tests have revealed that Ga attained high extraction yields (from 59 to >99%, Fig. 3) using NaOH 1 M. Except for #129 fly ash, the highest Ga extraction yields (81–99%) were attained after 6 h, being those reduced down to 59–79% after 24 h (Fig. 3). These results indicate that Ga speciation in IGCC fly ash controls significantly the Ga extraction yields. Note that the highest Ga extraction yields (81%) obtained for #70 fly ash agree with the proportion of both free Ga₂O₃ (58%) and Ga in sphalerite (24%) detected in this sample [16]. Therefore, free Ga₂O₃ and Ga in sphalerite easily releases from IGCC fly ash whereas NaOH > 1 M has to be applied to mobilises Ga occurring in Al–Si matrix (18% for #70 fly ash). Likewise, the extraction of >99.9% of the bulk Ga content in the rest of IGCC fly ash samples indicates that, in this samples, >99.9% Ga occurs as free Ga₂O₃ and Ga in sphalerite/wurtzite. Conversely to the other IGCC fly ash samples, #129 fly ash attained the highest Ga extraction yields (99%) at 24 h (Fig. 3). As stated above, in this fly ash sample, characterised by the highest Ga and Al bulk fly ash content and the lowest sphalerite/wurtzite ratio (Table 1), Ga is most probably more embedded in the wurtzite lattice than in the sphalerite one. Therefore, the results on Ga extraction yields as a function of extraction time obtained for #129 fly ash suggests lower kinetics solubility of wurtzite under alkaline media than that of sphalerite and may partially explain the high extraction times (24 h) needed to reach highest Ga extraction yields.

Despite the high Ga extraction yields obtained, the NaOH leachates on IGCC fly ash are characterised by a low selectivity, so that along with Ga, the leachates contain high levels of impurities, such as Zn, P, S, Ge, V, Pb, Sb, K, Mo, Si, Al, Ca, Mg, and Fe. To reduce impurity content and to optimise Ga extrac-

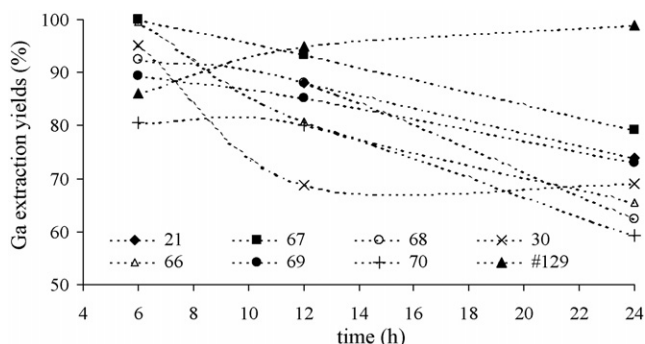


Fig. 3. Ga extraction yields (%) achieved at 25 °C, NaOH 1 M and 6, 12, and 24 h on eight fly ash samples from Puertollano IGCC power plant.

tion conditions from the Puertollano IGCC fly ash, a number of Ga extraction tests were carried out controlling the following parameters: temperature, NaOH concentration, NaOH/FA ratio and extraction time. For these tests the solid residue selected was that arising from the Ge extraction tests performed at semi-pilot plant at the optimal Ge extraction conditions (90 °C, W/FA ratio of 5 L/kg, 6 h) on #129 fly ash (representative of the current fly ash type produced at the Puertollano IGCC power plant).

The results of these tests have revealed Ga extraction yields ranging from 3 to 99% (Fig. 4). As expected the highest Ga extraction yield (99%) was obtained at 25 °C, NaOH/FA ratio of 10 L/kg, 1 M NaOH and 24 h. Furthermore, these Ga extraction tests showed that Ga extraction yields >60% were only obtained at 25 °C (Fig. 4). Thus the extraction temperature appears to be the most significant experimental parameter controlling Ga extraction yields. At this temperature (25 °C) Ga extraction yields >70% were obtained only when using NaOH/FA ratio of 10 L/kg, being those reduced, generally to <40% when using NaOH/FA ratios of 5 and 3 L/kg (Fig. 4). Consequently, the NaOH/FA ratio also has a significant influence of the on Ga extraction. Furthermore, Ga extraction yields attained >70% at different extraction times depending upon the NaOH concentration. Thus, Ga extraction yields >70% were reached at 24, ≥6, and ≥3 h using NaOH concentrations of 0.1, 0.5, and 0.7–1 M,

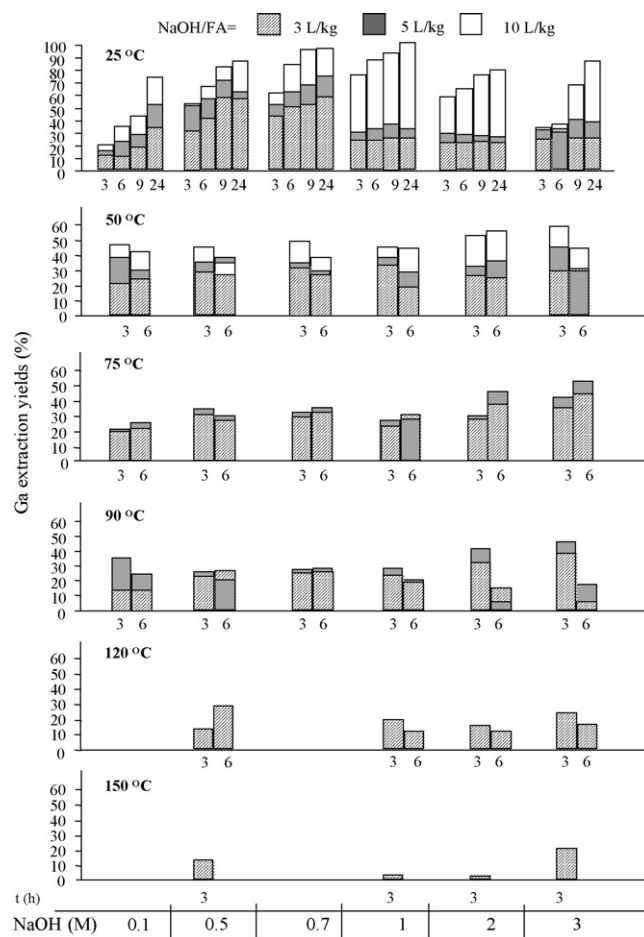


Fig. 4. Ga extraction yields (%) obtained at different temperatures, NaOH concentrations, NaOH/FA ratios and extraction times on IGCC fly ash #129.

respectively (Fig. 4). For NaOH 2–3 M Ga extraction yields >70% were reached at >6 and >9 h, respectively (Fig. 4). From these results it is deduced that increasing NaOH concentration from 0.1 up to 1 M, Ga will yield both high Ga values and reduce extraction time. On the other hand, by increasing NaOH concentration from 1 up to 3 M, Ga extraction yields increase with time, but yields are lower to that attained at the same extraction time for 1 M NaOH (Fig. 4).

This behaviour of Ga extraction yields as a function of NaOH concentration and extraction time suggests that:

- If NaOH < 0.7 M is used, the alkalinity is not high enough to dissolve large amount of Ga from IGCC fly ash and consequently to achieve high Ga extraction yields (>70%) at reasonable low extraction times (6 h).
- If NaOH concentrations > 1 M are used, these are high enough to dissolve large amounts of Ga but also Al and Si, with the subsequent precipitation of Na–Al–Si-species, decreasing NaOH concentration down to <0.7 M while reducing Ga extraction yields.

Therefore, the dissolution kinetics controls Ga extraction yields for NaOH < 0.7 M whereas for NaOH > 1 M, Ga extraction is mainly controlled by thermodynamic processes.

Both the low alkalinity and saturation and precipitation of Na–Al–Si species explain the low Ga extraction yields obtained when NaOH/FA ratios are reduced to 3 and 5 L/kg. Intermediate Ga extraction yields, from 40 to 70%, were obtained only for NaOH 0.5 and 0.7 M and NaOH/FA ratios of 3 and 5 L/kg at extraction times >6 and >3 h, respectively (Fig. 4). For NaOH concentrations of 0.1, 1, 2, and 3 M Ga extraction yields are drastically reduced to <40% (Fig. 4), due to the slight alkalinity given by NaOH = 0.1 M and to the alkalinity reduction due to the saturation and precipitation of Na–Al–Si species for NaOH ≥ 1 M.

Furthermore, the precipitation of Na–Al–Si species may also account for lower Ga extraction yields (<60%) when temperature progressively increased from 25 to 150 °C. The highest Ga extraction yields reached 58, 54, 47, 29, and 21% at 50, 75, 90, 120, and 150 °C, respectively (Fig. 4). The highest Ga extraction yields at 50, 75, 90, 120, and 150 °C reached 58, 54, 47, 29, and 21%, respectively (Fig. 4). Fixing the NaOH/FA ratio at 3 L/kg, the highest Ga extraction yields obtained at 50, 75, 90, 120, and 150 °C attained 33, 44, 39, 29, and 21%, respectively, demonstrating that Ga extraction yields decrease as temperature increases. Since the dissolution of Al and Si as well as Ga is enhanced when temperature is raised, the precipitation of Na–Al–Si–Ga species occurs easily. To demonstrate this fact, extraction tests at 75 and 90 °C, 3 M NaOH and NaOH/FA ratio of 10 L/kg as a function of extraction time were carried out. These tests demonstrated that the highest Ga extraction yields are attained at 0.5 h extraction time, reaching 60 and 56%, respectively, subsequently reducing to 37 and 33% after 6 and 3 h, respectively. The reduction on Ga, Al, Si, and Na content in the leachates demonstrated the saturation and precipitation of these elements at high extraction temperatures (Table 2).

The high correlation ($R^2 = 0.87$) among Ga and Al content in the leachates during the above mentioned extraction tests,

Table 2

Ga and impurities content (mg/L) on the leachates obtained from 0.5 to 6 h at 75 and 90 °C, NaOH 3 M and NaOH/FA = 10 L/kg

	Temperature					
	75 °C				90 °C	
	0.5	1	3	6	1	3
Al	1540	1474	1214	656	1057	894
Ca	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fe	19	20	2	5	<0.1	<0.1
Ga	17	14	14	11	15	11
Ge	16	17	27	16	19	17
K	604	727	1777	1440	1353	1426
Mg	<0.1	<0.1	0.1	<0.1	<0.1	<0.1
Mn	<0.01	<0.01	0.0	<0.01	<0.01	<0.01
Mo	2.5	3.9	2.8	2.5	4.0	<0.1
Na	67560	67150	52150	56340	63180	58710
P	162	149	277	147	173	154
S	310	333	132	293	309	239
Sb	13	12	21	<0.1	<0.1	<0.1
Si	3654	3867	6935	5002	5935	5954
V	92	124	245	246	241	262
Zn	177	178	22	41	66	8

the strong Ga–Al affinity as well as the formation of zeolites through NaOH leaching at temperatures >75 °C, as detected by XRD analysis of the solid residue arising from the Ga extraction, suggest that the incorporation of Ga in the zeolite framework structure is the main cause for the precipitation of Ga from the leachates and, consequently for the low Ga extraction yields obtained at these temperatures.

The results obtained on Ga extraction tests indicate that optimal Ga extraction conditions can be fixed at 25 °C, NaOH 0.7–1 M, NaOH/FA ratio of 5–10 L/kg and 6 h. Under these conditions Ga extraction yields of 60–86% may be achieved, equivalent to 197–275 mg of Ga/kg of fly ash. The main limitations of this Ga extraction process may arise from the low initial Ga concentration in the leachates (25–38 mg/L), the high NaOH/FA ratio needed (5–10 L/kg), and the high levels of impurities in the leachates. For this reason an attempt to concentrate Ga in the leachates while reducing NaOH consumption and impurities content was tested by re-circulating the solution.

3.1.2. Pre-concentration of Ga by re-circulation of the leachates

In order to apply a re-circulation process to the Ga leachates it needs to be remembered that, to yield constant Ga extraction efficiencies in each extraction step a similar NaOH concentration in the solution is required to maintain alkalinity. Only optimal NaOH concentration (0.7–1 M) for the Ga extraction deals with this constraint, since the starting NaOH concentration is not strongly reduced during the extraction step (<1%). Conversely, that of NaOH > 1 M is reduced by ≥12% in a single extraction step, as a consequence of the precipitation of Na–Si–Al species.

The results of the 13 Ga re-circulation cycles carried out at 25 °C, NaOH/FA ratio of 5 L/kg, 6 h extraction time and NaOH 0.7 M using the leachate obtained in the first Ga extraction cycle, show that Ga concentration can be raised up to 188–215 mg/L

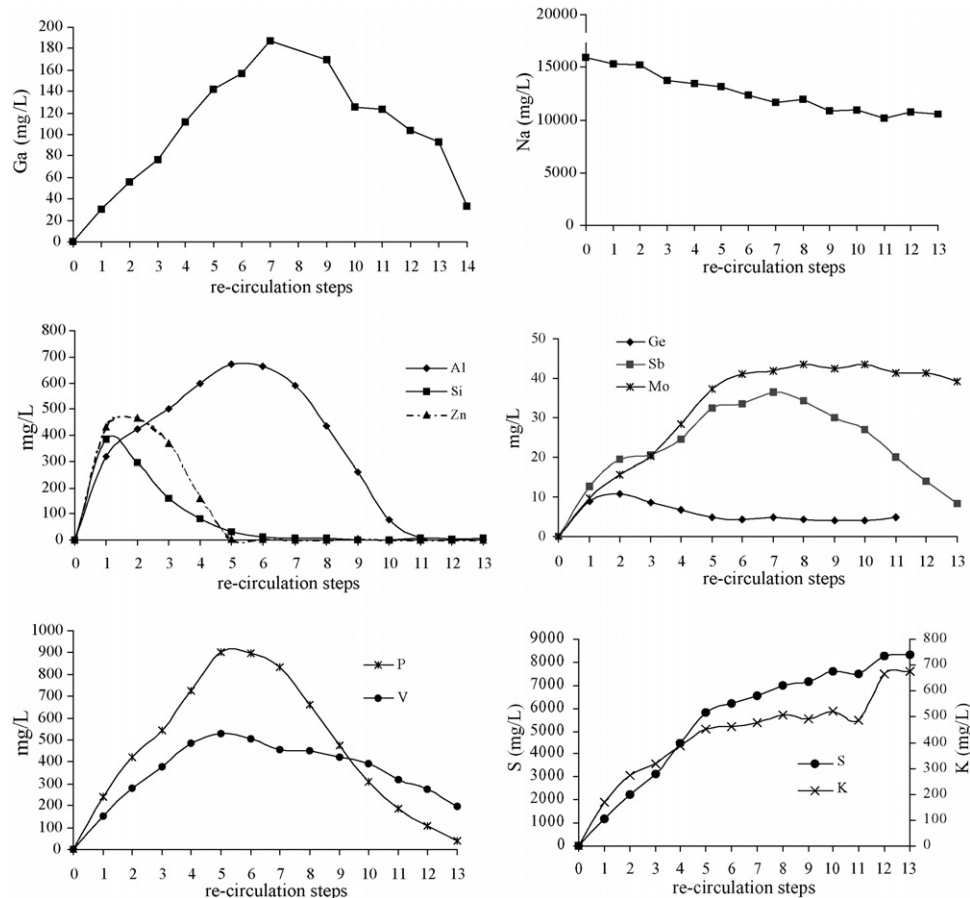


Fig. 5. Ga and impurities (Na, Al, P, Si, Zn, Ge, K, S, Mo, and V) content in the leachates during the re-circulation process.

after 7 cycles, keeping extraction yields over 50–55% (Fig. 5). If more than seven steps are applied Ga concentration falls to 34 mg/L after 13 re-circulation cycles (Fig. 5). During the first seven re-circulation steps certain impurities such as Si, Zn, and Ge precipitated progressively from the leachate. These elements attained very low leachate content (8, 2, and ≤ 5 mg/L, respectively) at the seventh re-circulation step, and Al and P achieved their highest leachate content at the fifth re-circulation step. However, Al and P still in a high contents (589, 833, and 457 mg/L, respectively) after 7 re-circulation cycles (Fig. 5). S and K attained high leachate contents (6555 and 477 mg/L, respectively) after 7 re-circulation cycles (Fig. 5).

The XRD spectra of the solid residue arising from each re-circulation step showed the following (Fig. 6):

- The occurrence of precipitated Na sulphate (Na_2SO_4) in the solid residue. This sulphate increased in content after each subsequent re-circulation step and its may be originated by the oxidation of sulphides during extraction process.
- Sphalerite and galena were dissolved in relatively high proportions during the first 6th re-circulation steps.
- Wurtzite was not dissolved to any appreciable degree during the 13th re-circulation steps.

Combining the leachate content and XRD spectra of the solid residues, it is deduced that the precipitation of Na (as Na_2SO_4)

and Si, probably as amorphous silica [23] ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$), results in a progressive reduction of the alkalinity during the subsequent re-circulation steps. In this way, alkalinity is reduced to 0.5 M NaOH by the 7th re-circulation step. Furthermore, sphalerite was dissolved when alkalinity reached 0.6 M NaOH (6 re-circulation steps), revealing that this Zn sulphide is soluble at $\text{NaOH} > 0.6$ M. Conversely the very low dissolution of wurtzite during the re-circulation process demonstrated that under low alkaline conditions ($\text{NaOH} < 0.7$ M), the dissolution kinetics of wurtzite is extremely low, as was suggested by the preceding Ga extraction tests. This fact contrasts, with the faster dissolution of wurtzite compared with sphalerite in slightly acidic conditions (Fig. 2). The partial dissolution of other sulphides, such as galena during the first 3 re-circulation cycles, resulted in the later precipitation of metal sulfates (Fig. 6). Therefore, the low solubility of wurtzite seems the most probable cause for the low Ga extraction yields attained for #129 fly ash at $\text{NaOH} < 0.7$ M. Both, the lack of sphalerite dissolution and the precipitation of Al–Na–Ga species, most probably Na–Al–Ga phosphates as deduced from Fig. 5, are the main causes for the strong reduction of the Ga content after seven re-circulation steps.

Since NaOH consumption is strongly reduced by re-circulating the leachates, the results suggest that a NaOH/FA ratio of 10 L/kg is feasible and increases Ga extraction yields up to 80–86%. The highest Ga leachate content (188–215 mg/L) obtained re-circulating the leachates is similar or even 1.5–1.7

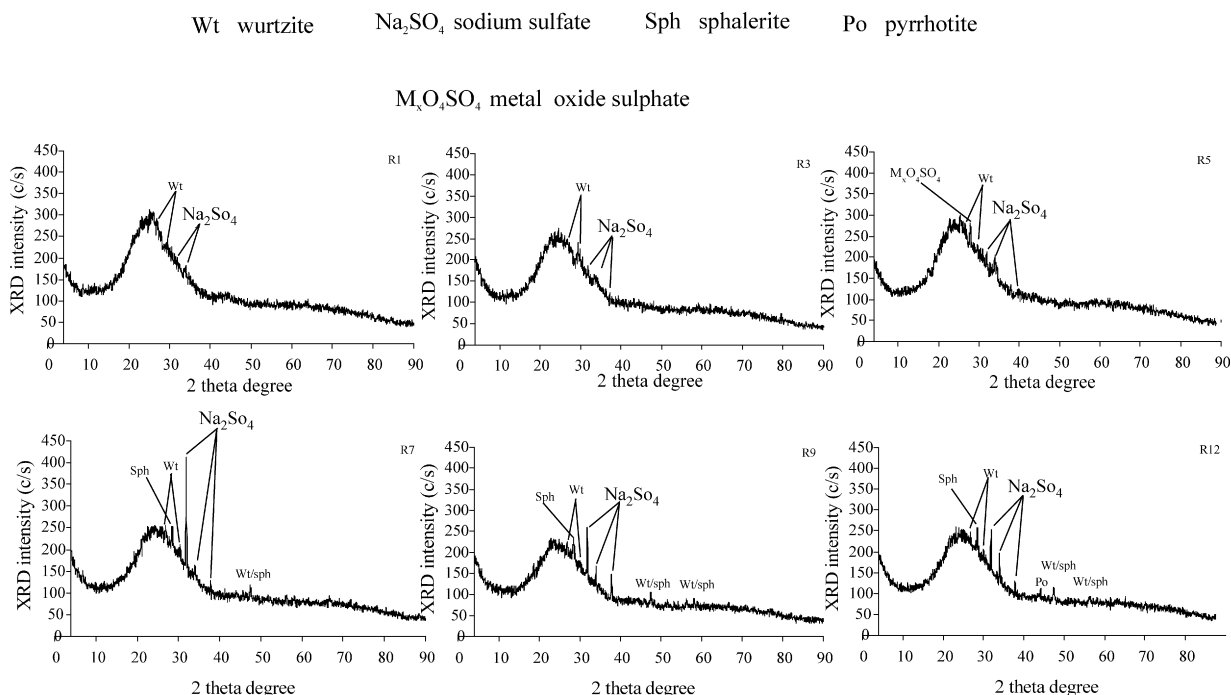


Fig. 6. XRD spectra from the solid residues arising from the Ga re-circulation tests.

times higher, than that obtained in currently used industrial Ga recovery process from bauxites [1–2]. Fly ash presents a chemical composition much more complex than bauxite, raising the amount of impurities in the starting leachate. However, as in the Bayer process case, only Al is expected to be a major inhibition to the attainment of a high Ga purity [1–2], emphasising the potential suitability of this re-circulating process.

3.1.3. Ga precipitation

Since the Ga precipitation tests were performed by carbonating intermediate Ga concentrate leachates (3–4 recirculation cycles), the leachates contain lower amounts of Ga (78–105 mg/L), Al (374–560 mg/L), and S (1695–4639 mg/L) than the optimal Ga concentrate leachate obtained by 7 re-circulation cycles, but contain higher amounts of Zn (36–272 mg/L), K (520–695 mg/L), and Ge (up to 16 mg/L,

Tables 3 and 4). The tests showed that >99% of the Ga content in the leachate can be precipitated at pH 7.5. The precipitation of Ga (2–3%) begins at 10.2 > pH < 10.7, increasing to 19, 25, 67, 68, 98, and 99% as pH decreases through 9.7–9.3, 8.6, 8.0, 7.5, and 7.4, respectively (Table 3 and Fig. 7). The carbonation of the leachate produced also produces precipitation of most of Al (88–99%), Zn (87–99.9%), P (27–63%), and Sb (14–25%) from pH 13 to 7.4, whereas elevated amounts of S, Na, K, and Mo remain in solution (Table 3 and Fig. 7). The results indicated that the precipitation of Ga and impurities are highly dependent on pH, with most of major impurities, such as Al (91%) and Zn (97%) as well as minor impurities, such as Si (98%), Sn (83%), Ge (81%), Pb (59%), and P (32%) can be removed from the leachate at pH 10.2 (Fig. 7), while Ga remains in solution. A second carbonation of the remaining solution at pH 7.4 allowed the precipitation of 98% of the Ga content (Fig. 7).

Table 3
Ga and impurities content (mg/L) in the leachates and precipitation yields obtained by carbonation of an intermediate Ga concentrated leachate as a function of pH

	pH									
	13.5 ^a	11.3	10.7	10.2	9.7	9.3	8.6	8	7.5	7.4
Al	374	43	61	32	8	5	<2	<2	<2	<2
Ga	79	79	76	78	64	59	26	9	1	1
Ge	16	3	3	3	3	4	6	7	9	10
K	406	514	509	504	485	497	442	455	506	493
Mo	7	8	7	7	7	7	7	7	7	7
Na	15300	14655	14559	14439	14001	14385	13416	13746	14619	14469
P	528	382	384	357	309	309	247	230	214	193
S	1687	1792	1751	1768	1673	1763	1588	1624	1752	1717
Sb	35	30	29	29	28	29	26	27	28	27
V	207	218	214	213	206	217	194	202	217	214
Zn	273	8	8	8	6	5	2	1	1	1

^a Starting solution.

Table 4

Ga and impurities content on the starting Ga concentrate leachate (mg/L) and the solid product (mg/kg) obtained from a single carbonation at pH 7.5 as well as the impurities content in precipitate obtained from Ga precipitation from olution of the re-dissolved solid product

	Starting Ga solution (mg/L)	Precipitate at pH 7.5		Precipitation of Ga from the solution in acid medium					
		mg/kg	%	Residual solution (mg/L)		Precipitate (mg/kg)		Precipitate (%)	
				pH 3	pH 4	pH 3	pH 4	pH 3	pH 4
Al	560	120314	99.4	377	254	21390	41630	14	41
Ga	99	21065	98.5	2	<0.1	63809	45781	97.8	>99.9
Ge	6	774	60	2	2	175	37	29	28
K	695	4911	3	25	22	576	619	<0.01	<0.01
Mo	31	32	1	0.1	<0.01	22	14	48	91
Na	22325	153288	3	1632	1822	1539	1694	<0.01	<0.01
P	951	78086	38	199	98	41520	47002	30	65
S	4639	4213	0.4	16	15	581	153	<0.01	1
Sb	43	264	3	1	1	180	162	<0.01	<0.01
V	338	553	1	2	1	212	223	0.4	50
Zn	183	17223	44	63	63	191	940	<0.01	<0.01

The formation of insoluble Al and Zn carbonates, such as hydrozincite and hydroxalcite accounts for the high removal efficiency of Al and Zn from the leachate. The high proportion of metal precipitates reduces the Al/Ga ratio in the leachate down to 0.08, but the leachate still contains high concentrations of Na, V, S, and P. Therefore, a second carbonation of the remaining solution can be carried out to precipitate 98% of the bulk Ga content in the starting solution, together with the remaining Al and relatively high proportions of P (Table 3 and Fig. 7). In this second precipitation step, Ga and Al mainly precipitate as hydroxides, whereas the precipitation of P is probably related due to the formation of Al phosphates such as variscite (AlPO_4), which has a low solubility at this pH, and/or by adsorption of PO_4^{3-} on $\text{Al}(\text{OH})_3$ surfaces [24–25]. Applying two precipitation steps would yield a Ga-rich product, with an Al/Ga ratio of 0.9, and containing 8% Ga, and 7% Al, 12% Na, and 9% P. Ga concentrations achieved by this method will be more than eight times higher than obtained by a similar precipitation procedure (the Beja process) from Bayer liquors (0.3–1% Ga) [4].

Although the Ga content of this product is greatly elevated, even higher Ga purity is required for further industrial applications of this element [1–2]. With this in mind a dissolution in acid media (pH 0) of a Ga precipitate was carried out to test for

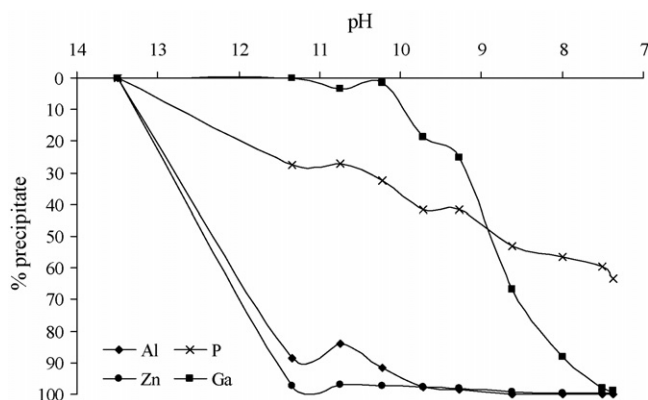


Fig. 7. Precipitation yields (%) obtained for Ga, Al, P and Zn by carbonation of a concentrated Ga leachate as a function of pH.

possible further increase in Ga purity. The dissolution was performed on a Ga product obtained by a single Ga precipitation by carbonation of a Ga concentrated leachate at pH 7.5 (Table 4). As expected, high precipitation of both Ga (98% of the bulk content) and impurities, Al (>99.9%), Zn (99.8%) and P (38%) were achieved. Low precipitation yields were achieved for Sn (14%), K, Na, and Sb (<3%), Mo, S, and V (<1%) and <0.1% of the bulk content for the rest of the elements (Table 4). The solid product obtained is of low Ga purity (2%) and contains high amounts of Al (12%), Na (15%), and P (8%) with lower proportions of Zn (2%), S (0.4%), and K (0.5%). Even given the lower Ga content with respect to that obtained by two carbonation steps, however, the Ga content is still double that obtained by the Beja process on the Bayer liquors [4].

In order to test for possible further increase of the purity of the Ga end solid product, sequential Ga precipitation from the dissolved Ga solution in acidic media was performed, increasing pH from 0 to 3–4. These tests showed that >97.8 and >99.9% of Ga contained in the acidic solution can be precipitated at pH 3 and 4, respectively. Together with high Ga precipitation, low Al (13.7%) and P (29.8%) optimum precipitation yields were obtained at pH 3. Therefore the dissolution process in acidic media and further selective precipitation controlling pH appears to be highly effective in reducing contents of impurities, allowing the achievement of a improved Ga product suitable for further purification by electrolysis in order to produce a marketable product.

3.2. V recovery process

The results on the V extraction tests attained V extraction yields ranging from 2 to 64%. The maximum V extraction yield (64%) was achieved at 90 °C, NaOH 3 M, NaOH/FA ratio of 5 L/kg and 9 h extraction time, equivalent to a 4005 mg of V/kg of fly ash. From these results it can be deduced that V extraction yields are highly dependent on the extraction temperature and NaOH concentration, while NaOH/FA ratio and extraction time have lower influence on the V extraction yields. Due to the lower solubility of V(III) than V(V) at alkaline pH [21], low V

extraction yields (<40%) are achieved with NaOH < 2 M at temperatures <75 °C. To obtain V extraction yields from 50 to 67% temperatures from 75 to 90 °C, NaOH concentrations >2 M and NaOH/FA ratio >5 L/kg have to be applied. The precipitation of V(III) substituting for Al(III) in the zeolitic material accounts for the low V extraction yields (<50%) at temperatures >90 °C. Given that relatively low V extraction yields are obtained even when using extreme (and expensive) alkaline extraction conditions, the current marked price of this element considerably limits the economic feasibility of V recovery from IGCC fly ash.

4. Conclusions

The results of the laboratory scale tests for the proposed Ga recovery process, based on NaOH extraction, concentration by re-circulation of the leachates and Ga precipitation by carbonation, show significant recovery yields and a Ga end product pure enough to justify the feasibility of this method for the recovery of Ga from IGCC fly ash. The main conclusions extracted from this study may be summarised as follows:

- The NaOH-based Ga extraction tests have revealed that >99% of the bulk Ga can be extracted from IGCC fly ash. However, high proportions of Ga (>70%) are extracted only under a narrow range of experimental conditions (25 °C, NaOH/FA = 10 L/kg). Applying this conditions Ga extraction yields >70% attained at different extraction times depending on the NaOH concentration. Intermediate Ga extraction yields (60–70%) can be obtained only at 25 °C, NaOH = 0.5–0.7 M, $t \geq 6$ h, reducing NaOH/FA ratio down to 5 L/kg. Increasing temperature from 25 to 150 °C achieves Ga extraction yields of <60%. Taking into account that along with high Ga extraction yields, any up-scaling of the process will require the minimization of both NaOH-solution consumption and extraction time, optimal Ga extraction conditions were fixed at 25 °C, NaOH 0.7–1 M, NaOH/FA ratio of 5 L/kg and 6 h. Under these conditions Ga extraction yields are 60–86%, equivalent to 197–275 mg of Ga/kg of fly ash.
- Re-circulation of leachates greatly reduced the NaOH-solution consumption, and the final Ga content obtained (188–215 mg/L) is similar, or even higher (1.5–1.7 times), than that currently achieved by industrial Ga recovery from bauxites. Thus the re-circulation of Ga leachates is recommended as a means to concentrate this element prior to precipitation.
- The Ga precipitation tests demonstrated that 99% of the bulk Ga content in the starting solution can be precipitated by bubbling CO₂ up to pH 7.4. At pH 10.5 significant proportions of impurities Al (91%), Zn (97%), Sb (17%), and Ge (88%) precipitated from the leachates while 98% of the bulk Ga remains in solution. A product containing 7% Ga, 12% Na, 12% Al, and 9% P can be obtained by a second carbonation of the remaining solution at pH 7.5, recovering 98% of the bulk Ga in the pre-concentrated solution and achieving an Al/Ga ratio to 0.9. The Ga concentration obtained is >8 times higher than the one obtained by a similar industrial precipitation procedure (the Beja process) from Bayer liquors (0.3–1%

Ga) [4]. Re-dissolving this product at pH 0 with HCl and using a Ga precipitation at pH 3, Al/Ga ratio in precipitate product is reduced increasing Ga purity to a level suitable for final purification by electrolysis.

- Using the proposed method, the final recovery yield obtained for Ga attained 132–152 mg Ga/kg fly ash, this being equivalent to 1582–1821 kg of Ga/year given the current annual production of Puertollano IGCC plant (12,000 tonnes). Furthermore, the extraction residue may be still used for other commercial applications, such as the production of fluxes or lightweight aggregates [26].
- Given the relatively high yields, the purity of the Ga end product, and the higher efficiency of the Ga recovery method tested when comparing with those currently applied in industry, the recovery process may be considered as a feasible method for the recovery of Ga from IGCC fly ash.
- In contrast, the relatively low V extraction yields even when using extreme alkaline extraction conditions, and the low price of this element, greatly constrain the economic feasibility of V recovery from IGCC fly ash.

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